A

TREATISE ON CHEMISTRY

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VOLUME III.

THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES

OR

ORGANIC CHEMISTRY

PART III.

> "*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

London:
MACMILLAN AND CO.
AND NEW YORK
1886

RICHARD CLAY AND SONS,
LONDON AND BUNGAY.

PREFACE TO VOL. III., PART III.

THIS part of the work commences the consideration of the complicated but most important series of bodies known as the Aromatic Compounds.

It contains, after an introduction, a description of the mode of formation, and of the properties, of the Aromatic Hydrocarbons and their derivatives, together with an historical discussion of their isomeric modifications. The constitution of Benzene and the characteristic reactions of its di-substitution products are then fully explained. Next follows a review of all the important Benzene Derivatives, so that the part now published forms a complete chapter of the ever-increasing volume of Aromatic Chemistry.

H. E. R.
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ORGANIC CHEMISTRY,

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PART III.

AROMATIC COMPOUNDS, OR COMPOUNDS RICH IN CARBON.

914 In the early years of our Science, the name "aromatic compounds" was given to a small group of naturally occurring bodies possessing an aromatic smell and taste. For in those days almost all chemical compounds were classed according to certain well-marked physical properties; and even now the pages of our manuals contain chapters on "colouring matters," "bitter principles," &c. There we find descriptions of substances possessing an unknown constitution, and, therefore, incapable of any more systematic classification, to which Gerhardt gave the title of *corps à sérier*. Thanks, however, to the progress of our science, this "chemical lumber-room" is rapidly being cleared out, and in time it will doubtless be found empty.

A similar sifting process has been going on with respect to the aromatic compounds. It was soon perceived that, in addition to certain analogies in their outward properties, such as smell and taste, these bodies are connected by intimate chemical ties. The first step towards this recognition was effected by Liebig and Wöhler in 1832 by the publication of their classical research "On the Radical of Benzoic Acid."[1] In the introduction to their memoir they remark: "We may congratulate

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[1] *Ann. Pharm.* 3. 219.

ourselves if we succeed in clearing a narrow-path through the dark domain of organic nature, which may perhaps lead to the recognition of the true method of surveying and examining this unknown district, although we are well aware of its illimitable extent. Nor indeed can we here reasonably expect at first to arrive at any very profound or wide generalisations, owing to the absence of previous investigations, as well as the difficulty of obtaining the necessary materials. Under these circumstances the experiments which are described in the sequel must be regarded, as far as their extent and connection with other branches of investigation are concerned, only as the opening out of a wide and fruitful field for future research."

This wide field embraces the whole of the aromatic compounds, and it has proved to be even more fruitful than Liebig and Wöhler could have even dreamed. Their first observation was that oil of bitter almonds is distinguished from all similar compounds by its power, first noticed by Stange, of absorbing oxygen, and of being converted into benzoic acid—a compound known so long ago as the seventeenth century, and prepared from the aromatic gum benzoin. The two chemists then showed that both these compounds contain the same radical, benzoyl, C_7H_5O, that the oil of bitter almonds must be regarded as benzoyl hydride, C_7H_6O, which on oxidation passes into benzoic acid, $C_7H_6O_2$. By replacing an atom of hydrogen in benzoyl hydride, by the elements of the chlorine group, by cyanogen, or by sulphur, other compounds of this same radical are obtained.

Mitscherlich prepared the hydrocarbon, C_6H_6, by distilling benzoic acid with slaked lime, it being formed by the separation of carbon dioxide from benzoic acid, and to this body he gave the name of benzin, which was altered by Liebig to benzol, but which in England is now usually written benzene. Mitscherlich also found that this hydrocarbon is converted by the action of nitric acid into nitrobenzene, $C_6H_5NO_2$. Zinin next showed that the oxygen in this body can be replaced by hydrogen, and that thus a basic oil is obtained which was soon proved to be identical with aniline, a compound which Fritsche had previously obtained by distilling indigo with caustic potash. The Russian chemist had also observed that indigo when treated with caustic potash yields an acid termed anthranilic acid, $C_7H_7NO_2$, and that this is decomposed on distillation into carbon dioxide and aniline.

Gerhardt afterwards noticed that when nitrous acid acts upon anthranilic acid, this latter is converted into salicylic acid, $C_7H_6O_3$, a body first obtained from the ethereal oil of *Spiræa Ulmaria*, together with salicyl hydride, $C_7H_6O_2$. These two compounds stand in the same relation to one another as benzoyl hydride does to benzoic acid; just as the latter is converted into benzene by the separation of carbon dioxide, so from salicylic acid, carbolic acid, C_6H_6O, is obtained. This latter substance is also found in coal-tar, together with benzene and toluene, C_7H_8, a body whose name is derived from the fact that it was first obtained by distilling the aromatic balsam of tolu. This compound closely resembles benzene; thus, by the action of nitric acid it is converted into nitrotoluene, and from this the base toluidine can readily be prepared. These investigations proved that an intimate relation exists between the two series of compounds, containing respectively six and seven atoms of carbon:—

Benzene. C_6H_6.	Nitrobenzene. $C_6H_5NO_2$.	Aniline. C_6H_7N.	Carbolic Acid. C_6H_6O.
Toluene. C_7H_8.	Nitrotoluene. $C_7H_7NO_2$.	Toluidine. C_7H_9N.	—
Benzoyl Hydride. C_7H_6O.	—	—	Salicyl Hydride. $C_7H_6O_2$.
Benzoic Acid. $C_7H_6O_2$.	—	—	Salicylic Acid. $C_7H_6O_3$.

In course of time the existence of many similar groups was discovered, and to all these the general title of "aromatic compounds" was given, although among them many are found which either possess no smell, or whose odour is anything but aromatic. The designation of aromatic is applied in the same sense as that of "fatty bodies," in which we now class almost all the organic substances not belonging to the aromatic series. (R. Meyer.)

It was at first difficult to find a sharp distinction between aromatic compounds and other groups, as many bodies were known which, according to their products of decomposition as well as their mode of combination, may equally well be placed either in the one or in the other division. Thus it came about that many compounds which clearly belong to the aromatic group were not classed under this head. On the other hand, however, the fact was not then recognised that bodies properly classed as aromatic could yield compounds belonging either to the group of fatty bodies, or to that of bodies containing less hydrogen. Nor was it understood that the reverse action could take place. (Kekulé.)

915 *Kekulé's Theory of the Constitution of Aromatic Bodies.*—No expression of opinion is to be found respecting the constitution of the aromatic compounds until Kekulé proposed a theory which shed an unexpected light on these hitherto neglected bodies.[1] The effect of the general recognition of the truth of Kekulé's theory has been that this special field of organic chemistry has since been, and still is, most industriously cultivated, perhaps to the undeserved neglect of other branches.

In justification, however, it must be remembered that the study of the aromatic compounds is full of practical interest, inasmuch as not only all the natural, but also all the artificial colouring matters, as well as the most valuable medicines and most potent poisons, belong to this class of bodies.

Kekulé's views are best given in his own words: "If we wish to form an idea of the constitution of the aromatic compounds we are bound to explain the following facts:—(1st) Even the simplest of aromatic compounds are comparatively richer in carbon than the compounds belonging to the fatty group; (2nd) Amongst the aromatic compounds as well as amongst the fatty bodies a large number of homologous substances exist; (3rd) The simplest aromatic compounds contain at least six atoms of carbon; (4th) All the derivatives of these substances exhibit a certain family resemblance, they all belong to the group of aromatic compounds. In cases where a more destructive reaction occurs, a portion of the carbon of the original compound may be eliminated, but the chief product invariably contains at least six atoms of carbon, and the decomposition stops with the formation of this product, unless, indeed, the aromatic group is completely destroyed. These facts justify the supposition that one and the same group of atoms occurs in all the aromatic compounds, or that they all contain a common nucleus of six atoms of carbon. In these bodies some of the carbon atoms are in more intimate connection than others, hence it follows that all aromatic compounds are proportionately rich in carbon. Other atoms of carbon may attach themselves to this nucleus

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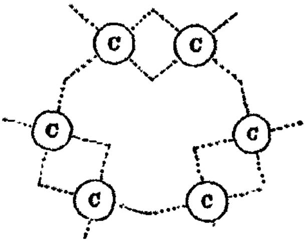
[1] *Bull. Soc. Chim.* 1865, 1, 98.

in the same way, and according to the same laws, as is the case in the group of fatty bodies, and in this way the existence of homologous compounds is readily explained."[1]

According to Kekulé, the six atoms of carbon in the aromatic nucleus are alternately connected by one and by two combining units to form a closed ring, as shown in the following graphic formula:—



916 *Explanation of Isomerism in the Aromatic Group.*—If the six free combining units of the nucleus are saturated with hydrogen, the simplest aromatic compound, viz., benzene, C_6H_6, is formed. From this all the other aromatic compounds may be derived by the same processes as the fatty bodies are derived from methane. Hence, benzene may be regarded as the marsh gas of the aromatic series, and this series is defined as group of the benzene derivatives. Kekulé's formula not only explains the above-named facts, but also the following, which will be mentioned in detail in the sequel:

(1) In the case of the mono-substitution products of benzene no case of isomerism occurs, as all the six atoms of hydrogen of this hydrocarbon are of equal value, and, therefore, indistinguishable one from the other.

(2) If two atoms of hydrogen be replaced by elements or radicals, termed "side chains," three isomeric compounds may be formed whether the entering element or side chain be identical or different, and this conclusion is borne out by experiment. This isomerism is due to the fact that the bodies replacing hydrogen take up different positions in the benzene ring. If we represent benzene by a hexagon, at each of whose angles a carbon atom is placed, and number these 1 to 6, it is clear that three different dibromobenzenes, $C_6H_4Br_2$, or nitrobromobenzenes,

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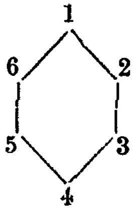
[1] Kekulé, *Lehrbuch*, ii. 195.

$C_6H_4(NO_2)Br$, can exist in which bromine or nitroxyl takes the following positions:—



Br : Br = 1 : 2
Br : Br = 1 : 3
Br : Br = 1 : 4
Br : NO_2 = 1 : 2
Br : NO_2 = 1 : 3
Br : NO_2 = 1 : 4

Every other position is identical with one of the above; hence, these may be distinguished as adjacent, alternate, and opposite. Tri-substitution products of benzene containing identical elements or side chains can also occur, but only in three modifications:—

1 : 2 : 3
1 : 2 : 4
1 : 3 : 5

These are distinguished as adjacent, asymmetrical, and symmetrical. It is also clear that if four atoms of hydrogen are replaced by some element or radical three isomeric compounds can also occur.

Supposing, however, that the entering elements or radicals are not identical, it is plain that the number of isomeric bodies will be increased; thus, for example, we are acquainted with six nitrodibromobenzenes, $C_6H_3(NO_2)Br_2$, in which, if the nitroxyl occupies position 1, the bromine atoms may occupy the following positions:—

1 : 2 : 3
1 : 2 : 4
1 : 2 : 5
1 : 2 : 6
1 : 3 : 4
1 : 3 : 5

Supposing, again, that all the three, or even more, elements or side chains are different, we see that the number of possible isomerides will of course be larger.

917 *Characteristic Properties of Aromatic Bodies.*—By the action of chlorine and bromine on benzene, substitution products are formed, but under certain conditions additive products may also be produced, inasmuch as benzene combines with

two, four, or six atoms of the halogen, but not with more. In support of his theory Kekulé adds: "Some few chemists incline to the view that benzene and hydrocarbons homologous with it are derived from hydrocarbons belonging to the class of fatty bodies by simple loss of hydrogen, and the consequent more intimate union of the carbon atoms. I do not share this view, but rather believe that the hydrocarbons of the family C_6H_6, prepared from C_6H_{12} by subtraction of hydrogen, will turn out to be only isomeric, and not identical with benzene." Such a hydrocarbon is in fact now known, and it is termed dipropinyl, $CH \equiv C.CH_2.CH_2.C \equiv CH$. (See vol. iii. Part II. p. 466.) This compound combines energetically with bromine to form a tetrabromide, $C_6H_6Br_4$, and on warming with bromine it yields an octobromide, $C_6H_6Br_8$. On the other hand, its isomeride benzene exhibits totally different reactions, inasmuch as it combines with bromine and chlorine only slowly, and moreover is incapable of taking up more than six atoms. The formation of this additive product is quite analogous to that of ethylene dibromide from ethylene: as in this instance so in the case of benzene, the double linkage of the carbon atoms is resolved into a single linkage, but the closed ring form remains unaltered. By acting on ethylene dibromide with alkalis, bromethylene is formed, and in like manner benzenehexbromide is converted into tribromobenzene.

The substitution products of benzene react quite differently from those of the paraffins. By the action of chlorine, monochlorobenzene, C_6H_5Cl, is formed, and this was formerly supposed to be the chloride of a monovalent alcohol radical and termed phenyl chloride. It does not, however, exhibit any of the properties of an alcoholic chloride, inasmuch as it holds its chlorine in a much more retentive form, and is not attacked when heated with caustic potash, silver salts, ammonia, &c.

The action of concentrated nitric acid serves as another characteristic test for the aromatic compounds, as these readily form nitro-compounds, bodies which in the fatty series are only obtained by indirect processes; thus benzene yields nitrobenzene, $C_6H_5NO_2$, this passes easily by reduction into aniline, $C_6H_5NH_2$, a body which was formerly called phenylamine, but now termed amidobenzene; for, although in some respects it possesses analogies with the compound ammonias, it differs widely from them in other respects, especially in not possessing any ammoniacal smell and having a perfectly neutral reaction.

Another characteristic property of the aromatic compounds is the formation of sulphonic acids when the hydrocarbons are treated with strong sulphuric; thus, for example, benzene yields benzenesulphonic acid, $C_6H_5SO_3H$.

If an atom of hydrogen in benzene be replaced by hydroxyl a body resembling the alcohols is obtained, and to this the name of phenyl alcohol, C_6H_5OH, was formerly given, though at the present day we prefer the name of phenol, it being distinguished from the alcohols, amongst other properties, by being an extremely stable compound which can only be oxidized with difficulty. Alcohol is converted by concentrated nitric acid into a nitrate, and by strong sulphuric acid into a sulphate; phenol, on the other hand, treated in like manner, yields nitrophenol, $C_6H_4(NO_2)OH$, and phenolsulphonic acid, $C_6H_4OH.SO_3H$. These examples suffice to show that well-defined differences are observable between the members of the fatty and those of the aromatic group of substances.

AROMATIC HYDROCARBONS.

918 The homologues of benzene are formed by the replacement of hydrogen by an alcohol radical, such as methyl, ethyl, propyl, &c.; the compounds thus obtained act on the one hand as aromatic, and on the other, as fatty bodies. When the hydrogen nucleus in methylbenzene or toluene, $C_6H_5CH_3$, is replaced by chlorine, hydroxyl or nitroxyl, bodies are formed which exhibit the closest similarity to the corresponding benzene derivatives. If, however, the replacement takes place in the methyl group, compounds of the alcohol radical, phenylmethyl or benzyl are produced, such as benzyl chloride, $C_6H_5.CH_2Cl$, a body which is converted by the action of ammonia into strongly alkaline benzylamine; similarly, the same body can be converted by oxidation into benzoyl hydride and benzoic acid. Thus the two following series are obtained:—

Toluene, Methylbenzene or Phenylmethane.

$C_6H_5.CH_3$.

Monochlorotoluene. C_6H_4Cl,CH_3.	Benzyl Chloride. C_6H_5,CH_2Cl.
Toluidine or Amidotoluene. $C_6H_4(NH_2)CH_3$.	Benzylamine. C_6H_5,CH_2,NH_2.

Cresol or Oxytoluene. $C_6H_4(OH)CH_3$.	Benzyl Alcohol. C_6H_5,CH_2,OH.
Nitrocresol. $C_6H_3(NO_2)(OH)CH_3$.	Benzyl Nitrate. $C_6H_5.CH_2O.NO_2$.
—	Benzaldehyde. $C_6H_5.COH$.
—	Benzoic Acid. $C_6H_5.CO.OH$.

Here we find several different isomeric compounds, but their number is really still greater, for each mono-substitution product of toluene exists in three isomeric forms.

Moreover, substitution can take place at the same time in the aromatic nucleus and in the alcohol radical, whereby bodies are obtained which act both as aromatic substitution-products and as compounds of alcohol radicals. Such a body is chlorobenzyl chloride, $C_6H_4Cl.CH_2Cl$, and this can be easily converted into chlorobenzylamine, chlorobenzyl alcohol, &c.

Moreover, not only one atom of hydrogen in benzene can be substituted by an alcohol radical, but all six can be consecutively substituted. If this take place with methyl, a series of homologous bodies is obtained whose members are isomeric with corresponding ones of the first series, thus:—

		Benzene . . .	C_6H_6
		Methylbenzene .	$C_6H_5.CH_3$
Ethylbenzene .	$C_6H_5.C_2H_5$	Dimethylbenzene .	$C_6H_4(CH_3)_2$.
Propylbenzene.	$C_6H_5.C_3H_7$	Trimethylbenzene .	$C_6H_3(CH_3)_3$.
Butylbenzene .	$C_6H_5.C_4H_9$	Tetramethylbenzene .	$C_6H_2(CH_3)_4$.
Pentylbenzene.	$C_6H_5.C_5H_{11}$	Pentamethylbenzene .	$C_6H(CH_3)_5$.
Hexylbenzene.	$C_6H_5.C_6H_{13}$	Hexmethylbenzene .	$C_6(CH_3)_6$.

Here we find two kinds of homologous bodies, those of the first series depend on the lengthening of the side chain, and the number of its members is only limited by the number of alcohol radicals which is known, whilst the homology of the second series depends upon an increase in the number of side chains, so that here hexmethylbenzene is the last member of the series.

The members of the first of these series of hydrocarbons beginning with the second term occur in isomeric forms dependent upon the isomerism of the radicals; thus we know of a normal propylbenzene and an isopropylbenzene, $C_6H_5.CH(CH_3)_2$, &c. In the second series the isomeric forms, as has been explained, commence with the first term and end with the last but one.

It is clear that two and more atoms of hydrogen in benzene can be replaced by alcohol radicals homologous with methyl. These may be either the same or different, and this gives rise to a number of isomeric bodies.

In all these hydrocarbons the hydrogen in the aromatic nucleus, as well as that in the side chain, can again be replaced, and from this it will be seen that the number of benzene derivatives may be extremely large, and the possibility of a further increase is evident when we remember that the hydrogen of the benzene is not merely capable of replacement by a monad alcohol radical, C_nH_{2n+1}, but also by groups containing less hydrogen. Thus for example we are acquainted with the following hydrocarbons:

Styrolene or phenylethylene . . .	$C_6H_5.CH{=}CH_2$.
Allylbenzene or phenylpropylene .	$C_6H_5.CH{=}CH.CH_3$.
Crotonylbenzene or phenylbutylene	$C_6H_5.CH_2.CH_2.CH{=}CH_2$.

And derivatives of these, such as:

Cinnamic alcohol or phenylallyl alcohol, $C_6H_5.CH{=}CH.CH_2.OH$.
Cinnamic aldehyde or phenylacrylaldehyde, $C_6H_5.CH{=}CH.COH$.
Cinnamic acid or phenylacrylic acid, $C_6H_5.CH{=}CH.CO.OH$.
Hydroxyphenylpropylene, $C_6H_4(OH)CH{=}CH.CH_3$.

These compounds exhibit the general properties of the olefines or of the compounds of the allyl series; they unite with hydrogen, the elements of the chlorine group and their hydracids, &c., forming saturated compounds.

The number of side chains which are contained in an aromatic hydrocarbon, or in its derivatives obtained by substitution in the side chains, may easily be ascertained by oxidation with chromic acid solution. If only one side chain be present as in toluene, ethylbenzene, propylbenzene, amylbenzene, phenylethylene or cinnamic alcohol, &c., the monobasic benzoic acid is produced. The constitution of the side chain in such hydrocarbons may also be ascertained in the same way; thus amylbenzene, $C_6H_5.CH_2.CH_2.CH(CH_3)_2$, in addition to benzoic acid, yields isobutyric acid.[1]

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[1] Popow and Zincke, *Ber. Deutsch. Chem. Ges.* v. 384.

If two side chains be present, one of the three phthalic acids or benzenedicarboxylic acids, $C_6H_4(CO_2H)_2$, is formed, and if three such side chains be present a tribasic benzenetricarboxylic acid, $C_6H_3(CO_2H)_3$, is formed. All the carboxylic acids of benzene yield, when distilled with slaked lime, carbon dioxide and benzene.

When dilute nitric acid or potassium permanganate is employed as the oxidizing agent, only one side chain is at first oxidized to carboxyl, and, if these side chains are different, the longest of them is attacked first. The dimethylbenzenes, $C_6H_4(CH_3)_2$, ethylmethylbenzenes, $C_6H_4\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right.$, and propylmethylbenzenes, $C_6H_4\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$, yield monobasic toluic acids, $C_6H_4\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$, and, of the last class, that which contains normal propyl yields in addition acetic acid.[1] One trimethylbenzene, $C_6H_3(CH_3)_3$, treated in a similar way, first yields a monobasic acid, $C_6H_3\left\{\begin{matrix}(CH_3)_2\\CO_2H\end{matrix}\right.$, and then a dibasic acid, $C_6H_3\left\{\begin{matrix}CH_3\\(CO_2H)_2\end{matrix}\right.$; the first of these yields dimethylbenzene when distilled with lime, and the second, like the toluic acids, yields toluene. In certain cases it has been observed that when the oxidation is carried on very slowly, a long side chain is not at once oxidized to carboxyl, but that intermediate products are formed; thus, for example, by oxidizing ethylbenzene, $C_6H_5CH_2CH_3$, some methylphenylketone, $C_6H_5.CO.CH_3$, is obtained,[2] whilst from triethylbenzene, $C_6H_5(C_2H_5)_3$, together with trimesitic acid, $C_6H_3(CO_2H)_3$, the tribasic isophthalacetic acid, C_6H_3, $\left\{\begin{matrix}(CO_2H)_2\\CH_2.CO_2H\end{matrix}\right.$, is obtained.[3]

919 *Formation of Aromatic Hydrocarbons.*—In addition to the above-mentioned mode of formation from the acids, a large number of the hydrocarbons can be obtained by simple synthesis, as is the case with paraffins, and by this means their constitution can be ascertained.

1st. A mixture of a brominated hydrocarbon and the iodide or bromide of an alcohol radical is treated with sodium thus:[4]—

$$C_6H_5Br + CH_3I + 2Na = C_6H_5.CH_3 + NaBr + NaI.$$

$$C_6H_4Br.CH_3 + C_2H_5Br + 2Na = C_6H_4\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right. + 2NaBr.$$

$$C_6H_4Br_2 + 2CH_3I + 4Na = C_6H_4\,(CH_3)_2 + 2NaBr + 2NaI.$$

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[1] Dittmar and Kekulé, *Ann. Chem. Pharm.* clxii. 337.

[2] Bahlson, *Bull. Soc. Chim.* xxxii. 615.

[3] *Ibid.* xxxiv. 625.

[4] Fittig and Tollens, *Ann. Chem. Pharm.* cxxxi. 303.

2nd. The zinc compound of the alcohol radical is allowed to act on benzyl chloride or benzylene chloride thus:—

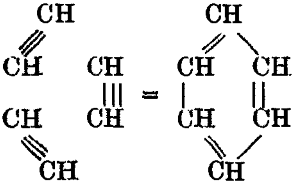
$$2C_6H_5.CH_2Cl + Zn(C_2H_5)_2 = 2C_6H_5.C_3H_7 + ZnCl_2.$$
$$C_6H_5.CHCl_2 + Zn(CH_3)_2 = C_6H_5.CH(CH_3)_2 + ZnCl_2.$$

3rd. By the action of a halogen compound of an alcohol radical upon a mixture of an aromatic hydrocarbon and aluminium chloride.

Thus, if methyl chloride be passed through a mixture of aluminium chloride and benzene the chief product is durene or tetramethylbenzene, whilst hydrochloric acid is evolved.[1]

Toluene treated in like manner yields dimethylbenzene, trimethylbenzene, tetramethylbenzene, pentamethylbenzene and hexmethylbenzene.[2] If ethylene be passed through a heated mixture of aluminium chloride and benzene, ethylbenzene, diethylbenzene and triethylbenzene are formed.[3] The part which aluminium chloride plays in this complicated reaction is not known.

4th. Aromatic hydrocarbons are also formed by the condensation of hydrocarbons of the acetylene series. Berthelot found that if acetylene be heated to a temperature at which glass softens, a considerable quantity of benzene is produced.



At the same time styrolene, C_8H_8, naphthalene, $C_{10}H_8$, and other hydrocarbons are formed.

If methylacetylene be dissolved in sulphuric acid and the mixture distilled, mesitylene or symmetrical trimethylbenzene is formed:

$$3CH \equiv C.CH_3 = C_6H_3(CH_3)_3.$$

Dimethylacetylene, $CH_3C \equiv C.CH_3$, when shaken with sulphuric acid, is converted into hexmethylbenzene, $C_6(CH_3)_6$, (see vol. iii. Part II. p. 463).

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[1] Friedel and Crafts, *Bull. Soc. Chim.* xxviii. 147; *Ann. Chim. Phys.* [6], i. 449.

[2] *Bull. Soc. Chim.* xxix. 481; Ador. u. Rilliet, *Ber. Deutsch. Chem. Ges* xii. 329; Jacobsen, *ibid.* xiv. 2624.

[3] Bahlson, *Bull. Soc. Chim.* xxxi. 539.

5th. The ketones containing methyl are converted by distillation with sulphuric acid into aromatic hydrocarbons, which contain three alcohol radicals in symmetrical position :—

$$3CH_3.CO.CH_3 = C_6H_3(CH_3)_3 + 3H_2O.$$
$$3CH_3.CO.C_2H_5 = C_6H_3(C_2H_5)_3 + 3H_2O.$$
$$3CH_3.CO.C_3H_7 = C_6H_3(C_3H_7)_3 + 3H_2O.$$

6th. Aromatic hydrocarbons occur in many balsams and ethereal oils, as well as in certain petroleums. They are formed by the dry distillation of organic substances, and hence they occur in wood-tar and in larger quantities in coal-tar, in which we find benzene, toluene, dimethylbenzenes, trimethylbenzenes, and a large number of other aromatic compounds.

In a memoir on the products obtained in the preparation of illuminating gas from resin, Pelletier and Walter so early as the year 1838 remark, that chemical operations conducted on the large scale offer opportunities for observing phenomena, investigating laws, and preparing new products which do not present themselves in laboratory experiments. Chemical industry, largely indebted to theory for its progress, repays the chemist whose assistance she needs, by presenting him with new compounds for investigation and thus science is widened and industry developed. In this way the manufacture of coal-gas has enriched organic chemistry with many new compounds, whose investigation has proved of the greatest interest. But for coal-gas Faraday's liquid hydrocarbons, butylene and benzene, Kidd's naphthalene and Dumas and Laurent's paranaphthalene (anthracene) would still have to be discovered.[1]

Pelletier and Walter discovered toluene in the oil obtained from distillation of resin. This body, together with its homologues, benzene, naphthalene, anthracene, are now obtained from coal-tar on the large scale. This black, tarry and foully smelling substance, an essential product of the coal-gas manufacture, and formerly a noxious and useless article, has now become not only of the greatest importance to the colour manufacturer but most valuable to the scientific chemist, as a means of carrying on the investigation of interesting and important bodies to an extent which would have been impossible but for the introduction of the gas manufacture. For this coal-tar has proved a source, as yet inexhaustible, of new aromatic compounds, from which valuable materials, such as the colouring matter of madder

[1] *Ann. Chim. Phys.* lxvii. 269.

and indigo, bodies previously only known as natural products, can now be artificially prepared.

Additive Products of the Aromatic Compounds.—When benzene and its homologues are heated to 280° with fuming hydriodic acid they combine with six atoms of hydrogen and give rise to a homologous series whose members are isomeric with the olefines.[1]

Hexhydrobenzene . . .	C_6H_{12}.
Hexhydromethylbenzene .	C_7H_{14}.
Hexhydrodimethylbenzene	C_8H_{16}. &c.

These bodies are distinguished from the olefines inasmuch as they do not combine directly with bromine, this element forming with them substitution products. The constitution of the compounds thus produced corresponds to that of the chlorine and bromine additive products which have been already described; like these they contain six carbon atoms in a closed ring, but connected by single linkages. These hydrocarbons are found in Baku petroleum,[2] and also probably, together with paraffins and with hydrocarbons of the benzene series, in that of Galicia.[3]

According to Markownikow and Oglobin, the hydrocarbons which occur in Caucasian petroleum are not hydrogen addition products of benzene and its homologues, but consist of a peculiar group of bodies, to which they gave the name of naphthenes.[4]

Ethereal oils contain hydrocarbons having the common formulæ $C_{10}H_{16}$, and termed terpenes; these stand in close connection with cymene or propylmethylbenzene, $C_{10}H_{14}$, and behave as hydrogen additive-products of this body.

DERIVATIVES OF AROMATIC HYDROCARBONS.

920 *Halogen Substitution Products.*—Derivatives may be obtained from aromatic hydrocarbons by replacing hydrogen either in the side chain or in the aromatic nucleus. We have already seen that in the first case chlorine is very powerfully combined, inasmuch as it cannot be removed by alkalis, silver salts, sodium sulphite, ammonia, etc.; on the other hand, the compounds obtained by substitution in the side chain react like the chlorides of radicals of the fatty group.

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[1] Wreden, *Liebig's Ann.* clxxxvii. 168.

[2] Beilstein and Kurbatow, *Ber. Deutsch. Chem. Ges.* xiii. 1818; xiv. 1620.

[3] Lachowicz, *Liebig's Ann.* ccxx. 188.

[4] *Ber. Deutsch. Chem. Ges.* xvi. 1873.

When benzene is treated by chlorine alone no regular substitution takes place, but if a small quantity of iodine be added it takes place quietly and step by step, the iodine acting as a carrier of the chlorine in consequence of the constant formation and decomposition of iodine chloride.[1] In this reaction some iodobenzene is always formed. In order to replace the last atoms of hydrogen, antimony chloride is advantageously employed as a carrier of chlorine (H. Müller). The reaction takes place even more easily and regularly if one per cent. of molybdenum chloride be employed instead of iodine.[2]

Chlorine reacts upon the homologues of benzene in a peculiar way; if this gas be passed through the liquid in the cold, substitution only takes place in the nucleus; but in presence of iodine and antimony chloride this same substitution occurs whether the saturation takes place in the cold or at the boiling point; if, however, free chlorine be allowed to act alone upon the boiling hydrocarbon, a replacement of hydrogen in the side chain is alone effected. If the mixture be allowed to cool, substitution again occurs in the nucleus; on heating a second time the chlorine reverts to the side chain. Thus we obtain as final products from toluene, tetrachlorobenzenyl trichloride, $C_6HCl_4.CCl_3$, and pentachlorobenzidene dichloride, $C_6.Cl_5.CHCl_2$. If an attempt be made further to chlorinate these bodies in presence of iodine, a decomposition into hexchlorobenzene, C_6Cl_6, and tetrachloromethane, CCl_4, takes place.[3] The homologues of toluene exhibit quite a similar behaviour, and when thoroughly chlorinated yield the two chlorides of carbon as final products.[4]

Bromine acts in the same manner as chlorine, only less quickly. In the cold, or in presence of iodine, the bromine takes its place in the nucleus: at the boiling point it appears in the side chain. As commercial bromine frequently contains iodine, it must be purified by distillation with potassium bromide when a substitution in the side chain has to be effected.[5] If bromine containing iodine be heated with benzene homologues, the formation of hexbromobenzene and tetrabromobenzene is observed.

Iodine cannot effect a direct substitution, but if benzene be

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[1] Hugo Müller, *Journ. Chem. Soc.* xv. 41.

[2] Aronheim, *Ber. Deutsch. Chem. Ges.* viii. 1400.

[3] Beilstein and Geitner, *Ann. Chem. Pharm.* cxxxix. 331.

[4] Krafft and Merz, *Ber. Deutsch. Chem. Ges.* viii. 1296.

[5] Thorpe, *Proc. Roy. Soc.* xviii. 123.

heated with iodine and iodic acid to a temperature of from 200 to 240° the following reaction occurs:

$$5C_6H_6 + HIO_3 + 2I_2 = 5C_6H_5I + 3H_2O.$$

In this case part of the benzene is oxidized by the iodic acid to carbon dioxide and water.[1] The iodine substitution products of the aromatic hydrocarbons are far more easily obtained by the action of hydriodic acid on the diazo-compounds. They are as stable as the chlorine and bromine derivatives, which latter may also be obtained by means of the diazo-reaction. Halogen substitution products of the aromatic hydrocarbons are also formed by action of phosphorus compounds of the halogens on phenol, or the aromatic alcohols; they may likewise be obtained from substituted acids, by heating the same with lime or baryta.

Nitro-Substitution Products are formed by the action of concentrated nitric acid on hydrocarbons, when nitroxyl, NO_2, replaces the hydrogen in the aromatic nucleus but not in the side chain.[2] When the action takes place in the cold, the mono-nitro compound is easily formed; when heated, or when a mixture of nitric and sulphuric acids is employed, higher substitution products are obtained. The larger the number of side chains which a compound contains, the more readily does the nitration take place, and the action may be moderated by previously dissolving the substance in glacial acetic acid.

The halogen substitution products are in like manner converted into nitro-compounds by the action of nitric acid; but if, on the other hand, the nitrated hydrocarbons be treated with chlorine or bromine, the reactions take place only on warming, and then the halogen takes the place of the nitroxyl group. The substitution is aided by the presence of iodine, and, as in the case of chlorine, the action takes place more readily in presence of antimony chloride.

921 *Sulphonic Acids.*—By acting with concentrated or fuming sulphuric acid on the hydrocarbons, or on their halogen substitution products, &c., monosulphonic acids or disulphonic acids are formed, the substitution taking place in the nucleus:

$$C_6H_6 + SO_2(OH)_2 = C_6H_5SO_2.OH + H_2O.$$
$$C_6H_5.CH_3 + 2SO_2(OH)_2 = C_6H_3(SO_2.OH)_2CH_3 + 2H_2O.$$

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[1] Kekulé, *Ann. Chem. Pharm.* cxxxvii. 161.

[2] Some compounds containing two carbon atoms in double linkage in the side chain form an exception, such as styrolene or phenylethylene, $C_6H_5.CH{=}CH_2$, which becomes converted by nitric acid into phenylnitroethylene, $C_6H_5.CH{=}CHNO_2$.

Trisulphonic acids are formed by heating with sulphuric acid and phosphorus pentoxide. Chlorosulphonic acid, $SO_2Cl(HO)$, acts in a similar way to sulphuric acid;[1] it may also be employed for the preparation of trisulphonic acids.[2]

The sulphonic acids of the aromatic group closely resemble those of the members of the fatty group and, like these, are easily soluble in water. On heating, they split up into sulphur trioxide and the original hydrocarbon, and this reaction may be employed for separating aromatic hydrocarbons from those containing more hydrogen. In cases, such as that of coal-tar, when the two series occur together,[3] this reaction depends on the fact that hydrocarbons rich in hydrogen are either, like the paraffins, unattacked by sulphuric acid or, like the olefines, either converted into the acid sulphates of the alcohol radicals or polymerised. When the sulphomic acids undergo dry distillation they always yield by-products, which diminish the yield of the hydrocarbon; better results are obtained when the sulphonic acid is dissolved in concentrated sulphuric acid and the mixture then treated with superheated steam.[4]

When acted upon by phosphorus pentachloride the sulphonic acids yield sulpho-chlorides and these are converted by zinc into sulphinic acids such as $C_6H_5SO_2H$; these are also readily formed by leading sulphur dioxide into a mixture of a hydrocarbon and aluminium chloride:[5]

$$C_6H_6 + SO_2 = C_6H_5SO_2H.$$

They readily take up oxygen again and are converted into sulphonic acids.

922 *Phenols.*—This name is applied to compounds containing one or more hydroxyls in the nucleus. They are obtained by fusing a sulphonic acid with caustic potash thus:

$$C_6H_5.SO_3K + HOK = C_6H_5OH + SO_3K_2.$$

They are also formed from amido-compounds by the action of aqueous nitrous acid:

$$C_6H_5.NH_2 + HO.NO = C_6H_5.OH + H_2O + N_2.$$

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[1] Beckurts and Otto, *Ber. Deutsch. Chem. Ges.* xi. 2061.
[2] Claeson, *Ibid.* xiv. 307.
[3] Beilstein, *Ann. Chem. Pharm.* cxxxiii. 34.
[4] Armstrong and Miller, *Journ. Chem. Soc.* 1884, ii. 148.
[5] Friedel and Crafts, *Compt. Rend.* lxxxvi. 1368.

In this case, however, the diazo-compound is formed as an intermediate product.

Aromatic oxyacids which contain an hydroxyl in the nucleus decompose when heated alone or with baryta into carbon dioxide and a phenol; this same decomposition takes place on heating with hydrobromic or hydriodic acids; thus salicylic acid readily yields common phenol or monohydroxybenzene:

$$C_6H_4\begin{cases}OH\\CO_2H\end{cases} = C_6H_5.OH + CO_2.$$

This substance is found, together with other phenols and their methyl ethers, in wood-tar and coal-tar. Thymol, $C_6H_3(OH)CH_3(C_3H_7)$, is a phenol which occurs as a constituent in a large number of ethereal oils. The phenols exhibit in certain relations strong analogies with the alcohols, and indeed were formerly classed amongst them.

In other respects, however, they differ from them very distinctly—*e.g.* the hydrogen of the hydroxyl is very easily replaced by metals. In order to prepare sodium ethylate, C_2H_5ONa, alcohol must be treated with sodium, whereas sodium phenate is formed at once by action of caustic soda upon phenol. A very characteristic reaction of the phenols is their behaviour with nitric and sulphuric acids. They do not form any acid ethers (or ethereal salts) with these acids, but yield substitution products, and these are more readily formed than is the case with the hydrocarbons; thus we obtain nitrophenol, $C_6H_4(NO_2)OH$, phenolsulphonic acid, $C_6H_4(OH)SO_3H$, &c. Whilst the nitro-hydrocarbons are only attacked by chlorine and bromine with difficulty, the nitrophenols readily yield substitution products. The phenols are moreover distinguished from the alcohols by the fact that they withstand the action of acid oxidizing agents, though in alkaline solutions they absorb oxygen, and those which contain many hydroxyls readily reduce the salts of the noble metals. These and similar reactions are of a complicated character, and greatly differ from the simple oxidation of the alcohols.

Phenol Ethers are obtained by heating the phenols with caustic potash and the alcoholic iodides:

$$C_6H_5OK + CH_3I = C_6H_5OCH_3 + KI.$$

By heating with the hydracids these bodies are converted into phenol and a haloid ether. They are acted upon by the elements of the chlorine group, nitric acid, sulphuric acid, and chromic acid, exactly as the hydrocarbons are; thus cresolmethyl ether, $C_6H_4\begin{cases} OCH_3 \\ CH_3, \end{cases}$ yields on oxidation methyloxybenzoic acid, $C_6H_4\begin{cases} OCH_3 \\ CO_2H. \end{cases}$

The acid phenol ethers are obtained by the action of chlorides or oxides of the acid radicals on the phenols:[1]

$$C_6H_5.OH + (C_2H_3O)_2O = C_6H_5.O.C_2H_3O + (C_2H_3O)OH.$$

They are very readily saponified by alkalis. The phenols when heated with zinc-dust are reduced to hydrocarbons:

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

Phenol ethers, on the other hand, may be distilled over zinc-dust without undergoing change. Neutral ferric chloride colours aqueous solutions of the phenols violet, blue, red, or green, but not that of its ethers. Many oxyacids which are at the same time phenols likewise exhibit this reaction.[2]

If a phenol be shaken with a solution of potassium nitrite in concentrated sulphuric acid (Liebermann's reagent) the solution first becomes brown, then green, and finally a bright blue.[3]

When the hydrogen in the nucleus of a phenol is substituted by a halogen or by nitroxyl, or other electro-negative radicals, its acid character becomes more marked; thus trinitrophenol or picric acid, $C_6H_2(NO_2)_3OH$, possesses all the properties of a powerful monobasic acid.

In addition to phenols containing one hydroxyl, others are known containing two and three hydroxyls; thus we are acquainted with three dihydroxybenzenes, $C_6H_4(OH)_2$, viz., pyrocatechol, resorcinol, and hydroquinol.

Thiophenols are obtained by the action of phosphorus pentasulphide on phenols; or, better, by treating the sulphonic chlorides with zinc and dilute sulphuric acid. Like mercaptans these are unpleasantly-smelling bodies, readily forming metallic salts or mercaptides.

On oxidation they are easily converted into sulphides and disulphides; thus ordinary thiophenol, C_6H_5SH, yields $(C_6H_5)_2S$ and $(C_6H_5)_2S_2$.

The monosulphides are oxidized by chromic acid solution to sulphones, such as diphenylsulphone, $(C_6H_5)_2SO_2$. These

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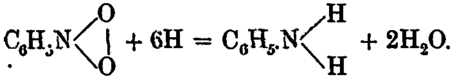
[1] Baeyer, *Ann. Chem. Pharm.* cxl. 295.
[2] H. Schiff, *ibid.* clxix. 161.
[3] Liebermann, *Ber. Deutsch. Chem. Ges.* vii. 248, 1098.

bodies are also obtained by the action of sulphur trioxide on a hydrocarbon, and are also produced together with a hydrocarbon when a sulphonic acid undergoes dry distillation.

923 *Amido-Compounds* are formed by the action of nascent hydrogen on nitro-compounds; thus from nitrobenzene we obtain aniline or amidobenzene:



$$C_6H_5N\left\langle\begin{matrix}O\\ |\\ O\end{matrix}\right. + 6H = C_6H_5.N\left\langle\begin{matrix}H\\ \\ H\end{matrix}\right. + 2H_2O.$$

Aniline and its homologues, such as toluidine or amidotoluene, $C_6H_4(CH_3)NH_2$, were formerly classed as amines. They are, however, as different from these as phenols are from alcohols, and hence Griess proposed to call them amido-compounds.[1]

They are only weak bases, although they combine readily with acids to form salts which easily crystallize but exhibit an acid reaction. On the other band benzylamine, $C_6H_5.CH_2NH_2$, an isomeride of toluidine, is a strong caustic liquid, miscible with water, possessing a powerful alkaline reaction, and rapidly absorbing carbon dioxide from the air. Aniline and its homologues, on the contrary, are only slightly soluble in water, possess an aromatic smell, exhibit no alkaline reaction, and do not form carbonates.

These bodies resemble the amines, however, inasmuch as the hydrogen of the amido-group can be replaced by alcohol radicals by the action of the haloid salts of the latter. The action of nitrous acid on the amido-bases is characteristic. The primary amines such as aniline are thus converted into phenols, as the primary amines are into alcohols. The secondary amides when treated with nitrous acid also behave as secondary amines do, thus methylaniline, $C_6H_5N(CH_3)H$, is converted into nitrosomethylaniline, $C_6H_5N(CH_3)NO$. The action of this same reagent on the tertiary compounds is, however, very different, the amines not being attacked, whilst in the amido-compounds nitrosyl replaces hydrogen in the nucleus; thus, from dimethylaniline we obtain nitrosodimethylaniline:

$$C_6H_4(NO)N(CH_3)_2.$$

The tertiary bases combine readily with the iodides of the alcohol radicals to form ammonium iodides and these are decomposed by moist silver oxide, with formation of strong alkaline and caustic hydroxides.

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[1] *Ann. Chem. Pharm.* cxxi. 258.

Secondary and tertiary bases are also formed when aniline hydrochloride is heated with methyl alcohol or other alcohols to from 250° to 300°. In this case the chloride of the alcohol radical is, doubtless, first produced. When wood-spirit is employed other bases containing the hydrogen in the nucleus replaced by methyl are produced in addition to methylaniline and dimethylaniline. Thus Hofmann and Martius found in the material which is prepared on the large scale for the manufacture of colours, dimethyltoluidine, $C_6H_4(CH_3)N(CH_3)_2$, dimethylxylidine, $C_6H_3(CH_3)_2N(CH_3)_2$ and dimethylcumidine, $C_6H_2(CH_3)_3N(CH_3)_2$.[1] In addition to these a non-volatile diacid base, $C_{10}H_{26}N_2$, occurs together with hexmethylbenzene.[2]

When trimethylphenyl ammonium iodide, $C_6H_5N(CH_3)_3I$, is heated to from 220° to 230°, two dimethyltoluidines are formed, together with a methylxylidine and dimethylxylidine; whilst at higher temperatures such as 335°, or the melting-point of lead, cumidine, $C_6H_2(CH_3)_3NH_2$,[3] is chiefly formed. At this temperature methylaniline hydrochloride passes into toluidine,[4] whilst ethylaniline, $C_6H_5N(C_2H_5)H$, is converted into amido-ethylbenzene, $C_6H_4(C_2H_5)NH_2$, and amylaniline, $C_6H_5N(C_5H_{11})H$, into amido-amylbenzene, $C_6H_4(C_5H_{11})NH_2$.[5] Xylidine hydrochloride when heated with methyl alcohol to from 250° to 300° is converted into cumidine.[6]

The hydrogen of the amido-group in the primary and secondary bases can be replaced by treatment with the chlorides or nitrates of the alcohol radicals. In the case of the tertiary compounds, no action of this kind can of course occur, and hence this reaction is employed for the separation of secondary and tertiary compounds which are often formed together.

The hydrogen in the nucleus of the amido-compounds can also be replaced by the halogen and nitroxyl groups, when the basic character of the original compound is weakened. This also occurs when the hydrogen of the amido-group in aniline is replaced by phenyl, thus diphenylamine, $(C_6H_5)_2NH$, yields salts which are decomposed by water, whilst triphenylamine, $(C_6H_5)_3N$, does not combine with acids.

The dinitro-substitution products of the aromatic hydrocarbons are converted by nascent hydrogen into diacid bases; such as diamidobenzene or phenylenediamine, $C_6H_4(NH_2)_2$,

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[1] *Ber. Deutsch. Chem. Ges.* iv. 742.

[2] *Ibid.* vi. 345.

[3] Hofmann, *Ibid.* v. 704.

[4] *Ibid.* v. 720.

[5] *Ibid.* vii. 526.

[6] *Ibid.* xiii. 1730.

which exists in three modifications. The nitrophenols are thus converted into amidophenols, which do not combine with bases to form salts, but unite with acids.

924 *Azo-Compounds* are formed under certain conditions by the reduction of nitro-substitution products; thus azobenzene, $C_{12}H_{10}N_2$, is obtained from nitrobenzene by acting upon it with caustic soda and zinc-dust, or by treating it in alcoholic solution with sodium amalgam:

$$\begin{array}{l} C_6H_5.NO_2 \\ C_6H_5.NO_2 \end{array} + 8H = \begin{array}{l} C_6H_5N. \\ \quad\;\; \| \\ C_6H_5.N \end{array} + 4H_2O.$$

The same body is also produced when aniline undergoes moderate oxidation:

$$\begin{array}{l} C_6H_5.NH_2 \\ C_6H_5.NH_2 \end{array} + 2O = \begin{array}{l} C_6H_5.N \\ \quad\;\; \| \\ C_6H_5.N \end{array} + 2H_2O.$$

This compound unites with nascent hydrogen to form hydrazobenzene, $C_{12}H_{10}(NH)_2$, which by further reduction yields aniline.

The hydrazo-compounds are colourless, whilst the azo-compounds have a yellow or red colour; but they do not possess the properties of colouring matters if they only contain hydrogen in the nucleus. If, however, this is replaced by hydroxyl, by an amido-group, &c., the *azo-colours* are formed, many of which are now made on the large scale, and concerning which more will be said in the sequel.

925 *Diazo-Compounds.*—These bodies form one of the most characteristic and important series of the aromatic group and possess a great theoretical as well as practical interest. They were discovered by Griess, who obtained them by action of nitrous acid on the amido-compounds. The action of this acid on ammonia is as follows:

$$NH_3 + NO.OH = N_2 + 2H_2O.$$

Now Piria found in 1849 that by the action of nitrous acid, asparagine, or amidosuccinamic acid, is converted into malic acid:

$$C_2H_3(NH_2)\left\{\begin{array}{l} CO.NH_2 \\ CO.OH \end{array}\right. + 2NO.OH = 2N_2 + C_2H_3(OH)\left\{\begin{array}{l} CO.OH \\ CO.OH \end{array}\right. \\ + 2H_2O.$$

Soon after this, Strecker in like manner obtained glycollic acid from amidoacetic acid, and now we know that all amido-compounds and amines are acted upon in a similar manner.

Analogous reactions had also been observed in the aromatic group. Thus Hunt in 1849 found that nitrous acid converted aniline into phenol.[1] This latter substance is, however, more easily formed if aniline hydrochloride be treated with silver nitrite;[2]

$$C_6H_5.NH_2 + NO.OH = N_2 + C_6H_5OH + H_2O.$$

In a similar way Gerland in 1853 prepared oxybenzoic acid, $C_6H_4(OH)CO_2H$, from amidobenzoic acid, $C_6H_4(NH_2)CO_2H$.[3]

Griess then showed in a series of researches, which have become classical, that when nitrous acid acts upon the aromatic amido-compounds no nitrogen is evolved, but that the resulting compounds contain the nitrogen both of the nitrous acid and of the amido-group, and that they very readily part with this nitrogen, frequently with explosive violence, though when treated with certain reagents they are converted into compounds the formation of which had been previously observed.[4]

By acting with nitrous acid on an aqueous solution of aniline nitrate, Griess obtained diazobenzene nitrate, its formation being represented as follows:

$$C_6H_7N.HNO_3 + NHO_2 = C_6H_4N_2.HNO_3 + 2H_2O.$$

According to Kekulé's view, now generally accepted by chemists, the group N_2 is dyad and has the following constitution: $-N{=}N-$. The formation of diazobenzene nitrate is then represented as follows:

$$C_6H_5.NH_3.O.NO_2 + NO_2H = C_6H_5.N{=}N.ONO_2 + 2H_2O.$$

Other chemists uphold the view that diazo-compounds contain pentad nitrogen.[5]

By acting with sulphuric acid on the nitrate, acid diazobenzene sulphate, $C_6H_5.N_2.SO_4H$, is obtained, and this is better suited for most reactions inasmuch as nitric acid is apt to yield nitro-products. In many cases, however, it is not necessary

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[1] *Jahresb.* 1849, 391; *Ann. Chem. Pharm.* lxxvi. 285.

[2] Hofmann, *ibid.* lxxv. 359.

[3] *Ibid.* lxxxvi. 143.

[4] Kekulé, *Lehrb.* ii. 703.

[5] Strecker, *Ber. Deutsch. Chem. Ges.* iv. 786; Erlenmeyer, *ibid.* vii. 1110; Blomstrand, *ibid.* viii. 51.

to use the pure salt, but the amido-compound may be dissolved in the requisite quantity of dilute sulphuric acid and the theoretical amount of potassium nitrite gradually added in aqueous solution.[1] The product is then boiled with water, when a phenol is formed:

$$C_6H_5.N_2.SO_4H + H_2O = C_6H_5OH + N_2 + SO_4H_2.$$

Hydriodic acid decomposes the salts of diazobenzene easily with formation of iodine substitution products, which are best obtained in this way:

$$C_6H_5.N_2.SO_4H + HI = C_6H_5I + N_2 + SO_4H_2.$$

Hydrobromic acid does not act so readily. If the diazo-salt be treated at the same time with hydrobromic acid and bromine, a diazobenzene perbromide is formed, which is easily decomposed on heating with alcohol:

$$C_6H_5.NBr-NBr_2 + C_2H_6O = C_6H_5Br + 2HBr + N_2 + C_2H_4O.$$

Hydrochloric acid acts with still greater difficulty on the diazo-salt, but if hydrochloric acid, platinic chloride and alcohol be added to its solution, a platinic chloride compound is precipitated, which on heating with caustic soda decomposes as follows:

$$(C_6H_5N_2)_2PtCl_6 = 2C_6H_5Cl + N_2 + Pt + 2Cl_2.$$

If the diazo-salt be boiled with absolute alcohol the corresponding hydrocarbon is produced:

$$C_6H_5.N_2.SO_4H + C_2H_6O = C_6H_6 + N_2 + SO_4H_2 + C_2H_4O.$$

Phenol ether is however often thus produced and sometimes in large quantity:[2]

$$C_6H_5.N_2.SO_4H + C_2H_5.OH = C_2H_5.O.C_6H_5 + N_2 + SO_4H_2.$$

Instead of converting the amido-compounds into diazo-salts, it is often possible to replace the amido-group directly by hydrogen. This is accomplished by heating the base with alcohol saturated with nitrogen trioxide and therefore containing ethyl nitrite, when the diazo-compound is first formed, but afterwards decomposed by the alcohol. In many cases the yield of hydrocarbon is only small, as a large quantity of resin is produced;

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[1] Meyer and Ambühl, *Ber. Deutsch. Chem. Ges.* viii. 1074.

[2] Haller, *ibid.* xvii. 1887; Hofmann, *ibid.* xvii. 1917.

this however may be avoided by decomposing the diazo-chloride with stannous chloride as follows:

$$C_6H_5.N_2Cl + H_2O + SnCl_2 = C_6H_6 + N_2 + SnOCl_2 + HCl.$$

926 *Diazoamido-Compounds* are formed when nitrous acid acts upon an alcoholic solution of a base, such as aniline, which must be present in excess, and also when a base is brought in contact with a diazo-salt in an aqueous or alcoholic solution:

$$C_6H_5N{=}NCl + NH_2.C_6H_5 = C_6H_5N{=}N.NH(C_6H_5) + HCl.$$

A large number of diazoamido-compounds can be prepared from other bases and diazo-salts. These are not colourless like the diazo-salts but possess a yellow tint; they do not combine with acids but form double platinum chlorides. They are converted into diazo-compounds by the further action of nitrous acid; when heated with water or acids they undergo a similar decomposition to the diazo-salts, amido bases being formed at the same time:

$$C_6H_5N_2.NH.C_6H_5 + H_2O = C_6H_5.OH + NH_2.C_6H_5 + N_2.$$

Some of these bodies readily pass into the isomeric amidoazo compounds. In the case of diazoamidobenzene this change occurs when its alcoholic solution is allowed to stand for a few days; the reaction takes place more readily if some aniline hydrochloride be added to the solution.[1] In this reaction the aniline residue $C_6H_4.NH_2$ takes the place of $NH.C_6H_5$; but as aniline hydrochloride is formed in the reaction, a small quantity of this salt is sufficient to convert a large quantity of diazoamidobenzene into amidoazobenzene:

$$\begin{gathered} C_6H_5.N{=}N.NH.C_6H_5 + (C_6H_5)NH_2.ClH = \\ C_6H_5.N{=}N.C_6H_4.NH_2 + NH_2(C_6H_5)ClH. \end{gathered}$$

Other diazo-compounds undergo similar changes more or less easily according to their constitution; thus diazopara-amidotoluene prepared from paratoluidine $C_6H_4(CH_3)NH_2$ is not converted by contact with a hydrochloride of this last-named salt into an amidoazotoluene as are the corresponding compounds prepared from the two isomeric toluidines, which are at once converted by nitrous acid into amidoazo-compounds. The same holds good for the homologues of this body and for other amido-compounds not containing hydrogen in the para position, compounds in this case being formed, of which many belong to the class of the azo-colours.

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[1] *Zeitschr. Chem.* 1866, 689.

When phenol acts upon diazobenzene *sulphate*, diphenyl oxide is produced.

$$C_6H_5.N_2.SO_4H + HO.C_6H_5 = N_2 + SO_4H_2 + C_6H_5.O.C_6H_5.$$

If, however, potassium phenate be used, oxyazobenzene is obtained:

$$C_6H_5.N_2.NO_3 + KO.C_6H_5 = KNO_3 + C_6H_5.N_2.C_6H_4OH.$$

A series of oxyazo-compounds, also used as colours, has recently been obtained from diazo-salts and alkaline solutions of phenols or their sulphonic acids.

Azylines are formed by the action of nitric oxide on tertiary amido-compounds, which are then partly oxidized:

$$2C_6H_5.(CH_3)_2N + 2NO = (CH_3)_2NC_6H_4.N{=}N.C_6H_4.N(CH_3)_2.$$

These are strong bases possessing well crystallizable coloured salts.

Diazoamines are formed when a diazo-salt acts on primary and secondary amines.[1]

Diazobenzene-ethylamine.

$$C_6H_5.N_2.NO_3 + H_2N.C_2H_5 = C_6H_5.N_2.NH.C_2H_5. + NO_3H.$$

Diazobenzene-dimethylamine.

$$C_6H_5.N_2.NO_3 + HN(CH_3)_2 = C_6H_5.N_2.N(CH_3)_2 + NO_3H.$$

These are converted into the isomeric amidoazo-compounds, but corresponding mixed nitroazo-compounds are known which are formed when the sodium compound of a nitro-paraffin is brought in contact with a diazo-salt.[2]

Azophenylnitroethyl.

$$C_6H_5.N_2.NO_3 + NaC_2H_4.NO_2 = C_6H_5.N_2.C_2H_4.NO_2 + NaNO_3.$$

The reactions of these bodies resemble those of the other azo-compounds; they are yellow colouring matters.

927 *Hydrazines* are formed by the action of an excess of acid potassium sulphite on a diazo-salt:[3]

$$\begin{aligned}&C_6H_5.N{=}N.NO_3 + 3KHSO_3 =\\&C_6H_5.NH{-}NHSO_3K + KHSO_4 + KNO_3 + SO_2.\end{aligned}$$

In this reaction the potassium salt of phenylhydrazinesulphonic acid is first formed, and this converted by boiling with hydrochloric acid into phenylhydrazine hydrochloride:

$$C_6H_5.N_2H_2.SO_3K + HCl + H_2O = C_6H_5.N_2H_3.ClH + KHSO_4.$$

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[1] Baeyer and Jager, *Ber. Deutsch. Chem. Ges.* viii. 148.
[2] Meyer and Ambuhl, *ibid.* viii. 751, 1073.
[3] E. Fischer, *Liebig's Ann.* cxc. 67.

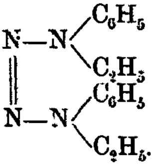
Hydrazines are also formed when a diazoamido-compound is treated with zinc-dust and acetic acid:

$$C_6H_5.N{=}N.NH.C_6H_5 + 4H = C_6H_5NH-NH_2 + H_2N.C_6H_5.$$

Secondary hydrazines are formed in a similar way from nitroso-bases; nitrosodiphenylamine yields diphenylhydrazine:

$$(C_6H_5)_2N-NO + 4H = (C_6H_5)_2N-NH_2 + H_2O.$$

Asymmetrical ethylphenylhydrazine, $C_6H_5N(C_2H_5)-NH_2$, is formed from nitrosoethylaniline. The same compound is also formed together with asymmetrical ethylphenylhydrazine, $(C_6H_5)NH-NH(C_2H_5)$, by the action of ethylbromide on phenylhydrazine. This latter compound is oixdized by mercuric oxide to azophenylethyl, $C_6H_5N=NC_2H_5$, and this compound unites with hydrogen to form the original compound, which may therefore be called hydrazophenylethyl.[1] The asymmetrical compound yields on oxidation with mercuric oxide, diethyldiphenyltetrazon, a body having the following composition:



The aromatic hydrazines resemble the same class of compounds belonging to the fatty series, and are, however, monacid bases. Aromatic compounds are also known containing phosphorus, arsenic, silicon and metals.

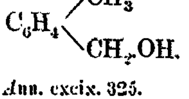
928 *Aromatic Alcohols and Acids.*—Aromatic alcohols are formed by replacement of hydrogen in the side chain of the hydrocarbon by hydroxyl; their mode of preparation corresponds exactly to that employed in the preparation of the alcohols of the fatty group, and, as in this latter case, primary, secondary and tertiary aromatic alcohols are known as well as those containing divalent and polyvalent radicals.

Phenylethyl alcohol.
$C_6H_5.CH_2.CH_2.OH.$

Phenyldimethyl carbinol.
$C_6H_5.C(OH)(CH_3)_2.$

Phenylmethyl carbinol.
$C_6H_5.CH(OH)CH_3.$

Tolyl alcohol.



$C_6H_4{<}^{CH_3}_{CH_2.OH.}$

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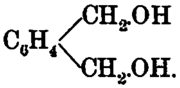
[1] Fischer and Erhard, *Liebig's Ann.* ccxix. 325.

Phenylethylene glycol.

$C_6H_5.CH(OH)CH_3.OH.$

Tolylene glycol.

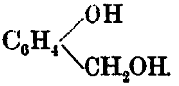


$$C_6H_4\begin{cases}CH_2.OH\\CH_2.OH.\end{cases}$$

Phenyl glycerol.

$C_6H_5.CH(OH)CH(OH)CH_2.OH.$

In these alcohols the hydrogen of the nucleus can be replaced by other elements or radicals and thus a series of compounds is obtained, which, on the one hand, act as fatty bodies, and on the other, like aromatic substances. Thus, some are known which are at once phenols and alcohols, to this class belongs orthoxybenzyl alcohol,



$$C_6H_4\begin{cases}OH\\CH_2OH.\end{cases}$$

Aromatic alcohols react with oxidizing agents in a manner depending on their constitution, as is the case with the fatty bodies corresponding to these.

929 *Aromatic Acids.*—These primary alcohols yield aldehydes and then acids, and these latter can be obtained according to other reactions characteristic of the bodies of the aromatic-group, viz:—

1st. They may be obtained from the hydrocarbons not only by oxidation of the side chain, but also synthetically by combination with carbon dioxide in presence of aluminium chloride.[1] Thus from benzene we obtain benzoic acid:

$$C_6H_6 + CO_2 = C_6H_5.CO_2H.$$

And if carbonyl chloride be employed in place of carbon dioxide benzyl chloride is formed:

$$C_6H_6 + COCl_2 = C_6H_5.COCl + HCl.$$

This cannot however be obtained in large quantity, as it acts further on the benzene with formation of diphenylketone,[2] $CO(C_6H_5)_2$.

2nd. Acids are obtained from monosubstitution products of the hydrocarbons by simultaneous action of sodium and carbon dioxide:[3]

$$C_6H_5Br + CO_2 + 2Na = C_6H_5.CO_2Na + NaBr.$$

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[1] Friedel and Crafts, *Compt. Rend.* lxxxvi. 1368.

[2] Friedel, Crafts, and Ador, *Ber. Deutsch. Chem. Ges.* x. 1854.

[3] Kekulé, *Ann. Chem. Pharm.* cxxxvii. 178.

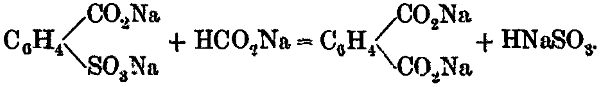
3rd. In place of carbon dioxide and sodium, ethylchloroformate and sodium amalgam may be used, when the ethyl ether is formed:[1]

$$C_6H_5Br + ClCO_2C_2H_5 + 2Na = C_6H_5.CO_2C_2H_5 + NaBr + NaCl.$$

4th. Monobasic acids are obtained from the sulphonic acids of hydrocarbons by heating them with sodium formate:

$$C_6H_5SO_3Na + HCO_2Na = C_6H_5CO_2Na + HNaSO_3.$$

If sulphobenzoic acid be employed, dibasic isophthalic acid is formed:[2]



$$C_6H_4\left\langle\begin{matrix}CO_2Na\\SO_3Na\end{matrix}\right. + HCO_2Na = C_6H_4\left\langle\begin{matrix}CO_2Na\\CO_2Na\end{matrix}\right. + HNaSO_3.$$

Isophthalic acid is also prepared by heating sodium bromobenzoate with sodium formate:[3]

$$C_6H_4Br.CO_2Na + 2CHO_2Na = C_6H_4(CO_2Na)_2 + NaBr + CH_2O_2.$$

5th. When an amido-compound is heated with oxalic acid formamide is obtained, thus phenylformamide or formanilide is obtained from aniline, which is converted on heating with hydrochloric acid into benzonitrile,[4] the carbamine which is at first formed suffering intermolecular change:

$$C_6H_5N(COH)H = C_6H_5.CN + H_2O.$$

6th. Amido-compounds can also be converted by Weith's method into acids, by preparing the thiocarbimide or mustard oil, and heating this with powdered or finely-divided copper:[5]

$$C_6H_5NCS + 2Cu = C_6H_5.CN + Cu_2S.$$

Aromatic nitriles are also formed when a sulphonic acid salt is heated with potassium cyanide,[6] as well as by the same reactions for the preparation of the nitriles of the fatty series. Like this latter class of bodies, they are converted into the corresponding acids by heating with alkalis or strong acids. Aromatic acids can also be synthetically obtained by means of the aceto-acetic ether, and the malonic acid reactions.

[1] Wurtz, *Ann. Chem. Pharm.* Suppl. vii. 125.
[2] V. Meyer, *Ber. Deutsch. Chem. Ges.* iii. 112.
[3] Ador and Meyer, *ibid.* iv. 259.
[4] Hofmann, *Ann. Chem. Pharm.* cxlii. 121.
[5] *Ibid.* vi. 210.
[6] Merz, *Zeitschr. Chem.* 1868, 33.

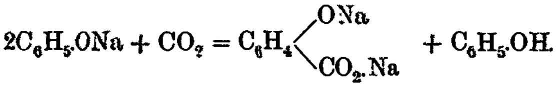
Aromatic acids containing less hydrogen corresponding to the acrylic acid series are formed, when aromatic aldehydes are heated with a sodium salt of a fatty acid together with a dehydrating substance such as acetic anhydride:

$$C_6H_5.COH + CH_3.CO_2H = \overset{\text{Cinnamic Acid.}}{C_6H_5.CH{=}CH.CO_2H} + H_2O.$$

In place of the salts of the fatty acids, those of malonic acid or of its homologues of analogous constitution may be employed, as these decompose into fatty acids and carbon dioxide.

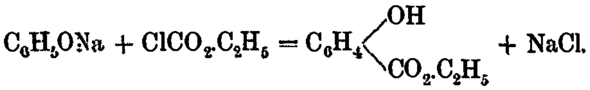
Aromatic oxyacids which are at the same time phenols, can be prepared from these bodies in various ways.

1st. Kolbe and Lautemann showed that when carbon dioxide and sodium simultaneously act upon phenol, salicylic acid or orthoxybenzoic acid is formed.[1] Kolbe then proved that this acid may be easily prepared by heating sodium phenate in a current of carbon dioxide to 180°:[2]



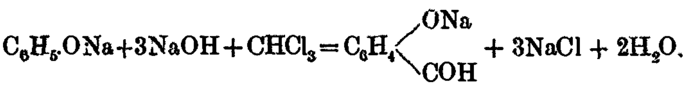
$$2C_6H_5.ONa + CO_2 = C_6H_4\begin{cases}ONa\\CO_2.Na\end{cases} + C_6H_5.OH.$$

2nd. Its *ethyl ether* is formed by the action of sodium on a mixture of phenol and ethylchloro-formate:[3]



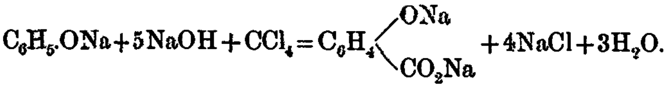
$$C_6H_5ONa + ClCO_2.C_2H_5 = C_6H_4\begin{cases}OH\\CO_2.C_2H_5\end{cases} + NaCl.$$

3rd. The aldehydes of these oxyacids are formed when a phenol is heated with caustic soda and chloroform:[4]



$$C_6H_5.ONa+3NaOH+CHCl_3=C_6H_4\begin{cases}ONa\\COH\end{cases} + 3NaCl + 2H_2O.$$

4th. If tetrachloromethane be employed instead of chloroform an acid is obtained:[5]



$$C_6H_5.ONa+5NaOH+CCl_4=C_6H_4\begin{cases}ONa\\CO_2Na\end{cases}+4NaCl+3H_2O.$$

5th. When an oxyacid is heated with caustic soda and

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[1] *Ann. Chem. Pharm.* cxv. 201.

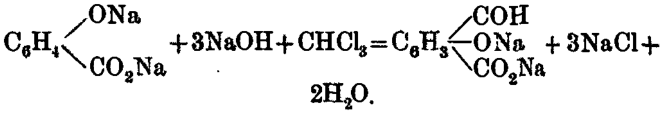
[2] *Journ. Prakt. Chem.* [2], x. 93.

[3] Wilm and Wischin, *Zeitschr. Chem.* 1868, vi.

[4] Reimer and Tiemann, *Ber. Deutsch. Chem. Ges.* ix. 824.

[5] *Ibid.* ix. 1285.

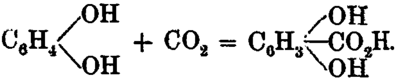
chloroform an aldehydo-acid is produced, and this is transformed on oxidation into a dibasic oxyacid.[1]



$$C_6H_4\left\langle\begin{matrix}ONa\\CO_2Na\end{matrix}\right. + 3NaOH + CHCl_3 = C_6H_3\left\langle\begin{matrix}COH\\ONa\\CO_2Na\end{matrix}\right. + 3NaCl + 2H_2O.$$

6th. Oxyacids are also formed when a sulphonic acid, such as sulphobenzoic acid, is fused with caustic potash.

7th. Certain dioxybenzenes are converted into dioxyacids when heated with ammonium carbonate and water to 110°. Thus resorcinol gives rise to a mixture of isomeric dioxybenzoic acids:[2]



$$C_6H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + CO_2 = C_6H_3\left\langle\begin{matrix}OH\\CO_2H.\\OH\end{matrix}\right.$$

ISOMERISM IN THE AROMATIC GROUP.

930 It has been already stated that experiment has shown that no isomeric mono-substitution products of benzene exist. It was indeed at one time thought that such bodies had been discovered, but careful investigation proved that in this case the observed differences were due to impurities.

Di-substitution products, on the other hand, can occur in three isomeric forms, and this conclusion is completely verified by experiment. The history of the di-substitution products is fully given in Richard Meyer's work entitled *Einleitung in das Studium der aromatischen Substanzen.* In this case also, some chemists assumed the existence of more than three modifications, but it turned out, as before, that, either on the one hand the bodies were impure, or mixtures of isomeric compounds, or, on the other, that the observed differences were due to physical isomerism, such as has been observed in the fatty group of bodies as well as in the case of inorganic compounds, and which in this instance is designated as dimorphism or trimorphism. When Kekulé proposed his theory, many substitution products of benzene were known, and amongst them several di-substitution products, such as certain derivatives of benzoic acid, which could be arranged in three classes according to their genetic relations. Kekulé gives the following

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[1] Reimer and Tiemann, *Ber. Deutsch. Chem. Ges.* ix. 1268.

[2] Senhofer and Brunner, *ibid.* xiii. 930.

arrangement, observing that in the condition of our knowledge at that time it was scarcely possible to determine the positions which the elements or radicals replacing the hydrogen in benzene occupy, with any degree of certainty.[1]

	(1)	(2)	(3)
$C_6H_4\left\{\begin{matrix}Cl\\CO_2H\end{matrix}\right.$ —	Chlorodracylic acid.	Chlorosalicylic acid.	Chlorobenzoic acid.
$C_6H_4\left\{\begin{matrix}OH\\CO_2H\end{matrix}\right.$ —	Para-oxybenzoic acid.	Salicylic acid.	Oxybenzoic acid.
$C_6H_4\left\{\begin{matrix}NH_2\\CO_2H\end{matrix}\right.$ —	Amidodracylic acid.	Anthranilic acid.	Amidobenzoic acid.

The members of the last series are direct derivatives of benzoic acid; by the action of nitric acid, nitrobenzoic acid, $C_6H_4(NO_2)CO_2H$, is obtained, and this on reduction is converted into amidobenzoic acid: this again is converted into oxybenzoic acid by the action of nitrous acid, from which chlorobenzoic acid is obtained by the diazo-reaction. It has already been stated that anthranilic acid is obtained by heating indigo with caustic potash; by the action of nitrous acid this is converted into the earlier known salicylic acid, and the latter substance when acted upon with phosphorus pentachloride and water yields chlorosalicylic acid. The members of the first series are obtained from toluene, $C_6H_5.CH_3$, by conversion first by nitric acid into nitrotoluene, $C_6H_4(NO_2)CH_3$, and then by oxidation into nitrodracylic acid, from which chlorodracylic acid is obtained in the same way as chlorobenzoic acid from nitrobenzoic acid. Para-oxybenzoic acid was previously known, and thus termed because it was found to be isomeric with oxybenzoic acid.

Bromotoluene can be obtained directly from toluene like nitrotoluene, and hence Kekulé assumed that both bodies have an analogous constitution. Bromotoluene when acted upon by sodium and methyl iodide, yields a dimethylbenzene (paraxylene), and when treated with sodium and carbon dioxide forms toluic acid, $C_6H_4(CH_3)CO_2H$, both derivatives being converted by oxidation into terephthalic acid, $C_6H_4(CO_2H)_2$. For this reason Kekulé supposed that both these bodies belong to the first series. Later investigation has, however, shown that an analogous mode of formation does not always give rise to similarly constituted compounds, but in the above cases Kekulé's view was found to be correct.

Cases of isomerism, similar to that of the substituted benzoic acids, were then observed in other compounds: thus, for example,

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[1] *Lehrbuch*, ii. 517 (1866).

two series of substituted anilines were known. To those which were obtained directly from aniline no special designation was given, whilst the others were termed para-compounds, although there was no intention of connecting this series in any way with the series of para-oxybenzoic acid. Various other compounds were obtained from these substituted anilines, such as halogen substitution products of benzene, substituted phenols, &c.

When Körner discovered a third iodophenol, he termed it meta-iodophenol and suggested for the first series the name of ortho-compounds. The same method of designation was then applied to the derivatives of benzoic acid obtained by direct substitution, and, as a para-series already existed, bodies connected with salicylic acid were termed meta-compounds. This led to much confusion, as it was supposed, without reason, that a similar mode of designation indicated an analogous constitution in the compounds of both groups.

The following table is, with some abbreviation, taken from Kekulé's *Lehrbuch*.[1]

	Ortho-series.	Para-series.	Meta-series.
$C_6H_4Cl_2$	Dichlorobenzene.	—	—
$C_6H_4Br_2$	Dibromobenzene.	—	—
$C_6H_4I_2$	Di-iodobenzene.	—	—
$C_6H_4(NO_2)_2$	—	Dinitrobenzene.	—
$C_6H_4(NO_2)Cl$	Nitrochlorobenzene	Paranitrochlorobenzene.	—
$C_6H_4(NO_2)Br$	Nitrobromobenzene	Paranitrobromobenzene.	—
$C_6H_4(NO_2)I$	Nitro-iodobenzene.	Paranitro-iodobenzene.	—
$C_6H_4(NH_2)Cl$	Chloraniline.	Parachloraniline.	—
$C_6H_4(NH_2)Br$	Bromaniline.	Parabromaniline	—
$C_6H_4(NH_2)I$	Iodaniline.	Paraiodaniline.	—
$C_6H_4(NH_2)NO_2$	Nitraniline.	Paranitraniline.	—
$C_6H_4(NH_2)_2$	Phenylenediamine.	Paraphenylenediamine.	—
$C_6H_4(OH)I$	Iodophenol.	Para-iodophenol.	Meta-iodophenol
$C_6H_4(OH)_2$	Hydroquinone.	Resorcin.	Pyrocatechin.

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[1] iii. 25 and 92.

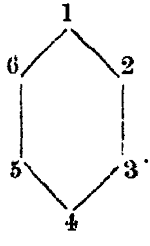
It has already been stated that the ortho-compounds are those which are obtained from aniline by direct substitution, or by means of the diazo-reaction.

The starting-point for the para-compounds is dinitrobenzene, which is easily converted by partial reduction into paranitraniline. This yields the nitro-halogen compounds by the diazo-reaction, and from these again the substituted anilines and phenols can be obtained. The phenylenediamines or diamidobenzenes are obtained by further reduction of the nitranilines. The ortho-compound of the iodophenols, in addition to its production from iodaniline, was prepared by Körner by the action of iodine and iodic acid on phenol, a small quantity of meta-iodophenol being produced at the same time. The earlier known dihydroxybenzenes were obtained by Körner by fusing the iodophenols with caustic potash.

Hydroquinone on oxidation forms quinone, $C_6H_4O_2$, and this may also be obtained by the oxidation of phenylenediamine, a further proof that hydroquinone belongs to the first series.

ORIENTATION IN THE AROMATIC SERIES.

931 As soon as the fact was recognised that the di-substitution products exist in three isomeric forms, and that they can be arranged in series whose members can be converted by simple reactions into the others, it became necessary to investigate the orientation or the relative position of the substituted radicals or elements. This indeed Kekulé attempted to effect, and he was of opinion that when two similar elements or radicals replace the hydrogen in benzene, they take up positions in the molecule removed as far as possible from one another, inasmuch as all the atoms lying within the sphere of action of the first bromine atom would have their affinity for bromine weakened.

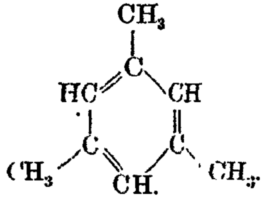


Let us suppose that in monobromobenzene, C_6H_5Br, the bromine takes up position 1, then in dibromobenzene the second atom of bromine will occupy position 4.[1]

Baeyer opposed this view, pointing out that when ethyl chloride is chlorinated, ethidene dichloride, $CH_3.CHCl_2$, and not ethylene dichloride, $CH_2Cl.CH_2Cl$, is formed, so that the second chlorine atom instead of being repelled by the first, is rather attracted to it.[2] In the above case, however, both views are correct; for when bromobenzene is brominated, 1, 4, dibromobenzene is the chief product; but a certain quantity of 1, 2, dibromobenzene is also formed, though this was not known at the time, and these considerations did not exert any influence on the problem. On the other hand, the views held by Baeyer respecting the constitution of mesitylene, C_9H_{12}, exerted considerable influence.[3] This hydrocarbon is formed when acetone is heated with sulphuric acid:

$$3C_3H_6O = C_9H_{12} + 3H_2O.$$

Fittig had previously found that mesitylene yields on oxidation trimesitic acid, $C_6H_3(CO_2H)_3$, and that this when heated with lime yields benzene and carbon dioxide. Hence it is proved that mesitylene is trimethylbenzene, $C_6H_3(CH_3)_3$. The formation of this body is explained by Baeyer by supposing that each molecule of acetone gives rise, with separation of water, to the residue $CH{\equiv}C{-}CH_3$, and that three of these are so arranged as to form symmetrical trimethylbenzene, in which the methyl groups are in the positions 1, 3, 5,



This view, though probable, was not proved to be correct, any more than another idea which was at one time entertained, namely, that trichlorobenzene, derived from benzene hexchloride, $C_6H_6Cl_6$, by removal of three molecules of hydrogen chloride, contains the chlorine atoms symmetrically arranged. Ladenburg, however, afterwards proved the truth of Baeyer's hypothesis, and it now stands as one of the most important methods of effecting orientation (see p. 46).

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[1] *Lehrbuch*, ii 553.

[2] *Ann. Chem. Pharm.* Suppl. v. 84.

[3] *Ibid.* cxl. 306.

Mesitylene yields on moderate oxidation a monobasic and a dibasic acid.

Mesitylenic Acid. Uvitic Acid.

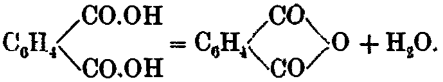
$$C_6H_3\left\{\begin{matrix}(CH_3)_2\\CO_2H.\end{matrix}\right. \qquad C_6H_3\left\{\begin{matrix}CH_3\\(CO_2H)_2.\end{matrix}\right.$$

The former of these when distilled with lime yields a dimethylbenzene, which is identical with the metaxylene contained in coal-tar oils, and yields on oxidation the dibasic isophthalic acid $C_6H_4(CO_2H)_2$, isomeric with phthalic and terephthalic acids.

Assuming the above constitution of mesitylene, it follows that the side chains of metaxylene and of isophthalic acid occupy alternate positions:

$$1 : 3 = 1 : 5 = 3 : 5.$$

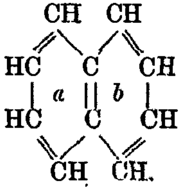
932 Phthalic acid differs from terephthalic acid, and, as was afterwards found, also from isophthalic acid, inasmuch as when heated, it is readily resolved into water and an anhydride:



$$C_6H_4\begin{matrix}\diagup CO.OH\\ \diagdown CO.OH\end{matrix} = C_6H_4\begin{matrix}\diagup CO \diagdown\\ \diagdown CO \diagup\end{matrix}O + H_2O.$$

From this reaction Gräbe concluded that the carboxyls are adjacent or occupy the positions 1, 2,[1] and this conclusion he corroborated in his valuable research on naphthalene, $C_{10}H_8$.

Erlenmeyer had previously expressed the opinion that this latter hydrocarbon contains two benzene rings, having two carbon atoms in common.[2] These two rings we may designate as *a* and *b*:



Now from Gräbe's investigations it appears very probable that this formula does represent the constitution of naphthalene; and as this hydrocarbon yields phthalic acid on oxidation, the two carboxyls must occupy the positions 1 and 2.[3] Gräbe's proof will be given hereafter under napthalene. Nölting and Reverdin[4] have, however, since given a much simpler proof, as follows: nitronaphthalene, $C_{10}H_7NO_2$, yields on oxidation nitrophthalic acid, $C_6H_3(NO_2)(CO_2H)_2$. If we now assume that the nitroxyl is contained in the nucleus *a*, it follows that the nucleus *b* has

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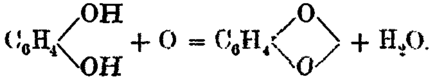
[1] Gräbe and Born, *Ann. Chem. Pharm.* cxlii. 330. [2] *Ibid.* cxxxvii. 346.

[3] *Ibid.* cxlix. 1. [4] *Constitution of Naphthalene and its derivatives*, 1880.

been destroyed. By reduction nitronaphthalene is converted into amidonaphthalene, $C_{10}H_7NH_2$, and this on oxidation does not yield amidophthalic acid, or an oxidation product of it, but phthalic acid. Hence it follows that in this latter case, the nucleus *a* has been oxidized to carboxyl. Now as we are acquainted with the constitution of phthalic and isophthalic acids, it is clear that that of terephthalic acid is also known, as well as that of the bromotoluene which can be converted into toluic acid, and of a dimethylbenzene which on oxidation yields terephthalic acid.

933 Hydroquinone, $C_6H_4(OH)_2$, is distinguished from its isomerides inasmuch as it readily passes by oxidation into quinone, $C_6H_4O_2$, and this can again be easily reduced to hydroquinone. From these facts Gräbe concluded that in the formation of quinone the two oxygen atoms combine together :



$$C_6H_4\begin{cases}OH\\OH\end{cases} + O = C_6H_4\begin{cases}O\\O\end{cases} + H_2O.$$

This peculiar reaction of hydroquinone is most simply explained, according to Gräbe, by the supposition that in this body the hydroxyls occupy the adjacent positions of 1 and 2. But as hydroquinone is formed by fusing ortho-iodophenol with potassium, we may conclude that the substitution in ortho-compounds takes place in the adjacent position.

At the end of his memoir on naphthalene Gräbe gives the following table. The expressions, ortho, meta, para, are here employed in the sense we now use them.

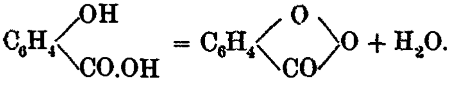
	Ortho-series. 1 : 2.	Meta-series. 1 . 3.	Para-series. 1 : 4.
$C_6H_4\begin{cases}OH\\OH\end{cases}$	Hydroquinone.	Pyrocatechin.	Resorcin.
$C_6H_4\begin{cases}OH\\CO_2H\end{cases}$	Oxybenzoic acid.	Salicylic acid.	Para-oxybenzoic acid.
$C_6H_4\begin{cases}CO_2H\\CO_2H\end{cases}$	Phthalic acid.	Isophthalic acid.	Terephthalic acid.

It has already been stated that Kekulé assumed that para-oxybenzoic and terephthalic acids belong to the same series; the former of these was obtained from nitrotoluene, which on reduction yields a toluidine, from which Hofmann obtained the same toluic acid which is formed by Kekulé's reaction from bromotoluene, and which on oxidation yields terephthalic acid, thus corroborating Kekulé's supposition. The connection between bromotoluene and nitrotoluene is further shown, inasmuch as the former is converted by oxidation into a bromobenzoic acid, which is identical with that obtained by the diazo-reaction from amidodracylic acid; hence all these compounds belong to the para-series.

A connection between resorcin and terephthalic acid was not at that time proved, but Irelan [1] and Garrick [2] soon showed that bromobenzenesulphonic acid and benzenedisulphonic acid yield resorcin when fused with caustic potash, whilst when they are heated with potassium cyanide and the product decomposed by caustic potash terephthalic acid is obtained. But if hydroquinone is an ortho-compound and resorcin a para-compound, then pyrocatechin must belong to the meta-series.

The insertion of oxybenzoic and salicyclic acids was, on the other hand, purely arbitrary.

934 The relations existing between the di-substitution products of benzene and the mono-substitution products of benzoic acid were at that time only determined in so far as that both were placed in the para-series. The assumption that the same relative position of the substituents held good for the ortho- and meta-compounds of the two groups was in no way proved, as was pointed out by Victor Meyer, who then drew attention to the fact that in the meta-derivatives of benzoic acid the adjacent position of the side chains must be assumed with the same degree of probability as in the case of phthalic acid, inasmuch as, of the three isomeric oxybenzoic acids, only salicylic acid yields an anhydride on heating.



$$C_6H_4\left\langle\begin{matrix}OH\\CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}O\\CO\end{matrix}\right\rangle O + H_2O.$$

It therefore appeared to Meyer more probable that oxybenzoic acid belongs to the series 1, 3, and of this he discovered the proof; for Barth had shown that sulphobenzoic acid when fused with caustic potash only yields oxybenzoic acid,[3] whilst on heating it with sodium formate, Meyer obtained isophthalic acid,[4] which is also formed when ordinary bromobenzoic acid is employed in place of the sulphonic acid.[5]

He also proved that the crystallized dibromobenzene belongs to the para-series, inasmuch as when acted upon by sodium and methyl iodide it is converted into paradimethylbenzene, and this body yields terephthalic acid when oxidized.

Of the three known nitrotoluenes the solid one yields on

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[1] *Zeitschr. Chem.* 1869, 164. [2] *Ibid.* 549. [3] *Ann. Chem. Pharm.* 148, 30.
[4] *Ibid.* 156, 268. [5] Adler and Meyer, *ibid.* 159, 1.

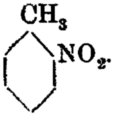
oxidation paranitrobenzoic acid (nitrodracylic acid). The second, liquid one, yields common or metanitrobenzoic acid, and the third, also a liquid body, is decomposed completely, a property characteristic of the ortho-compounds, which are either scarcely attacked by oxidizing agents, or else completely burned. Hence there can no longer be any doubt respecting the classification of the nitrobenzenes and of the toluidenes which are formed from them.

The three dimethylbenzenes or xylenes were also known at the time referred to. It has been already stated that one yields on oxidation terephthalic acid, whilst the second is converted into isophthalic acid, the third, or orthoxylene, being entirely decomposed. Finally, by the dry distillation of two diamidobenzoic acids, Griess obtained the third diamidobenzene, which up to that time had not been prepared, and this was naturally considered to be a meta-compound. The following table exhibits the views respecting the constitution of the di-substitution products which were held about the year 1870; only some of the compounds contained in the table on p. 35 being mentioned:—

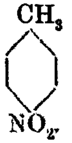
	Ortho-series. 1 : 2	Meta-series. 1 : 3	Para-series. 1 : 4
$C_6H_4Br_2$	—	—	Dibromobenzene, M.P. 89°.
$C_6H_4(NO_2)_2$	—	—	Dinitrobenzene.
$C_6H_4(NO_2)Br$	Bromonitrobenzene M.P. 126°.	Bromonitrobenzene, M.P. 41°·5.	Bromonitrobenzene, M.P. 56°.
$C_6H_4(NH_2)Br$	Bromaniline, from aniline.	Metabromaniline, from bromonitrobenzene.	Parabromaniline, from dinitrobenzene.
$C_6H_4(NH_2)_2$	Phenylenediamine, M.P. 147°.	Phenylenediamine, M.P. 99°.	Paraphenylenediamine, M.P. 63°.
$C_6H_4I(OH)$	Ortho-iodophenol, from phenol.	Meta-iodophenol, from phenol.	Para-iodophenol, from dinitrobenzene.
$C_6H_4(OH)_2$	Hydroquinone.	Pyrocatechin.	Resorcin.
$C_6H_4Br(CH_3)$	—	Metabromotoluene.	Parabromotoluene.
$C_6H_4(NO_2)CH_3$	Nitrotoluene, from toluene (liquid).	Metanitrotoluene.	Paranitrotoluene, from toluene (solid).
$C_6H_4(NH_2)CH_3$	Orthotoluidine (liquid).	Metatoluidine (liquid).	Paratoluidine (solid).
$C_6H_4Cl.CO_2H$	Chlorosalicylic acid.	Chlorobenzoic acid.	Chlorodracylic acid.
$C_6H_4BrCO_2H$	—	Bromobenzoic acid.	Bromodracylic acid.
$C_6H_4(NH_2)CO_2H$	Anthranilic acid.	Amidobenzoic acid.	Amidodracylic acid.
$C_6H_4(OH)CO_2H$	Salicylic acid.	Oxybenzoic acid.	Para-oxybenzoic acid.
$C_6H_4(CH_3)_2$	Orthoxylene.	Metaxylene.	Paraxylene.
$C_6H_4(CO_2H)_2$	Phthalic acid.	Isophthalic acid.	Terephthalic acid.

935 The arrangement of the compounds mentioned in this table was chiefly founded on experimental evidence, and those compounds for which this was not the case were classified from analogy. But, notwithstanding this, many emendations were soon found necessary. Thus the para-derivatives of benzene, with the exception of paradibromobenzene and resorcin, had not been brought into close connection with the para-derivatives of toluene or of benzoic acid. Petersen then showed that the two nitrotoluenes, of which the one yields on oxidation orthonitrobenzoic acid and the other paranitrobenzoic acid, yield on further nitration the same dinitrotoluene, and for this reason the nitroxyls must occupy the meta-position:

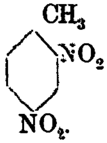
Orthonitrotoluene.



Paranitrotoluene.

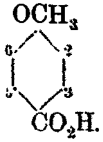


Dinitrotoluene.



Now, dinitrobenzene so closely resembles dinitrotoluene that an analogous position of the nitroxyls may well be assumed in both compounds. If this be correct, dinitrobenzene and the compounds connected with it must also belong to the meta-series. The same chemist then proved that the phenylene-diamine melting at 99°, is not a meta-compound but belongs to the ortho-series.

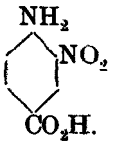
Anisic acid, or methylpara-oxybenzoic acid, $C_6H_4(OCH_3)CO_2H$, yields nitranisic acid, in which the nitroxyl can only occupy the position 2 or 3 = 6 or 5.



By heating nitranisic acid with ammonia Salkowski obtained a nitro-amidobenzoic acid:

$$C_6H_3(NO_2)(OCH_3)CO_2H + NH_3 =$$
$$C_3H_3(NO_2)(NH_2)CO_2H + CH_3OH.$$

By means of the diazo-reaction the amido-group can be replaced by hydrogen; in this way metanitrobenzoic acid is obtained, and from this it follows that the above-mentioned nitro-amidobenzoic acid has the following constitution:



By reducing this, diamidobenzoic acid, $C_6H_3(NH_2)_2CO_2H$, is formed, and if carbon dioxide be then eliminated, orthodiamidobenzene or phenylenediamine is obtained, a body melting at 99°. Meyer and Wurster, as well as Salkowski, had shortly before come to the conclusion that this belongs to the series 1 : 2. The same substance is also obtained from the bromonitrobenzene, $C_6H_4(NO_2)Br$, melting at 41°·5, by heating it with ammonia, when it is converted into nitraniline, and reducing this. The same nitrobromobenzene when heated with caustic potash yields a nitrophenol melting at 45°; this may be converted into amidophenol and afterwards into chlorophenol, which latter on fusion with caustic potash yields pyrocatechin, $C_6H_4(OH)_2$, which, therefore, is orthodioxybenzene.

936 The nitroxyl in the bromonitrobenzene melting at 126° can be replaced by bromine, paradibromobenzene being formed; hence bromonitrobenzene is a para-compound. When heated with caustic potash it gives a nitrophenol which melts at 115°, yielding on reduction an amidophenol, which, like phenylenediamine, yields quinone on oxidation. This same paranitrobenzene can also be obtained from the nitraniline, which melts at 146°, and which, according to Hofmann, also yields a large quantity of quinone. Hence, then, Petersen concluded that all these compounds, and therefore hydroquinone, belong to the series 1 : 4.

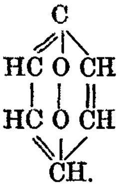
From this and former statements it follows that resorcin ought to be classed in the 1 : 3 series, for it can be obtained from dinitrobenzene, which, according to Petersen, is a meta-compound. Now, resorcin is also formed by fusing benzenedisulphonic acid with caustic potash; but this acid yields on heating with potassium cyanide the nitrile of terephthalic acid, which latter is undoubtedly a para-compound. This contradiction was explained by Petersen by the supposition that, on fusing the sulphonic acid with caustic potash intramolecular changes take place; and this idea is borne out in many cases by experiment, especially where the reaction requires a high temperature.

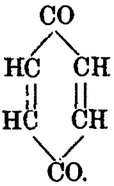
Wurster next prepared the diamidobenzene melting at 63° by oxidizing the above-named dinitrotoluene to form a dinitrobenzoic acid, which on reduction and elimination of carbon-dioxide yielded this diamidobenzene, so that there can no doubt that it is a meta-compound.

Moreover, Wurster and Ambühl showed that this body, like orthodiamidobenzene, can be obtained from two different diamidobenzoic acids, whilst the para-compound

corresponds to only one such acid.

Salkowski also concluded that the common phenylenediamine is metadiamidobenzene, and he proved that hydroquinone belongs to the same series as para-oxybenzoic acid. He reduced the methyl ether of the nitrophenol melting at 115°, or nitro-anisol, $C_6H_4(NO_2)OCH_3$, to amido-anisol, $C_6H_4(NH_2)OCH_3$, substituted in this, the amido-group by bromine, and then, by means of sodium and methyl iodide, replaced this bromine by methyl, thus obtaining a cresolmethyl ether, $C_6H_4(CH_3)OCH_3$, which on oxidation yielded anisic acid. He then converted the amido-anisol into a diazo-compound, and decomposed this by water, when methyl was eliminated, and hydroquinone formed. It follows from this that the hydroxyls of hydroquinone and therefore the oxygen atoms of quinone occupy the positions 1 : 4. The constitution of this latter body is, therefore, expressed by one of the following formulæ:





Which of these is the more probable we shall learn hereafter.

From the results of these and similar investigations it follows that the former table must be revised as below, only a portion being here given and the lacunæ being filled up:—

$C_6H_4Br_2$	Orthodibromobenzene, B.P. 224°.	Metadibromobenzene, B.P. 219°.	Paradibromobenzene, M.P. 89°.
$C_6H_4(NO_2)_2$	Orthodinitrobenzene, M.P. 118°.	Metadinitrobenzene, M.P. 89°·8.	Paradinitrobenzene, M.P. 172°.
$C_6H_4(NO_2)Br$	Orthobromonitrobenzene, M.P. 41°·5.	*Metabromonitrobenzene*, M.P. 56°·4.	*Parabromonitrobenzene*, M.P. 126°.
$C_6H_4(NH_2)_2$	Orthodiamidobenzene, M.P. 99°.	Metadiamidobenzene, M.P. 63°.	Paradiamidobenzene, M.P. 147°.
$C_6H_4(OH)_2$	Pyrocatechin, M.P. 104°.	Resorcin, M.P. 110°.	Hydroquinone, M.P. 169°.
$C_6H_4Br(CH_3)$	Orthobromotoluene, B.P. 182°.	Metabromotoluene, B.P. 184°.	Parabromotoluene, M.P. 28°·3.
$C_6H_4(NO_2)CH_3$	Orthonitrotoluene, B.P. 223°.	Metanitrotoluene, M.P. 16°.	Paranitrotoluene, M.P. 54°.
$C_6H_4(NH_2)CH_3$	Orthotoluidine, B.P. 199°·5.	Metatoluidine, B.P. 197°.	Paratoluidine, M.P. 45°.
$C_6H_4(OH)CO_2H$	Salicylic acid, M.P. 156°.	Meta-oxybenzoic acid, M.P. 200°.	Para-oxybenzoic acid, M.P. 210°.
$C_6H_4(CH_3)_2$	Orthoxylene, B.P. 140°.	Metaxylene, B.P. 137°.	Paraxylene, B.P 137°.
$C_6H_4(CO_2H)_2$	Phthalic acid.	Isophthalic acid.	Terephthalic acid.

937 So far all attempts at orientation had been directed towards placing the compounds in genetic connection with one of the phthalic acids. We have already seen that the constitution of terephthalic acid and of the para-series connected with it had been placed on a sure foundation.

On the other hand, the views concerning the constitution of phthalic and isophthalic acids rested on hypotheses which had not been verified. As common phthalic acid is the only one which yields an anhydride, it was assumed that in this the carboxyls occupy the adjacent position. But a similar argument was employed to show that the hydroxyls in hydroquinone also occupy the same position, and this conclusion was proved to be erroneous; hence the argument lost weight in the case of phthalic acid. The conclusions based upon the constitution of naphthalene stood on a firmer basis, but it still was a question whether they were final.

The case of isophthalic acid is a similar one: its constitution depends upon that of mesitylene in which we know that the three methyls are contained in symmetrical position, or, what is the same thing, that the three hydrogen atoms in direct combination with the nucleus are of equal value. Ladenburg proved this as follows:—"Let us indicate the three hydrogen atoms by the letters *a*, *b* and *c*, and assume that in dinitromesitylene, $C_6(CH_3)_3\overset{a}{N}O_2(\overset{b}{N}O_2)H$, *a* and *b* are replaced by nitroxyl, and that by partial reduction *b* is converted into an amido-group; we then obtain the formula $\overset{a}{N}O_2\overset{b}{N}H_2\overset{c}{H}$ for amidonitromesitylene. Now, the hydrogen atom marked *c* in this may be replaced by nitroxyl, and the amido-group by hydrogen, a dinitromesitylene, having the formula $\overset{a}{N}O_2\overset{b}{H}\overset{c}{N}O_2$, being thus obtained, and as this is identical with the former one, it is clear that the hydrogen atoms *b* and *c* are of equal value.

Supposing now that the amido-group in amidonitromesitylene be replaced by hydrogen, we obtain nitromesitylene, which on reduction is converted into amidomesitylene, $\overset{a}{N}H_2\overset{b}{H}\overset{c}{H}$. If this body be nitrated only one amidonitromesitylene, $\overset{a}{N}H_2\overset{b}{N}O_2\overset{c}{H} = \overset{a}{N}H_2\overset{b}{H}\overset{c}{N}O_2$, can be formed, as both *b* and *c* are of equal value. The compound thus obtained proves, however, to be identical with the amidonitromesitylene, having the following formula: $\overset{a}{N}O_2\overset{b}{N}H_2\overset{c}{H}$. Hence the hydrogen atoms *a* and *b* are also of equal value, or the three hydrogen atoms belonging to the aromatic nucleus of mesitylene are of equal value."

938 Before Ladenburg's memoir appeared, Körner published a valuable research on the isomerism of the aromatic compounds containing six atoms of carbon.[1] In this he criticised the methods of orientation then in vogue, founded on the constitution of the three phthalic acids, of mesitylene and of naphthalene, &c. He expressed doubt whether the constitution of these compounds was ascertained with sufficient certainty to serve as a foundation for orientation and he, therefore, doubted the conclusions and experiments by which the acids containing eight atoms of carbon were brought into connection with the di-substitution products of benzene obtained by direct methods. Körner prepared 126 new compounds, and in addition revised all the researches which had hitherto been published, especially those concerning the simplest benzene derivatives, in the preparation of which it happened that the formation of two or

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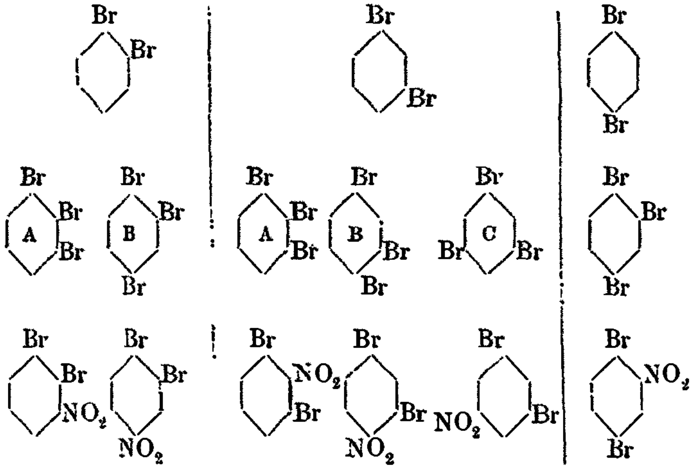
[1] *Gazz. Chim. Ital.* 1874, 305; *Jahresb.* 1875, 299; *Journ. Chem. Soc.* 1876, i. 204.

three isomerides had been overlooked. Assuming the equal value of the hydrogen atoms of benzene, he employed a method of orientation depending on the following principles:

An ortho-compound (1:2) with similar substituents can yield two tri-derivatives, when a third hydrogen atom is replaced. Under the same conditions a meta-compound (1 : 3) yields three tri-derivatives; whereas a para-compound can only yield one. In this case, where the entering element or radical is identical with the two already present, only three substitution products can be formed; but when a different element or radical is introduced, six may be obtained, as is seen from the following table:



From this it follows that the dibromobenzene which yields three tribromobenzenes or three nitrodibromobenzenes, and which, on the other hand, is formed from three dibromanilines, by elimination of the amido-group, contains the bromine atoms in the position 1 : 3.

Orthodibromobenzene having the position 1 : 2 can only yield two tribromobenzenes or two nitrodibromobenzenes, and can be obtained only from two dibromanilines. Lastly paradibromobenzene (1:4) can only be obtained from one dibromaniline and yields only one tribromobenzene, and only one nitrodibromobenzene.

Now, the solid dibromobenzene, melting at 89°, yields only one nitro-derivative;[1] the liquid compound obtained together with

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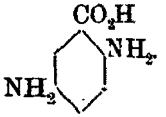
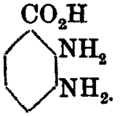
[1] Zincke and Sintenis, *Ber. Deutsch. Chem. Ges.* vi. 123.

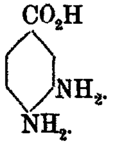
the former by the action of bromine on benzene[1] yields, on the other hand, two; and the third, obtained by Meyer and Stüber from dibromaniline,[2] forms three nitrodibromobenzenes.

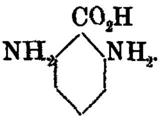
Körner showed, moreover, that when the dibromobenzenes are further brominated, the above conditions are fulfilled, so that the solid corresponds to one; the liquid, formed at the same time, to two; and the third to three dibromanilines. Solid dibromobenzene is, therefore, (1 : 4); that obtained by Riese, (1 : 2); and that prepared by Meyer and Stüber, (1 : 3). No. 1 corresponds to hydroquinone, No. 2 to pyrocatechin, and No. 3 to resorcin.

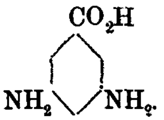
939 In a similar way Körner has determined the constitution of a large number of compounds, and this without reference to the views respecting the positions of the carboxyls in the three phthalic acids. Almost at the same time Griess employed the same principle to ascertain the constitution of the three diamidobenzenes, by preparing them from the six diamidobenzoic acids by elimination of carbon dioxide:

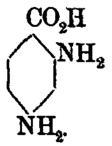






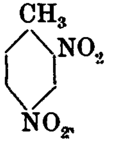






From the first of these he obtained paradiamidobenzene melting at 147°, the two next yielded orthodiamidobenzene melting at 99°, and the last three gave rise to common metadiamidobenzene melting at 63°.[3]

In close connection with these researches Nölting has given a direct proof of the constitution of phthalic acid.[4] We have already seen that dinitrotoluene has the following constitution:



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[1] Riese, *Ber. Deutsch. Chem. Ges.* ii. 61.

[2] Meyer and Stüber, *ibid.* v. 52.

[3] Meyer and Stüber, *ibid.* vii. 1226.

[4] R. Meyer, *Einl. Arom. Verb.* 73.

This is deduced from the facts that it has been obtained by the further nitration of the two mononitrotoluenes obtained directly from toluene, of which the solid one yields paranitrobenzoic acid on oxidation, and that it was converted by Wurster, by reduction and elimination of methyl, into ordinary metamidobenzene. From this it follows that the liquid nitrotoluene, and therefore the orthotoluidine obtained from it, contain the side chains in the position 1 : 2. This latter substance, however, Weith converted by means of the mustard-oil reaction into orthotoluic acid, $C_6H_4(CH_3)CO_2H$, which on oxidation with potassium permanganate yields phthalic acid; this substance must therefore also contain the carboxyls in the position 1 : 2.

Kekulé had previously converted orthotoluidine into orthoiodotoluene and obtained orthotoluic acid from it by Wurtz's reaction, while by oxidizing this iodotoluene he obtained iodobenzoic acid, $C_6H_4I(CO_2H)$, which when fused with caustic potash yielded salicylic acid.[1]

Another very simple proof of the constitution of the phthalic acids has been given by Nölting,[2] using the method of Körner and Griess (see page 46). These acids are readily obtained by oxidizing the corresponding xylenes with potassium permanganate. Now isoxylene yields three mononitroxylenes, orthoxylene two, and paraxylene only one. It follows from this that the side chains in isoxylene, and, therefore, in isophthalic acid, have the position 1 : 3, in orthoxylene and orthophthalic acid 1 : 2, and in paraxylene and paraphthalic acid, 1 : 4.

940 Adopting the principles of orientation above explained, many chemists have extended their researches in this direction, so that the constitution of the more important di-substitution products of benzene is now known with a great degree of probability. As, however, higher substitution products can be obtained from these by simple reactions, and these again can easily be reconverted into di-substitution products, as has been shown above, it is clear that the constitution of a large number of aromatic compounds containing three or more side chains is also known.

For the further consideration of this point we must refer to the special description of the compounds.

941 In the case of penta-substitution products which contain identical elements or radicals, as in that of mono-substitution derivatives, no isomerides occur. From this we may conclude that the six hydrogen atoms of benzene are of equal value. But this conclusion is here founded on negative evidence only,

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[1] *Ber. Deutsch. Chem. Ges.* vii. 1006.

[2] *Ibid.* xviii. 2687.

and it is of importance that it should be proved directly. For this purpose Ladenburg adopted the same principle as that which he employed for proving the equality of the three hydrogen atoms of mesitylene.[1] He first showed that two of the hydrogen atoms of benzene occupy a symmetrical position with regard to a third atom; or, in other words, that it is immaterial whether one or other be replaced by a radical or element, inasmuch as the bodies thus obtained are identical.

Hübner and Petermann[2] found that when ordinary bromobenzoic acid is nitrated, two isomeric bromonitrobenzoic acids are formed, in which the nitroxyl, therefore, occupies two different positions, *a* and *b*:

$$C_6H_3Br(\overset{a}{N}O_2)CO_2H\,; \qquad C_6H_3Br(N\overset{b}{O}_2)CO_2H.$$

Both bodies are converted by nascent hydrogen into anthranilic acid, bromine being replaced by hydrogen and the nitroxyl being reduced to the amido-group. Hence it follows that both *a* and *b* occupy a symmetrical position as regards the carboxyl.

But as regards the hydrogen atom replaced by carboxyl, there exists another pair of symmetrically placed hydrogen atoms. Thus, it has been shown by Wroblewski[3] that if one atom of hydrogen in paratoluidine be replaced by bromine, a bromotoluidine is obtained, which is converted by the diazo-reaction into metabromotoluene, and that this on oxidation yields metabromobenzoic acid. This bromotoluidine also yields a nitrobromotoluidine, and this by the same reaction is converted into a nitrobromotoluene, yielding on reduction an amidobromotoluene, in which the bromine can be replaced by hydrogen. A toluidine is thus obtained, and it is found that this yields by means of the diazo-reaction the same bromotoluene which, as has been described, was obtained from paratoluidine.

Parabromotoluidine.

$$C_6\overset{a}{H}\overset{b}{H}\overset{c}{H}\overset{d}{Br}(\overset{e}{CH_3})\overset{f}{N}H_2.$$

Metabromotoluene.

$$C_6HHHBr(CH_3)H.$$

Metabromobenzoic Acid.

$$C_6HHHBr(CO_2H)H.$$

Nitrobromotoluidine.

$$C_6HH(NO_2)Br(CH_3)NH_2.$$

Nitrobromotoluene.

$$C_6HH(NO_2)Br(CH_3)H.$$

Amidobromotoluene.

$$C_6HH(NH_2)Br(CH_3)H.$$

Amidotoluene.

$$C_6HH(NH_2)H(CH_3)H.$$

Metabromotoluene.

$$C_6HHBrH(CH_3)H.$$

Metabromobenzoic Acid,

$$C_6HHBrH(CO_2H)H.$$

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[1] *Ber. Deutsch. Chem. Ges.* ii. 140.

[2] *Ann. Chem. Pharm.* 149, 129.

[3] *Ibid.* clxviii. 153 : cxcii. 196.

This proves that the positions *c* and *d* lie symmetrically as regards the methyl or carboxyl.

Hübner and Petermann commenced their experiments with the same bromobenzoic acid which Wroblewski obtained by oxidizing bromotoluene. But as the two nitrobenzoic acids contain the two nitroxyls placed symmetrically, with regard to the carboxyls, and as the acids obtained by Wroblewski contain two bromine atoms in the same positions, it is clear that two pairs of hydrogen atoms exist in benzene, which occupy a symmetrical position with regard to the fifth atom, whilst the sixth atom occupies an isolated position.

As Hübner and Petermann obtained anthranilic acid, or orthoamidobenzoic acid, but Wroblewski metabromobenzoic acid, we conclude that there are in benzene two symmetrical ortho- and meta-positions, whilst the para-position only occurs once.

942 Ladenburg has brought forward another proof for which we must refer to the original memoir.[1] He further showed that four hydrogen atoms in benzene are of equal value.

Phenol, C_6H_5OH, which occurs in large quantities in coal-tar, when acted upon by phosphorus pentabromide is converted into bromobenzene, C_6H_5Br, and this, by the action of sodium and carbon dioxide, into benzoic acid:

$$C_6H_5Br + Na_2 + CO_2 = C_6H_5.CO_2Na + NaBr.$$

The hydroxyl, therefore, has the same position *a* in the phenol, as the carboxyl in the benzoic acid. In this latter, however, hydrogen can be replaced by hydroxyl, and thus the three isomeric oxybenzoic acids can be obtained, in which the carboxyl occupies the same position as in the benzoic acid and phenol; whilst the hydroxyls replace different hydrogen atoms of the benzoic acid; these we may designate by *b*, *c*, and *d*. All three oxybenzoic acids, however, yield phenol with elimination of carbon dioxide; and this is identical with that found in coal-tar; hence the positions, *a*, *b*, *c*, and *d*, are of equal value. From what has been said, however, we may conclude that of the three last, no two can occupy a symmetrical position with regard to *a*. Hence we must come to the conclusion that all six hydrogen atoms of benzene are of equal value; and further, that one

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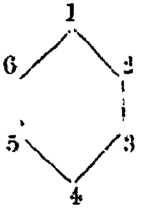
[1] *Ber. Deutsch. Chem. Ges.* v. 322; viii. 1666; *Theorie Arom. Verb.*, Vieweg and Sohn, 1876.

hydrogen atom corresponds to two symmetrical pairs, and this is indicated in the formula of benzene:



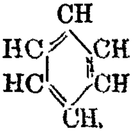
The symmetrical pairs to (1) are 2 : 6, and 3 : 5; to (2) 1 : 3, and 4 : 6, &c. With reference to (1) the positions which occur twice are:—

$$1:2 = 1:6$$
$$1:3 = 1:5$$

The position 1 : 4 only occurs once.

THE CONSTITUTION OF BENZENE.

943 According to Kekulé the constitution of benzene is expressed by the following formula:



Soon after this formula had been proposed, other chemists gave their views concerning the constitution of this compound and expressed them by certain graphical formulæ. Of these the following may be mentioned:

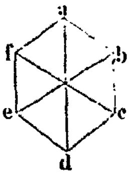


Fig. A.

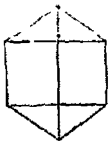


Fig. B.

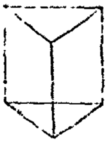


Fig. C.

Claus proposed the formulæ illustrated by Figs. A and B, giving the preference to the former of these;[1] a similar formula was

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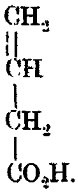
[1] *Theoret. Betracht. System. Org. Chemie*, Freibr. 1867.

suggested by Körner, which cannot, however, be represented on a plane surface, but may be readily put together by means of Kekulé's glyptic models. According to Körner's view, and in accordance with Claus's first formula, each carbon atom is directly combined with three others. The former assumes that the carbon atoms *a*, *c*, *e*, and *b*, *d*, *f*, lie in two parallel planes.[1] Claus's second formula is identical with that proposed by Ladenburg (Fig. C), except that the latter assumes an arrangement in space of the six carbon atoms, in supposing that they lie in the angles of a three-sided prism.[2]

According to Claus's first formula only two isomeric di-substitution products can exist, and for this reason we need not further consider it.[3] Ladenburg raises an objection to Kekulé's formula inasmuch as it requires, not three, but four isomeric substitution products, the positions 1 : 2 and 1 : 6 not being perfectly identical; for it is clear that two substituents occupying the position 1 : 2 are combined with two carbon atoms which are connected together by single linkage, whereas between the positions 1 : 6 the carbon atoms are doubly linked. The question whether 1 : 3 is equal to 1 : 5 is a simpler one and may be answered in the affirmative.

Ladenburg thinks that if the first two positions are identical, the two crotonic acids must also be identical:

$$\begin{array}{c} CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ CO_2H. \end{array}$$



$$\begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ CH_2 \\ | \\ CO_2H. \end{array}$$

But this argument is not unanswerable, as the difference observed does not merely depend on the arrangement of the linkage of the carbon atoms, but also on the distribution of the hydrogen among the carbon atoms.

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[1] Körner, *loc. cit.*

[2] *Ber. Deutsch. Chem. Ges.* ii. 141, 272.

[3] Compare Claus. *ibid.* xv. 1405; R. Meyer, *ibid.* 1823.

Victor Meyer opposed Ladenburg's view, insisting that the difference between the positions 1 : 2 and 1 : 6 was not brought about by a variation in the position of the atoms, but only by a varying arrangement of the combining units of the carbon, and, that it was of so very subtle a character that it was doubtful whether such minute differences could exert a perceptible influence on the properties of the compound.[1]

944 In reply to these remarks,[2] Kekulé says that the apparent difference between the positions 1 : 2 and 1 : 6, originates rather from the model employed than from the ideas, of which this model affords only an imperfect representation, and in order to show that no such difference exists he brings forward the following hypothesis.[3] The atoms in the systems which we call molecules must be assumed to be continually in motion, but hitherto no explanation as to the nature of this intramolecular motion has been given, which of course must be in accordance with the law of the linking of atoms. A planetary motion seems, therefore, inadmissible; the movement must be of such a kind, that all the atoms forming the system retain the same relative arrangement; in other words, that they return to a mean position of equilibrium. The most probable assumption, and one which is in accordance with the view held by physicists, is that the motion of the atoms takes place in straight lines and that on striking each other, they recoil like elastic bodies. What we call valency would then be nothing but the number of contacts experienced by one atom with other atoms in the unit of time. In the same time that the monad atoms of a diatomic molecule like H_2 strike each other once, the dyad atoms of a diatomic molecule come in contact with each other twice, the temperature in both cases being the same. In a molecule consisting of one dyad and two monads, as H_2O, the number of contacts in the unit of time is 2 for the former and 1 for each of the latter.

If two atoms of carbon are linked together by one combining unit of each, they strike against each other once in the unit of time, or in the same time in which monad hydrogen makes a complete vibration; during the same time they encounter three other atoms. Carbon atoms linked together by two bonds of each come in contact twice in the unit of time, and encounter

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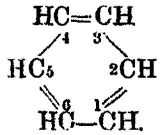
[1] *Ann. Chem. Pharm.* clvi. 265; clix. 24.
[2] *Ibid.* clxii. 77; *Journ. Chem. Soc.* 1872, 612.
[3] *Ann. Chem. Pharm.* clxii. 86.

during the same time two other atoms. Applying these views to benzene we come to the following. Each carbon atom strikes against two others in the unit of time, once against the one and twice against the other. In the same unit of time it comes once in contact with the hydrogen atom, which during the same period makes a complete vibration. Accordingly in the graphic formula



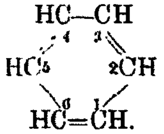
the contacts of the atom 1 in the unit of time may be thus represented, if *h* stands for hydrogen:

1 : 2, 6, *h*, 2.

In the second unit of time they are:

2 : 6, 2, *h*, 6,

which would be represented by the following formula:



The same carbon atom is therefore, during the first unit of time, linked to one of the adjoining ones by one, and during the second unit of time by two of its combining units; and *vice versâ* with regard to the other adjoining carbon atom.

The variation of these contacts undergone by a carbon atom exhausts itself in these two units of time; its sum, viz:

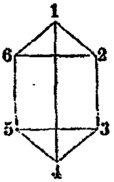
2, 6, *h*, 2, 6, 2, *h*, 6

represents the whole series of possible contacts under these circumstances, and therefore repeats itself continually. From this it is evident that the carbon atom strikes against the two others, with which it is directly combined, an equal number of times, *i.e.* that it bears the same relation to both. The ordinary graphic formula only represents the contacts made during the first unit of time, and thus the view has sprung up that in the di-substitution products, the positions 1, 2 and 1, 6, must produce different compounds. If the above, or some similar conception be correct, it follows that no real difference exists.

945 Michaelis opposed Kekulé's views, which, according to him, possess, from physical considerations, little probability, especially from the point of view of the kinetic theory of gases, as according to this, the square of the velocity of the atoms at equal temperatures is, in a perfect gas, inversely proportional to the atomic weights. Hence it follows that hydrogen atoms have the greatest velocity, but according to Kekulé they impinge less often than the oxygen atoms for example, and hence they must describe a much larger orbit than these; and further, their molecules must be larger than those of the oxygen. But, according to the kinetic theory of gases, the hydrogen molecules are only half as large as those of oxygen and are probably the smallest of all the gaseous molecules. Kekulé's ideas on atomic motion cannot, according to Michaelis, be regarded as representing a stable condition of dynamical equilibrium, and are moreover improbable, because then benzene should readily decompose into three molecules of acetylene.[1]

In comparing the formulæ of Kekulé and Ladenburg, we find that both explain equally well the formation of benzene from acetylene, and of mesitylene from acetone, as well as the formation of addition-products; in both cases the existence of a closed ring of six carbon atoms is assumed in which each atom is connected with two others by a single bond.

Ladenburg's formula also explains the equal value of the six hydrogen atoms, besides showing as clearly as Kekulé's the existence of the three isomeric di-substitution products. If we number the six angles of the prism, or, to simplify matters, those of Claus's hexagon:



we have:

$$1 : 2 = 1 : 6 = \text{Meta.}$$
$$1 : 3 = 1 : 5 = \text{Ortho.}$$
$$1 : 4 = \text{Para.}$$

This is also easily shown by employing the proof given by Körner:

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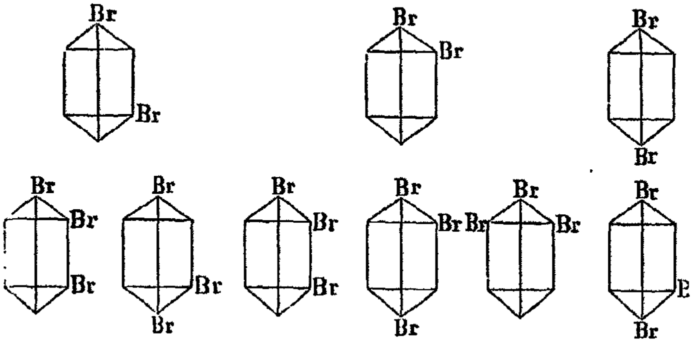
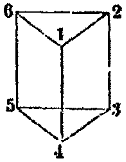
[1] *Ber. Deutsch. Chem. Ges.* v. 463.



In the case of the triderivatives we obtain the following results, similar to those previously obtained:



1 : 2 : 3 adjacent,
1 : 3 : 4 asymmetrical,
1 : 2 : 6 symmetrical.

If we assume that one of the triangular faces of the prism be revolved in its plane through 180°, whilst the other remains in its original position, and at the same time the figure thus obtained be projected on the surface whose position has been unchanged, the following graphic formula is obtained:

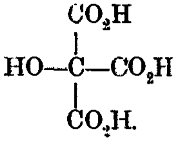
This possesses the advantage that the numbers have the same meaning as in Kekulé's formula, and otherwise expresses all that the prism formula can.

946 *Physical Methods.*—An attempt has recently been made to determine the constitution of benzene by physical methods. Brühl has investigated the refractive power of compounds

containing carbon in single, double, or treble linkage, and has arrived at the conclusion that benzene contains three doubly-linked carbon atoms; hence he considers the accuracy of Kekulé's views to be proved.[1]

Lossen and Zander arrived at the same conclusion from investigations on the specific volume of certain hydrocarbons,[2] whilst Julius Thomsen, in determining the heat of combustion of similar bodies, arrived at the opposite conclusion; for according to him benzene contains nine single links, and, therefore, Ladenburg's formula is correct.[3] Further investigations must decide whether the question can thus be solved.

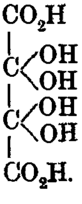
Another interesting observation which seemed likely to afford satisfactory proof has also failed. An acid termed carboxytartronic acid, $C_4H_4O_7$, is obtained by the action of nitrous acid on protocatechuic acid, $C_6H_3(OH)_2CO_2H$,[4] or catechol, $C_6H_4(OH)_2$.[5] This acid is very unstable in the free state, quickly decomposing into carbon dioxide and tartronic acid, and for this reason Gruber and Barth proposed for it the following constitution:



$$\begin{array}{c} CO_2H \\ | \\ HO—C—CO_2H \\ | \\ CO_2H. \end{array}$$

According to these chemists it contains one carbon atom in direct linkage with three others, and as it is formed by a simple reaction it appeared very probable that this form of linkage also occurred in the aromatic nucleus, as expressed by the prism formula.

Kekulé, however, showed that the correct formula of this acid is $C_4H_6O_8$, and that it is not a tribasic but a dibasic acid, which on reduction yields racemic acid together with inactive tartaric acid. Kekulé then obtained it as a decomposition product of the so-called nitrotartaric acid, $C_2H_2(ONO_2)_2(CO_2H)_2$. Its constitution is, therefore, as follows:



$$\begin{array}{l} CO_2H \\ | \\ C\begin{cases} OH \\ OH \end{cases} \\ | \\ C\begin{cases} OH \\ OH \end{cases} \\ | \\ CO_2H. \end{array}$$

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[1] *Liebig's Ann.* cc. 93.
[2] *Ibid.* ccxxv. 119.
[3] *Ber. Deutsch. Chem. Ges.* xiii. 1808.
[4] Gruber, *ibid.* xii. 514.
[5] Barth, *Monatsch. Chem.* i. 869.

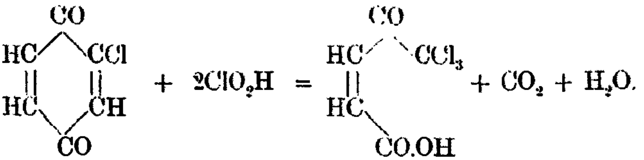
and it is dioxytartaric acid or tetroxysuccinic acid.[1] Although its constitution does not exactly contradict the truth of the prismatic formula, its formation from catechol is certainly more easy to explain if we assume the hexagon formula for benzene.

947 The same is true for the formation of another acid obtained by Carius by acting with chlorous acid on benzene, and afterwards investigated by Kekulé and Strecker,[2] who have found that it is β-trichloracetylacrylic acid, $CCl_3CO.CH{=}CH.CO_2H$, for on warming with baryta-water it decomposes into chloroform and maleic acid;

$$C_3H_3Cl_3O_3 + H_2O = C_4H_4O_4 + CCl_3H.$$

It combines with bromine, forming trichloracetyldibromopropionic acid, $CCl_3CO.CHBr.CHBr.CO_2H$, which on boiling with lime-water is converted into chloroform and inactive tartaric acid.

β-trichloracetylacrylic acid is not obtained from benzene by a simple reaction, as several by-products are formed, amongst others, chlorinated quinones. The acid is produced by the action of chlorous acid on quinone, and its formation is most simply explained by the supposition that monochloroquinone yields it, according to the following equation:



If we attempt to explain this reaction by means of the prism formula, Kekulé and Strecker have shown that if we do not meet with insuperable difficulties we are, at any rate, surrounded by distinct improbabilities. "We must then assume that five single links of carbon are liberated, three by the separation of the carbon atom which is set free and separates out. This cannot be said to be remarkable, but two other links are liberated so as to form the normal chain of carbon atoms which is contained in β-trichloracetylacrylic acid." Hence the improbable supposition must be made, that a double linkage of the carbon atoms is brought about from a single linkage under conditions in which we should rather expect to find the formation of a

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[1] *Liebig's Ann* ccxxi. 230.

[2] *Ibid.* ccxxiii. 170.

single from a double linkage. If the formation of the above-named acid does not prove the truth of Kekulé's views concerning the constitution of benzene, it renders this view certainly far more probable than any other which has hitherto been given. In most cases a simple hexagon can be used to explain the constitution of the benzene derivatives, and we imply by this either Kekulé's formula or the star prismatic formula.

948 Kekulé's formula has, moreover, the advantage of satisfactorily explaining the constitution of naphthalene, $C_{10}H_8$, phenanthrene, $C_{14}H_{10}$ and other hydrocarbons which contain more than six atoms of carbon in aromatic linkage. Of these bodies we shall speak at length in a subsequent portion of this treatise, We only wish to point out that they are derived in several ways from benzene, viz:—

1. The hydrogen in benzene can be replaced by phenyl;

Phenylbenzene	$C_6H_5.C_6H_5$
Diphenylbenzene	$C_6H_4.(C_6H_5)_2$
Triphenylbenzene	$C_6H_3(C_6H_5)_3$

Compounds are also found containing alcohol radicals as side chains;

Phenyltoluene	$C_6H_5.C_6H_4.CH_3$
Methylphenyltoluene . . .	$CH_3.C_6H_4.C_6H_4.CH_3$

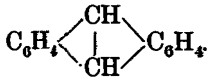
2. In others the aromatic nuclei are not combined directly but through a carbon atom:

Diphenylmethane	$CH_2(C_6H_5)_2$
Triphenylmethane	$CH(C_6H_5)_3$
Diphenylethane	$CH_3.CH.(C_6H_5)_2$
Phenyltolylmethane . . .	 $CH_2\begin{cases} C_6H_5 \\ C_6H_4.CH_3 \end{cases}$

3. The aromatic nuclei are united by two carbon atoms:

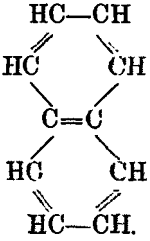
Dibenzyl	$C_5H_0.CH_2—CH_2.C_6H_5$
Toluylene	$C_6H_5.CH{=}CH.C_6H_5$
Tolane	$C_6H_5.C{\equiv}C.C_6H_5$
Tetraphenylethane	$(C_6H_5)_2CH—CH(C_6H_5)_2$

And to this group belongs anthracene:

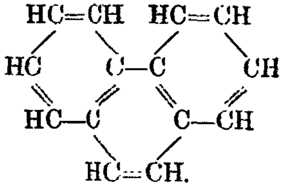


4. Of the hydrocarbons with condensed nuclei, it is sufficient to mention here, two,

Naphthalene.



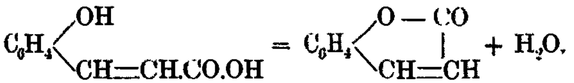
Phenanthrene.



Many others besides these are known, and from each of these a large number of derivatives can be obtained, affording a further proof of the very large number of the aromatic bodies.

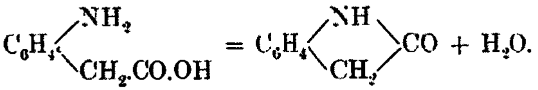
CHARACTERISTIC REACTIONS OF THE DI-SUBSTITUTION PRODUCTS.

949 A characteristic property of the ortho-compounds is their easy transformation with separation of water into inner anhydrides, such as have been mentioned under salicylic and phthalic acids. As another example we may mention cumaric acid or orthocinnamic acid, whose anhydride, cumarin, gives to sweet woodruff its pleasant smell:



$$C_6H_4\left\langle\begin{matrix}OH\\CH{=}CH.CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}O-CO\\ \quad\;\;|\\CH{=}CH\end{matrix}\right. + H_2O.$$

The amido-acids of this group also exhibit a similar reaction; thus ortho-amidophenylacetic acid passes readily into an anhydro-compound, which has been termed oxindol from the fact that it was first obtained from indigo:

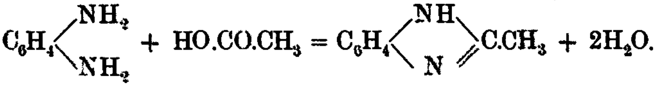


$$C_6H_4\left\langle\begin{matrix}NH_2\\CH_2.CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}NH\\CH_2\end{matrix}\right\rangle CO + H_2O.$$

The ortho-compounds having carbon side-chains are distinguished from those of the two other series, inasmuch as when heated with chromic acid solution, they do not undergo a simple oxidation, but are completely decomposed with formation of carbon dioxide, acetic acid and oxalic acid, &c. Dilute nitric acid, or an alkaline solution of potassium permanganate, on the other hand, easily bring about an oxidation in which the side chains are converted into carboxyl.

Ladenburg found that orthodiamido-compounds when heated with monobasic organic acids give rise to peculiar condensation products:

Ethylenephenylenediamine.



$$C_6H_4\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + HO.CO.CH_3 = C_6H_4\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle C.CH_3 + 2H_2O.$$

In the meta- and para-compounds, however, a hydrogen atom of each amido-group is replaced by an acid radical, and thus, *e.g.*, β diacetyldiamido-benzene, $C_6H_4(NH.CO.CH_3)_2$, is obtained.

The orthodiamines also form with aldehydes a series of monoacid bases to which Ladenburg has given the name of aldehydines:

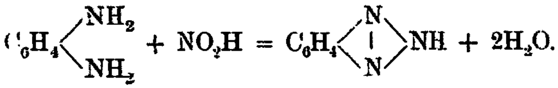
Benzaldehyde. Phenylbenzaldehydine.

$$C_6H_4(NH_2)_2 + 2COH.C_6H_5 = C_6H_4(NCH.C_6H_5)_2 + 2H_2O.$$

The diamines of the two other series act similarly; but the compounds thus obtained are so unstable that it is impossible to prepare their salts since they decompose readily into their constituents with assumption of water.

If the hydrochloride of an orthodiamine be heated with benzaldehyde from 100° to 120°, half the hydrochloric acid is evolved, whilst the salts of the two other series yield no trace of acid when thus treated.

Ladenburg found that the orthodiamido-compounds are distinguished from the other isomerides by the action of nitrous acid, inasmuch as only one molecule of the base enters into the reaction,[1] and inner condensation occurs accompanied by elimination of water. Orthodiamidobenzene yields amidoazophenylene or azoamidobenzene:



$$C_6H_4\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + NO_2H = C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle NH + 2H_2O.$$

950 In the case of meta-compounds on the other hand, two molecules take part in the reaction, and yellow or brown azocolours are formed. From metadiamidobenzene, triamidoazobenzene or phenylene-brown is obtained:

$$2C_6H_4(NH_2)_2 + NO_2H = C_6H_4(NH_2)N = NC_6H_3(NH_2)_2 + 2H_2O.$$

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[1] *Ber. Deutsch. Chem. Ges.* ix. 219, 1524; xvii. 147.

According to Griess this reaction is so characteristic and delicate that it may be used to detect the nitrites in potable water; for this it is necessary to mix the solution of the base with the solution of the nitrite.[1]

Another characteristic reaction for the metadiamidobenzenes is that they unite with diazo-salts to form diamidoazo-compounds, yellow or yellowish red colours, one of which is well known as chrysoidine.

Nitrous acid acts quite differently on paradiamido-compounds; if potassium nitrite be added to a solution of hydrochloride of paradiphenylamine, a brown powder separates out after some time, the amount of this being increased on warming with violent evolution of gas and formation of quinone (Ladenburg).

In the para-series many compounds occur which yield quinone, $C_6H_4O_2$, on oxidation with manganese dioxide and dilute sulphuric acid; this substance being recognised by its powerful smell, as well as by the ease with which it sublimes in yellow needles. It is, however, not only obtained from para-substitution products, such as hydroquinone, paradiamidobenzene, &c., but also from monosubstitution products, such as aniline.

The influence of the nitroxyl is remarkable when it occurs in the ortho- or para-positions with respect to the halogens.

When the latter replace hydrogen in the aromatic group, the compounds formed are usually not capable of double decomposition, but they become so when nitroxyl occupies the above position. Ortho- and para-bromonitrobenzene when heated with alcoholic potash are converted into the corresponding nitrophenols:

$$C_6H_4(NO_2)Br + KOH = C_6H_4(NO_2)OH + KBr.$$

If the former be heated with alcoholic ammonia nitranilines are formed, which may be also obtained from the corresponding nitranisols:

$$C_6H_4(NO_2)OCH_3 + NH_3 = C_6H_4(NO_2)NH_2 + HO.CH_3.$$

These reactions do not take place in the meta-series.

The orthodinitro-compounds readily exchange a nitroxyl for other radicals.[2]

If orthodinitrobenzene be boiled with caustic soda orthonitrophenol is formed, and on heating the former with ammonia, orthonitraniline and ammonium nitrite are obtained.

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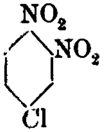
[1] *Ber. Deutsch. Chem. Ges.* xi. 625.

[2] Laubenheimer, *ibid.* ix. 761; xi. 303, 1151; xv. 597.

If dinitrochlorobenzene, $C_6H_3Cl(NO_2)_2$, which has the following constitution—



be boiled with a solution of sodium sulphite, sodium nitrochlorobenzenesulphonate, $C_6H_3(NO_2)Cl(SO_3Na)$, and sodium nitrite are produced.

BENZENE GROUP.

BENZENE, C_6H_6.

951 *Historical.*—It has already been stated that the oil obtained from portable gas contained a liquid, in which Faraday in 1825 discovered two new hydrocarbons (Vol. iii. Part II. p. 162), the first of which was afterwards found to be butylene. To the second, Faraday gave the name of bicarburet of hydrogen, as he found its empirical formula to be C_2H ($C = 6$). By exploding its vapour with oxygen, he observed that one volume contains 36 parts by weight of carbon, to 3 parts by weight of hydrogen, and its specific gravity compared with hydrogen is therefore 39.[1]

Mitscherlich, in 1834, obtained the same hydrocarbon by distillation of benzoic acid, $C_7H_6O_2$, with slaked lime, and termed it benzin. He assumed that it is formed from benzoic acid, simply by removal of carbon dioxide.[2] Liebig denied this, adding the following editorial note to Mitscherlich's memoir: "We have changed the name of the body obtained by Professor Mitscherlich by the dry distillation of benzoic acid and lime, and termed by him benzin, into benzol, because the termination 'in' appears to denote an analogy between strychnine, quinine, &c., bodies to which it does not bear the slightest resemblance, whilst the ending in 'ol' corresponds better to its properties and mode of production. It would have been perhaps better if the name which the discoverer, Faraday, had given to this body had been retained, as its relation to benzoic acid and benzoyl compounds is not any closer than it is to that of the tar or coal from which it is obtained."

Almost at the same time Péligot found that the same hydro-

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[1] *Phil. Trans.* 1825, 440; *Pogg. Ann.* iii. 306.

[2] *Ann. Chem. Pharm.* ix. 43.

carbon occurs, together with benzone, $C_{13}H_{10}O$ (diphenylketone $CO(C_6H_5)_2$), in the products of the dry distillation of calcium benzoate.[1]

The different results obtained by Mitscherlich and Péligot are represented by the following formulæ:

$$C_7H_6O_2 + CaO = C_6H_6 + CaCO_3.$$
$$(C_7H_5O_2)_2Ca = C_{13}H_{10}O + CaCO_3.$$

Péligot obtained benzene only as a by-product, exactly as in the preparation of acetone (dimethylketone) from calcium acetate, a certain quantity of marsh gas is always formed.

It is not clear how Liebig became acquainted with the fact that benzene is formed by the dry distillation of coal, as his pupil Hofmann, who obtained it in 1845 from coal-tar, observes: "It is frequently stated in memoirs and text-books that coal-tar oil contains benzene. I am, however, unacquainted with any research in which this question has been investigated."[2] It is, however, worthy of remark that about the year 1834, at the time when Mitscherlich had converted benzene into nitrobenzene, the distillation of coal-tar was carried out on a large scale in the neighbourhood of Manchester; the naphtha which was obtained was employed for the purpose of dissolving the residual pitch, and thus obtaining black varnish. Attempts were made to supplant the naptha obtained from wood-tar, which at that time was much used in the hat factories at Gorton near Manchester for the preparation of "lacquer," by coal-tar naphtha. The substitute however did not answer, as the impure naphtha left on evaporation so unpleasant a smell, that the workmen refused to employ it. It was also known about the year 1838, that wood-naphtha contained oxygen, whilst that from coal-tar did not, and hence Mr. John Dale attempted to convert the latter into the former, or into some similar substance. By the action of sulphuric acid and potassium nitrate, he obtained a liquid possessing a smell resembling that of bitter-almond oil, the properties of which he did not further investigate.[3] This was, however, done in 1842 by Mr. John Leigh, who exhibited considerable quantities of benzene, nitrobenzene, and dinitrobenzene to the chemical section of the British Association meeting that year in Manchester. His communication is, however, so printed in the Report, that it

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[1] *Ann. Chim. Phys.* [3], lvi. 59.

[2] *Ann. Chem. Pharm.* lv. 200.

[3] Private communication.

is not possible from the description to identify the bodies in question.[1]

952 Coal-tar is obtained, as is well known, together with ammonia-liquor in the manufacture of coal-gas. The same products are also produced in the coking process, now usually carried on in ovens connected with vessels in which the aqueous distillate and the tar are collected. It is interesting to learn that these products were collected even before the manufacture of gas became known. Thus De Gensanne describes coke ovens connected with the ironworks at Sulzbach, near Saarbrücken, about 1764, in connection with which was an arrangement for collecting the volatile products "les huiles et le bitume." The oil thus obtained resembled distilled petroleum, had a strong bituminous odour, and burnt with a smoky flame; the miners and peasants in the neighbourhood used it for their lamps.

These are probably the same ovens which Goethe, in 1771, saw in the neighbourhood of the burning hill near Dutweiler, a village near Sulzbach.[2] Here he met old Stauf, a coal philosopher —"philosophus per ignem," as it was formerly called—"who complained that the enterprise did not pay," for as Goethe says, they not only wanted to desulphurize the coal for the use in iron-works, "but at the same time they wished to turn the oil and resin to account; nay, they would not lose the soot, and thus all failed together, on account of the many ends in view."[3]

Large quantities of benzene were prepared in 1848, under Hofmann's direction, by Mansfield, who proved that the naphtha in coal-tar contains homologues of benzenes, which may be separated from it by fractional distillation.[4]

On the 17th of February, 1856, Mansfield was occupied with the distillation of this hydrocarbon, which he foresaw would find further applications, for the Paris Exhibition, in a still, whose construction is shown in Fig. 1. The liquid in the retort boiled over and took fire, burning Mansfield so severely that he died in a few days.[5]

Sources of Benzene.—Benzene is also found in the products of distillation of wood and many organic bodies. It is likewise pro-

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[1] Private communication. *Brit. Assoc. Report*, 1842, 39. See also *Moniteur Scient.* 1865, 446.

[2] Private communication of Dr. Gurlt to Watson Smith. The title of Gensanne's work is: *Traité de la fonte des Mines par le feu du Charbon de Terre.* 2 vols. Paris, 1770 et 1776.

[3] *Aus Meinem Leben*, "Wahrheit and Dichtung." Oxenford's Translation, vol. i. 364.

[4] *Quart. Journ. Chem. Soc.* i. 244.

[5] *Ibid.* viii. 110.

duced when the vapours of its homologues and other aromatic compounds are passed through a red-hot tube. Even the simplest compounds of the fatty group, such as marsh gas, alcohol and acetic acid, yield some benzene together with a variety of other bodies when thus treated.[1]

Of special interest is its synthesis from acetylene, C_2H_2, discovered by Berthelot. If this gas be heated for some time at the temperature at which glass begins to soften, it is converted into a mixture of polymerides, amongst which benzene is present in considerable quantity.[2] Marignac has shown that it is also formed by the distillation of phthalic acid, $C_8H_6O_4$, with caustic lime.[3] The reaction is quite similar to that by which it is formed from benzoic acid:

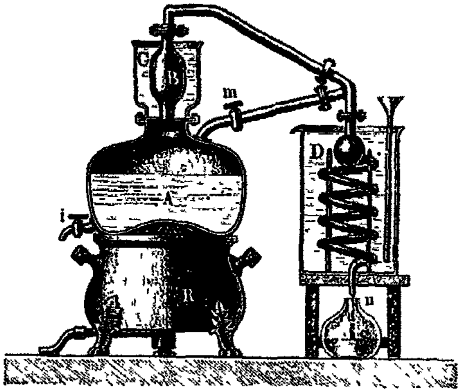

FIG. 1.

$$C_6H_5.CO_2H = C_6H_6 + CO_2$$
$$C_6H_4(CO_2H)_2 = C_6H_6 + 2CO_2.$$

Since that time, it has been observed that all benzenecarboxylic acids, or acids which are derived from benzene by replacement of hydrogen by carboxyl, are in this way converted into benzene.

Benzene also occurs, together with its homologues, in small quantities in petroleum from Burmah (Rangoon tar),[4] in that

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[1] Berthelot, *Jahresb.* 1851, 437, 504; 1868, 333.
[2] *Ibid.* 1870, 1.
[3] *Ann. Chem. Pharm.* xlii. 217.
[4] Warren de la Rue and H. Müller, *Roy. Soc. Proc.* viii. 221.

from Galizia,[1] and in that from Canadian and Pennsylvanian wells. (Schorlemmer.)

Manufacture.—Benzene is largely employed in the arts, especially in the manufacture of aniline. In preparing it, coal-tar, or tar from certain coking processes, is distilled in large retorts made of malleable iron. The usual English retort is shown in Figs. 4 and 5, whilst those used in France and Germany are represented in Figs. 2 and 3.

The vapours are cooled by passing through lead or copper pipes, or by means of a system of iron pipes as shown in Fig. 6.

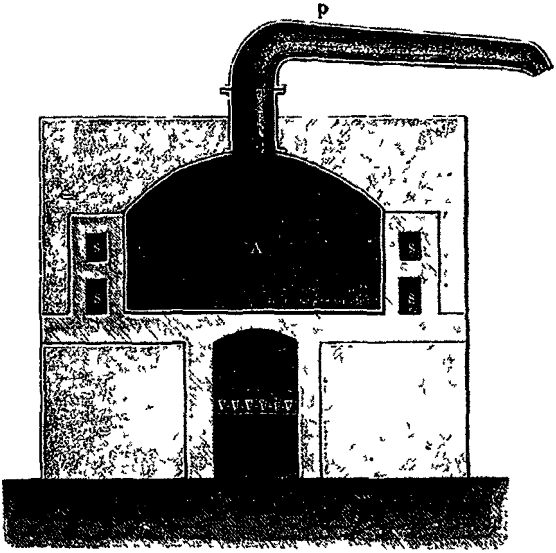

FIG. 2.

In this process the following products are obtained, combustible gases being evolved at the commencement of the distillation

The *first runnings* amount to about 2 to 4 per cent. of the tar, and consist of carbon disulphide, paraffins, olefines, benzene and other hydrocarbons, acetonitril, ethyl alcohol &c At the same time ammonia-water comes over, and for this reason the distillate separates into two layers. When a thermometer is used

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[1] Freund, *Ann. Chem. Pharm.* cxv. 19.

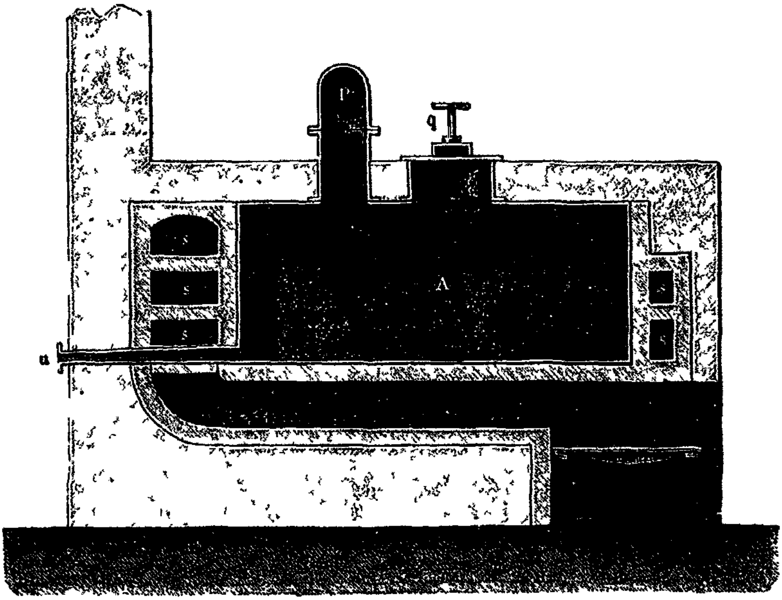

Fig. 3.

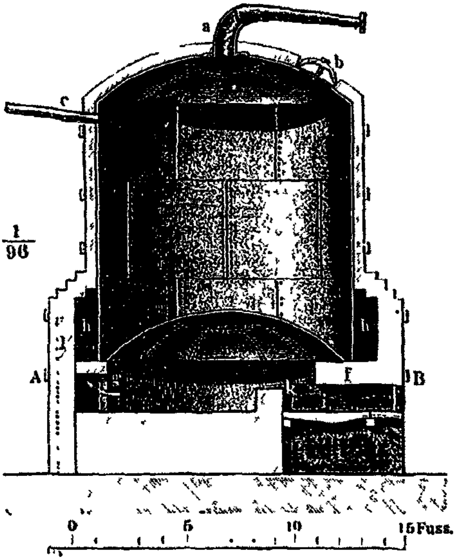

Fig. 4.

in working, the receiver is changed when the temperature rises to about 110°.

The next product is termed *light oil* or *crude naphtha*. As soon as the water is removed, the peculiar hissing noise ceases, and the light oil (which swims on water) now comes over, and amounts to about 7 to 8 per cent. of the tar, the temperature rising to about 210°. In some works the light oil is collected below 170°, and that coming over between 170° and 230° is called *middle oil*.

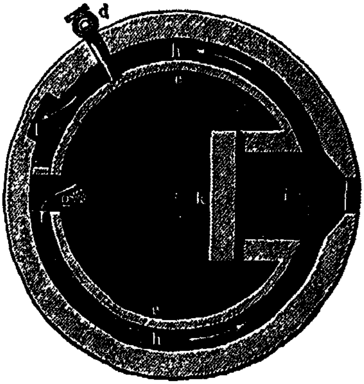

Fig. 5.

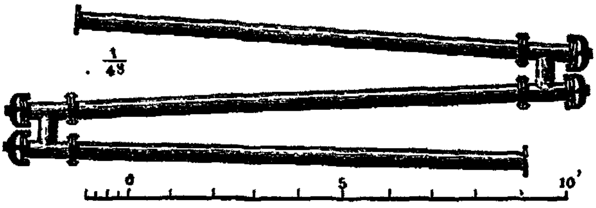

Fig. 6.

Between 210° and 400° *heavy* or *dead oil* comes over, which sinks in water. This is also frequently collected in two portions, that which comes over below 270° being known as *creasote oil*, whilst the higher boiling portion is termed *anthracene oil*. The further treatment of these oils, as well as that of pitch, will be referred to hereafter.

953 Benzene mixed with other hydrocarbons is obtained from the first runnings by fractional distillation. The *light oil*, however,

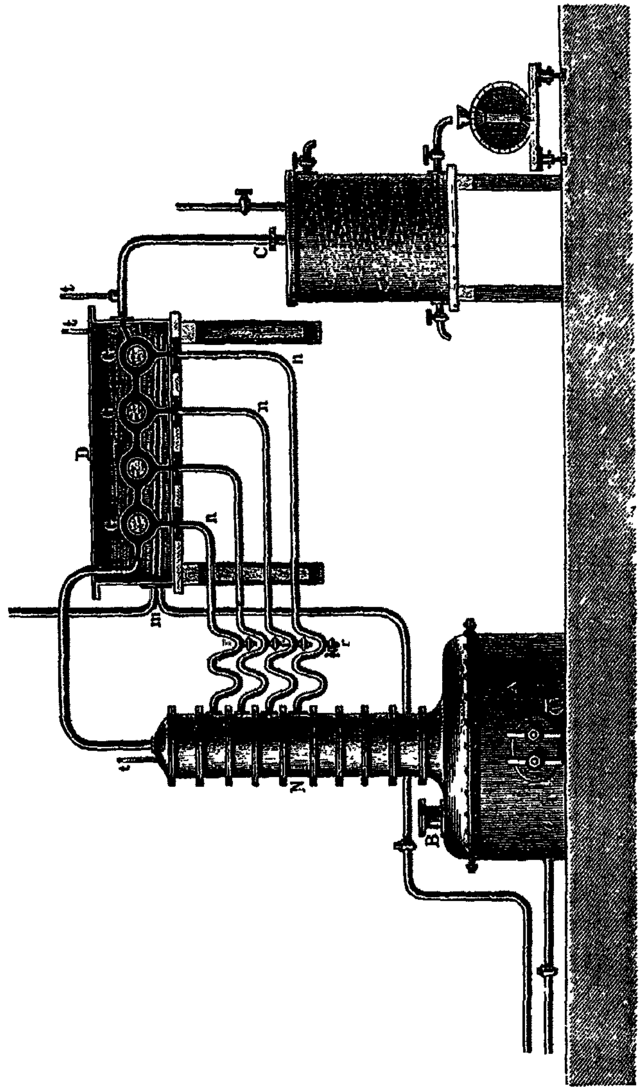

FIG. 7.

is the chief source of crude benzene. This oil contains a small quantity of paraffins, olefines, benzene and its homologues, phenol, cresol, naphthalene and bases. It is first rectified once or several times in light oil stills, which are similar in structure to the tar stills, but usually smaller. The portion boiling between 80° and 150°, together with that fraction of the first runnings which boils above 80°, and the portion of the creasote oils which, on rectification, boils below 150°, are then worked up for benzene and its homologues. The first boiling portions of the light oils are frequently collected separately and brought into commerce as crude naphtha, being employed for carburetting gas, and as a solvent.

The rectified light oils are then treated with 5 per cent. of concentrated sulphuric acid, for the purpose of freeing them from bases, olefines and other hydrocarbons; well washed with water and thoroughly agitated with caustic soda, which dissolves phenol and its homologues.

In 1860, E. Kopp suggested the employment of an apparatus used in the rectification of alcohol for the purpose of fractionating the neutral oils thus obtained, and this suggestion was first carried out on the large scale by Coupier at Poissy, near Paris, in 1863.

The apparatus he employed, Fig. 7, consists of a boiler heated by steam and a column that serves as a dephlegmator, in which a partial separation takes place. The vapours which do not here liquefy pass into a series of condensers surrounded by a solution of calcium chloride, which for the purpose of obtaining benzene is heated to a temperature of 80°.

When this has all distilled over, the bath of calcium chloride is heated to 110°, when toluene passes over. To obtain the mixture of the xylenes, a paraffin bath is employed heated by high pressure steam to a temperature of 140°. Coupier obtained the following results with this apparatus:

100 litres of light oil boiling between 80° and 150° gave :—

			B.P.
6	litres of	crude benzene	62° to 80°
44	„	benzene	80° „ 82°
6	„	intermediate product. .	82° „ 110°
17	„	toluene	110° „ 112°
5	„	intermediate	112° „ 137°
9	„	xylenes	137° „ 140°
5	„	intermediate	140° „ 148°
8 to 9	„	trimethylbenzenes . . .	148° „ 150°[1]

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[1] These, however, boil from 163° to 166°.

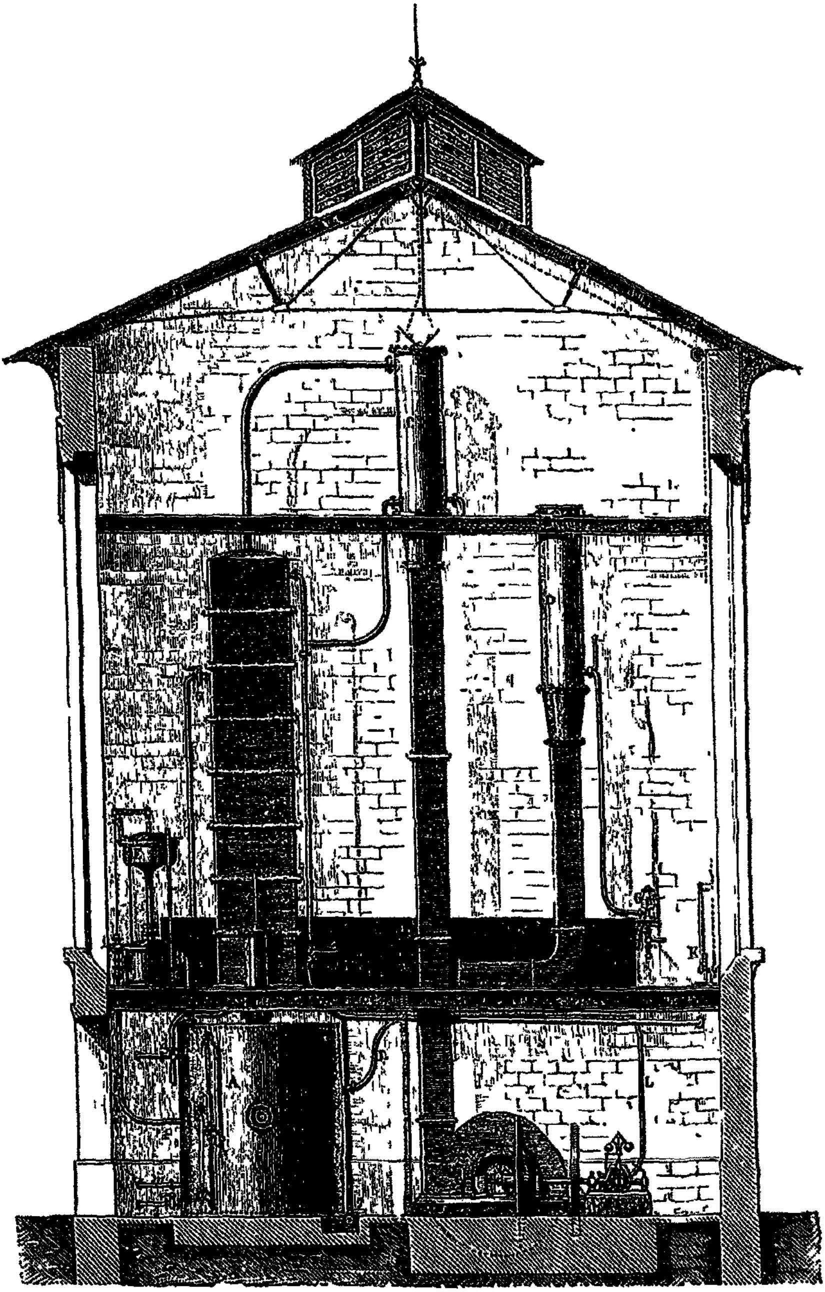

Fig. 8.

In larger works the hydrocarbons are separated by means of large copper column apparatus (similar to those employed in the rectification of spirits). Fig. 8 shows one employed by Savalle, in Paris, a vertical section being shown in Fig. 9. The condensation of the vapours is effected by a current of air, the strength of which can be regulated.

The benzene boiling from 80° to 82° is pure enough for the preparation of pure aniline. It always, however, contains a small quantity of paraffins and other non-saturated hydrocarbons. In order to purify it Mansfield's process is employed. This consists in crystallizing the crude benzene in a freezing mixture, when the impurities remain liquid and can be separated from the pure solidified benzene. A simple apparatus for this purification has been described by Hofmann.[1]

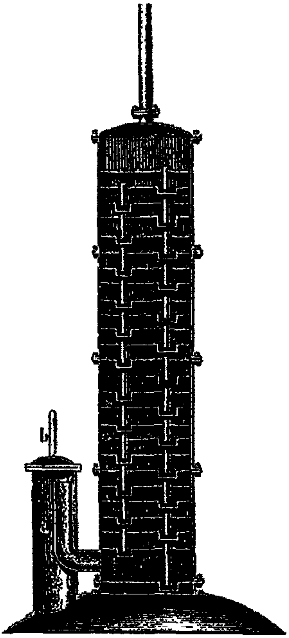

FIG. 9.

Chemically pure benzene, obtained from benzoic acid, does not colour sulphuric acid brown, though that obtained from coal-tar

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[1] *Ber. Deutsch. Chem. Ges.* iv. 162.

does so even after crystallization. This latter product exhibits a very characteristic reaction. If one grain of isatine, $C_8H_5NO_2$, be dissolved in concentrated sulphuric acid, and benzene added, the liquid after a short time becomes of a fine blue colour; if, however, the benzene be previously shaken with sulphuric acid, until it is no longer coloured brown, or if the benzene obtained from benzoic acid be used, the isatine reaction is not given.[1]

The body which produces this reaction is thiophene, C_4H_4S, a liquid possessing a most remarkable similarity to benzene.

Mention has already been made of this substance, Vol. III. Part II, p. 631.

954 *Properties.*—Benzene is a colourless, mobile, strongly refracting liquid, possessing a peculiar smell, boiling at 80°·5, and solidifying, when cooled, to rhombic crystals which melt at 4°·5. It is easily inflammable, burning with a luminous and smoky flame. Like other hydrocarbons, it is very slightly soluble in water, but dissolves in alcohol, ether, chloroform, &c. On the other hand, it serves as an excellent solvent for iodine, sulphur, phosphorus, fats, resins, various alkaloids, and many other organic compounds. Its specific gravity at 0° is 0·900 and at 15° is 0·885.

Benzene taken internally is found in the urine, as a salt of phenylsulphonic acid. If the vapour of about 10 grammes be inhaled, dizziness and sickness, as well as a tendency to sleep, occur. In doses from 40 to 50 grammes it produces a similar action to chloroform, accompanied by profuse perspiration; the same quantity given to cats acts fatally, with epileptic seizures. In works in which the fat is extracted from woollen fibre by benzene, the vapours of this substance produce intoxication amongst the workmen, who also suffer from a peculiar irritation and dryness of the skin, due, according to Perrin, to the solution of its fatty constituents.[2]

When the induction spark is passed through benzene a solid substance is formed, together with carbon, whilst a mixture of 42 to 43 per cent. of acetylene, and 57 to 58 per cent. of hydrogen, is given off.[3]

If benzene be oxidized with manganese dioxide and sulphuric acid various products are formed, amongst which are formic,

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[1] V. Meyer, *Ber. Deutsch. Chem. Ges.* xvi. 1465, 2172, 2968.

[2] Grandhomme, *Die Farbwerke von Meister, Lucius und Brüning in sanitärer und socialer Beziehung.*

[3] Destrem, *Compt. Rend.* xcix. 138.

benzoic, and phthalic acids.[1] If formic acid be added to the above oxidizing mixture a larger proportion of benzoic acid is formed, from which Carius concluded that it is produced by a simultaneous oxidation of benzene and formic acid.

$$C_6H_6 + CHO.OH + O = C_6H_5.CO.OH + H_2O.$$

It appears, however, more probable that a part of the benzene is oxidized to diphenyl, $C_6H_5.C_6H_5$, and that this on further oxidation yields benzoic acid, whilst phthalic acid, $C_6H_4(CO.OH)_2$, is formed from diphenylbenzene, $C_6H_4(C_6H_5)_2$, which is probably formed at the same time as the diphenyl.

Benzene, when brought into contact with a glowing spiral of platinum wire, in presence of air, is oxidized to benzaldehyde and benzoic acid.[2]

By the action of potassium chlorate and sulphuric acid on benzene, Carius obtained a peculiar acid, which he considered to be a chlorine substitution product of an acid homologous with malic acid, and to which he gave the name of trichlorophenomalic acid, $C_6H_7Cl_3O_5$. He believed it to be produced according to the following equation:

$$C_6H_6 + 3ClO_2H = C_6H_7Cl_3O_5 + H_2O.$$

At the same time he obtained chlorobenzene, oxalic acid, chlorinated quinols, and quinones, amongst which was dichloroquinone, $C_6H_2Cl_2O_2$, and other bodies.

By heating trichlorophenomalic acid with baryta water, phenaconic acid, $C_6H_6O_6$, a substance isomeric with aconitic acid, was produced:

$$C_6H_7Cl_3O_5 + H_2O = C_6H_6O_6 + 3HCl.$$

When, however, this body was heated with hydriodic acid it was completely converted into succinic acid, whilst by the action of bromine two isomeric dibromosuccinic acids were formed. These, as well as the succinic acid, must be produced from phenaconic acid by "polymeric rearrangements." On warming a mixture of the two dibromosuccinic acids with baryta water Carius obtained racemic acid and bromomaleic acid.

A short time after this Carius concluded, from some experiments made on the acid potassium salt of fumaric acid, that it was clear that phenaconic acid is identical with fumaric acid. Hence phenaconic acid disappeared from the list of chemical

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[1] *Ann. Chem. Pharm.* cxlviii. 50.

[2] Coquill. *Compt. Rend.* lxxx. 1089.

compounds; trichlorophenomalic acid remained, however, as a mysterious body, and its decomposition into hydrochloric acid and fumaric acid was unexplained.

In 1877 Krafft repeated Carius' experiments, and found in the product of the reaction a large quantity of trichloroquinone, $C_6HCl_3O_2$, and trichlorohydroquinone, $C_6H_3Cl_3O_2$, which latter substance he considered to be identical with trichlorophenomalic acid. This compound then disappeared from chemical literature, the fact being overlooked that Krafft had only proved the formation of trichloroquinone and trichlorohydroquinone. The identity of this latter substance with Carius' acid had not been shown, and he did not try the only decisive experiment, *i.e.* to convert trichlorophenomalic acid into fumaric acid.

The investigation of trichlorophenomalic acid was next taken up by Kekulé and Strecker. In the introduction to their memoir they say: "To express shortly the results of our critical studies, we may state that it is nothing but a comedy of errors. Trichlorophenomalic acid is not formed according to the equation given by Carius, neither has it the formula which Carius ascribed to it; on the other hand, it is not, as Krafft believed, identical with trichlorohydroquinone. It does not yield hydrochloric acid or fumaric acid when decomposed by alkalis, but, notwithstanding, Carius' phenaconic acid is identical with fumaric acid."

It has already been stated that trichlorophenomalic acid proved to be β-trichloracetylacrylic acid, $C_5H_3Cl_3O_3$, which is soluble with difficulty in cold, but more readily in hot water, and crystallizes in small glistening scales, which possess a pleasant smell, and melt from 131° to 132°.

On warming with baryta water it decomposes into chloroform and maleic acid, $C_4H_4O_4$, and it unites with bromine to form trichloracetyldibromopropionic acid, $C_5H_3Cl_3Br_2O_3$, which on heating with lime-water splits up into chloroform and inactive tartaric acid. Carius' statements can now be simply explained. In his first experiments part of the maleic acid was converted into fumaric acid; by the action of bromine on this mixture he obtained dibromosuccinic acid together with isodibromosuccinic acid, the former of which yielded inactive tartaric acid, then believed to be racemic acid. In his later experiments the conversion of the maleic acid was complete, and his pure phenaconic acid consisted entirely of fumaric acid.[1]

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[1] *Liebig's Ann.* ccxxiii. 170 (where also the complete literature will be found).

If boiling benzene be saturated with picric acid (trinitrophenol), the compound, $C_6H_6 + C_6H_2(NO_2)_3OH$, separates out on cooling in bright yellow crystals, which give off benzene on exposure to air (Fritzsche).

If antimony chloride be dissolved in hot benzene, transparent monoclinic tables of the compound, $(C_6H_6)_2(SbCl_3)_3$, separate out on cooling, which deliquesce on exposure to air.[1]

When a current of hydrochloric acid is passed into a mixture of benzene and aluminium chloride, a compound, $6C_6H_6 + Al_2Cl_6$, is obtained as a thick orange-coloured liquid, which crystallizes at $-5°$, and is decomposed by water into its constituents. Aluminium bromide forms a similar compound.[2]

When benzene is heated with potassium from 230° to 250°, a bluish-black crystalline body is formed without any hydrogen being evolved; on exposure to air this substance spontaneously ignites with explosive violence. If this body be covered with benzene, and water slowly added, diphenylbenzene, $C_6H_4(C_6H_5)_2$, is formed together with a small quantity of diphenyl, $(C_6H_5)_2$, and of a hydrocarbon, $C_{12}H_{16}$, which is a thick liquid smelling like aniseed and boiling at 222°. From this it would appear that the above blue body is a mixture of monopotassium benzene, C_6H_5K, dipotassium benzene, $C_6H_4K_2$, and potassium hydrogenide, K_4H_2 (Vol. II. Part I. p. 61)[3].

ADDITIVE PRODUCTS OF BENZENE.

955 *Benzene hexhydride*, or *Hexhydrobenzene*, C_6H_{12}, was first obtained by Berthelot, and believed by him to be hexane. It is formed when benzene is heated with a large excess of aqueous hydriodic acid, saturated at 0°, for five hours, to 280°. It forms a constituent of Caucasian petroleum,[4] and is a liquid boiling at 69°, and having a specific gravity 0·76 at 0°.[5]

Benzene hexchloride, $C_6H_6Cl_6$, was first prepared by Mitscherlich,[6] Peligot,[7] and Laurent,[8] by exposing benzene in large flasks

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[1] Smith and Davis, *Journ. Chem. Soc.* 1882, i. 412.

[2] Gustavson, *Ber. Deutsch. Chem. Ges.* xi. 2151.

[3] Abeljanz, *ib.* ix. 10.

[4] Beilstein and Kurbatow, *ib.* xiii. 1818.

[5] Wreden and Znatowicz, *Ann. Chem. Pharm.* clxxxvii. 163.

[6] *Pogg. Ann.* xxxv. 370.

[7] *Ann. Chim. Phys.* [2], lvi. 66.

[8] *Ann. Chem. Pharm.* xxiii. 68.

filled with chlorine to the action of sunlight. It is also obtained when chlorine is passed into boiling benzene.[1]

According to Hugo Müller, benzene dichloride, $C_6H_6Cl_2$, and benzene tetrachloride, $C_6H_6Cl_4$, bodies which have not been more closely examined, together with substitution products, are first formed.[2] Additive products are also formed when hydrochloric acid and potassium bichromate act upon benzene.[3]

In order to prepare benzene hexchloride, chlorine is allowed to act in the sunlight on the surface of benzene contained in large flasks.[4] The crystalline mass thus formed is then recrystallized from hot benzene. It forms large monoclinic prisms melting at 157° and boiling, with liberation of hydrochloric acid, at 288°; alcoholic potash decomposes it completely into hydrochloric acid and asymmetrical trichlorobenzene. Fuming nitric acid does not attack it even on warming, whilst zinc reduces it in alcoholic solution to benzene.[5]

On passing chlorine into boiling benzene in the sunlight an isomeric benzene hexchloride is formed, which crystallizes in regular octahedra and tetrahedra, etc. This body melts at 300° and volatilizes about the same temperature; it is only slowly attacked by boiling alcoholic potash, and is unaltered by a boiling alcoholic solution of potassium cyanide, by which reaction it can be separated from the ordinary hexchloride, as this is at once converted into trichlorobenzene.[6]

According to Schüpphaus, Meunier's compound, which Hübner previously observed, is perhaps diphenyl dodecachloride, $C_{12}H_{10}Cl_{12}$.[7]

Benzene hexbromide, $C_6H_6Br_6$, was obtained by Mitscherlich by the action of bromine on benzene in sunlight.[8] It separates from its ethereal solution in microscopic, opaque, rhombic prisms (Lassaigne), and is decomposed by alcoholic potash into tribromobenzene and hydrobromic acid.

Benzene trichlorohydrin, $C_6H_6Cl_3(OH)_3$, is formed when benzene is brought into contact with aqueous hypochlorous acid. It is difficultly soluble in water, but readily in ether, and crystallizes

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[1] Lesimple, *Ann. Chem. Pharm.* cxxxvii. 123; Heys, *Zeitsch. Chem.* 1871, 293.

[2] *Jahresb.* 1862, 414.

[3] Jungfleisch, *ib.* 1868, 355.

[4] Leeds and Everhart, *Journ. Americ. Chem.* ii. 205.

[5] Zinin, *Zeitsch. Chem.* 1871, 284; ii. 205.

[6] Meunier, *Compt. Rend.* xcviii. 436.

[7] *Ber. Deutsch. Chem. Ges.* xvii. 2256.

[8] *Ann. Chem. Pharm.* xvi. 173.

in fine scales which melt at 10°, and are volatile without decomposition. Very dilute alkalis decompose it with formation of various products, among which phenose, $C_6H_{12}O_6$, a body isomeric with glucose, is found. This is an amorphous, hygroscopic mass, which possesses a sweetish taste and reduces an alkaline copper solution. Concentrated hydriodic acid is said to convert it into secondary hexyl iodide on heating.[1]

CHLORINE SUBSTITUTION PRODUCTS OF BENZENE.

956 It has already been stated that by the action of chlorine on benzene a mixture of additive and substitution products is obtained. When iodine is added, a smooth and regular substitution takes place in consequence of a continuous decomposition and reformation of iodine chloride. Still more energetic is the action of antimony chloride, which is, therefore, used in the preparation of higher chlorinated derivatives.[2]

By this direct substitution all the theoretically possible compounds are not formed. Monochlorobenzene which is first formed is chiefly converted into paradichlorobenzene, some orthodichlorobenzene being produced at the same time. On further chlorination both yield asymmetrical trichlorobenzene, and this again yields symmetrical tetrachlorobenzene, in which the two hydrogen atoms are in the para-position. This is then further converted into pentachlorobenzene and hexchlorobenzene.

Monochlorobenzene is also formed by the action of pentachloride of phosphorus on phenol, as well as when the amido-group of aniline is replaced by chlorine, by means of the diazo-reaction. In the same way other chlorobenzenes are obtained from chlorine substitution products of aniline and phenol.

Monochlorobenzene, C_6H_5Cl, was obtained by Laurent and Gerhardt by the action of phosphorus chloride on phenol (phenyl alcohol) and called chloride of phenyl (chlorure de phènyle).[3]

The product thus obtained, however, was a mixture of chlorobenzene with phenyl orthophosphate,[4] and probably also the

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[1] Carius, *Ann. Chem. Pharm.* cxxxvi. 323; cxl. 322.
[2] Hugo Müller, *Journ. Chem. Soc.* xv. 41.
[3] *Ann. Chem. Pharm.* lxxv. 79.
[4] Scrugham, *Chem. Soc. Journ.* vii. 237.

chlorides of monophenyl- and diphenyl-phosphoric acid;[1] this explains the statements of the above chemists that chloride of phenyl when treated with alkalis is again converted into phenyl alcohol.

In order to prepare chlorobenzene, rather less than the theoretical amount of chlorine is passed into a solution of one part of iodine in four parts of benzene, and the product washed with caustic soda, and purified by fractional distillation.[2]

It is also formed when benzene is heated with sulphuryl chloride to 150°.[3]

$$C_6H_6 + SO_2Cl_2 = C_6H_5Cl + HCl + SO_2.$$

Monochlorobenzene is a pleasant smelling liquid, which boils at 132°, and has a specific gravity of 1·12387 at 0°.[4] It solidifies to a crystalline mass, melting at −40°.

Concentrated nitric acid converts it into a mixture of solid parachloronitrobenzene and liquid orthochloronitrobenzene.

957. *Monochlorobenzene hexchloride*, $C_6H_5Cl_7$, is formed when diphenyl sulphone, $(C_6H_5)_2SO_2$, is treated with chlorine in the sun-light. It crystallizes from hot alcohol in small quadratic prisms which melt at 255° to 257°.[5]

Paradichlorobenzene, $C_6H_4Cl_2$, was obtained by H. Müller by passing chlorine into a solution of iodine in benzene until a sample of the product sank rapidly in water; it was then washed with caustic soda, any benzene and monochlorobenzene still present removed by distillation, and the portion boiling above 160° cooled to 0°. The compound crystallized out, and was purified, after removing the mother liquor, by re-crystallization from alcohol. Paradichlorobenzene is also readily obtained when the requisite quantity of chlorine is passed into benzene, to which 1 per cent. of molybdenum chloride has been added.[6] It is also formed, with other products, by the action of phosphorus pentachloride on parachlorophenol[7] and paraphenolsulphonic acid, $C_6H_4(OH)SO_3H$.[8]

Paradichlorobenzene crystallizes in monoclinic plates, which possess a pleasant sweet smell, and sublime in closed vessels, at the ordinary temperature, in large, four-sided tables. It melts at

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[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* viii. 1519.
[2] Hugo Müller, *Zeitsch. Chem.* 1864, 65.
[3] Dubois, *ibid.* 1866, 705.
[4] Adrieenz, *Ber. Deutsch. Chem. Ges.* vi. 441.
[5] Otto, *Ann. Chem. Pharm.* cxli. 101.
[6] Aronheim, *Ber. Deutsch. Chem. Ges.* viii. 1400.
[7] Beilstein and Kurbatow, *Ann. Chem. Pharm.* clxxvi. 40.
[8] Kekulé, *Ber. Deutsch. Chem. Ges.* vi. 944.

56·4° and boils at 173·2°.[1] It is converted by fuming nitric acid into paradichloronitrobenzene, melting at 54·5°.

Orthodichlorobenzene, $C_6H_4Cl_2$, was first prepared by Beilstein and Kurbatow by the action of phosphorus pentachloride on orthochlorophenol.[2] They also found it in the mother liquor obtained in the preparation of paradichlorobenzene by Müller's method. In order to prepare it from this, the liquid is heated for two days with fuming sulphuric acid to 210°, when orthodichlorobenzenesulphonic acid is formed, any paradichlorobenzene still present not being acted upon. The sulphonic acid, which is obtained in the pure state from the barium salt, yields pure orthodichlorobenzene[3] on dry distillation. It is a liquid boiling at 179° and not solidifying at −14°. Fuming nitric acid converts it into the dichloronitrobenzene which melts at 43°.

Metadichlorobenzene, $C_6H_4Cl_2$, was obtained by Körner, by converting metanitraniline into the diazo-chloride and fusing its platinum chloride with soda. He thus obtained metachloronitrobenzene, which he reduced to metachloraniline, in which he then replaced the amido-group by chlorine. It is also formed when the corresponding dichloraniline is covered with absolute alcohol, nitrogen trioxide passed in, and the solution, after saturation, heated to boiling. It is a liquid boiling at 172°, and having a specific gravity of 1·307 at 0°. On nitration it yields a dichloronitrobenzene melting at 33°, which on reduction is converted into the original dichloraniline.[4]

Dichlorobenzene hexchloride, $C_6H_4Cl_8$, was obtained by Jungfleisch, by the action of chlorine on benzene in the sunlight. It crystallizes from chloroform in oblique rhombic prisms which do not melt at 250°.[5]

Trichlorobenzenes, $C_6H_3Cl_3$.

			Melting-point.	Boiling-point.
[6] Symmetrical	(1.3.5)	long needles	63·4°	208·5°
[7] Asymmetrical	(1.2.4)	rhombic crystals	16·0°	213·0°
[8] Adjacent	(1.2.3)	large tables	53-54°	218-219°

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[1] Körner, *Jahresb.* 1875, 318.

[2] *Ann. Chem. Pharm.* clxxvi. 42.

[3] *Ibid.* clxxxii. 94.

[4] *Ibid.* clxxxii. 97.

[5] Jungfleisch, *Zeitsch. Chem.* 1868, 486.

[6] Jungfleisch, *Ann. Chim. Phys.* [4], xv. 186; Beilstein and Kurbatow, *Ann. Chem. Pharm.* cxcii. 236.

[7] Mitscherlich, *Ann. Chem. Pharm.* xvi. 172; Otto, *ibid.* clxi. 105; Jungfleisch, *loc. cit.*; Beilstein and Kurbatow.

[8] Beilstein and Kurbatow.

Tetrachlorobenzenes, $C_6H_2Cl_4$.

			Melting-point.	Boiling-point.
[1] Symmetrical	(1.2.4.5)	monoclinic crystals	137-138°	243-246°
[2] Asymmetrical	(1.3.4.5)	needles	50-51°	246°
[3] Adjacent	(1.2.3.4)	needles	45-46°	254°

Pentachlorobenzene, C_6HCl_5, crystallizes from hot alcohol in fine needles, melting at 85° to 86°, and boiling at 275° to 276°.[4]

958 *Hexchlorobenzene*, C_6Cl_6, was obtained by Hugo Müller as a final product of the action of chlorine on benzene in presence of iodine, or better, of antimony pentachloride. He expressed the opinion that it was identical with the compound already known under the name of Julin's chloride of carbon, which was prepared in a very peculiar way. Julin manufactured nitric acid in Åbo, in Finland, by heating crude saltpetre in cast-iron retorts with calcined green vitriol, obtained from the drainage water of the mines of Fahlun, in Sweden. He thus obtained a body of which he sent a small sample to Richard Phillips, editor of the *Annals of Philosophy*, stating that it was a similar substance to the perchloride of carbon discovered by Faraday.[5]

Faraday and Phillips investigated the compound more accurately, but, owing to the small quantity they possessed, they were unable to come to any satisfactory conclusion respecting its composition. They noticed, however, that it possessed such peculiar properties that they came to the conclusion that it probably contained a new modification of carbon, or perhaps some analogous element.[6] Julin gave them a larger quantity after his return from the Continent, and they then found that the body was a chloride of carbon, whose vapour on being passed through a red-hot tube, filled with small pieces of rock crystal, is decomposed into its elements. Analysis showed that the formula was $C_4Cl_2(C=6)$, but they gave the compound no name.[7] Gmelin described it as dichloride of carbon; according to him the carbon needed for its formation was probably

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[1] Jungfleisch; Beilstein and Kurbatow.

[2] Otto; Jungfleisch; Beilstein and Kurbatow.

[3] Beilstein and Kurbatow.

[4] Jungfleisch; Otto and Ostrop, *Ann. Chem. Pharm.* cxli. 93; cliv. 182; Beilstein and Kuhlberg, *ibid.* clii. 247; Ladenburg, *ibid.* clxxii. 344.

[5] *Ann. Phil.* xvii. 216.

[6] *Ibid.* 217.

[7] *Phil. Trans.* 1821, 392.

derived from the cast iron, and the chlorine from the crude saltpetre.[1]

Regnault obtained this compound by passing the vapour of chloroform, or of tetrachlorethylene, through a red-hot tube filled with pieces of porcelain,[2] and Bassett showed that it is hexchlorobenzene.[3]

It is also formed when acetylene tetrachloride, $C_2H_2Cl_4$, is heated for 100 hours to 360°,[4] as well as by the prolonged chlorination of methylbenzene and of dimethylbenzene in presence of antimony chloride.[5] It is likewise formed when several benzene derivatives are heated with iodine chloride to 350°. Several aromatic hydrocarbons, and oil of turpentine, $C_{10}H_{16}$, also yield it by exhaustive chlorination, together with tetrachloromethane, or hexchloromethane.[6]

If secondary hexyl iodide be heated with excess of iodine chloride for a long time to 240°, hexchlorobenzene, together with tetrachloromethane, is formed.[7]

Hexchlorobenzene is insoluble in cold, slightly soluble in hot alcohol, but readily in benzene. From a mixture of the two it crystallizes in long thin prisms, and from carbon disulphide in rhombic prisms. It melts at 226°, and boils at 326°, and is not attacked either by boiling concentrated acids or by alkalis.

BROMINE SUBSTITUTION PRODUCTS OF BENZENE.

959 Bromine acts on benzene in a similar manner to chlorine, but more slowly; the presence of iodine quickens the reaction.

Monobromobenzene, C_6H_5Br, was first obtained by Couper by the prolonged action of bromine on benzene in diffused daylight.[8]

Riche obtained it from phenol and phosphorus pentachloride,[9] and Griess by the decomposition of diazobenzene perbromide.[10]

It is produced when a mixture of equal molecular weights of bromine and benzene are allowed to act upon one another for a week; the product is then washed with caustic potash, and

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[1] Gmelin, *Handbook*, viii. 160.
[2] *Ann. Chem. Pharm.* xxx. 350.
[3] *Journ. Chem. Soc.* [2], v. 443.
[4] Berthelot and Jungfleisch, *ibid.* Suppl. vii. 256.
[5] Beilstein and Kuhlberg, *ibid.* cl. 309.
[6] Ruoff, *Ber. Deutsch. Chem. Ges.* ix. 1483.
[7] Krafft, *ibid.* ix. 1085.
[8] *Ann. Chem. Pharm.* clv. 225.
[9] *Ibid.* cxxi. 359.
[10] *Ibid.* cxxxvii. 86.

the unaltered benzene, and a small quantity of dibromobenzene, removed by distillation.[1]

According to Michaelis it is best prepared by heating 2,500 grams of benzene, and 50 grams of iodine, in a bolthead connected with an inverted condenser, and gradually adding 2,500 grams of bromine. As soon as no further evolution of hydrobromic acid takes place on continued boiling, the excess of benzene is distilled off, the residue washed with caustic soda, and distilled in a current of steam. The dry distillate is finally purified by fractionation.[2]

Monobromobenzene is a liquid boiling from 154·8° to 155·5°, and having at 0° a specific gravity 1·51768.[3]

On nitration it yields chiefly paranitrobromobenzene, together with a small quantity of orthonitrobromobenzene. If from three to four grams of bromobenzene be given to a large dog daily, several different bodies make their appearance in the urine; amongst these are parabromophenylsulphuric acid, $C_6H_4BrSO_4H$, and bromophenylmercapturic acid, $C_{11}H_{10}BrNSO_3$. This latter substance crystallizes from hot water in long needles, decomposing on boiling with caustic soda into parabromothiophenol, C_6H_4BrSH, ammonia, acetic acid, and other bodies as yet unexamined;[4] according to Jaffé chlorobenzene acts on the animal economy in a similar manner.

Paradibromobenzene, $C_6H_4Br_2$, was discovered by Couper.[5] It is produced when one part of benzene and eight parts of bromine are boiled for some days in an apparatus connected with an inverted condenser; the excess of bromine is removed by heating, the residue washed with caustic soda, and cooled down, until paradibromobenzene crystallizes out. This is purified by pressing out the mother liquor, and recrystallized from alcohol.[6] It is also formed by heating parabromophenol with phosphorus pentabromide,[7] and from paradibromaniline by the diazo-reaction.[8] It crystallizes in monoclinic tables or prisms melting at 89·3° and boiling at 219°.

Orthodibromobenzene, $C_6H_4Br_2$, is formed in small quantities during the preparation of the para-compound,[9] but more

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[1] Fittig, *Ann. Chem. Pharm.* cxxxii. 201. [2] Fittig, *ibid.* clxxxi. 289.

[3] Adrieenz, *Ber. Deutsch. Chem. Ges.* vi. 443.

[4] Baumann and Preusse, *ibid.* xii. 806; Jaffé, *ibid.* 1092.

[5] *Ann. Chem. Pharm.* civ. 225.

[6] Riche and Bérard, *ibid.* cxxxiii. 51.

[7] Mayer, *ibid.* cxxxvii. 221.

[8] Griess, *Jahresb.* 1866, 454; Körner, *ibid.* 1875, 303.

[9] Riese, *Ann. Chem. Pharm.* clxiv. 176.

readily from orthobromaniline.[1] It is a light mobile liquid having at 0° a specific gravity 2·003, boiling at 224°, and on cooling forming crystals melting at −1°.

Metadibromobenzene, $C_6H_4Br_2$, was obtained by V. Meyer and Stüber, by heating an alcoholic solution of metadibromaniline with ethyl nitrite.[2]

$$C_6H_3.Br_2.NH_2 + C_2H_5.NO_2 = \\ C_6H_4Br_2 + C_2H_4O + N_2 + H_2O.$$

It has also been prepared from metabromaniline.[3] It is a liquid boiling at 219·4°, not solidifying at −26°, and at 18·6° having a specific gravity of 1·955.

Tribromobenzenes, $C_6H_3Br_3$.

			Melting-point.	Boiling-point.
[4] Symmetrical	(1.3.5)	needles	119·6°	278°
[5] Asymmetrical	(1.2.4)	needles	44·0°	275—276°
[6] Adjacent	(1.2.3)	rhombic tables	87·4°	—

Tetrabromobenzenes, $C_6H_2Br_4$.

[7] Symmetrical	(1.2.4.5)	long needles	137—140°	—
[8] Asymmetrical	(1.3.4.5)	fine needles	98·5°	329°
[9] Adjacent	(1.2.3.4)	small needles	160°	—

Pentabromobenzene, C_6H_5Br, was obtained by Kekulé, together with symmetrical tetrabromobenzene, by heating nitrobenzene with bromine to 250°. It is also formed together with tribromobenzenesulphonic acid, when symmetrical tribromobenzene is heated, for from eight to fourteen days, with fuming sulphuric acid to 100°.[10] It crystallizes in needles, melting at 260°.

Hexbromobenzene, C_6Br_6, is formed by the action of bromine chloride on benzene, phenol, azobenzene, and toluene at a temperature of from 350° to 400°.[11] It is obtained from secondary hexyl iodide in this manner, together with carbon and tetrabromomethane, at a temperature of 200°.[12]

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[1] Körner, *Jahresb.* 1875, 503.

[2] *Ann. Chem. Pharm.* clxv. 161.

[3] Körner, Wurster, *ibid.* clxxvi. 170.

[4] Körner; Meyer and Stüber, *loc. cit.*

[5] Mitscherlich; Meyer; Körner; Griess; Wurster, *Ber. Deutsch. Chem. Ges.* vi. 1490; Wroblewsky, *ibid.* vii. 1060.

[6] Körner.

[7] Riche and Bérard; Kekulé, *Ann. Chem. Pharm.* cxxxvii. 172.

[8] Körner, *ibid.* 218; Mayer, *ibid.* 227; Wurster and Nölting, *Ber. Deutsch. Chem. Ges.* vii. 1564.

[9] Halberstadt, *ibid.* xiv. 911.

[10] Bässman, *Liebig's Ann.* cxci. 208.

[11] Gessner, *Ber. Deutsch. Chem. Ges.* ix. 1505.

[12] Wahl, *ibid.* ix. 1506.

It is also obtained when symmetrical tribromobenzene is boiled with sulphuric acid, by which no sulphonic acid is formed, but a portion of the tribromobenzene is decomposed with evolution of carbon dioxide.[1] It is most easily obtained when a few milligrams of aluminium are added to bromine free from chlorine and cooled by ice, two-thirds of the calculated amount of benzene being gradually added. The reaction is completed in a day.[2]

It is almost insoluble in hot alcohol, and crystallizes from toluene in long needles melting above 315°.

IODINE SUBSTITUTION PRODUCTS OF BENZENE.

960 *Moniodobenzene*, C_6H_5I.—Scrugham obtained this substance by the action of iodine and phosphorus on phenol,[3] and Kekulé, by heating benzene with iodine, iodic acid and water from 200° to 240°. The following reaction takes place.

$$5C_6H_6 + HIO_3 + 2I_2 = 5C_6H_5I + 3H_2O.$$

At the same time a part of the iodic acid acts as an oxidizing agent, converting the benzene into water and carbon dioxide.[4] Iodobenzene is also formed when sodium benzoate is treated with iodine chloride.[5]

$$C_6H_5.CO_2Na + ICl = C_6H_5I + NaCl + CO_2.$$

It is also formed, together with higher substitution products, by gradually adding iodine chloride to a mixture of aluminium chloride and benzene.[6] It is, however, best obtained by the action of concentrated hydriodic acid on acid diazobenzene sulphate.[7]

It is a liquid which turns red on exposure to light, and boils at 190°—190·5°. Sodium amalgam converts it, in an alcoholic solution, into benzene, while by heating with caustic potash it remains unchanged.

Paradi-iodobenzene, $C_6H_4I_2$, is formed, with mon-iodobenzene, in

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[1] Herzig, *Monatsh. Chem.* ii. 192.

[2] Gustavson, Beilstein's *Organ. Chem.* 822.

[3] *Ann. Chem. Pharm.* xcii. 318.

[4] *Ibid.* cxxxvii. 162.

[5] Schützenberger, *Jahresb.* 1862, 251.

[6] Greene, *Compt. Rend.* xc. 40.

[7] Griess, *Ann. Chem. Pharm.* cxxxvii. 76.

the preparation of the latter, according to the methods of Kekulé and Schützenberger.

It is also easily obtained from para-iodaniline by the diazo-reaction. It crystallizes in plates, melting at 129·4°, and boiling at 285°.[1]

Orthodi-iodobenzene, $C_6H_4I_2$, was obtained by Körner from ortho-iodaniline: it crystallizes easily, and boils at a higher temperature than its isomerides.[2]

Metadi-iodobenzene, $C_6H_4I_2$, can be obtained by means of the diazo-reaction from meta-iodaniline[3] and metadi-iodaniline.[4] It crystallizes from a mixture of alcohol and ether in rhombic tables, melting at 40·4°, and boiling at 284·7°.

Tri-iodobenzene, $C_6H_3I_3$, probably the asymmetrical modification, was obtained by Kekulé by heating benzene with iodine and iodic acid. It crystallizes in small needles which melt at 76°, and volatilize without decomposition.

FLUORINE SUBSTITUTION PRODUCTS OF BENZENE.

961 *Monofluobenzene*, C_6H_5F, has been obtained by means of paramidobenzenesulphonic acid, which is converted by the diazo-reaction into fluobenzenesulphonic acid, a body not known in the free state.

Its potassium salt, when heated with concentrated hydrochloric acid in a sealed tube, yields fluobenzene, a liquid smelling like benzene, and boiling at 85° to 86°.[5]

NITROSO-SUBSTITUTION PRODUCTS OF BENZENE.

962 *Nitrosobenzene*, C_6H_5NO, has hitherto only been prepared in solution. It is obtained when a solution of nitrosyl bromide, NOBr, or nitrosyl chloride, NOCl, in benzene, is added to a solution of mercury phenyl, $(C_6H_5)_2Hg$. The compound $SnCl_4$ + NOCl,

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[1] Kekulé, *Zeitsch. Chem.* 1866, 688; Körner, *Jahresb.* 1875, 357.

[2] Körner, *ibid.* 318.

[3] Körner; Rudolph, *Ber. Deutsch. Chem. Ges.* xi. 81.

[4] Paternò and Oliveri, *ibid.* xvii. ref. 109.

[5] Paternò and Oliveri, *ibid.* xi. ref. 109.

which is easily obtained in large yellow crystals by passing the vapours of aqua regia over stannic chloride, acts still better. On distillation with steam a beautiful green liquid is obtained, smelling like mustard oil, which on treatment with tin and hydrochloric acid yields aniline.[1]

NITRO-SUBSTITUTION PRODUCTS OF BENZENE.

963 *Nitrobenzene*, $C_6H_5NO_2$, was first obtained by Mitscherlich in 1834, by the action of fuming nitric acid on benzene and termed nitrobenzide.[2] In order to prepare it in small quantities equal parts of fuming nitric acid and benzene are gradually mixed, the vessel being kept cool; the mixture is then poured into water, and the heavy oil separating, washed first with water and then with caustic soda, after which it is distilled with steam. It is now prepared on the large scale, by a process which will be subsequently described.

Nitrobenzene is a light-yellow, strongly refractive liquid, having at 0° a specific gravity, 1·200. It has a peculiar smell, similar to that of oil of bitter almonds, at the same time reminding one of oil of cinnamon, and possesses a sweet and burning taste. It boils at 210°, and at a low temperature solidifies in large needles, melting at 3°. In water it is scarcely soluble, but it dissolves readily in alcohol, ether, benzene, and concentrated nitric acid; and is itself an excellent solvent for many organic substances, which are sparingly or not at all soluble in the ordinary solvents.

Nitrobenzene is poisonous, especially when the vapour is inhaled; it produces a burning sensation in the mouth, nausea and giddiness, also cyanosis of the lips and face, and in serious cases, which frequently end fatally, symptoms of a general depression, such as fright, coma, humming in the ears, convulsions, and pallor, are observed, the breath and vomited matter smelling of nitrobenzene.[3] When introduced into the animal organism, nitrobenzene is transformed into aniline, whilst its homologues, such as paranitrotoluene, are oxidized to acids, and are not poisonous.[4]

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[1] Baeyer, *Ber. Deutsch. Chem. Ges.* vii. 1638.

[2] *Pogg. Ann.* xxxi. 625.

[3] Grandhomme, *Die Theerfabriken des Herren Meister Lucius, und Brüning in sanitärer und socialer Beziehung.*

[4] Jaffé, *Ber. Deutsch. Chem. Ges.* vii. 1673.

Nitrobenzene was first introduced into commerce by Collas under the name of essence of mirban, or artificial bitter-almond oil; and Mansfield, in 1874, patented a process for its preparation from coal-tar. It is now prepared on a very large scale and employed for a variety of purposes.

Nitrobenzene is manufactured by allowing a well-cooled mixture of fuming nitric acid, free from chlorine, and concentrated sulphuric acid to flow into benzene, contained in cast-iron vessels provided with agitators (Fig. 10); the mixture must be kept cool. Towards the end of the reaction, however, the temperature may rise to from 80° to 90°. When the reaction is over the product is run into tanks; the acid mixture separates as a layer at the bottom, whilst nitrobenzene, being insoluble in the acid, goes to the top.

The acid layer is drawn off, and the nitric acid recovered. Crude nitrobenzene contains more or less benzene which has escaped the reaction. To remove the latter, the crude product is treated with steam, when the benzene distils over with a small quantity of nitrobenzene, and this mixture is used again for the preparation of nitrobenzene. The residual nitrobenzene is washed with caustic soda and water, and if necessary purified by distillation in high pressure steam.

Nitrobenzene is employed in perfumery, especially for scenting toilet soaps, but is much more extensively used in the manufacture of pure aniline for the colours known as aniline blue and aniline black, also in the manufacture of magenta by the recent process, and for various other purposes to be hereafter mentioned.

The nitrobenzene prepared from pure benzene is used in commerce under the name of *light nitrobenzene*, or *nitrobenzene for blue or black*. The *heavy nitrobenzene*, or *nitrobenzene for red*, is obtained in a similar way from a mixture of toluene and benzene, containing about 40 per cent. of the latter, and is used for the preparation of magenta by the older processes. Finally, *very heavy nitrobenzene* consists principally of paranitrotoluene and *orthonitrotoluene*, from which the pure compounds can be prepared by fractional distillation. This is likewise used in the manufacture of colours.

We may here remark that the above technical terms are not chosen with respect to the specific gravity of the different products, since that of the pure nitrobenzene is greater than that of its homologues.[1]

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[1] Schultz, *Chemie des Kohlentheers*, 350.

964 *Dinitrobenzene*, $C_6H_4(NO_2)_2$, was obtained by Deville by boiling benzene with fuming nitric acid for a long time, and was called by him binitrobenzide or "nitrobenzinèse."[1] It was then more accurately investigated by Hofmann and Muspratt, who prepared it by dissolving benzene in a mixture of equal parts of fuming nitric and sulphuric acids, and then heating for a few minutes.[2] The product, however, contains in addition to metadinitrobenzene, orthodinitrobenzene, and a small quantity of paradinitrobenzene.

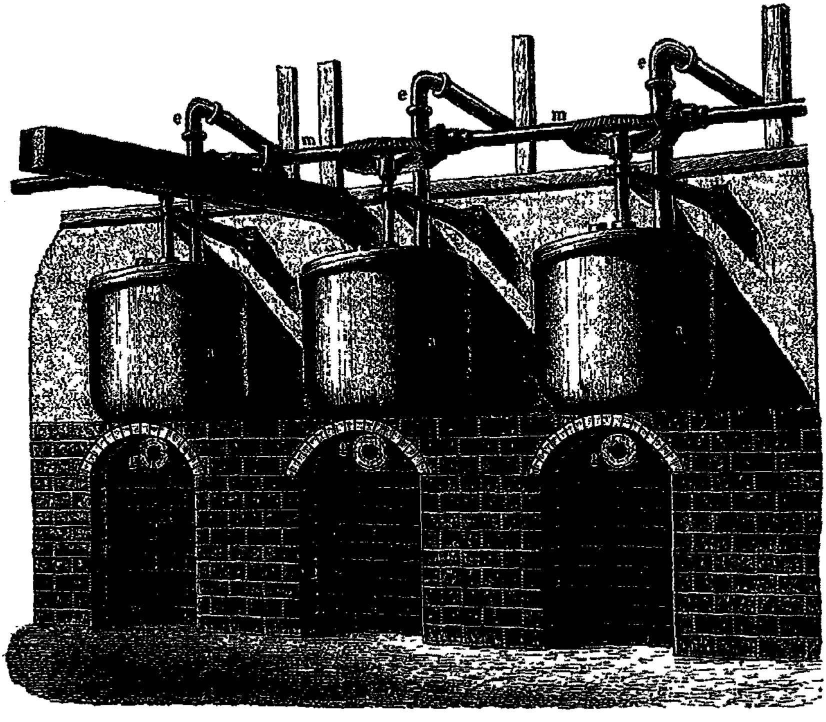

FIG. 10.

In order to prepare the crude product, benzene is run without cooling into a mixture of concentrated nitric and sulphuric acids and then boiled for a short time. It is purified by washing with

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[1] *Ann. Chim. Phys.* [3], iii. 187.

[2] *Ann. Chem. Pharm.* lvii. 214.

[3] Rinne and Zincke, *Ber. Deutsch. Chem. Ges.* vii. 869, 1372 ; Korner, *Gazz. Chim. Ital.* iv. 305; *Abstract Journ. Chem. Soc.* 1876, i. 204 ; *Jahresb.* 1875.

water, pressing and crystallizing from alcohol, when the meta-compound separates out first. After standing for some time paradinitrobenzene crystallizes out from the mother liquor, and may be purified by recrystallization from absolute alcohol. The first mother liquor of the para-compound is freed from alcohol by distillation, when some of the meta-compound separates out; the orthodinitrobenzene is then deposited and may be purified by recrystallization from 25 per cent. acetic acid (Rinne and Zincke).

Orthodinitrobenzene crystallizes from hot water or acetic acid in needles, and from alcohol or chloroform in monoclinic tables,[1] melting at 117·9°. On boiling with caustic soda it is converted into orthonitrophenol, $C_6H_4(NO_2)OH$, and on heating with alcoholic ammonia into orthonitraniline,[2] $C_6H_4(NO_2)NH_2$, whilst its isomerides are not affected by this reagent.

Metadinitrobenzene is best obtained, according to Beilstein and Kurbatow, by dissolving one volume of benzene in two volumes of nitric acid of sp. gr. 1·52, and finishing the reaction by heating. After cooling, 3·3 volumes of sulphuric acid are added. The whole is then boiled up, and after again cooling, precipitated with water. The washed precipitate is purified by recrystallization from alcohol. It crystallizes in long needles or thin rhombic tables (Bodewig), melting at 89·9° (Körner). It is somewhat more readily soluble in alcohol than its isomerides; nevertheless when these are present only in small quantity it separates out first. It is used in the colour industry, and is prepared on the large scale, in the apparatus used for the preparation of nitrobenzene; the usual method is to run a mixture of 100 kilos of nitric acid of sp. gr. 1·38, and 156 kilos of concentrated sulphuric acid into 100 kilos of benzene. After the completion of the reaction the acids separate out, and can be again used for another quantity of benzene. It is now gently warmed for some time, and the product separated in the liquid state. It is then repeatedly washed with hot and cold water, and is not generally further purified.

It dissolves in alcohol, and on addition of a few drops of caustic potash to this solution, gives a magenta colouration, caused by some adhering dinitrothiophen. This reaction is given by all nitrobenzene prepared from benzene containing thiophen.[3]

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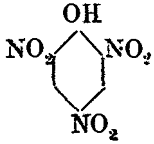
[1] Bodewig, *Pogg. Ann.* clviii. 239.
[2] Laubenheimer, *Ber. Deutsch. Chem. Ges.* ix. 1828; xi. 1155.
[3] V. Meyer and Stadler, *Ber. Deutsch. Chem. Ges.* xvii. 2778.

Paradinitrobenzene forms monoclinic needles melting at 171°—172° and subliming readily.

965 *Symmetrical Trinitrobenzene*, $C_6H_3(NO_2)_3(2 : 4 : 6)$, is obtained by heating two parts of metadinitrobenzene with six parts of the most concentrated nitric acid, and fifteen parts of pyrosulphuric acid to 80°—120°. It crystallizes from hot alcohol in white silky plates, or fern-like needles; when the cold saturated solution is allowed to evaporate slowly, small rhombic tables are obtained, melting at 121°—122°.[1]

When oxidized with potassium ferricyanide in a weak alkaline solution, it is converted into picric acid or symmetrical trinitrophenol, $C_6H_2(NO_2)_3OH$, which, as will be shown later, has the following constitution:



Trinitrobenzene forms with benzene the compound $C_6H_3(NO_2)_3 + C_6H_6$, crystallizing in hard shining prisms, quickly decomposing on exposure to the air. With other hydrocarbons it forms analogous compounds.[2]

Chloronitrobenzenes, $C_6H_4ClNO_2$.

		Melting-point.	Boiling-point.
Ortho	(3) needles	32·5°	243°
Meta	(4) rhombic crystals . .	44·4°	235·6°
Para	(5) rhombic plates . . .	83°	242°

Bromnitrobenzenes, $C_6H_4Br.NO_2$.

		Melting-point.	Boiling-point.
Ortho	(6) lance-like crystals . .	43·1°	261°
Meta	(7) light yellow plates .	56·4°	256·5°
Para	(8) needles	126—127°	255—256°

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[1] Hepp, *Liebig's Ann.* ccxv. 344.

[2] *Ibid.* ccxv. 375.

[3] Engelhardt and Latschinow, *Zeitsch. Chem.* 1870, 229; Beilstein and Kurbatow, *Ann. Chem. Pharm.* clxxxii. 107.

[4] *Ibid.* 102; Griess, *Jahresb.* 1866, 457; Laubenheimer, *Ber. Deutsch. Chem. Ges.* vii. 1765; viii. 1622; ix. 764.

[5] Riche, *Ann. Chem. Pharm.* cxxi. 357; Sokolow, *Zeitsch. Chem.* 1866, 621; Beilstein and Kurbatow, *loc. cit.* 105.

[6] Hübner and Alsberg, *Ann. Chem. Pharm.* clvi. 316; Walker and Zincke, *Ber. Deutsch. Chem. Ges.* v. 114; Fittig and Mayer, *ibid.* vii. 1179; Körner, *Jahresb.* 1875, 302.

[7] Griess, *ibid.* 1863, 423; Wnrster and Grubenmann, *Ber. Deutsch. Chem. Ges.* vii. 416; Körner, *loc. cit.*; Fittig and Mayer, *Ber. Deutsch. Chem. Ges.* viii. 364.

[8] Couper, *Ann. Chem. Pharm.* civ. 225; Griess, *loc. cit.*; Hübner and Alsberg, *loc. cit.*; Körner, *loc. cit.*

Iodonitrobenzenes, $C_6H_4INO_2$.

		Melting-point.	Boiling-point.
Ortho (1)	yellow needles . . .	49·4°	—
Meta (2)	small monoclinic plates	36°	—
Para (3)	needles	171·5°	—

These disubstitution products, which are of great theoretical interest, can be easily converted into the corresponding amido-compounds, and these are transformed by means of the diazo-reaction into many other bodies whose constitution has been thus ascertained.

With regard to the formation of these compounds it may be remarked that by the action of concentrated nitric acid on chlorobenzene and bromobenzene, the para-compound is obtained, together with small quantities of the ortho-compound. Metachloronitrobenzene, on the other hand, is formed when nitrobenzene, containing iodine or antimony chloride, is treated with chlorine. They can also be obtained from the nitrophenols by replacing the hydroxyl by chlorine or bromine, and, in a similar way, from the nitranilines by the diazo-reaction.

By heating the ortho-compounds with caustic soda, the halogen is replaced by hydroxyl, and orthonitrophenol is obtained, whereas by heating with alcoholic ammonia, orthonitraniline is formed. The para-compound is acted upon by the above reagents in an exactly similar manner, but with greater difficulty, the meta-compounds not being attacked by them (951).

BENZENE SULPHONIC ACIDS.

966 *Monobenzenesulphonic acid*, $C_6H_5.SO_2.OH$. Mitscherlich obtained this compound by the action of fuming sulphuric acid on benzene, and called it benzinsulphuric acid. He states that, like Faraday, he did not succeed when ordinary strong sulphuric acid[4] was used; but Freund has shown that on long standing in the cold it may thus be obtained.[5] It is more quickly prepared by heating benzene with sulphuric acid.[6] For this purpose a mixture of equal volumes of sulphuric acid and benzene are allowed to

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[1] Körner, *Jahresb.* 1875, 302. [2] Griess, *Zeitsch. Chem.* 1866, 218; Körner.

[3] Kekulé, *Ann. Chem. Pharm.* cxxxvii. 168; Griess.

[4] *Pogg. Ann.* xxxi. 283 and 634.

[5] *Ann. Chem. Pharm.* cxx. 76. [6] Stenhouse, *Proc. Roy. Soc.* xiv. 351.

boil gently for from twenty to thirty hours in a flask connected with an inverted condenser, when about 0·8 of the benzene passes into solution. Further heating does not increase the yield.[1] From the solution thus obtained the barium, lead, or calcium salt is prepared and other benzenesulphonates or the free acid obtained.

Monobenzenesulphonic acid crystallizes in small four-sided tables, which deliquesce in damp air, and when dried over sulphuric acid contain two molecules of water of crystallization.[2] When its aqueous solution is distilled water passes over first, and then decomposition sets in with formation of benzene, phenyl sulphone, $(C_6H_5)_2SO_2$, sulphur dioxide, and carbonization of the residue (Freund).

Barium benzenesulphonate, $(C_6H_5.SO_3)_2Ba + H_2O$, crystallizes in pearly tablets which are slightly soluble in alcohol.

Copper benzenesulphonate, $(C_6H_5.SO_3)_2Cu + 6H_2O$, forms large light blue tables.

Ethyl benzenesulphonate, $C_6H_5SO_2.C_2H_5$, is formed by the action of benzenesulphonyl chloride on sodium ethylate, and is a peculiarly smelling, oily liquid, which on boiling with water decomposes into alcohol and benzenesulphonic acid.[3]

Benzenesulphonic chloride, $C_6H_5SO_2Cl$, is formed by the action of phosphorus pentachloride on benzenesulphonate,[4] and is an oily liquid, which, on standing for a long time at 0°, solidifies to large rhombic crystals.[5] It is insoluble in water and is scarcely affected by it.

Under diminished pressure it can be distilled without decomposition; at the ordinary pressure it boils, undergoing considerable decomposition, at 246°—247° (Otto).

Benzenesulphonamide, $C_6H_5.SO_2.NH_2$, was obtained by Chancel and Gerhardt by trituration of the chloride with ammonium carbonate.[6] It is also easily obtained by treating the chloride with alcoholic ammonia. It is readily soluble in alcohol, slightly in water, and crystallizes from the latter in thin rhombic prisms, melting at 149° (Otto); with an ammoniacal solution of silver it forms the compound $C_6H_5.SO_2.NHAg$—a crystalline precipitate (Gerhardt and Chiozza).

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[1] Michael and Adair, *Ber. Deutsch. Chem. Ges.* x. 585.
[2] Hübner, *Liebig's Ann.* ccxxiii. 235.
[3] Schiller and Otto, *Ber. Deutsch. Chem. Ges.* ix. 1638; Hübner, *loc. cit.*
[4] Gerhardt and Chiozza, *Ann. Chem. Pharm.* lxxxvii. 299.
[5] Otto, *ibid.* cxlv. 321.
[6] *Ibid.* lxxxvii. 296; *Jahresber.* 1852, 434.

967 *Benzenedisulphonic acids*, $C_6H_4(SO_3H)_2$. By heating benzonitril with fuming sulphuric acid, Buckton and Hofmann obtained an acid of this composition[1] consisting chiefly of the para-compound.[2] It is also formed as chief product when the vapour of benzene, heated to 240°, is passed into sulphuric acid.[3] If benzene, on the other hand, be heated with fuming sulphuric acid, the meta-acid is chiefly formed, and this on heating more strongly is partly converted into the para-compound. The isomerides can be separated by converting the mixture into the potassium salt, separating the crystals mechanically and purifying by recrystallization.[4]

Benzeneparadisulphonic acid is a very hygroscopic crystalline mass.

		Melting-point.
$C_6H_4(SO_3K)_2 + H_2O$	small thin plates	—
$C_6H_4(SO_2Cl)_2$	long needles	131°
$C_6H_4(SO_2NH_2)_2$	—	288°

By heating the potassium salt with potassium cyanide, the nitrile of terephthalic acid, $C_6H_4(CO_2H)_2$ which is a para-compound, is formed; whilst by fusing the salt with caustic potash an intramolecular change takes place and metadihydroxybenzene or resorcinol, $C_6H_4(OH)_2$, is formed.

Benzenemetadisulphonic acid is formed almost exclusively when benzene is dissolved in an equal volume of fuming sulphuric acid, another volume of the latter added, and the liquid strongly heated in a retort with an upright neck for two to three hours, till the vessel is filled with white vapours.[5] The free acid is a very deliquescent crystalline mass containing 2½ molecules of water.

		Melting-point.
(6) $C_6H_4(SO_3K)_2 + 1\frac{1}{2}\, H_2O$	needle-shaped oblique prisms	—
$C_6H_4(SO_2Cl)_2$	large prisms	63°
$C_6H_4(SO_2NH_2)_2$	needles	229°

Benzene-orthodisulphonic acid is obtained from the corresponding amidobenzenedisulphonic acid by the diazo-reaction. Its potassium salt is readily soluble in water and crystallizes tolerably well.[7]

		Melting-point.
$C_6H_4(SO_2Cl)_2$	large 4-sided tables	105°
$C_6H_4(SO_2NH_2)_2$	needles	233°

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[1] *Ann. Chem. Pharm.* c. 157.

[2] Garrick, *Zeitschr. Chem.* 1869, 550 ; Fittig, *Ann. Chem. Pharm.* clxxiv. 123.

[3] Egli, *Ber. Deutsch. Chem. Ges.* viii. 817.

[4] Barth and Senhofer, *ibid*, viii. 1478 ; Körner and Monselise, *ibid.* ix. 583.

[5] Heinzelmann, *Ann. Chem. Pharm.* clxxxviii. 157.

[6] Reiche, *ibid.* cciii. 69.

[7] Drebes, *Ber. Deutsch. Chem. Ges.* ix. 552.

Benzenetrisulphonic acid, $C_6H_3(SO_3H)_3 + 3H_2O$, is formed by heating benzene with sulphuric acid and phosphorus pentoxide for some hours to 280°—290°. The free acid crystallizes in flat, very hygroscopic needles. The potassium salt, $C_6H_3(SO_3K)_3 + 3H_2O$, forms oblique prisms.[1]

Diphenylsulphone, $(C_6H_5)_2SO_2$, was obtained by Mitscherlich, together with benzenesulphonic acid, by the action of fuming sulphuric acid, or sulphur trioxide, on benzene, and termed by him sulphobenzide.[2] Subsequently Stenhouse obtained it by oxidizing diphenyl sulphide, $(C_6H_5)_2S$, and gave to it the name of sulphobenzolene;[3] Kekulé and Szuch then showed that this body is identical with sulphobenzide.[4] It is also formed in small quantities by the dry distillation of ammonium benzenesulphonate[5] and in larger quantities by the action of sulphuryl chloride, SO_2Cl_2, on benzene.[6] It is insoluble in cold water, and soluble only with difficulty in hot, and crystallizes from benzene in large prisms melting at 128°—129° and sublimes easily. It is attacked by aqueous or alcoholic solutions of the alkalis even in the cold, and concentrated sulphuric acid dissolves it without decomposition; on heating it forms benzenesulphonic acid.

Benzenesulphinic acid, $C_6H_5.SO_2H$.—By the action of zinc ethyl on benzenesulphonyl chloride, Kalle expected to form the compound, $C_6H_2.SO_2C_2H_5$, but instead of this he obtained the zinc salt of the above acid, which he called benzylsulphurous acid.[7]

$$2C_6H_5.SO_2Cl + (C_2H_5)_2Zn = (C_6H_5.SO_2)_2Zn + 2C_2H_5Cl.$$

It is also formed by the direct combination of sulphur dioxide and benzene in the presence of aluminium chloride.[8]

It is more easily obtained by gradually adding zinc-dust to a well-cooled alcoholic solution of benzenesulphonic chloride, and then washing out the alcohol and zinc chloride from the thick mass with cold water. The zinc salt is almost insoluble in cold water, and is converted into the sodium salt by the addition of carbonate of soda, the benzenesulphinic acid being precipitated from the concentrated solution by the addition of hydrochloric acid.[9]

It is soluble with difficulty in cold water and crystallizes from hot water in stellated prisms, which melt at 68°—69° and are

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[1] Senhofer, *Ann. Chem. Pharm.* clxxiv. 243.

[2] *Pogg. Ann.* xxxi. 625.

[3] *Roy. Soc. Proc.* 1865, xiv. 354.

[4] *Zeitschr.* 1867, 193 and 300.

[5] Freund, *ibid.* cxx. 81.

[6] Knapp, *ibid.* 1869, 41.

[7] *Ann. Chem. Pharm.* cxix. 153.

[8] Friedel and Crafts, *Jahresb.* 1878, 739.

[9] Otto, *Ber. Deutsch. Chem. Ges.* ix. 1584.

readily soluble in alcohol and ether. Oxidizing agents easily convert it into benzenesulphonic acid, even the oxygen of the air gradually transforming it. Phosphorus pentachloride converts it into benzenesulphonic chloride.

$$C_6H_5.SO_2H + PCl_5 = C_6H_5.SO_2Cl + HCl + PCl_3.$$

By fusing with caustic potash it is decomposed, forming benzene and potassium sulphite

Nitrobenzenesulphonic Acids, $C_6H_4.(NO_2).SO_3H$.

968 An acid of this composition was first obtained by Laurent by treating benzenesulphonic acid with nitric acid,[1] and Schmitt showed that it is also obtained[2] by warming nitrobenzene with fuming sulphuric acid. This was supposed to be a single definite compound until Limpricht pointed out that, while the chief product in both cases is the meta-acid, the other two isomerides are formed at the same time. These may be roughly separated by means of their barium salts, but the separation is only rendered complete by conversion into the amides, which are decomposed by heating with hydrochloric acid to 150°.[3]

According to Limpricht these compounds are prepared by mixing 200 grms. of benzene with 300 grms. of fuming sulphuric acid, removing the undissolved benzene after two to three hours, and adding to the solution nitric acid, of about sp. gr. 1·5, drop by drop till the action ceases; water is then added and the liquid poured off from the dinitrobenzene formed at the same time. The solution is neutralized with milk of lime, and concentrated, when the calcium salt of the meta-acid crystallizes out first. This is decomposed with potassium carbonate and the dry potassium salt ground up with phosphorus pentachloride; the product is washed with water, which scarcely attacks the nitrobenzenesulphonic chloride; it is then dissolved in ether and dried over calcium chloride. On evaporation the chloride crystallizes out in large, shining prisms. By treating these with strong ammonia the amide is obtained and this is purified by recrystallization.

The last crystallizations of the calcium salt are worked up in the same way, but the mixed chlorides are at once converted into the amido-compounds which are separated by frequent recrystallizations from hot water—the ortho-acid being the least

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[1] *Jahresb.* 1850, 418.

[2] *Ann. Chem. Pharm.* cxx. 163.

[3] *Ibid.* clxxvii. 60.

soluble, the para-acid the most, and the solubility of the meta-acid lying between that of the other two.

Of the free acids metanitrobenzenesulphonic acid is the only one which has been prepared pure; it crystallizes in large, flat, deliquescent tables, and it is not attacked when boiled with fuming nitric acid.

The properties of the chlorides and amides are given in the following table:

Nitrobenzenesulphonyl chlorides, $C_6H_4(NO_2)SO_2.C$

		Melting-point.
Ortho.	white prisms	67°
Meta.	4-sided prisms	60·5°
Para.	red oil	—

Nitrobenzenesulphonamides, $C_6H_4(NO_2)SO_2.NH_2$.

Ortho.	fine needles	186°
Meta.	needles or prisms	161°
Para.	fine needles	131°.

HYDROXYBENZENES AND ALLIED BODIES.

969 *Phenol*, C_6H_5OH.—This compound was discovered by Runge in 1834 in coal-tar, and called by him "Kohlenölsäure" or carbolic acid.[1] Laurent obtained it pure in 1841 and determined its composition; he gave it the name of phenylhydrate (hydrate de phényle) or phenic acid (acide phénique),[2] from φαίνειν, to emit light, probably because it was found as a by-product in the oils from the manufacture of illuminating gas. Gerhardt named it phenol in order to mark the fact that this body is a kind of alcohol, whence it has also been termed phenyl alcohol. Phenol was for a long time confounded with creosote, discovered by Reichenbach in 1832, although Runge had already pointed out that phenol is distinguished from wood creosote by having an acid reaction and by the fact that, if used instead of creosote for the preservation of meat, it imparts to it a strong and very unpleasant taste. Later investigations have proved that wood creosote is a mixture of different compounds and only contains very small quantities of phenol. This latter is a product of the dry distillation of many organic bodies, being found in largest

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[1] *Pogg. Ann.* xxxi. 65; xxxii. 308.

[2] *Ann. Chim. Phys.* [3], 195.

quantities in the tar obtained by the dry distillation of coal, lignite, and peat.

Wöhler found it in small quantities in castoreum,[1] a substance secreted by the præputial glands in the beaver, and Städler has indicated its presence in the urine of man, the horse, and the cow.[2] It occurs in urine as the potassium salt of the unstable phenyl-sulphuric acid,[3] and for this reason it can only be detected by distillation with hydrochloric acid.[4] Healthy urine from a mixed diet contains 0·004 grm. of phenol per litre,[5] but under pathological conditions it may rise as high as 1·5575 grm. (Salkowski). Phenol is also formed when albuminoid bodies are allowed to putrify in presence of some water and pancreas,[6] and hence it is found in small quantities in excrements.[7]

According to Griffiths it also occurs in the trunk, leaves, and sap of the Scotch fir (Pinus sylvestris).[8]

When benzene and water are shaken up in the air with palladium hydride (Vol. II. Part II. p. 425), a little phenol, together with other products, is formed.[9] It is obtained in larger quantities, together with oxalic acid, when water is poured on to phosphorus, some benzene added, and the whole exposed to the action of sunlight. In both cases the oxidation is effected by hydrogen dioxide, which also oxidizes benzene directly.[10]

$$C_6H_6 + HO.OH = C_6H_5.OH + HOH.$$

Phenol is also readily formed when oxygen is passed into an agitated mixture of benzene and aluminium chloride.[11]

Hofmann[12] and Hunt[13] obtained it from aniline by treating a hydrochloric acid solution with silver nitrite, when diazobenzene chloride, which had been previously obtained by Griess, is first formed.

Wurtz[14] and Kekulé[15] found that phenol may be easily obtained by fusing benzenesulphonic acid with caustic potash; caustic soda gives a smaller yield than potash, and the best

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[1] *Ann. Chem. Pharm.* lxvii. 360.

[2] *Ibid.* lxxvii. 18.

[3] Baumann, *Ber. Deutsch. Chem. Ges.* ix. 55.

[4] Salkowski, *ibid.* ix. 1595.

[5] Munk, *ibid.* 1596.

[6] Baumann, *ibid.* x. 685; Odermatt, *Journ. Prakt. Chem.* [2], xviii. 249.

[7] Prieger, *ibid.* [2], xvii. 133.

[8] *Chem. News*, xlix. 59.

[9] Hoppe-Seyler, *Ber. Deutsch. Chem. Ges.* xii. 1551.

[10] Leeds, *ibid.* xiv. 975.

[11] Friedel and Crafts, *Bull. Soc. Chim.* xxxi. 463.

[12] *Ann. Chem. Pharm.* lxxv. 356.

[13] Silliman, *Americ. Journ.* 1849.

[14] *Ann. Chem. Pharm.* cxliv. 121.

[15] *Lehrb. Org. Chem.* iii. 13.

proportions are six molecules of the latter to one molecule of potassium benzenesulphonate. The excess of alkali assists the reaction and by dilution prevents the overheating of the melt.[1]

Berthelot obtained phenol from acetylene by dissolving in fuming sulphuric acid and fusing the product with caustic potash.[2] It is also formed in smaller quantities, together with glycerin ether (Vol. III. Part II. p. 351), and other products, when glycerin is distilled with calcium chloride.[3]

Phenol was first prepared about forty years ago in larger quantities from coal-tar by Sell[4] in Offenbach, and Brönner in Frankfort.[5] Its manufacture in large quantities was commenced in England in 1861, by Messrs. Crace Calvert and Charles Lowe, at Bradford, near Manchester. The latter discovered in 1862 that phenol forms a hydrate with water which crystallizes at a low temperature, a property which is not possessed by its homologues. This hydrate splits up on distillation into water and pure phenol, and the latter compound was thus first brought into commerce by Messrs. Charles Lowe and Co., Lowe's carbolic acid melting at a higher temperature and boiling at a lower temperature than the ordinary commercial product. At present pure phenol is prepared by many firms.

It was formerly obtained by distilling the portions of tar boiling between 150°—250°, but it is now prepared from the portion boiling between 150°—200°, or the so-called middle oil, which, after the larger quantity of the naphthalene contained in the oil has crystallized out, is treated with caustic soda, of sp. gr. 1·34, and the mixture well worked in a cylinder by means of an agitator. After standing for some time, the lower layer is drawn off from the upper, which consists of hydrocarbons, diluted with water and allowed to stand in contact with air, when naphthalene and tarry products separate. The aqueous solution is fractionally precipitated by dilute sulphuric acid, tarry matters separating out first, then the homologues of phenol, and, lastly, phenol itself.

In other works the decomposition is completed in one operation and the tar-acids separated by distillation, the portion boiling between 175° to 200° being collected separately as the

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[1] Degener, *Journ. Prakt. Chem.* [2], xvii. 394.

[2] *Compt. Rend.* lxviii. 539.

[3] *Ann. Chem. Pharm.* Suppl. viii. 254.

[4] Hofmann, *Report London Exhibition*, 1862.

[5] C. Brönner prepared "creosote as clear as water," which was frequently returned, because it crystallized in winter. Lunge, *Dist. Coal-Tar*, &c.

crude carbolic acid of commerce. By repeated fractional distillation, and by cooling the portions boiling between 180° to 190°, crystalline phenol is obtained, which, however, still contains more or less paracresol. In order to prepare chemically pure phenol, either Coupier's apparatus is employed, or the above-mentioned hydrate is decomposed by distillation.

Phenol crystallizes in long rhombic needles melting at 42° and boiling at 182° (Lowe). Its melting-point is lowered by the admixture of even insignificant quantities of its homologues, as well as of naphthalene and water. A few drops of the latter suffice to liquefy a large quantity of phenol. The above-mentioned hydrate, $2C_6H_6O + H_2O$, solidifies on cooling to crystals melting at 17° (Lowe). The specific gravity of liquid phenol at 46° is 1·0560, and at 56° is 1·0469.[1]

970 Phenol combines with liquid carbon dioxide to form a crystalline compound,[2] which is also obtained when salicylic acid, or the isomeric para-oxybenzoic acid, is heated for two hours to 250° to 260° in a closed tube, when this acid decomposes easily into phenol and carbon dioxide. On cooling, the compound separates out as a crystalline mass, similar to the pyramidal form of common salt, and melting at 37°. The compound is, of course, only stable under pressure.[3]

Phenol also forms with sulphur dioxide a compound which crystallizes in yellow, rhombic tables melting at 25° to 30° and distilling at 140° in a stream of sulphur dioxide. On exposure to air it quickly gives off sulphur dioxide. Its composition is probably $SO_2 + 4C_6H_6O$.[4]

Phenol possesses a peculiar smell and has a burning, caustic taste; it is soluble at the ordinary temperature in fifteen parts of water; its solubility increases with increase of temperature, so that at 84° both liquids may be mixed in all proportions.[5] It is readily soluble in the fatty oils and glycerol, and dissolves in alcohol and ether in every proportion.

Pure phenol remains colourless on exposure to light and air, but if it contains a trace of impurity it is quickly coloured red or brown, and deliquesces in moist air.

It acts on the skin as a powerful caustic; it coagulates albumen and precipitates solutions of gelatine. Taken internally

[1] Ladenburg, *Ber. Deutsch. Chem. Ges.* vii. 1687.
[2] Barth, *Wien. Akad. Ber.* lviii. 2, 16.
[3] Klepl, *Journ. Prakt. Chem.* [2], xxv. 464.
[4] Holzer, *ibid.* xxv. 463.
[5] Alexejew, *Ber. Deutsch. Chem. Ges.* ix. 1810.

it is a violent poison; a few drops kill a dog, and plants expire in a dilute aqueous solution (Frerichs and Wöhler). In cases of poisoning by carbolic acid, which not unfrequently occur, Crace Calvert recommends olive or almond oil as an antidote; Husemann advises the use of sucrate of lime prepared by adding five parts of slaked lime to sixteen parts of sugar in forty parts of water; after digesting for three days it is filtered, the solution evaporated, and the residue dried at 100°.[1]

When the vapour of phenol is passed over red hot zinc dust it is reduced to benzene.[2] In this way all phenols and various other oxidized aromatic compounds can be converted into the corresponding hydrocarbons. This reaction, discovered by Baeyer, is of great interest, as it led to the discovery of artificial alizarin, the colouring matter of madder. When phenol is merely passed through a red-hot tube it forms benzene, toluene, C_7H_8, xylene, C_8H_{10}, naphthalene, $C_{10}H_8$, anthracene, $C_{14}H_{10}$, and a small quantity of phenanthrene, $C_{14}H_{10}$.[3]

Reactions of Phenol.—It has been remarked in the introduction that most of the phenols give characteristic colours with a solution of ferric chloride, this property having been first noticed in phenol *par excellence* by Runge, who obtained a violet colouration with ferric salts. This reaction is, however, not a delicate one, and does not occur in presence of alcohol.[4] By adding some ammonia, and then a solution of bleaching powder to an aqueous solution of phenol a blue colouration is obtained.[5] Millon's reagent (a solution of mercuric nitrate containing nitrous acid) gives on boiling with a phenol solution a yellow precipitate, which dissolves in nitric acid, yielding a deep red coloured solution. By this reaction, $\frac{1}{2000000}$ of phenol can be detected. Salicylic acid likewise gives this reaction and the presence of phenol must therefore be confirmed by adding to the solution ammonia and sodium hypochlorite. When the solution contains not less than $\frac{1}{50000}$ of phenol, the blue colour is obtained after standing for twenty-four hours.[6]

By dissolving 6 per cent. of potassium nitrite in strong sulphuric acid and adding phenol, the liquid is coloured brown, then green, and afterwards blue.[7] The colouring matters here formed

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[1] Schultz, *Steinkohlentheer*, 446.

[2] *Ann. Chem. Pharm.* cxl. 295.

[3] Kramers, *ibid.* clxxxix. 129.

[4] Hesse, *Liebig's Ann.* clxxxii. 161.

[5] Berthelot, *Rép. Chim. Appl.* i. 284; Lex, *Ber. Deutsch. Chem. Ges.* iii. 458; also Salkowski, *Fresenius' Zeitschr.* xi. 316.

[6] Almén, *Pharm. Journ. Trans.* [3], vii. 812.

[7] Liebermann, *Ber. Deutsch. Chem. Ges.* vii. 247.

will be subsequently described. On adding bromine water to an aqueous solution of phenol a yellowish white precipitate of tribromophenol is obtained, which disappears until an excess of bromine has been added. If the solution contains 1 part of phenol to 50,000 to 60,000 parts of water, a crystalline precipitate separates out in a few hours. Aniline, and some other bodies, give similar precipitates, but these may be easily distinguished from tribromophenol by bringing some of the washed precipitate into a test tube with some water and sodium amalgam, shaking and warming the mixture. The liquid is then poured into a basin and dilute sulphuric acid added, when the characteristic smell of free phenol is noticed, and, if the quantity is not too small, it separates out in oily drops.[1]

The easy transformation of phenol into tribromophenol can be used for the quantitative estimation of phenol by determining the weight of the tribromophenol (Landolt). It is, however, simpler to add to the phenol solution a normal solution of bromine in caustic soda, and hydrochloric acid, and titrate the excess of bromine with potassium iodide and sodium thiosulphate.[2]

Uses of Phenol.—This body, commonly known as carbolic acid, is used in the pure state, mixed with water, glycerol, or olive oil, as a powerful antiseptic in medicine and surgery, its dilute aqueous solution being employed as a spray in surgical operations (Lister's dressing). It is also used for destroying parasitic and other organisms infesting both animals and plants. Its aqueous solution is also employed in a more or less pure state for impregnating or creosoting wood, &c. For the latter purpose the crude carbolic acid which contains cresol can be used in many cases, or cresol alone may be employed. For certain purposes it is desirable to have the antiseptic in a solid form, and phenol is then mixed with such substances as marl, clay, chalk, infusorial earth, saw-dust, &c. McDougall's disinfecting powder is a mixture of calcium phenate and magnesium sulphite.

A considerable quantity of phenol is now used for the manufacture of salicylic acid, and of various colouring matters, such as picric acid, aurin, azo-colours, &c.

971 *Phenates.*—These bodies, which are also called carbolates, were first prepared by Runge and Laurent.

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[1] Landolt, *Ber. Deutsch. Chem. Ges.* iv. 770.

[2] Koppeschar, *Fresenius' Zeitschr.* xv. 233; see also Degener, *Journ. Prakt. Chem.* [2], xvii. 390; Chandelon, *Bull. Soc. Chim.* xxxviii. 69.

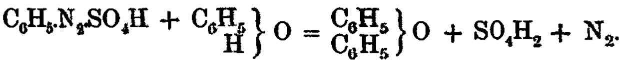
Potassium phenate, or *phenol potassium*, C_6H_5OK, is obtained by warming equal equivalents of phenol and caustic potash, or by dissolving potassium in phenol. In order to prepare the pure compound, phenol is gradually heated with the requisite quantity of the metal in an atmosphere of hydrogen. As soon as this is completely dissolved, the solution is cooled, when a radiating, crystalline mass is obtained, containing cavities in which well-developed needles have been formed.[1] The salt is extremely hygroscopic. It was formerly supposed that phenol does not decompose potassium carbonate, inasmuch as an alkaline phenate rapidly absorbs carbon dioxide (Runge). But Baumann has shown that the crystalline phenate can be obtained by boiling phenol with a solution of potassium carbonate.[2]

Sodium phenate, C_6H_5ONa, is prepared in a similar way to the potassium compound. It is obtained in large quantities by dissolving the calculated quantity of phenol in strong caustic soda, an excess of phenol being avoided, as, otherwise, a dark-coloured product is obtained. On evaporating the solution to dryness, and continually stirring the heated residue, the whole falls to a dry powder. Sodium phenate is very hygroscopic, and must, therefore, be placed while hot in an air-tight vessel.[3] It is employed in the manufacture of salicylic acid.

The phenates of calcium, barium, lead (Runge, Laurent), thallium,[4] and aluminium,[5] have likewise been prepared.

PHENYL ETHERS.

972 *Phenyl oxide*, or *diphenyl ether*, $(C_6H_5)_2O$, was first obtained by Limpricht and List, in small quantities, together with other products, by the dry distillation of copper benzoate. It is prepared by warming a solution of diazobenzene sulphate with phenol:[6]



$$C_6H_5.N_2.SO_4H + \left.\begin{matrix}C_6H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}O + SO_4H_2 + N_2.$$

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[1] Hartmann, *Journ. Prakt. Chem.* [2], xvi. 36.
[2] *Ber. Deutsch. Chem. Ges.* x. 686.
[3] H. Kolbe, *Journ. Prakt. Chem.* [2], x. 89.
[4] Kuhlmann, *Jahresb.* 1864, 254.
[5] Gladstone and Tribe, *Journ. Chem. Soc.* 1881, i. 9.
[6] Hofmeister, *Ann. Chem. Pharm.* clix. 191.

Phenyl oxide is also formed, together with other products, by warming phenol with aluminium chloride.[1] It separates out from its solutions as an oil, which solidifies at a low temperature to needles or four-sided prisms melting at 28°. It smells like geranium, and boils at 252°—253°.

Phenyl oxide is an extremely stable body, which is neither attacked by phosphorus pentachloride nor by a solution of chromium trioxide in acetic acid. Even hydriodic acid does not act on it at 250°, and it remains unchanged when ignited with zinc-dust.

Phenyl methyl ether was first obtained by Cahours by distilling anisic acid (methylparoxybenzoic acid) with baryta, and was therefore called anisol.[2]

$$C_6H_4\left\{\begin{matrix}OCH_3\\CO_2H\end{matrix}\right. = C_6H_5OCH_3 + CO_2.$$

In the same way he obtained it from wintergreen oil, which chiefly consists of methyl salicylate, which is metameric with anisic acid.[3] He then found that anisol is also formed by using Williamson's method of preparing mixed ethers, viz., by heating potassium phenate with methyl iodide, or by distilling it with potassium methyl sulphate.[4] It is obtained in larger quantities by heating sodium phenate to 190°—200°, and passing methyl chloride through the mass by a tube reaching to the bottom of the vessel as rapidly as it is absorbed.[5]

Anisol is a pleasantly-smelling liquid, boiling at 152°, and having a sp. gr. of 0·991 at 15°. It is not attacked by concentrated hydrochloric acid at 120°—130°, but hydriodic acid decomposes it at 130°—140° into phenol and methyl iodide.[6] Heated zinc-dust does not decompose it.[7]

Phenyl ethyl ether, $C_6H_5OC_2H_5$.—Baly first obtained this compound by the action of ethyl salicylate on anhydrous baryta, and by the distillation of the product; the new compound he termed salithol.[8] Soon afterwards Cahours obtained it by the same process and called it phenetol (phénétol[9]), and then prepared it from ethyl iodide and potassium phenate.[10] It is also easily obtained by heating sodium phenate with sodium methyl sulphate for

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[1] Merz and Weith, *Ber. Deutsch. Chem. Ges.* xiv. 189.

[2] *Ann. Chem. Pharm.* xli. 69.

[3] *Ibid.* xlviii. 65.

[4] *Ibid.* lxxviii. 226.

[5] Vincent, *Bull. Soc. Chim.* xl. 106.

[6] Gräbe, *Ann. Chem. Pharm.* cxxxix. 149.

[7] Ders, *ibid.* clii. 66.

[8] *Journ. Chem. Soc.* ii. 28; *Ann. Chem. Pharm.* lxx. 269.

[9] *Ann. Chem. Pharm.* lxxiv. 314.

[10] *Ibid.* lxxviii. 226.

several hours to 150°.[1] It is a liquid possessing similar properties to anisol, and boiling at 172°.

We are also acquainted with the following mixed phenyl ethers containing monatomic alcohol radicals:

		Boiling-point.
Phenyl isopropyl ether,[2]	$\left.\begin{matrix}(CH_3)_2CH\\C_6H_5\end{matrix}\right\}O$	176°
Phenyl propyl ether,[3]	$\left.\begin{matrix}C_3H_7\\C_6H_5\end{matrix}\right\}O$	190—191°
Phenyl isobtuyl ether,[4]	$\left.\begin{matrix}(CH_3)_2C_2H_3\\C_6H_5\end{matrix}\right\}O$	198°
Phenyl amyl ether,[5]	$\left.\begin{matrix}C_5H_{11}\\C_6H_5\end{matrix}\right\}O$	224—225°
Phenyl allyl ether,[6]	$\left.\begin{matrix}C_3H_5\\C_6H_5\end{matrix}\right\}O$	192—195°

Diphenyl methylene ether, $(C_6H_5O)_2CH_2$, is obtained by heating methylene bromide with potassium phenate. It is a liquid with a faint odour resembling that of phenol, and boiling at 293°—295°.[7]

Diphenyl ethylene ether, $(C_6H_5O)_2C_2H_4$, is formed when potassium phenate is heated with ethylene bromide to 140°. It forms crystals melting at 98·5°, difficultly soluble in cold, but readily in hot alcohol, and ether.[8]

By allowing equal molecules of sodium phenate and ethylene bromide to act upon one another in alcoholic solution, phenyl bromethyl ether, $C_6H_5OC_2H_4Br$, is formed. It crystallizes in colourless needles melting at 39°, boils with slight decomposition at 240°—250°, and easily loses its bromine. By heating the ether with alcoholic ammonia to 100°—120°, the hydrobromide of imidodiethylene phenyl ether, $(C_6H_5OC_2H_4)_2HN$, is formed, and by acting on this with soda the free base is obtained as a thick, strongly basic oil.[9]

Phenolglucoside, $C_6H_{11}O_5(OC_6H_5)$, is formed by the action of alcoholic potassium phenate on acetochlorohydrose (Vol. III. Part II. p. 545):

$$C_6H_7(C_2H_3O)_4ClO_5 + C_6H_5OK + 4C_2H_5OH$$
$$= C_6H_{11}O_5(OC_6H_5) + 4C_2H_5.OC_2H_3O + KCl.$$

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[1] Kolbe, *Journ. Prakt. Chem.* [2], xxvii. 425.

[2] Silva, *Zeitsch. Chem.* 1870, 249. [3] Cahours, *Bull. Soc. Chim.* xxi. 78.

[4] Riess, *Ber. Deutsch. Chem. Ges.* iii. 780.

[5] Cahours, *Ann. Chem. Pharm.* lxxviii. 227.

[6] Henry, *Ber. Deutsch. Chem. Ges.* v. 455 a.

[7] Henry, *Ann. Chim. Phys.* [5], xxx. 266.

[8] Burz, *Zeitsch. Chem.* 1869, 165; Lippmann, *ibid.* 447.

[9] Weddige, *Journ. Prakt. Chem.* [2], xxiv. 241.

It is soluble in cold, but still more so in hot water, and crystallizes from its aqueous solution in concentrically grouped needles which melt at 171°—172°.[1] By heating it with acetic anhydride and sodium acetate, the triacetyl-compound, $C_6H_7(C_2H_3O)_4O_5(OC_6H_5)$, which crystallizes from hot alcohol in long shining needles, is formed.[2]

We have already remarked that dextrose frequently occurs as a product of decomposition of bodies belonging to the vegetable kingdom, termed glucosides, which are split up by dilute acids, or by certain ferments, with assumption of water, yielding sugar-like substances and other bodies. (Vol. III. Part II. p. 538.)

Phenolglucoside is not only the simplest compound of this group, but also the first one which was artificially prepared. When boiled with dilute acids, or when its solution, warmed to 40°, is brought into contact with emulsin, a ferment contained in almonds, it splits up into phenol and dextrose.

$$C_6H_{11}(OC_6H_5)O_5 + H_2O = HO.C_6H_5 + C_6H_{12}O_6.$$

ETHEREAL SALTS OF PHENYL WITH INORGANIC ACIDS.

973 *Sulphate of Phenyl.*—According to theory, two sulphates should exist, viz., the normal and the acid ethereal salt; these bodies, however, cannot be prepared in a similar way to the corresponding ethyl compounds, for phenyl iodide (iodobenzene) does not act on silver sulphate, and sulphuric acid converts phenol into the phenolsulphonic acid. It appeared therefore very doubtful whether it was possible to obtain sulphate of phenyl, till Baumann found in the urine of herbivora, and in smaller quantities in that of man and the dog, the potassium salt of an acid which he first believed to be a phenolsulphonic acid, but afterwards found to be *phenylsulphuric acid*, $SO_4(C_6H_5)H$. He observed moreover that the quantity of this compound is greatly increased if phenol be taken internally, and that if sufficient be taken the sulphates disappear from the urine. He then prepared phenylsulphuric acid artificially.[3]

Its potassium salt is obtained by mixing 100 parts of phenol

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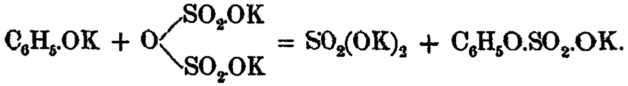
[1] A. Michael, *Jahresb.* 1879, 858.

[2] *Ber. Deutsch. Chem. Ges.* xvi. 2510.

[3] *Ibid.* ix. 54, 1715; xi. 1907.

and 60 parts of caustic potash with from 80—90 parts of water, and gradually adding 125 parts of finely powdered potassium disulphate as soon as the solution has cooled to 60°—70°. The mass is kept at this temperature for from eight to ten hours, and frequently agitated, after which it is extracted with boiling 95 p. c. alcohol, and the salt which separates out on cooling recrystallized from alcohol. Its formation is shown by the following equation:



$$C_6H_5.OK + O\begin{cases} SO_2.OK \\ SO_2.OK \end{cases} = SO_2(OK)_2 + C_6H_5O.SO_2.OK.$$

It crystallizes in small shining tablets which feel greasy to the touch; it is obtained in transparent rhombic tables from alcohol at 60°. At 15° it dissolves in seven parts of water; in cold absolute alcohol it is scarcely soluble, but in boiling alcohol somewhat more readily.

It decomposes on exposure to moist air, sometimes in a few minutes, into phenol and acid potassium sulphate. This change is also effected by heating the salt with water for some hours to 100°, or by warming it with dilute hydrochloric acid for a few minutes. Towards alkalis it is, on the contrary, very stable, and is only gradually attacked on treatment with caustic potash at 150°. By heating it to 150°—160°, in absence of moisture, it is converted into the isomeric potassium paraphenolsulphonate, $C_6H_4(OH)SO_3K$.

Free phenylsulphuric acid is so unstable that its aqueous or alcoholic solution decomposes almost immediately.

Phosphate of Phenyl.—By the action of phosphorus pentoxide on phenol, mono- and di-phenylphosphoric acids are formed; these can be separated by means of their copper salts, since that of the former acid is more readily soluble than that of the latter.[1]

Monophenylphosphoric acid, $PO(OC_6H_5)(OH)_2$, crystallizes in thick needles, readily soluble in water and alcohol, and melting at 97°—98°. On distillation it decomposes into phenol and metaphosphoric acid.

Diphenylphosphoric acid, $PO(OC_6H_5)_2OH$, forms crystals melting at 50°, soluble with difficulty in water, but readily in alcohol. It has a great tendency to remain in the fused condition, and hence it has been described as an oily liquid.[2] The chlorides of this acid

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[1] Reinbold, *Zeitsch. Chem.* 1866, 651.

[2] Rapp, *Ann. Chem. Pharm.* ccxxiv. 156.

are formed by the action of phosphorus oxychloride on phenol, and can be separated by fractional distillation.

Phenylphosphoric chloride, $PO(OC_6H_5)Cl_2$, is a heavy, strongly refractive, not unpleasantly smelling liquid, boiling at 241°—243°, and is easily decomposed by water.

Diphenylphosphoric chloride, $PO(OC_6H_5)_2Cl$, is a thick liquid boiling at 314°—316°, and having a similar smell to the preceding compound. It is only slowly attacked by water and cold dilute alkalis.[1]

Normal phenyl phosphate, $PO(OC_6H_5)_3$, is formed, together with chlorobenzene, by the action of phosphorus pentachloride on phenol.[2]

$$4C_6H_5OH + PCl_5 = C_6H_5Cl + PO(OC_6H_5)_3 + 4HCl.$$

It crystallizes in small needles melting at 45° (Jacobsen), is readily soluble in alcohol and ether, and can be recrystallized from strong sulphuric acid without alteration.

Phenyl carbonate, $CO(OC_6H_5)_2$, is formed when phenol is heated with carbonyl chloride to 140°—150°. It crystallizes from alcohol in silky needles melting at 78°.[3]

Phenyl ethylcarbonate, $CO\left\{\begin{matrix}OC_2H_5\\OC_6H_5\end{matrix}\right.$, is formed by the action of ethyl chlorocarbonate on potassium phenate, as well as by that of aluminium chloride on a mixture of phenol and ethyl carbonate.[4] It is an oily liquid boiling at 234°.[5]

Phenyl carbamate, $CO(NH_2)OC_6H_5$.—In the preparation of the carbonates phenyl chlorocarbonate is also formed, and this comes over first on distilling the product, though it is not pure. On passing ammonia through its ethereal solution, sal-ammoniac separates out, and on evaporating the ether, phenyl carbamate crystallizes out in tablets which melt at 141°, and are readily soluble in hot, but with difficulty in cold water. By heating it with ammonia to 140° phenol and carbamide are formed (Kempf).

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[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* viii. 1519.

[2] Scrugham, *Ann. Chem. Pharm.* xcii. 317.

[3] Kempf, *Journ. Prakt. Chem.* [2], i. 404.

[4] Pawlewsky, *Ber. Deutsch. Chem. Ges.* xvii. 1205.

[5] Fatianow, *Jahresb. Chem.* 1864, 477.

ETHEREAL SALTS OF PHENYL WITH ORGANIC ACIDS.

974 *Phenyl orthoformate*, $CH(OC_6H_5)_3$, is formed, together with salicylaldehyde, parabenzaldehyde and other products, when an alkaline solution of phenol is heated with chloroform. It crystallizes from alcohol in long white needles melting at 71·5°, and, under diminished pressure, distils without decomposition.

It is not saponified by continued boiling with alkalis, but acids transform it very readily into phenol and formic acid.[1]

Phenyl acetate, $C_2H_3O_2.C_6H_5$.—Cahours obtained this substance by the action of acetyl chloride on phenol,[2] and Scrugham by heating phenyl phosphate with potassium acetate and alcohol.[3] It is also prepared by boiling phenol with acetamide,[4] and by heating phenol with lead acetate and carbon disulphide to 170°.[5]

$$4C_6H_5OH + 2Pb(C_2H_3O_2)_2 + CS_2$$
$$= 4C_6H_5.C_2H_3O_2 + 2PbS + CO_2 + 2H_2O.$$

Phenyl acetate is a peculiarly smelling liquid boiling at 193° (Perkin and Hodgkinson), and possessing the same refractive index as ordinary soda-lime glass, so that a tube of this glass dipped in the liquid is invisible (Broughton). Sodium acts violently upon it, with formation of acetic acid, acetic ether, phenol, salicylic acid, and two crystalline bodies, $C_{15}H_{12}O_3$, and $C_{18}H_{14}O_4$, which have not yet been examined.[6]

Phenyl chloracetate, $C_2H_2ClO_2.C_6H_5$.—Provost obtained this compound by the action of chloracetyl chloride on phenol. It is readily soluble in alcohol, and crystallizes in needles melting at 40·2° and distilling without decomposition at 230°—235°. By heating it with alcoholic ammonia it forms phenyl amidacetate, $C_2H_2(NH_2)O_2.C_6H_5$, which crystallizes in needles and dissolves in weak acids and water, but is scarcely soluble in alcohol.[7]

Phenylglycollic acid, $C_6H_5OCH_2.CO_2H$, is formed by the action of sodium phenate on chloracetic acid.[8] It is best obtained by mixing an aqueous solution of sodium chloracetate with sodium

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[1] Tiemann, *Ber. Deutsch. Chem. Ges.* xv. 2685.

[2] *Ann. Chem. Pharm.* xcii. 316.

[3] *Ibid.* xcii. 317.

[4] Guareschi, *Ann. Chem. Pharm.* clxxi. 142.

[5] Broughton, *ibid.* Suppl. iv. 121.

[6] Perkin and Hodgkinson, *Journ. Chem. Soc.* 1880, i. 487.

[7] *Journ. Prakt. Chem.* [2], iv. 579.

[8] Heintz, *Jahresb.* 1859, 361; Giacosa, *Journ. Prakt. Chem.* [2], xix. 369.

phenate, and evaporating until the whole becomes thick; it is difficultly soluble in cold water, readily in alcohol and ether, and crystallizes from hot water in long shining needles which are acid and bitter to the taste, and smell peculiarly. It melts at 96°, and boils with slight decomposition at 285°. Phenyloxyacetic acid is not poisonous, but acts as a strong antiseptic.[1] It forms salts which crystallize well.

Ethyl phenylglycollate, $C_6H_5.OCH_2.CO_2.C_2H_5$, may be obtained by passing hydrochloric acid through a hot alcoholic solution of the above acid. It is a thick oily liquid, having a peculiar, not unpleasant, but persistent smell, and boiling at 251°. The methyl ether is a similar body, boiling at 245° (Fritzsche).

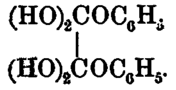
Phenyllactic acid, $CH_3.CH(OC_6H_5)CO_2H$, is obtained in a similar way to its analogue, the preceding acid, from *a*-chloropropionic acid. It crystallizes from hot water in long needles melting at 112°—113°. Its ethyl ether is a body smelling like chloroform and boiling at 243°—244°.

Phenyl oxalate, $C_2.O_2(OC_6H_5)_2$, is formed when phenol is heated with anhydrous oxalic acid and phosphorus oxychloride:

$$\begin{aligned}&2C_6H_5.OH + C_2O_4H_2 + POCl_3\\ &= C_2O_4(C_6H_5)_2 + PO_3H + 3HCl.\end{aligned}$$

It crystallizes from absolute alcohol in fine prisms, is insoluble in water, but on long boiling it decomposes, or more rapidly in presence of alkalis or acids.[2]

By distilling a mixture of one molecule of anhydrous oxalic acid and two molecules of phenol, thin shining plates are obtained melting at 126°—127°. This body is also formed when the two compounds are dissolved in glacial acetic acid. It distils between 150°—180°, partly decomposing into phenol and formic acid. Water and alcohol decompose it into its components. Its empirical formula is $C_2H_2O_4 + 2C_6H_6O$, and it may be regarded as the phenyl ether of orthoxalic acid, $C_2(OH)_6$:[3]



$$\begin{array}{c}(HO)_2COC_6H_5\\ |\\ (HO)_2COC_6H_5.\end{array}$$

Phenyl succinate, $C_4H_4O_2(OC_6H_5)_2$, is formed by warming phenol with succinyl chloride. It is insoluble in water, and crystallizes from boiling alcohol in pearly plates; these melt at 118°, and the liquid boils without decomposition at 330°.[4]

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[1] Fritzsche, *Journ. Prakt. Chem.* [2], xx. 269.

[2] Nencki, *Journ. Prakt. Chem.* [2], xxv. 282.

[3] Claparède and Smith, *Journ. Chem. Soc.* 1883, i. 358; Staub and Smith, *Ber. Deutsch. Chem. Ges.* xvii. 1740.

[4] Weselsky, *ibid.* ii. 518.

CHLORINE SUBSTITUTION PRODUCTS OF PHENOL.

975 *Monochlorophenols*, $C_6H_4Cl(OH)$.—By the action of chlorine on phenol, parachlorophenol, together with a small quantity of the ortho-compound, is formed.[1] These bodies, as well as metachlorophenol, are also obtained by means of the diazo-reaction from the corresponding chloranilines[2] as well as from the amidophenols.[3]

Orthochlorophenol is formed, together with α- and γ-dichlorophenol and trichlorophenol, by the action of sodium hypochlorite on an aqueous solution of phenol.[4] It is a liquid having an unpleasant, persistent smell, boiling at 175°—176°, and at a low temperature solidifying in needles, melting at 7°. By the action of phosphorus pentachloride it is converted into orthodichlorobenzene.

Metachlorophenol crystallizes in white needles, melting at 48°[5] and boiling at 214°.

Parachlorophenol is prepared, in addition to the above-mentioned method, by the action of sulphuryl chloride on phenol.[6]

$$C_6H_5.OH + SO_2Cl_2 = C_6H_4Cl.OH + SO_2 + HCl.$$

It forms crystals which melt at 37° and boil at 217°; it has a weak but unpleasant and very persistent smell.

α-Dichlorophenol, $C_6H_3Cl_2OH$. Laurent obtained this compound by the action of chlorine on phenol, and named it "*Acide chlorophénesique*."[7] It was afterwards prepared by F. Fischer, by passing chlorine through phenol for several days and fractionating the product. It is insoluble in water and crystallizes from benzene in long six-sided needles which have an unpleasant persistent smell, melt at 43° and boil at 209°—210°. Its solution in alcohol is acid, and it decomposes carbonates on boiling with water, though its salts are almost completely decomposed by carbon dioxide in the cold. Phosphorus pentachloride converts it into the asymmetrical trichlorobenzene.

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[1] Faust and Müller, *Ann. Chem. Pharm.* clxxiii. 303.
[2] Beilstein and Kurbatow, *ibid.* 176.
[3] Schmitt, *Ber. Deutsch. Chem. Ges.* i. 67.
[4] Chandelon, *ibid.* xvi. 1479.
[5] Uhlemann, *ibid.* xi. 1161.
[6] Dubois, *Zeitschr. Chem.* 1866, 705; 1867, 205.
[7] *Ann. Chim. Phys.* lxiii. 27.
[8] *Ann. Chem. Pharm.* Suppl. vii. 180.

Two other dichlorophenols are known, obtained from the dichloramidophenols.

		Melting-point.	Boiling-point.
β-Dichlorophenol,[1]	thin needles.	54°—55°	—
γ-Dichlorophenol,[2]	fine needles.	65°	218°—220°

Trichlorophenol, $C_6H_2Cl_3(OH)$, was likewise discovered by Laurent and named *Acide chlorphénisique*;[3] it is obtained by the action of chlorine, not only on phenol, but also on aniline,[4] indigo,[5] and other aromatic compounds. It is prepared by passing chlorine into phenol, warming gradually until the melting point rises to about 67°, and isolating the pure compound by fractional distillation.[6] It is easily soluble in alcohol and ether, and crystallizes in needles, melting at 67°—68°, boiling at 243·5°—244·5°, and having an acid reaction. Its salts are only slightly soluble in water.

An isomeric trichlorophenol is obtained from trichloramidophenol, it melts at 54·1°—54·5° and boils at 248·5°—249·5°.[7]

Perchlorophenol, $C_6Cl_5(OH)$. Erdmann obtained this compound by the continued action of chlorine on isatin and on trichlorophenol (chlorindoptic acid), and named it chlorinated indoptic acid.[8] Laurent who likewise prepared it from isatin named it *Acide Chlorphénusique*.[9] It is also prepared by the action of iodine chloride on phenol,[10] or, better, by passing chlorine continuously through a mixture of three parts of phenol and one part of antimony trichloride at 100° to 110° till the action ceases. The antimony chloride is then dissolved in strong hydrochloric acid, the residue treated with boiling soda solution, precipitated by hydrochloric acid, and the separated perchlorophenol purified by distillation in superheated steam and recrystallization from petroleum spirit.[11] It crystallizes in rhombic prisms which melt at 187°, and are readily soluble in alcohol, the solution having an acid reaction. When heated it first has a pungent smell and then produces coughing; its powder excites violent sneezing. By carefully heating it may be sublimed in white needles; it does not boil until a higher

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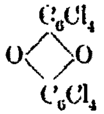
[1] Hirsch, *Ber. Deutsch. Chem. Ges.* xi. 1981.
[2] Seifart, *Ann. Chem. Pharm.* Suppl. vii. 203.
[3] *Ann. Chim. Phys.* [3], iii. 206.
[4] *Ann. Chem. Pharm.* liii. 8.
[5] Erdmann, *Journ. Prakt. Chem.* xix. 332; xxii. 276; xxv. 472.
[6] Faust, *Ann. Chem. Pharm.* cxlix. 149.
[7] Hirsch, *Ber. Deutsch. Chem. Ges.* xiii. 1908.
[8] *Journ. Prakt. Chem.* xxii. 272.
[9] *Ann. Chim. Phys.* [3], iii. 497.
[10] Schützenberger, *Bull. Soc. Chim.* iv. 102.
[11] Merz and Weith, *Ber. Deutsch. Chem. Ges.* v. 458.

temperature is reached, when it decomposes with separation of hydrochloric acid and perchlorophenylene oxide, which is described below. Phosphorus pentachloride converts it into perchlorobenzene. Its salts are for the most part only slightly soluble in water.

Potassium perchlorophenate, C_6Cl_5OK, crystallizes from concentrated caustic potash in prisms with a diamond lustre. At a high temperature it decomposes into potassium chloride and *perchlorophenylene oxide*, $(C_6Cl_4)_2O_2$, which is scarcely soluble in alcohol and ether, and crystallizes from hot nitrobenzene in broad needles resembling benzoic acid. It melts about 320°, and boils above the boiling point of mercury. Its constitution is probably the following:



Perchlorophenol chloride, $C_6Cl_5(OH)Cl_2$, is obtained by the continued action of chlorine on acetonietachloranilide, $C_6H_4Cl.N(C_2H_3O)H$, and crystallizes from petroleum spirit in large, thick prisms melting at 78·5° to 80°. By heating it with absolute alcohol to 230° it is converted into perchlorophenol.[1]

BROMINE SUBSTITUTION PRODUCTS OF PHENOL.

976 *Monobromophenols*, $C_6H_4Br(OH)$, are obtained in a similar way to the corresponding chlorophenols.

Orthobromophenol is an oily liquid having an unpleasant, strong and persistent smell, and boiling at 194° to 195°.[2]

Metabromophenol crystallizes in scales melting at 33° and boiling at 236·5°; it does not smell so unpleasantly as the ortho-compound.[3]

Parabromophenol crystallizes from chloroform in large octohedra resembling those of alum, melting at 63° to 64°. It is easily soluble in alcohol and boils at 238°.[4]

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[1] Beilstein, *Ber. Deutsch. Chem. Ges.* xi. 2182.

[2] Fittig and Mager, *Ber. Deutsch. Chem. Ges.* viii. 362.

[3] Wurster and Nölting, *ibid.* vii. 905; Fittig and Mager, *loc. cit.*

[4] Hubner and Brenken, *ibid.* vi. 171; Fittig and Mager, *ibid.* vii. 1176.

	Melting-point.
[1] Dibromophenol, $C_6H_3Br_2(OH)$, snow-white crystals	40°
[2] Tribromophenol, $C_6H_2Br_3(OH)$, very long hair-like needles	95°
[3] Tetrabromophenol, $C_6HBr_4(OH)$, needles	120°
[4] Pentabromophenol, $C_6Br_5(OH)$, needles	225°

These bodies are all obtained by the direct bromination of phenol. It is singular, that in the last three, the hydrogen atom of the hydroxyl can be easily replaced by bromine giving rise to the following compounds:

Tribromophenol bromide, $C_6H_2Br_3(OBr)$, is obtained by treating an aqueous solution of phenol, or better salicylic acid, $C_6H_4(OH)CO_2H$, with strong bromine water. The precipitate thus obtained crystallizes from carbon disulphide in lemon coloured scales which are not attacked by a boiling aqueous solution of an alkali. By dissolving it in benzene and adding caustic potash or ammonia, tribromophenol is formed. On heating with sulphuric acid it is converted into the isomeric tetrabromophenol.[5]

Tetrabromophenol bromide, $C_6HBr_4(OBr)$, is obtained by dissolving tetrabromophenol in caustic potash, adding hydrochloric acid and then quickly an excess of bromine water. It crystallizes from chloroform in yellow monoclinic tables; boiling alcohol converts it into tetrabromophenol, and on heating with sulphuric acid it is converted into pentabromophenol.

Hexbromophenol or Perbromophenol bromide, $C_6Br_5(OBr)$, is obtained from pentabromophenol in a similar way to the preceding compound, and forms granular yellow crystals, which are insoluble in cold alcohol, but are converted by boiling alcohol into pentabromophenol (Benedikt).

IODINE SUBSTITUTION PRODUCTS OF PHENOL.

977 *Mono-iodophenols*, $C_6H_4I(OH)$. Respecting these bodies, the published statements are at variance. According to Körner,[6] the para-compound is obtained, together with a little of the ortho-compound and tri-iodophenol, by adding hydrochloric acid

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[1] Körner, *Ann. Chem. Pharm.* cxxxvii. 205.

[2] Laurent, *ibid.* xliii. 212; Körner, *loc. cit.*

[3] Körner, *loc. cit.* 209.

[4] Körner, *loc. cit.* 210.

[5] Benedict, *Liebig's Ann.* cxcix. 128; *Monatsch. Chem.* i. 360.

[6] *Ann. Chem. Pharm.* cxxxvii. 211; *Jahresb.* 1867, 615; *ibid.* 1875. 356.

to phenol, iodine, and iodic acid, dissolved in a dilute solution of caustic potash:

$$5C_6H_5.OH + 2I_2 + HIO_3 = 5C_6H_4I.OH + 3H_2O.$$

Lobanow found that the meta-compound is also formed in this reaction. By distilling the product with steam, the liquid ortho-iodophenol comes over first, and then the solid meta-iodophenol, while the para-iodophenol is contained in the water which distils over, and also in the residual solution, to which caustic potash is added and the residue, after evaporation, decomposed by hydrochloric acid.[1]

By mixing together dry sodium phenate, iodine, and pure carbon disulphide, ortho-iodophenol, together with β-di-iodophenol and tri-iodophenol, is obtained.[2]

Ortho-iodophenol is, according to Lobanow, a liquid which does not solidify at – 23°; it is decomposed by chlorine or nitric acid, and when fused with caustic potash is converted into catechol (Körner). Nölting and Wrzesinski, on the other hand, observed that ortho-iodophenol, prepared by means of the diazo-reaction from orthonitrophenol, forms fine crystals which melt at 43°.[3]

Meta-iodophenol forms flat lustrous needles melting at 64°—66° (Lobanow). When fused with caustic potash these are transformed into resorcinol (Körner).

Para-iodophenol was first obtained by Griess from para-iodo-aniline.[4] It is also obtained by the action of iodine chloride on phenol,[5] and crystallizes from alcohol in large six-sided tables, and from carbon disulphide in short, thick prisms melting at 89° (Lobanow). On fusion with caustic potash it is converted into quinol (Körner), but at a higher temperature into resorcinol (Nölting and Wrzesinski).

	Melting-point.
[6] α-Di-iodophenol, $C_6H_3I_2(OH)$, crystals . .	150°
β-Di-iodophenol, $C_6H_3I_2(OH)$, crystals . .	68°
[7] Tri-iodophenol, $C_6H_2I_3(OH)$, needles . . .	156°

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[1] *Ber. Deutsch. Chem. Ges.* vi. 1251.

[2] Schall, *Ber. Deutsch. Chem. Ges.* xvi. 1897.

[3] *Ibid.* viii. 820.

[4] *Zeitschr. Chem.* 1865, 425.

[5] Schützenberger and Sengenwald, *Jahresb.* 1862, 413.

[6] Hlasiwetz and Weselsky, *Ber. Deutsch. Chem. Ges.* ii. 524.

[7] Lautemann, *Ann. Chem. Pharm.* cxx. 307; Schützenberger, *Jahresb.* 1865, 521; Körner, *Ann. Chem. Pharm.* cxxxvii. 213.

NITRO-SUBSTITUTION-PRODUCTS OF PHENOL.

978 *Mononitrophenol*, $C_6H_4(NO_2)OH$. In 1839 Fritzsche, by acting with nitric acid on indigo, obtained a peculiar smelling, volatile, yellow, crystalline body, which he subsequently found to be identical with Hofmann's nitrophenol, obtained by the action of nitrous acid on aniline, and of nitric acid on phenol.[1] Fritzsche afterwards found that by the latter reaction two isomeric bodies are formed of which nitrophenic acid can be volatilised in a current of steam, whilst isonitrophenic acid cannot.[2] These bodies were afterwards distinguished as volatile and non-volatile nitrophenol, until it was found that the first is the ortho- and the second the para-compound.

It may be prepared, by gradually adding one part of pure phenol to a well cooled mixture of two parts of nitric acid of Sp. gr. 1·34 and four parts of water, stirring, and after some time separating the heavy oil from the aqueous solution, washing it with water, and distilling in a current of steam, till the distillate is no longer coloured yellow.

Paranitrophenol may be obtained from the residue by extracting with boiling water. The yield amounts to 30 per cent. of orthonitrophenol and 32 per cent. of paranitrophenol on the phenol taken.[3]

The higher the temperature rises during the operation, the larger is the yield of orthonitrophenol, whilst if the temperature be kept low, more of the para-compound is formed.[4]

The two nitrophenols are also obtained, together with diazobenzene nitrate, when nitrogen trioxide is passed into an ethereal solution of phenol,[5] as well as when sodium phenate is mixed with a solution of nitrogen peroxide in carbon disulphide (Schall).

By warming a mixture of 5 parts of phenol and an equal weight of ethyl nitrate with 16 parts of water, and 32 parts of concentrated sulphuric acid for a long time, 22 p. c. of orthonitrophenol and only 0·5 p. c. of paranitrophenol is obtained.[6] According to Fittica a fourth isomeric nitrophenol is formed at the same time. We shall refer to this subject in the sequel.

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[1] Körner, *Ann. Chem. Pharm.* lxxv. 359; ciii. 347.

[2] *Ann. Chem. Pharm.* cx. 150.

[3] Schmitt and Cooke; Körner, Kekulé's *Lehrb. Org. Chem.* iii. 40.

[4] Goldstein, Beilstein's *Handb. Org. Chem.* 1015.

[5] Weselsky, *Ber. Deutsch. Chem. Ges.* viii. 89.

[6] Natanson, *Ber. Deutsch. Chem. Ges.* xiii. 415.

Orthonitrophenol is also obtained, as already stated, when orthochloronitrobenzene, orthobromonitrobenzene, or orthodinitrobenzene is heated with dilute alkalis. It is soluble with difficulty in cold, readily in hot water, as also in alcohol and ether, and crystallizes in sulphur-yellow needles or prisms, having a peculiar aromatic smell and melting at 45°. It boils without decomposition at 214°, and is converted by phosphorus pentachloride into orthonitrophenyl phosphate, only a little orthochloronitrobenzene being formed.

Its salts, which for the most part crystallize well, have a scarlet-red to an orange-yellow colour.

As already stated, according to Fittica,[1] a fourth nitrophenol exists. This body melts at 31°, and boils at 205° to 207°. By repeated distillation it is converted into orthonitrophenol; this would therefore seem to be a case of dimorphism.

Methyl orthonitrophenate or *Nitranisol*, $C_6H_4(NO_2)OCH_3$, is obtained, together with the para-compound, by the nitration of anisol, as well as by heating orthonitrophenol with caustic potash and methyl iodide.[2] It is a yellowish oil, boiling at 276·5°; it solidifies on cooling, and melts at + 9°. When heated with ammonia to 200° it forms orthonitraniline.[3]

Metanitrophenol is obtained by the diazo-reaction from metanitraniline;[4] it separates out from an ethereal solution in thick, sulphur-yellow crystals, melting at 96°. It can only be distilled without decomposition under diminished pressure, and is not volatile in a current of steam. Its salts are of an orange-yellow colour.

Methyl metanitrophenate, $C_6H_4(NO_2)OCH_3$, crystallizes from alcohol in flat needles, melting at 38° and boiling at 258°. It is easily volatilised by steam, and when heated with ammonia yields a small quantity of metanitrophenol together with humus-like products but no metanitraniline.[5]

Paranitrophenol is obtained, like orthonitrophenol, from the corresponding haloid compound by heating with alkalis. It crystallizes from boiling water in colourless needles or in monoclinic prisms, which melt at 114° and on again cooling separate out as monoclinic crystals, which, however, are dimorphous with the ordinary form.[6] It boils almost without decomposition but is not

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[1] *Journ. Prakt. Chem.* [2], xxiv. 1.

[2] Mühlhauser, *Ann. Chem. Pharm.* ccvii. 237. [3] Salkowski, *ib.* clxxiv. 278.

[4] Bantlin, *Ber. Deutsch. Chem. Ges.* xi. 2100.

[5] Salkowski, *Ber. Deutsch. Chem. Ges.* xii. 135.

[6] Lehmann, *Jahresb.* 1877 549.

volatile in a current of steam. On boiling it with water and barium carbonate it decomposes the last-named compound more rapidly than the ortho-compound, and this again acts more rapidly than metanitrophenol.[1] Its salts are not so deeply coloured as those of its isomerides.

Methyl paranitrophenate, $C_6H_4(NO_2)OCH_3$, crystallizes in large rhombic prisms melting at 51° and boiling at 258° to 260°, and forms paranitraniline on heating with ammonia.[2]

HALOGEN SUBSTITUTION PRODUCTS OF THE MONONITROPHENOLS.

Of these only those containing one halogen will be mentioned. The first number gives the position of the halogen, the second that of the nitroxyl, the hydroxyl occupying position one.

			Melting-point
Chloronitrophenols	2 : 6	yellow needles[3]	70°
	2 : 4	white needles[4]	110—111°
	3 : 6	lemon-yellow needles[5]	39°
	4 : 2	monoclinic prisms[6]	86—87°
Bromonitrophenols	2 : 4	long white needles[7]	102°
	5 : 2	yellow prisms[8]	44°
	4 : 6	yellow monoclinic prisms[9]	88°

IODONITROPHENOLS.

The first two of these are obtained by the action of iodine and mercuric oxide on a solution of orthonitrophenol in glacial acetic acid, and the third in the same way from paranitrophenol.[10]

		Melting-point.
α-Iodorthonitrophenol,	long, yellow needles	90—91°
β-Iodorthonitrophenol,	short, yellow needles	66—67°
Iodoparanitrophenol,	thick, light yellow crystals	154—155°

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[1] Post and Mehrtens, *Ber. Deutsch. Chem. Ges.* viii. 1549.

[2] Brunck, *Zeitschr. Chem.* 1867, 205; Willgerodt, *Ber. Deutsch. Chem. Ges.* xiv. 2632.

[3] Faust and Müller, *Ann. Chem. Pharm.* clxxiii. 309.

[4] Faust, *Zeitschr. Chem.* 1871. 591; Armstrong, *ibid.* 596; Faust and Müller.

[5] Uhlemann, *Ber. Deutsch. Chem. Ges.* xi. 1161.

[6] Faust and Saame, *Ann. Chem. Pharm.* Suppl. vii. 190; Laubenheimer, *Ber. Deutsch. Chem. Ges.* vii. 1601; Bodewig, *Jahresb. Chem.* 1879, 511.

[7] Brunck and Körner, *Zeitschr. Chem.* 1868, 323.

[8] Laubenheimer.

[9] Brunck; Körner; Laubenheimer; Hüfner and Brenken, *Ber. Deutsch. Chem. Ges.* vi. 170; Azruni, *Jahresb. Chem.* 1877, 547.

[10] Busch, *Ber. Deutsch. Chem. Ges.* vii. 462.

DINITROPHENOLS, $C_6H_3(NO_2)_2OH$.

Of the six theoretically possible compounds the following are known. The subjoined figures give the position of the nitroxyls when the hydroxyl occupies position 1.

Ordinary or *a-Dinitrophenol* (2:4) is obtained by nitrating phenol[1] as well as from both ortho- and para-nitrophenol, by which its constitution is shown.[2] It is best obtained by warming paranitrophenol with an equal weight of nitric acid of sp. gr. 1·37.[3] It crystallizes from hot water in yellowish-white rectangular tables which melt at 113° to 114°.

β-Dinitrophenol (2:6) is obtained, together with the former, by the nitration of orthonitrophenol, and crystallizes from hot water in fine, bright yellow needles melting at 63° to 64°.

γ-Dinitrophenol (3:6) is obtained together with the two following, when metanitrophenol is heated with nitric acid.[4] They can be separated by means of their barium salts, and the γ-compound can also be separated from the other two by distilling in a current of steam. It crystallizes from hot water in light yellow needles melting at 104°.

δ-Dinitrophenol (3:4) crystallizes in long, colourless, silky needles melting at 134°.

ε-Dinitrophenol (2:3) separates from hot water in small yellow needles, and from alcohol in thick crystals which melt at 144°.

TRINITROPHENOLS, $C_6H_2(NO_2)_3OH$.

979 We are now acquainted with three of these bodies. Of these the following has been known for a long time.

Symmetrical or *a-Trinitrophenol* (2:4:6). Woulfe found in 1771, that by the action of nitric acid on indigo a liquid is obtained which dyes silk yellow.[5] Similar observations were made by other chemists; thus Quatremère Disjonval in 1780 laid before the Paris Academy the results of an investigation on indigo, in which he remarks that this body forms with nitric acid a substance which stains the skin a saffron-yellow colour. Hausmann then observed that in this reaction a bitter acid compound is formed.

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[1] Laurent, *Ann. Chem. Pharm.* xliii. 213.

[2] Körner, *Zeitschr. Chem.* 1868, 322.

[3] Körner, Kekulé's *Lehrb.* iii. 42.

[4] Bantlin, *Ber. Deutsch. Chem. Ges.* viii. 21; xi. 2102; see also Henriques, *Liebig's Ann.* ccxv. 321.

[5] (*Phil. Trans.*) 1771.

Indigo-bitter was then further investigated by Fourcroy and Vauquélin[1] as well as by Chevreul.[2] The latter chemist considered it to be a compound of nitric acid with a peculiar organic substance. Welter, by treating silk with nitric acid, had already obtained a yellow, crystallized acid, whose potassium salt exploded when heated, like gunpowder.[3] Liebig found that Welter's bitter body is identical with indigo-bitter and aloe-bitter, which Braconnot had obtained by heating aloes with nitric acid, and called it "Kohlenstickstoffsäure" (carbazotic acid),[4] while Berzelius named it "Pikrinsalpetersäure," and Dumas gave it the name by which it is now universally known, picric acid (πικρός, bitter).[5] Laurent first obtained it by the action of nitric acid on phenol, and showed that picric acid (*Acide nitrophénisique*) is trinitrophenol.[6] This is the final product of the action of nitric acid on a large number of substances containing the benzene ring, just as oxalic acid is the result of the oxidation of many fatty bodies. Amongst those which give a good yield of the acid is the acaroïd resin (from *Xanthorrhoea hastilis*),[7] and before phenol was manufactured on a large scale, this resin was employed for the preparation of picric acid. This body is also obtained by the action of nitric acid on orthonitrophenol, paranitrophenol and the dinitrophenols (2:4) and (2:6), but not on metanitrophenol, and this fact indicates its constitution.

Picric acid was formerly obtained by the action of nitric acid on phenol; phenolsulphonic acid is now used, since this substance, as Laurent had already pointed out, is easily converted into picric acid. In its manufacture the apparatus is employed which is used for making nitrobenzene. A mixture of equal parts of phenol and concentrated sulphuric acid is placed in the vessel, the contents then heated to 100°, and nitric acid of sp. gr. 1·3 allowed to flow in. After cooling, the product solidifies to a crystalline mass, which is filtered and drained, and then washed with cold water. It is further purified by recrystallizing from water containing 0·1 p.c. of sulphuric acid. Another useful mode of purification consists in exactly saturating the crude acid with sodium carbonate and adding to the hot filtered solution a few crystals of sodium carbonate, when almost the whole of the sodium

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[1] Gehlen, *N. Journ.* ii. 231.

[2] *Ann. Chim. Phys.* lxxii. 113.

[3] *Ann. Chim. Phys.* xxix. 301.

[4] *Pogg. Ann.* xlii. 191.

[5] *Ann. Chem. Pharm.* xxxix. 350.

[6] *Ann. Chim. Phys.* [3]. iii. 221.

[7] Stenhouse, *Mem. Chem. Soc.* iii. 12.

picrate separates out and can be decomposed with hydrochloric acid.[1]

Picric acid is difficultly soluble in cold, easily in hot water, and crystallizes from aqueous solution in pale yellow, shining scales, whilst it crystallizes from an ethereal solution in rhombic prisms melting at 122·5°. When carefully heated it sublimes, but on strongly heating it decomposes with detonation, and on warming with calcium hypochlorite and water it yields chloropicrin, $CCl_3(NO_2)$, and chloranil, $C_6Cl_4O_2$. It has an intensely bitter taste, an acid reaction, and colours animal fibre, the skin, etc. pure yellow. As its tinctorial power is very great it is largely used as a dyeing material for wool, silk, leather, etc., either alone, or in combination with red and blue for dyeing oranges, greys, etc. It does not by itself adhere to vegetable fibre, and it is therefore employed to distinguish cotton from wool and silk, and to detect the presence of cotton in mixed fabrics, by steeping these for some time in a hot solution of the acid, washing with water and then examining under the microscope.

Both its intensely bitter taste and its power of dyeing wool yellow, serve to detect picric acid, but the best test is to add ammoniacal copper sulphate to the solution under examination; this gives a greenish precipitate, which can be seen even when only 1 part of picric acid is contained in 5,000 of water (C. Lea). By warming a solution of picric acid with ammonia and potassium cyanide, a deep red colour is produced, isopurpuric acid being formed (v. p. 126). Picric acid unites with other aromatic hydrocarbons, as it does with benzene, to form compounds, many of which are distinguished by their crystalline form or colour. This property indeed is frequently employed as a test for, and as a means of separating, some of these hydrocarbons. All such compounds are decomposed by ammonia, and some of them by alcohol, whilst others again may be recrystallized without decomposition. Of these latter one of the most characteristic is the naphthalene compound, $C_{10}H_2 + C_6H_3(NO_2)_3O$, crystallizing in golden needles, often united in a stellate mass, and melting at 149°. This peculiar compound may be employed to distinguish picric acid from similar nitro-compounds.

Picric acid is poisonous, rabbits and dogs being killed by doses of from 0·06 gram to 0·6 gram. It is said that it is sometimes added to beer to give it a bitter taste, 0·012 gram sufficing to give to a litre of beer an insupportable bitterness. In order to detect the

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[1] Carey Lea, *Sill. Amer. Journ.* [2], xxxii. 180.

picric acid, the beer is warmed and a skein of white woollen yarn steeped in it; if this becomes coloured yellow it is treated with ammonia, washed with water, the solution concentrated on the water-bath and some potassium cyanide added, when, if picric acid be present, the red colour of isopurpuric acid will be seen. Picric acid can also be detected by shaking some cubic centimetres of beer with half its volume of amyl alcohol, which takes up the picric acid; after evaporation of the alcohol the residue is tested as above.[1]

Wöhler in 1828 made the remarkable discovery that on boiling picric acid with water and baryta, hydrocyanic acid is formed.[2] This observation has been almost entirely forgotten, probably because it seemed to be highly unlikely, considering the very stable character which the benzene derivatives enjoy in other respects, and it was not until Hübner and Post lately carefully repeated and confirmed it that Wöhler's observation obtained the recognition of chemists. They also found that even dinitrobenzene yields prussic acid on boiling with caustic potash, and that it is also obtained by fusing nitrobenzene for a short time with caustic potash.[3]

PICRATES.

980 Picric acid forms salts having a yellow colour, which, for the most part, crystallize well and are explosive.

Potassium Picrate, $C_6H_2(NO_2)_3OK$, crystallizes in long, yellow, four-sided, lustrous needles, which, obtained from dilute solutions, appear sometimes red and sometimes green (Liebig). It dissolves in 260 parts of water at 15°, and in 4 parts at the boiling point. It is not soluble in alcohol. On account of its sparing solubility it was formerly employed as a reagent for potassium salts. On heating, it becomes of a red colour and then explodes like gunpowder; on being struck with a hammer it detonates powerfully. It is sometimes used mixed with saltpetre for blasting purposes.

Sodium Picrate, $C_6H_2(NO_2)_3ONa$, forms yellow needles, which dissolve at the ordinary temperature in about twelve parts of water, but as already stated the addition of soda precipitates the greater portion of it.

Ammonium Picrate, $C_6H_2(NO_2)_3ONH_4$, is sparingly soluble in water and still less so in alcohol, and crystallizes in rhombic

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[1] Vitali, *Ber. Deutsch. Chem. Ges.* x. 83.

[2] *Pogg. Ann.* xiii. 488.

[3] *Ber. Deutsch. Chem. Ges.* v. 408.

scales. It is employed mixed with the nitrates of barium, strontium, &c., for bengal fire. Brugère's picrate-powder consists of 54 parts of this salt to 46 parts of saltpetre; 2·6 grains of this is said to equal 5·5 grains of gunpowder. According to Abel this mixture is valuable for the blasting charge in shells.

Silver Picrate, $C_6H_2(NO_2)_3OAg + H_2O$, crystallizes from hot water in yellow shining needles, which dissolve at 15° in 113 parts of water.[1]

Lead Picrate, $[C_6H_2(NO_2)_3O]_2Pb + H_2O$, crystallizes in brown needles which dissolve at 15° in 113 parts of water. It is employed mixed with saltpetre as a blasting agent in the place of potassium picrate.

Methyl picrate or *trinitranisol*, $C_6H_2(NO_2)_3OCH_3$, was obtained by Cahours by the action of concentrated nitric acid on anisol; it is also obtained by the action of methyl iodide on silver picrate, and crystallizes in yellow monoclinic tables, melting at 64°.

Ethyl picrate, $C_6H_2(NO_2)_3OC_2H_5$, is formed in a similar way to the methyl ether,[2] and also by adding caustic potash to a solution of chlorotrinitrobenzene (picryl chloride) in absolute alcohol.[3] It crystallizes in long, almost colourless needles which melt at 78·5°; by heating it with alcoholic ammonia it is converted, like the methyl ether, into trinitraniline.[4]

Phenyl picrate, $C_6H_2(NO_2)_3OC_6H_5$, is obtained in a similar way to the preceding compound, using potassium phenate, and crystallizes in colourless needles (Willgerodt).

Trinitrophenyl acetate, $C_6H_2(NO_2)_3OC_2H_3O$, is formed by boiling picric acid with acetic anhydride, and separates from ether in dark yellow crystals, melting at 75°-76°.[5]

Picryl chloride or *Chlorotrinitrobenzene*, $C_6H_2(NO_2)_3Cl$, was first prepared by Pisani by the action of phosphorus pentachloride on picric acid and called "*Chlorure de picryle*," because he found that, like other acid chlorides, it is converted by water into hydrochloric acid and picric acid.[6]

According to Clemm, the latter observation is not accurate; Pisani's product contained, without doubt, some free picric acid,

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[1] Post and Mehrtens, *Ber. Deutsch. Chem. Ges.* viii. 1549.
[2] H. Müller and Stenhouse, *Ann. Chem. Pharm.* cxii. 80.
[3] Willgerodt, *Ber. Deutsch. Chem. Ges.* xii. 1277.
[4] Salkowski, *Ann. Chem. Pharm.* clxxiv. 259.
[5] Tomassi and David, *ibid.* clxix. 167.
[6] *Compt. Rend.* xxxix. 852; *Ann. Chem. Pharm.* xcii. 326.

which naturally enters into solution when water is added, while the pure compound is not attacked even by boiling water.[1]

Chlorotrinitrobenzene crystallizes from alcohol in almost colourless needles, and from ether in amber-coloured monoclinic tables, melting at 83°.[2]

By boiling it with soda solution it gives picric acid, and by heating it with an aqueous solution of ammonia it is converted into trinitraniline or picramide, $C_6H_2(NO_2)_3NH_2$.

Picryl chloride, like picric acid, forms compounds with aromatic hydrocarbons, which crystallize well.[3] The benzene compound $C_6H_2(NO_2)_3Cl + C_6H_6$, crystallizes in large, pale yellow prisms, which very quickly lose benzene in the air.[4]

981 *Isopurpuric acid* or *Picrocyamic acid*, $C_8H_5N_5O_6$, is as little known in the free state as its isomeride purpuric acid (Vol. III. Part II. pp. 307, 313), but many of its salts, which are very similar to the purpurates, have been prepared.

Potassium isopurpurate, $C_8H_4KN_5O_6$, is obtained when picric acid is warmed with water and potassium cyanide:[5]

$$C_6H_3N_3O_7 + 3KCN + 2H_2O = C_8H_4KN_5O_6 + K_2CO_3 + NH_3.$$

It crystallizes in brownish-red scales, having a greenish metallic lustre; is slightly soluble in cold water, more readily in hot, forming a fine red solution; on heating, or in contact with concentrated sulphuric acid, it explodes. On adding an acid to the aqueous solution it is coloured brownish-yellow, evolving a pungent odour, and then deposits a brown flocculent precipitate. On evaporating the solution, a brownish-yellow amorphous mass remains behind.

Ammonium Isopurpurate, $C_8H_4(NH_4)N_5O_6$, is obtained by the addition of sal-ammoniac to a concentrated solution of the potassium salt. It forms small brownish-red crystals, with a green metallic lustre, which are analogous in optical properties and crystalline form to murexide (ammonium purpurate). It is employed as a dye for wool and silk, and called in commerce *Grénat soluble.*

982 *β-Trinitrophenol*, $C_6H_2(NO_2)_3OH(3:4:6)$, is obtained by nitrating γ- and δ-dinitrophenol; it crystallizes from hot water in white, satin-like needles or scales, melting at 96°. The

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[1] *Journ. Prakt. Chem.* [2], i. 145.

[2] Bodewig, *Jahresb.* 1879, 394.

[3] Liebermann and Palm, *Ber. Deutsch. Chem. Ges.* viii. 377.

[4] Mertens, *ibid.* xi. 844.

[5] Baeyer, *Jahresb.* 1859, 458; Hlasiwetz, *Ann. Chem. Pharm.* cx. 289; Kopp, *Ber. Deutsch. Chem. Ges.* v. 644.

potassium salt forms light red, brilliantly-shining crystals, which are soluble with difficulty in water, forming a light-yellow solution.

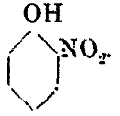
γ-Trinitrophenol, $C_6H_2(NO_2)_3OH(2 : 3 : 6)$, is obtained from γ- and ε-dinitrophenol, and forms white needles, melting at 117°-118°. The potassium salt, easily soluble in water, forms brilliant red needles; its aqueous solution colours wool and silk a fine orange shade.

Both trinitrophenols taste bitter and detonate on heating; their salts are, like the picrates, very explosive.[1] By the continued action of nitric acid they are converted into styphnic acid or trinitroresorcinol, $C_6H(NO_2)_3(OH)_2$. By nitrating γ-dinitrobenzene, besides trinitroresorcinol and the two trinitrophenols, a tetranitrodihydroxybenzene, $C_6(NO_2)_4(OH)_2$, probably tetranitroresorcinol, is formed.

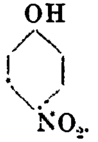
The production of styphnic acid by the nitration of dinitrophenol had already been observed by Bantlin, and the compound described under the name of isopicric acid.

The following graphic formulæ show the connection between the different nitro-substitution products of phenol:

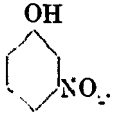
Orthonitrophenol.



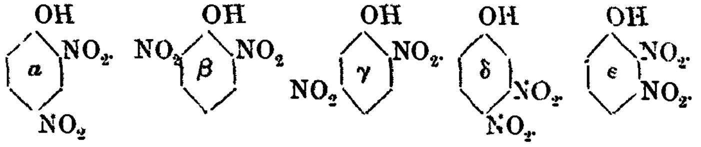
Paranitrophenol.



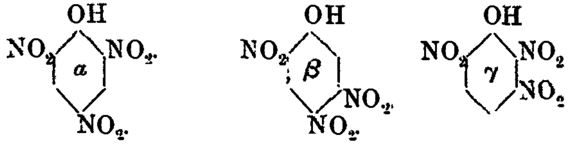
Metanitrophenol.



Dinitrophenols.



Trinitrophenols.



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[1] Henriques, *Ann. Chem. Pharm.* ccxv. 321.

PHENOLMONOSULPHONIC ACIDS, $C_6H_4(OH)SO_3H$.

983 By dissolving phenol in sulphuric acid Laurent obtained his "Acide sulphophénique."[1] Kekulé then found that a mixture of ortho- and parasulphonic acids[2] is thus formed.

Orthophenolsulphonic acid is principally formed in the cold; it is not known in the free state, because by evaporating its solution on the water-bath it is partly, and by strong heating, completely, converted into the para-compound.[3] In order to prepare the potassium salt, equal volumes of phenol and sulphuric acid are mixed, diluted with water and, after some days, the excess of sulphuric acid removed by lead oxide, and the filtrate neutralized with potassium carbonate. On concentrating the solution the para-salt separates out in anhydrous plates, and then the ortho-salt crystallizes in rhombic prisms, which contain two molecules of water of crystallization and effloresce in the air; by this means the para-salt is easily separated.[4]

Metaphenolsulphonic acid is formed by heating the potassium salts of the two phenoldisulphonic acids with some water and two or three times their quantity of caustic potash to 178° to 180°, till a uniform thick mass is produced.[5] The acid, which crystallizes in fine needles containing two molecules of water, produces a violet colour with ferric chloride, and on heating with caustic potash to 250° is converted into resorcinol.

Paraphenolsulphonic acid.—The preparation of this body has already been described. It is also obtained by the action of chlorosulphonic acid on phenol,[6] as well as by warming paradiazobenzenesulphonic acid with water.[7] In the free state it is a syrup. By oxidizing its sodium salt with manganese dioxide and sulphuric acid quinone is obtained.[8]

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[1] *Ann. Chim. Phys.* [3], 293.

[2] *Zeitschr. Chem.* 1867, 199.

[3] Kekulé, *Ber. Deutsch. Chem. Ges.* ii. 330.

[4] Post, *Liebig's Ann.* ccl. 64.

[5] Barth and Senhofer, *Ber. Deutsch. Chem. Ges.* ix. 969.

[6] Engelhardt and Latschinow, *Zeitschr. Chem.* 1869, 298.

[7] Schmitt, *Ann. Chem. Pharm.* cxx. 148.

[8] Schrader, *Ber. Deutsch. Chem. Ges.* viii. 760.

PHENOLDISULPHONIC ACIDS, $C_6H_3(OH)(SO_3H)_2$.

984 *a-Phenoldisulphonic acid* is formed by the action of concentrated sulphuric acid on diazobenzene sulphate.[1]

In order to prepare it, one part of phenol is heated with four parts of a mixture of ordinary and fuming sulphuric acids on the water-bath, until sulphur dioxide is evolved; it is then diluted with water and saturated with baryta.[2] From the barium salt, purified by recrystallization, the free acid is easily prepared; it crystallizes in deliquescent warty needles and is coloured a ruby red by ferric chloride.[3]

β-Phenoldisulphonic acid is obtained by heating phenoltrisulphonic acid with caustic potash and water. It forms a syrup and decomposes on heating.

Phenoltrisulphonic acid, $C_6H_2(OH)(SO_3H)_3$, is formed when two parts of phenol are heated with ten parts of sulphuric acid and five parts of phosphorus pentoxide to 180°.[4] It crystallizes *in vacuô* in needles containing water or in short prisms, which give an intense blood-red colour with ferric choride.

Hydroxysulphobenzide or *Hydroxyphenylsulphone*, $(C_6H_4OH)_2SO_2$, is a by-product of the action of sulphuric acid on phenol.[5] In order to prepare it, fuming sulphuric acid is heated with double its weight of phenol for from three to five hours at 180°-190° and the still warm mass gradually poured into a little water. It is almost insoluble in cold water, crystallizes from boiling water in long prismatic needles, and from glacial acetic acid in rhombic prisms melting at 239°. On heating with fuming sulphuric acid it is converted into phenoltrisulphonic acid.[6] Like phenol, it forms salts, which have been examined by Glutz.

Substituted Phenolsulphonic Acids.—The phenolsulphonic acids being phenols and powerful acids at the same time, form various series of salts. By the action of chlorine, bromine and nitric acid, substitution products may be obtained, which may also be prepared from the substituted phenols by the action of sulphuric acid. As in the case of phenol, so it is found that in these

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[1] Griess, *Ann. Chem. Pharm.* cxxxvii. 69.

[2] Kekulé, *Lehrb.* iii. 263.

[3] Senhofer, *Jahresb.* 1879, 749.

[4] Senhofer, *Ann. Chem. Pharm.* clxx. 110.

[5] Glutz, *ibid.* cxlvii. 52.

[6] Annaheim, *ibid.* clxxii. 36; *Ber. Deutsch. Chem. Ges.* ix. 1148.

bodies the larger the number of negative elements or hydroxyls in the compound, the more easily is the hydrogen of the phenol hydroxyl replaceable by metals; the stability of the compound is, however, correspondingly decreased.

SULPHUR COMPOUNDS OF PHENOL.

985 *Phenyl hydrosulphide*, or *Thiophenol*, $C_6H_5.SH$.—Vogt first obtained this compound, which is also called phenyl mercaptan, by the action of zinc and dilute sulphuric acid on benzenesulphonyl chloride, and named it benzyl mercaptan.[1] In order to obtain a good yield, the chloride is first reduced to benzenesulphinic acid, and the crude zinc salt so obtained put into a well-cooled mixture of zinc and hydrochloric acid. It is thus obtained together with phenyl disulphide. To the liquid, which now only contains a little free hydrochloric acid, zinc-dust is added to convert the disulphide into zinc thiophenate:

$$(C_6H_5)_2S_2 + Zn = (C_6H_5S)Zn.$$

It is then treated with hydrochloric acid and the thiophenol distilled off.[2] Stenhouse obtained it, together with phenyl sulphide and diphenylene sulphide, $C_{12}H_8S$, by the dry distillation of sodium benzenesulphonate in an iron retort, but when he used one of copper he only obtained a trace of thiophenol.[3] It is also formed by the action of phosphorus pentasulphide on phenol.[4] The reaction, according to Geuther, is as follows:

$$8C_6H_5.OH + P_2S_5 = 2C_6H_5.SH + 2PO_4(C_6H_5)_3 + 3H_2S.$$

At the same time, small quantities of phenyl sulphide and phenyl disulphide, which are decomposition products of thiophenol, and also some benzene, are produced by the action of the intermixed phosphorus trisulphide; when phenol is heated with the latter, the following reaction takes place:

$$8C_6H_5OH + P_2S_3 = 2C_6H_6 + 2PO_4(C_6H_5)_3 + 3H_2S.$$

A little thiophenol and phenyl sulphide are formed at the same time.[5] Thiophenol is also formed, together with the

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[1] *Ann. Chem. Pharm.* cxix. 142.
[2] Otto, *Ber. Deutsch. Chem. Ges.* x. 939.
[3] *Roy. Soc. Pro.* xvii. 62.
[4] Kekulé and Szuch, *Zeitschr. Chem.* 1867, 193.
[5] *Liebig's Ann.* ccxxi. 55.

sulphide, when benzene is warmed with sulphur and aluminium chloride.[1]

Thiophenol is a colourless, strongly refractive liquid, boiling at 172·5° and having at 24° a specific gravity 1·078. In the pure state it has an aromatic and somewhat aliaceous odour; it produces on the skin a burning pain. Its vapour attacks the eyes and causes temporary dizziness. It is readily converted by oxidation into phenyl disulphide; even the oxygen of the air effects this conversion in presence of ammonia.

As with other mercaptans, the hydrogen combined with the sulphur is easily replaceable by metals. It acts quickly on mercuric oxide, with formation of mercury thiophenate, $(C_6H_5S)_2Hg$, which crystallizes from boiling alcohol in white, silky needles.

Lead thiophenate $(C_6H_5S)_2Pb$, is obtained by the addition of thiophenol to an alcoholic solution of lead acetate, as a yellow, crystalline precipitate, which decomposes on dry distillation, forming lead sulphide and phenyl sulphide.

Ethyl thiophenate, $C_6H_5.SC_2H_5$, is formed when sodium thiophenate is heated with ethyl iodide to 120°; it is an unpleasantly smelling liquid, boiling at 204°.[2]

Phenyl orthothioformate, $CH(SC_6H_5)_3$, is prepared by heating an aqueous solution of sodium thiophenate with chloroform. It crystallizes from a mixture of alcohol and a small quantity of benzene in short, thick prisms, melting at 39·5°. Like the corresponding oxy-compound, it is not decomposed at 120° by caustic soda, but fuming hydrochloric acid decomposes it at 120°, under pressure, into formic acid and thiophenol.[3]

Phenyl thiacetate, $C_2H_3O.SC_6H_5$, is formed by the action of acetyl chloride on thiophenol; it is an unpleasantly smelling oily liquid, boiling at 228°-230° and dissolving in alcohol and ether; phenyl disulphide separates out from the solution on standing exposed to the air. When the ethereal salt is boiled with concentrated caustic potash it is decomposed into thiophenol and acetic acid.[4]

986 *Phenyl sulphide*, $(C_6H_5)_2S$, was first obtained by Stenhouse by the dry distillation of sodium benzenesulphonate.[5] Other methods of preparation have already been described under

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[1] Friedel and Crafts, *Bull. Soc. Chim.* xxxi. 464.
[2] Beckmann, *Journ. Prakt. Chem.* [2], xvii. 457.
[3] Gabriel, *Ber. Deutsch. Chem. Ges.* x. 185.
[4] *Ann. Chem. Pharm.* clxxvi. 177.
[5] *Ibid.* cxl. 287.

thiophenol. To prepare it, sodium benzenesulphonate is treated with phosphorus pentasulphide, the crude product rectified over powdered copper and then purified by fractional distillation.[1]

Phenyl sulphide is a liquid possessing an aliaceous odour, boiling at 272·5° and having a sp. gr. 1·119. Nitric acid oxidizes it to sulphobenzide, $(C_6H_5)_2.SO_2$.

Phenyl disulphide, $(C_6H_5)_2S_2$, is obtained, as already stated, by the oxidation of thiophenol; it is best to employ nitric acid of sp. gr. 1·11 to 1·12.[2] It is also obtained by the action of iodine on sodium thiophenate:[3]

$$\begin{array}{l} C_6H_5.SNa \\ \\ C_6H_5.SNa \end{array} + I_2 = \begin{array}{c} C_6H_5.S \\ | \\ C_6H_5.S \end{array} + 2NaI.$$

It is further formed when benzenesulphinic acid is heated with thiophenol to 110°.[4]

$$C_6H_5.SO_2H + 3C_6H_5.SH = 2(C_6H_5)_2S_2 + 2H_2O.$$

This reaction explains the fact that, by the action of nascent hydrogen on hot benzenesulphinic acid, the disulphide is formed, but that when the solution is kept cool, thiophenol is formed. Phenyl disulphide crystallizes from alcohol in brilliant needles, melting at 60°-61°. It boils at 310°[5] and decomposes on continued boiling into sulphur and phenyl sulphide. Reducing agents quickly convert it into thiophenol, and concentrated nitric acid oxidizes it to benzenesulphonic acid.

On heating it with alcoholic potash it forms thiophenol and benzenesulphinic acid. Its solution in concentrated sulphuric acid is coloured cherry-red and then blue on warming. Thiophenol gives the same reaction,[6] as it is oxidized by the acid to phenyl disulphide (Stenhouse).

Thiopicric acid, $C_6H_2(NO_2)_3SH$.—The potassium salt of this body separates in reddish-brown needles when a hot alcoholic solution of picryl chloride is gradually added to an alcoholic solution of potassium sulphide, which must be well cooled, and the whole allowed to stand; it detonates violently at 140° and on percussion. The acid thus obtained, or *a-trinitrothiophenol*,

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[1] Spring and Krafft, *Ber. Deutsch. Chem. Ges.* vii. 384.
[2] Otto, *Ann. Chem. Pharm.* clxiii. 213.
[3] Hübner and Alsberg, *ibid.* clvi. 330.
[4] Schiller and Otto, *Ber. Deutsch. Chem. Ges.* ix. 1589.
[5] Grabe, *Ann. Chem. Pharm.* clxxiv. 189.
[6] Baumann and Preusse, *Zeitschr. Phys. Chem.* v. 321.

is easily soluble in water, alcohol, and ether, tastes bitter, and crystallizes in yellowish needles, melting at 114° and exploding at 115°.

Picryl sulphide, $[C_6H_2(NO_2)_3]_2S$, is formed by mixing 10 cc. of an alcoholic solution of 10 grms. potassium sulphide with 4·4 grms. of picryl chloride dissolved in alcohol. It crystallizes from glacial acetic acid in golden-coloured leaves or whitish-yellow prisms, melting at 266°.[1]

DIHYDROXYBENZENES, $C_6H_4(OH)_2$, AND RELATED COMPOUNDS.

ORTHODIHYDROXYBENZENE, PYROCATECHIN OR CATECHOL.

987 Reinsch first obtained this body by the dry distillation of catechin,[2] and it was further examined by Zwenger, who named it "Brenzcatechin."[3] In his investigations on morintannic acid contained in fustic, R. Wagner observed that it is converted on heating into pyromorintannic acid,[4] which, he afterwards found, was identical with pyrocatechin, which he had prepared by heating catechu, and named, according to Erdmann's proposal, oxyphenic acid.[5] He obtained it also by the dry distillation of gum-ammoniac, from the aqueous extract of the bilberry plant, and generally from the extracts of all plants which contain tannic acid.[6] It is also obtained when filter paper, starch, or sugar is heated to 200°—280°,[7] as well as by the dry distillation of wood; it therefore occurs in crude pyroligneous acid.[8]

Catechol is also found in the autumnal leaves of the Virginia creeper (*Ampelopsis hederacea*)[9] and in kino, the boiled juice of different species of Pterocarpus, Butea and Eucalyptus.[10]

It is likewise obtained when ortho-iodophenol[11] or orthophenolsulphonic acid[12] is fused with caustic potash. In order

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[1] Willgerodt, *Ber. Deutsch. Chem. Ges.* xvii.; *ref.* 353.
[2] *Rep. Pharm.* lxviii. 54.
[3] *Ann. Chem. Pharm.* xxxvii. 327; and also Wackenroder, *ibid.* 309.
[4] *Journ. Prakt. Chem.* lii. 450.
[5] *Ibid.* lv. 65.
[6] Uloth, *Ann. Chem. Pharm.* cxi. 215.
[7] Hoppe-Seyler, *Ber. Deutsch. Chem. Ges.* iv. 15.
[8] Pettenkofer, *Jahresb.* 1854, 651; Buchner, *Ann. Chem. Pharm.* xcvi. 188.
[9] Gorup-Besanez, *Ber. Deutsch. Chem. Ges.* iv. 906.
[10] Flückiger, *ibid.* v. 1.
[11] Körner, *Zeitschr. Chem.* 1868, 322.
[12] Kekulé, *ibid.* 1867, 613.

to prepare it according to the latter method, the proportion of 1 molecule of the acid to 24 molecules of caustic potash is taken and the melt heated for some time to 320°—360°, when the yield amounts to 20 per cent. of the theoretical. By using less potash or by not heating so strongly, the yield is rendered smaller, as is also the case when the mass is heated to 400°.[1]

It is best obtained from the fraction of beechwood-tar creosote, boiling between 200°—205°, the chief portion of which consists of the monomethyl ether of catechol, by heating it to 195°—200° and passing in hydriodic acid as long as methyl iodide distils over. The catechol is separated by fractional distillation from the product.[2]

Catechol is readily soluble in water, and crystallizes therefrom in thin prisms, and from benzene in broad plates. It is very soluble in alcohol and ether, melts at 104°, and boils at 240°—245°. Its alkaline solution quickly turns brown in the air; it readily reduces solutions of the noble metals, and precipitates Fehling's solution on warming. On passing nitrogen trioxide through its ethereal solution it forms dioxytartaric acid (p. 58). Ferric chloride produces in an aqueous solution of catechol an emerald green colour, which on addition of sodium carbonate, or better, bicarbonate, gives a beautiful violet red.

The metallic compounds of catechol are very unstable, with the exception of the lead salt, $C_6H_4O_2Pb$., which forms a white precipitate readily soluble in acetic acid.

988 *Catechol monomethyl ether* or *Guaiacol*, $C_6H_4\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right.$, was first found in the distillation products of guaiacum,[3] and was afterwards noticed as an ingredient of beechwood-tar creosote. This is a mixture of phenols with the monomethyl ethers of catechol and its homologues, and will be further described under creosol, $C_6H_3(CH_3)OH(OCH_3)$.

In order to prepare guaiacol, the crude compound, obtained from creosote by fractional distillation, is repeatedly shaken with moderately strong ammonia, washed and rectified. The oil is then dissolved in an equal volume of ether, and a small excess of concentrated alcoholic potash added to it. The potassium salt separates out, and is then recrystallized from alcohol and decomposed by dilute sulphuric acid.[4]

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[1] Degener, *Journ. Prakt. Chem.* [2], xx. 304.

[2] Baeyer, *Ber. Deutsch. Chem. Ges.* viii. 153.

[3] Unverdorben, *Pogg. Ann.* viii. 402; *Ann. Chem. Phys.* [3], xii. 228; Sobrero, *Ann. Chem. Pharm.* xlviii. 19; Volkel, *ibid.* lxxxix. 345.

[4] Hlasiwetz, *ibid* cvi. 865.

It is also obtained when equal molecules of catechol, caustic potash and potassium methyl sulphate are heated together,[1] or when vanillic acid, $C_6H_3(OCH_3)(OH)CO_2H$, is distilled with lime.[2]

Guaiacol is a strongly refractive liquid, having an aromatic smell, reminding one of Peru balsam. It boils at 200°, has at 13° a sp. gr. of 1·117, is slightly soluble in water, but readily in alcohol; its solution gives with ferric chloride an emerald green colouration.

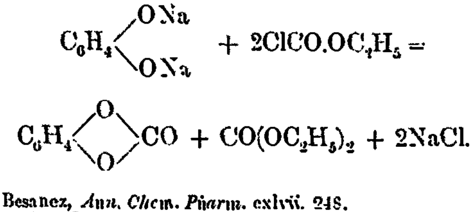
The metallic compounds of guaiacol are not very stable; the formation of potassium guaicate, $C_7H_7O_2K + 2H_2O$, is described above. By adding a little potash or potassium to guaiacol heated to 90°, the compound $C_7H_8O_2 + C_7H_7O_2K + H_2O$ is formed, which crystallizes from alcohol in shining prisms and dissolves in water with decomposition (Gorup-Besanez).

Catechol dimethyl ether, or *Veratrol*, $C_6H_4(OCH_3)_2$, was first obtained by distilling veratric acid, $C_6H_3(OCH_3)_2CO_2H$, with caustic baryta,[3] and is also formed when potassium guaicate is heated with methyl iodide.[4] It is a liquid with an aromatic odour, boils at 205°—206°, and solidifies at + 15° to a crystalline mass.

Catechol sulphuric acids are not known in the free state. On warming a solution of catechol in caustic potash with potassium disulphate, the salts $C_6H_4(SO_4K)_2$ and $C_6H_4(OH)SO_4K$ are formed. On treating the mixture with absolute alcohol, the first salt remains behind as a crystalline powder, and on evaporating the solution the second separates out in shining plates.[5]

These salts, or one of them, form a normal constituent of the urine of the horse and man.[6]

Catechol carbonate, $C_6H_4CO_3$, is obtained by the action of ethyl chlorocarbonate on a mixture of caustic potash and catechol or on the sodium salt:



$$C_6H_4\begin{cases}ONa\\ONa\end{cases} + 2ClCO.OC_2H_5 =$$

$$C_6H_4\begin{cases}O\\O\end{cases}CO + CO(OC_2H_5)_2 + 2NaCl.$$

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[1] Gorup-Besanez, *Ann. Chem. Pharm.* cxlvii. 248.
[2] Tiemann, *Ber. Deutsch. Chem. Ges.* viii. 1123.
[3] Merck, *Ann. Chem. Pharm.* cviii. 60; Kölle, *ibid.* clix. 243.
[4] Marasse, *ibid.* clii. 74. [5] Baumann, *Ber. Deutsch. Chem. Ges.* xi. 1913.
[6] Baumann, *Zeitschr. Phys. Chem.* i. 244.

It crystallizes from alcohol or benzene in fine four-sided prisms, melting at 118°, and boils without decomposition between 225°—230°.[1] By the action of acetyl chloride on catechol, the diacetate, $C_6H_4(OC_2H_3O)_2$, is formed, which crystallizes in needles.[2]

On heating guaiacol with acetic anhydride, aceto-guaiacol, $C_6H_4(OCH_3)OC_2H_3O$, a limpid liquid, boiling at 235°—240°,[3] is formed.

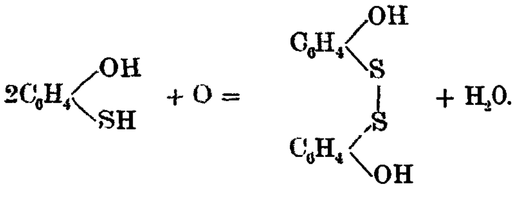
Tetrabromocatechol, $C_6Br_4(OH)_2$, is obtained by triturating together catechol and bromine,[4] as well as by heating protocatechuic acid, $C_6H_3(OH)_2CO_2H$, with bromine[5]; it crystallizes in long needles which melt at 187° and are insoluble in water. Its alcoholic solution is coloured dark blue by ferric chloride.

Nitrocatechol, $C_6H_3(NO)_2(OH)_2$, is obtained by the addition of sulphuric acid to an aqueous solution of catechol and potassium nitrate. It is readily soluble in water, and crystallizes from benzene in yellowish needles, melting at 157°. It dissolves in caustic potash, forming a splendid purple solution. This reaction is so delicate that nitrocatechol makes an excellent indicator for volumetric analysis.[6]

989 *Orthohydroxyphenyl hydrosulphide*, $C_6H_4\left\{\begin{matrix}OH\\SH\end{matrix}\right.$, is obtained when sodium phenate is heated with sulphur to 180°—200°.

$$2C_6H_5ONa + S = C_6H_4\left\{\begin{matrix}ONa\\SNa\end{matrix}\right. + C_6H_5OH.$$

This body can be indirectly separated from the product by oxidation, the effect of which is to form dihydroxyphenyl disulphide.



The latter is isolated by acidifying with sulphuric acid and distilling with steam. The distillate is neutralised with soda

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[1] Bender, *Ber. Deutsch. Chem. Ges.* xiii. 697; Wallach, *Ann. Chem. Pharm.* ccxxvi. 34.

[2] Nachbaur, *ibid.* cvii. 246.

[3] Tiemann and Koppe, *Ber. Deutsch. Chem. Ges.* xiv. 2020.

[4] Hlasiwetz, *Ann. Chem. Pharm.* cxlii. 250.

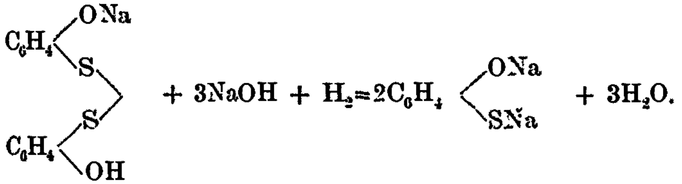
[5] Stenhouse, *Chem. News*, xxix. 95.

[6] Benedikt, *Ber. Deutsch. Chem. Ges.* xi. 362.

and concentrated to obtain the salt $(C_6H_4)_2S_2(OH)ONa$, which forms in white crystalline crusts, dissolving in water and producing an intensely yellow solution. On addition of sulphuric acid and extraction with ether, the free dihydroxyphenyl disulphide is obtained; it is a thick oil, possessing a faint smell, and decomposing at 200°. It forms two series of salts; of these the normal are decomposed by carbon dioxide.

The dimethyl ether, $S_2(C_6H_4OCH_3)_2$, is obtained when the sodium salt is heated with caustic soda, ethyl iodide, and methyl alcohol. It crystallizes from alcohol in odourless needles, melting at 119°. It is also formed by replacing the hydrogen of the hydroxyl in potassium orthophenolsulphonate, $C_6H_4(OH)SO_3K$, by methyl, converting the potassium anisolsulphonate so obtained, by means of phosphorus chloride, into the corresponding sulphonyl chloride, and treating this, in alcoholic solution, with zinc dust. On oxidation with chromic acid, the methyl ether is reconverted into anisolorthosulphonic acid, which, on fusion with caustic potash, yields catechol.

In order to prepare orthohydroxyphenylmercaptan, sodium amalgam is added to a solution of the above-mentioned sodium salt.



$$\begin{matrix} C_6H_4\left\langle\begin{matrix}ONa\\S\end{matrix}\right. \\ \bigg\rangle \\ C_6H_4\left\langle\begin{matrix}S\\OH\end{matrix}\right. \end{matrix} + 3NaOH + H_2 = 2C_6H_4\left\langle\begin{matrix}ONa\\SNa\end{matrix}\right. + 3H_2O.$$

By the decomposition of the product with dilute sulphuric acid, orthohydroxyphenyl hydrosulphide is obtained as a strongly refractive liquid, having a penetrating smell and, like phenol, corroding the skin. It solidifies at a low temperature to a crystalline mass, similar to phenol, which melts at 5°—6°. It is a tolerably strong acid, decomposing carbonates; its aqueous solution reddens litmus. On the addition of a little ferric chloride and carbonate of soda a very intense green colour is obtained, which, by adding caustic soda, is changed to a deep red. Oxidizing agents readily convert it again into dihydroxyphenyl disulphide, which is also formed by exposing an alkaline solution of the mercaptan to the air.[1]

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[1] Haitinger, *Monatsh. Chem.* iv. 135.

METADIHYDROXYBENZENE, RESORCIN, OR RESORCINOL, $C_6H_4(OH)_2$.

990 This body was first obtained by Barth and Hlasiwetz by fusing galbanum or gum-ammoniac with caustic potash, and since it is very similar to orcin (dihydroxytoluene), its higher homologue, and is obtained from resins, it was named resorcin.[1] It is also obtained in a similar way from *Asafœtida*,[2] *Sagapenum*, and *Acaroïd*.[3] It is also abundantly produced when impure brazilin, which separates as a crust from Brazil wood extract on standing, is subjected to dry distillation.[4]

Resorcinol is further obtained by fusing meta-iodophenol,[5] phenolmetasulphonic acid,[6] or benzenemetadisulphonic acid with caustic potash. But it is also formed in this way from benzeneparadisulphonic acid[7] and parabromophenol, while metabromophenol and orthobromophenol give catechol in addition.[8] During fusion with potash, intermolecular changes frequently take place. On fusing phenol for a long time with an excess of caustic soda, hydrogen is evolved, and resorcinol, catechol, phloroglucinol, $C_6H_3(OH)_3$, and diresorcinol, $C_{12}H_6(OH)_4$,[9] are formed.

That resorcinol belongs to the meta-series is shown by the fact that it is easily obtained by the diazo-reaction from meta-amidophenol.[10]

Resorcinol is employed in the manufacture of different colouring matters. To prepare it on the large scale, 90 kilos of fuming sulphuric acid, of sp. gr. 2·244, are put into a cast-iron apparatus furnished with an agitator, and 24 kilos of pure benzene gradually added, the mixture gently heated for some hours, and the temperature then raised to 275°, in order to convert the benzene completely into the disulphonic acid. After cooling, the mass is poured into 2,000 kilos of water, heated to boiling, neutralized with milk of lime, and the gypsum removed by the filter press. The calculated quantity of soda is then added to the solution, the calcium carbonate separated by the filter press, the solution evaporated to dryness, and 60 kilos of the product thus obtained fused with 150

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[1] *Ann. Chem. Pharm.* cxxx. 354.

[2] *Ibid.* cxxxviii. 63.

[3] *Ibid.* cxxxix. 78.

[4] Kopp, *Ber. Deutsch. Chem. Ges.* vi. 446.

[5] Körner, *Zeitschr. Chem.* 1868, 322.

[6] Barth and Senhofer, *Ber. Deutsch. Chem. Ges.* ix. 969.

[7] Barth and Senhofer, *ibid.* viii. 1483.

[8] Fittig and Mager, *ibid.* vii. 1175; viii. 365.

[9] Barth and Schreder, *ibid.* xii. 417.

[10] Bantlin, *ibid.* xi. 2101.

kilos of caustic soda in an iron vessel for eight to nine hours at 270°. The cooled melt is then dissolved in 500 kilos of boiling water and the solution boiled with hydrochloric acid as long as sulphur dioxide is given off. The cooled liquid is then systematically extracted with ether in a copper extraction-apparatus and the ether distilled off. The crude resorcinol thus obtained is heated up to 215°, in order to free it from water and adhering ether, the loss of which amounts on the whole to about 1 per cent. The residue, which contains 92 to 94 per cent. of resorcinol, forms the commercial product.[1] In order to prepare the pure compound, this crude product is distilled, when first water, then phenol, and, lastly, resorcinol comes over. This can be further purified by recrystallization from benzene, or by sublimation.

Resorcinol is very readily soluble in water, still more readily in alcohol and ether, but only with difficulty in cold benzene. It crystallizes in large rhombic prisms or tablets. It melts at 118°, boils at 276·5°, but readily sublimes at a lower temperature in lustrous silky needles. Its taste is intensely sweet, but causes subsequent irritation. In the warm state it reduces ammoniacal silver solution and Fehling's solution. It is distinguished from catechol by the fact that its solution produces a violet colour with ferric chloride, and is not precipitated by lead acetate.

In order to detect small quantities of resorcinol, it is heated for some minutes with phthalic anhydride almost to boiling, and the residue dissolved in dilute sulphuric acid. If resorcinol be present, the alkaline solution exhibits a fine green fluorescence, fluoresceïn, which will be subsequently described, being formed.

991 *Resorcinol ether*, $C_{12}H_{10}O_3$, is the name given to a body which is obtained by heating resorcinol with fuming hydrochloric acid to 180°, when it separates out like a resin.[2] It is also formed when resorcinol is heated with resorcinoldisulphonic acid[3] as well as by the action of fuming sulphuric acid on resorcinol.[4] By dissolving the latter in a large excess of the acid an orange-coloured solution is obtained, which gradually darkens, and turns greenish-blue, green, and finally a beautiful blue. On then heating it to 100° it is coloured purple-red, and on the addition of water, yellow (Kopp). The resorcinol ether obtained by

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[1] Binschedler and Busch, *Jahresb.* 1878, 1137, and 1184.
[2] Barth, *Ann. Chem. Pharm.* clxiv. 122; *Ber. Deutsch. Chem. Ges.* ix. 308.
[3] Hazura and Julius, *Monatsb. Chem.* v. 191.
[4] Kopp, *Ber. Deutsch. Chem. Ges.* vi. 447; Annaheim, *ibid.* x. 976.

means of hydrochloric acid contains the compound $C_{24}H_{18}O_5$. To separate these bodies, the crude product is dissolved in strong alcohol, and an alcoholic solution of lead acetate added, the lead compound of the ether being precipitated, filtered off, dissolved in glacial acetic acid and decomposed by hydrochloric acid; or it may be covered with alcohol and treated with sulphuretted hydrogen gas.[1] Resorcinol ether is a resinous mass, or a fiery, brownish-red powder, showing when pressed a greenish metallic lustre. It dissolves in alkalis forming a deep red solution, which, when dilute, exhibits a beautiful green fluorescence. On fusing it with caustic alkali, resorcinol, together with other bodies, is obtained.

Resorcinol monomethyl ether, $C_6H_4(OH)OCH_3$, is formed, together with the dimethyl ether, when resorcinol is heated with caustic potash and potassium methylsulphate,[2] or when resorcinol and sodium are dissolved in methyl alcohol and then boiled with methyl iodide.[3] The monomethyl ether is an oily liquid, soluble with difficulty in cold water, but readily soluble in hot water; its solution is coloured light violet by ferric chloride. It is readily soluble in dilute caustic soda, and boils at 243°—244°.

Resorcinol dimethyl ether, $C_6H_4(OCH_3)_2$, is a light mobile liquid, having an aromatic smell. It boils at 214°, is not soluble in caustic soda and is not coloured by ferric chloride.

Resorcinol diethyl carbonate, $C_6H_4(O.CO.C_2H_5)_2$, is obtained by the action of ethyl chloroformate on the sodium compound of resorcinol. It is a thick oily liquid boiling at 298°—302°.[4]

Diacetoresorcinol, $C_6H_4(OC_2H_3O)_2$, is obtained by the action of acetyl chloride on resorcinol and is a strongly refractive liquid, boiling with slight decomposition at 278°.[5]

Thioresorcinol, $C_6H_4(SH)_2$, is obtained by the action of tin and hydrochloric acid on benzenemetadisulphonic chloride, $C_6H_4(SO_2Cl)_2$,[6] and forms crystals, which have a penetrating odour. It melts at 27°, and boils at 243°. Its lead salt, $C_6H_4S_2Pb$, is a yellowish-red precipitate which on heating with cyanogen iodide and alcohol yields the thiocyanate, $C_6H_4(SCN)_2$, which crystallizes in shining needles and melts at 54°.[7]

Thioresorcinol is sometimes found in commercial resorcinol.

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[1] Barth and Weidel, *Ber. Deutsch. Chem. Ges.* x. 1464.

[2] Habermann, *ibid.* x. 867.

[3] Tiemann and Parrisino, *ibid.* xiii. 2362.

[4] Wallach, *Ann. Chem. Pharm.* ccxxvi. 84.

[5] Malin, *ibid.* cxxxviii. 78; Nencki and Sieber, *Journ. Prakt. Chem.* [2], xxiii. 149.

[6] Körner and Monselise, *Jahresb.* 1876, 450; Pazschke, *Journ. Prakt. Chem.* [2], ii. 418.

[7] Gabriel, *Ber. Deutsch. Chem. Ges.* x. 184.

CHLORINE SUBSTITUTION PRODUCTS OF RESORCINOL.

		Melting-Point.	Boiling-Point.
Monochlororesorcinol, $C_6H_3Cl(OH)_2$,	indistinct crystals	89°	256°
Dichlororesorcinol, $C_6H_2Cl_2(OH)_2$,	rhombic prisms	77°	249°
Trichlororesorcinol, $C_6HCl_3(OH)_2$,	fine needles	83°	—

992 These bodies are obtained by the action of sulphuryl chloride on resorcinol. Trichlororesorcinol is also obtained when chlorine is passed through an aqueous solution of resorcinol. The aqueous solutions of the first two are coloured a bluish-violet by ferric chloride.[1]

Pentachlororesorcinol, $C_6HCl_3(OCl)_2$, is obtained by the action of potassium chlorate and hydrochloric acid on resorcinol.[2] It crystallizes from carbon disulphide in flat prisms, melting at 92·5°. It may be heated to its boiling-point without decomposition, but a concentrated solution of acid potassium sulphite converts it into isotrichlororesorcinol, $C_6HCl_3(OH)_2$, which crystallizes in needles melting at 69°.[3]

Pentachlororesorcinol effloresces in the air, being converted into a modification which melts at 65°. This is obtained directly when pentachlororesorcinol is dissolved in hot water, and separates out on cooling in indistinct crystals.[4]

BROMINE SUBSTITUTION PRODUCTS OF RESORCINOL.

			Melting-Pt.
α-Dibromoresorcinol (5)	$C_6H_2Br_2(OH)_2$	needles	92°—93°
β-Dibromoresorcinol (6)	$C_6H_2Br_2(OH)_2$	long needles .	83°—85°

993 *Tribromoresorcinol*, $C_6HBr_3(OH)_2$, is obtained by the action of bromine water on resorcinol.[7] It crystallizes in small needles

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[1] Reinhard, *Journ. Prakt. Chem.* [2], xvii. 321.
[2] Stenhouse, *Roy. Soc. Pro.* xx. 72.
[3] Claassen, *Ber. Deutsch. Chem. Ges.* xi. 1441.
[4] Liebermann and Dittler, *Ann. Chem. Pharm.* clxix. 265.
[5] Baeyer, *ibid*, clxxxiii. 57 ; Hofmann, *Ber. Deutsch. Chem. Ges.* viii. 64.
[6] Zehenter, *Monatsb. Chem.* ii. 478.
[7] Hlasiwetz and Barth, *Ann. Chem. Pharm.* cxxx. 357.

which melt at 104°, are soluble with difficulty in cold water, and readily in alcohol.

Tetrabromoresorcinol, $C_6Br_4(OH)_2$, is obtained on warming pentabromoresorcinol with sulphuric acid;[1] it crystallizes from dilute alcohol in needles melting at 167°.

Pentabromoresorcinol, $C_6HBr_3(OBr)_2$, separates out when a concentrated aqueous solution of resorcinol[2] is poured into bromine; it crystallizes from carbon disulphide in tetragonal tables melting at 113·5°.

Hydriodic acid and other reducing agents convert it into tribromoresorcinol.[3] On heating to 160° it gradually decomposes into bromine and tribromoresoquinone, $C_6HBr_3O_2$, crystallizing from alcohol in small orange-coloured needles, which are decomposed on heating.[4]

Hexbromoresorcinol, $C_6Br_4(OBr)_2$, is obtained by dissolving tetrabromoresorcinol in caustic potash, and then adding hydrochloric acid and bromine water. It forms monoclinic crystals which melt at 136°, and by the action of tin and hydrochloric acid are again converted into tetrabromoresorcinol.[5]

IODINE SUBSTITUTION PRODUCTS OF RESORCINOL.

Mono-iodoresorcinol, $C_6H_2I(OH)_2$, was obtained by Stenhouse by gradually adding lead oxide to a solution of resorcinol and iodine in ether. It crystallizes in rhombohedral prisms melting at 67°.[6]

Tri-iodoresorcinol, $C_6HI_3(OH)_2$, is obtained when chloride of iodine is added to an aqueous solution of resorcinol,[7] or when this body is placed in a solution of potassium iodate and iodine in potassium iodide.[8] It crystallizes from carbon disulphide in needles melting at 154°.

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[1] Claassen, *Ber. Deutsch. Chem. Ges.* xi. 1440.
[2] Stenhouse, *Roy. Soc. Pro.* xx. 72.
[3] Benedikt, *Monatsb. Chem.* i. 351.
[4] Liebermann and Dittler, *Ann. Chem. Pharm.* clxix. 259.
[5] Benedikt, *Monatsb. Chem.* i. 366.
[6] Stenhouse, *Chem. News*, xxvi. 279.
[7] Michael and Norton, *Ber. Deutsch. Chem. Ges.* ix. 1752.
[8] Claassen, *ibid.* ii. 1442.

NITRO-SUBSTITUTION PRODUCTS OF RESORCINOL.

934 *Mononitroresorcinol*, $C_6H_3(NO_2)(OH)_2$, is obtained in two isomeric forms, together with other products, which will be described later on, when an ethereal solution of resorcinol is treated with nitric acid containing nitrous acid. They can readily be separated by distillation with steam. The volatile nitro-resorcinol, $(OH : NO_2 : OH = 1 : 2 : 3)$, crystallizes from dilute alcohol in orange-red prisms melting at 85°, and having an intense smell like that of orthonitrophenol.

The non-volatile nitroresorcinol, (1 : 4 : 3), forms lemon-coloured, hair-like needles melting at 115°. Its salts, which crystallize well, have a deep yellow to orange-red colour.[1]

Fuming sulphuric acid converts it into nitroresorcinol ether, $[C_6H_3(NO_2)OH]_2O$, which crystallizes in light rose-coloured needles, or in brown warty masses containing one molecule of water. It forms two barium salts, and is converted by concentrated nitric acid into trinitroresorcinol.[2]

Dinitroresorcinol, $C_6H_2(NO_2)_2(OH)_2$, is formed by passing nitrogen trioxide through an ethereal solution of dinitrosoresorcinol. It crystallizes from alcohol in small, light yellow plates which melt at 142°, and are converted by dilute nitric acid into trinitroresorcinol.[3]

Isodinitroresorcinol, $C_6H_2(NO_2)_2(OH)_2$, is obtained when diacetylresorcinol is converted by the action of concentrated nitric acid into the dinitro-compound, and this decomposed by hydrochloric acid.[4] It forms small, light-brown, shining plates, which melt at 212·5°, and are not attacked by boiling nitric acid (Benedikt and Hübl).

Trinitroresorcinol, or *Styphnic Acid*, $C_6H(NO_2)_3(OH)_2$.—On boiling logwood extract with nitric acid, Chevreul in 1808 obtained a crystalline body, which he considered to be a compound of an oil, or resinous matter with nitric acid; not only is its mode of preparation very nearly identical with that of Welter's Bitter (Picric Acid), but it also forms explosive salts like this

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[1] Flitz, *Ber. Deutsch. Chem. Ges.* viii. 631.

[2] Weselsky and Benedikt, *Monatsb. Chem.* i. 887; Hazura and Julius, *Monatsb. Chem.* v. 188.

[3] Benedikt and Hübl, *Monatsb. Chem.* ii. 323.

[4] Typke, *Ber. Deutsch. Chem. Ges.* xvi. 551.

body.[1] Erdmann then found, in 1846, that by the action of nitric acid on euxanthic acid, $C_{19}H_{16}O_{10}$, the magnesium salt of which occurs in commerce under the name Purrée or Indian yellow, an acid is obtained to which he gave the name of oxypicric acid, because it contained an atom of oxygen more than picric acid.[2] About this time Böttger and Will observed that when certain gum-resins or vegetable gums, as well as the extracts of different dye-woods, bodies which we now know yield resorcinol on fusion with potash, are boiled with nitric acid, an acid similar to picric acid is obtained, which they named styphnic acid, because it does not taste bitter, but astringent (στύφνος).[3] They perceived that this body is identical with Chevreul's substance, and supposed that this was also the case with oxypicric acid, a view which Erdmann confirmed.[4] Schreder showed that it is trinitroresorcinol,[5] and Stenhouse afterwards obtained it by the action of nitrosulphuric acid on resorcinol.[6] It is also formed by the continued action of fuming nitric acid on metanitrophenol [7]

To prepare styphnic acid, dissolve finely-powdered resorcinol, gradually and with continual stirring, in 5 to 6 parts of concentrated sulphuric acid warmed to about 40°; then cool down to 10°—12°, and add by degrees 2 to 2·5 times the theoretical quantity of nitric acid, adding at first concentrated acid mixed with 10 per cent. by weight of water, then concentrated acid without admixture of water, and finally fuming acid; during this operation the mixture must be continually agitated. It is now allowed to stand overnight, and is then brought into 1·5 to 2 volumes of cold water and passed through a vacuum filter to separate the crystals from the mother-liquor. On evaporation a further crop of crystals is obtained.[8]

Styphnic acid separates from its solution in dilute alcohol in large, sulphur-coloured, hexagonal crystals, which melt at 175·5°, and dissolve in 165 parts of water at 14°, more abundantly in hot water, and readily in alcohol and ether. From its aqueous solution, which has an acid reaction, it is precipitated by even a small quantity of a strong acid (Stenhouse).

The Styphnates.—Styphnic acid forms two series of yellow coloured salts, most of which are only slightly soluble, and, on

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[1] *Ann. Chem.* lxvi. 246 ; lxxiii. 43.
[2] *Journ. Prakt. Chem.* xxxvii. 409.
[3] *Ann. Chem. Pharm.* lviii. 273.
[4] *Journ. Prakt. Chem.* xxxviii. 355.
[5] *Ann. Chem. Pharm.* clviii. 244.
[6] *Chem. News*, xxii. 98.
[7] Bantlin, *Ber. Deutsch. Chem. Ges.* xi. 2101 ; Henriques, *Liebig's Ann.* 215, 321.
[8] Merz and Zetter, *Liebig's Ann.* xii. 2037.

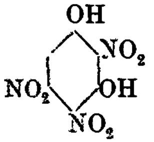
heating, explode more violently than the picrates (Böttger and Will).

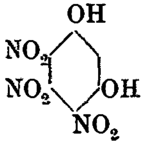
Dimethyl styphnate, $C_6H(NO_2)_3(OCH_3)_2$, was obtained by König by the action of nitrosulphuric acid on resorcinol dimethyl ether; it crystallizes in small plates, melting at 123°—124°.[1]

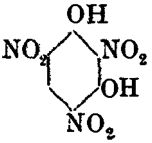
Diethyl styphnate, $C_6H(NO_2)_3(OC_2H_5)_2$, is obtained by the action of ethyl iodide on silver styphnate, and crystallizes in long plates, which melt at 120·5°, and are quickly coloured orange-brown in the light (Stenhouse).

By the action of alcoholic ammonia it is easily converted into trinitrometadiamidobenzene, $C_6H(NO_2)_3(NH_2)_2$, a yellow crystalline powder, which is only soluble with difficulty in the ordinary solvents, and on heating with dilute caustic soda is converted into sodium styphnate.

Styphnic acid can only have one of the following formulæ, because it is obtained from metanitrophenol.







In the first, as well as in the second formula, two nitroxyls are found in adjacent positions; and, according to Laubenheimer's rule, by the action of ammonia or alkalis one of these should be replaced by the amido-group or hydroxyl, which is not the case; therefore the third formula represents the constitution of styphnic acid.[2]

Resorcinol indophane, $C_9H_4N_4O_6$.—The potassium salt, $C_9H_2K_2N_4O_6 + H_2O$, separates as a dark-brown, metallic-looking, crystalline mass, when warm solutions of potassium cyanide and potassium styphnate are mixed. It explodes on heating, and yields, on decomposition with dilute sulphuric acid, free resorcinol indophane, which forms needles having a metallic lustre and dissolving in water forming a bluish-violet solution.[3]

Tetranitroresorcinol, $C_6(NO_2)_4(OH)_2$, is obtained, as already stated, together with trinitrophenol and styphnic acid, by the further nitration of γ-dinitrophenol. It is only slightly soluble in water, but readily in alcohol, and crystallizes in colourless or

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[1] *Ber. Deutsch. Chem. Ges.* xi. 1042.
[2] Nölting and Collin, *ibid.* xvii. 259.
[3] Schreder, *Ann. Chem. Pharm.* clxiii. 298.

yellowish needles, which melt at 166° and sublime easily. It is, however, still questionable whether this compound is a derivative of resorcinol.

PARADIHYDROXYBENZENE, HYDROQUINONE, OR QUINOL, $C_6H_4(OH)_2$.

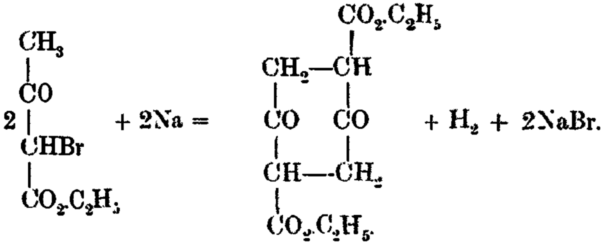
995 By the dry distillation of quinic acid, Caventou and Pelletier obtained a crystalline body, which they did not thoroughly examine, but named pyroquinic acid. Wöhler,[1] however, gave it the name of hydroquinone, because it is readily formed by the combination of hydrogen and quinone, $C_6H_4O_2$, which is an oxidation product of quinic acid and will be described later on. He found that this reduction can be performed with hydriodic acid and telluretted hydrogen, but that hydroquinone is best obtained when sulphur dioxide is passed through a warm saturated solution containing some undissolved quinone,

$$C_6H_4O_2 + 2H_2O + SO_2 = C_6H_6O_2 + SO_4H_2.$$

Besides these, almost all other reducing agents convert quinone into quinol.

Quinol is also formed by fusing para-iodophenol with caustic potash,[2] and by boiling paradiazobenzene sulphate with dilute sulphuric acid.[3]

The formation of quinol from succinic acid and acetoacetic acid is very interesting. By the action of sodium on the ethylether of the former, succino-succinic ether (Vol. III. Part II. p. 189) is obtained, which is also formed when bromaceto-acetic ether is treated with sodium.[4]



$$2\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHBr \\ | \\ CO_2.C_2H_5 \end{array} + 2Na = \begin{array}{ll} & CO_2.C_2H_5 \\ & | \\ CH_2— & CH \\ | & | \\ CO & CO \\ | & | \\ CH— & CH_2 \\ | & \\ CO_2.C_2H_5. & \end{array} + H_2 + 2NaBr.$$

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[1] *Ann. Chem. Pharm.* li. 145; lxv. 349.

[2] Körner, *Zeitsch. Chem.* 1866, 622 and 731.

[3] Weselsky and Schuler, *Ber. Deutsch. Chem. Ges.* ix. 1159.

[4] Duisberg, *ibid.* xvi. 133.

By the action of bromine this is converted into the diethylether of quinoldicarboxylic acid, $C_6H_4O_2(CO_2H)_2$. The free acid crystallizes from hot water in hair-like needles. Its solution is coloured pure blue by ferric chloride. On dry distillation the acid is decomposed into quinol and carbon dioxide.[1]

Quinol is also found in the distillation products of the salts of succinic acid.[2]

In order to prepare it, quinone, which is best obtained by the oxidation of aniline, is employed: 1 part of aniline is dissolved in 8 pts. of sulphuric acid and 30 pts. of water, and a solution of 2·5 pts. of powdered potassium bichromate gradually added to the cooled solution. Potassium sulphite is added to the brown liquid thus obtained, and the whole extracted with ether.[3] The latter is then distilled off, the residue dissolved in the smallest possible quantity of hot water, sulphurous acid and animal charcoal added, and the solution boiled and filtered.[4] On standing, the quinol separates out from the filtrate in hexagonal rhombohedral prisms, which sublime on heating in monoclinic plates. These, on recrystallization from hot water, reproduce crystals of the former kind.[5] Quinol is therefore dimorphous; it has a slightly sweet taste, melts at 169°, and distils without decomposition. It is readily soluble in hot water, alcohol, and ether, and slightly in cold benzene. On fusing with caustic potash it remains unchanged; if its vapour be passed through a tube at a low red heat it is decomposed into hydrogen and quinone.[6] The latter is also very easily formed by the action of oxidizing agents, for which reason quinol reduces silver nitrate solution on warming, and Fehling's solution even in the cold. Ferric chloride also easily oxidizes it, by means of which reaction it can be readily distinguished from its isomerides. It also differs from catechol in not being precipitated by lead acetate. On dissolving it in a hot solution of this salt, the compound $2[C_6H_6O_2 + (C_6H_5O_2)_2Pb] + 3H_2O$ separates out on cooling in oblique, rhombic prisms (Wöhler). On passing sulphuretted hydrogen through a cold saturated solution of quinol, gently warming until crystals appear, and then allowing the gas to

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[1] Herrmann, *Ber. Deutsch. Chem. Ges.* xvi. 1411; *Ann. Chem. Pharm.* ccxi. 308.

[2] Richter, *Journ. Prakt. Chem.* [2], xx. 207.

[3] Nietzki, *Ber. Deutsch. Chem. Ges.* x. 2003; xi. 1102.

[4] Ekstrand, *ibid.* xi. 713; see also Seyda, *ibid.* xvi. 687.

[5] Lehmann, *Jahresb. Chem.* 1877, 566.

[6] Hlasiwetz, *Ann. Chem. Pharm.* clxxv. 68; clxxvii. 336; Hesse, *ibid.* cxiv. 297.

stream through until these are redissolved, the compound $(C_6H_6O_2)_3SH_2$ separates out on cooling in colourless, transparent rhombohedra, which are odourless, and stable in the dry state. Cold water decomposes them slowly, hot water quickly, into their constituents. By employing a saturated solution warmed to 40°, long, colourless prisms of the composition $(C_6H_6O_2)_2SH_2$ are obtained, which behave like the preceding compound.[1] On passing sulphur dioxide through a solution of quinol, yellow rhombohedra of the composition $(C_6H_6O_2)_3SO_2$, are formed, which decompose on heating.[2]

996 *Quinol methyl ether*, $C_6H_4(OCH_3)OH$, was first obtained, together with quinol, as a decomposition product of *arbutin*. It is formed together with the dimethyl ether by heating quinol with caustic potash and potassium methyl sulphate to 170°.[3] It is more easily obtained by digesting 1 pt. of potash, 2 pts. quinol, 3 pts. methyl iodide, and some methyl alcohol in a flask connected with an inverted condenser, until the alkaline reaction disappears. The methyl alcohol is evaporated off and the residue distilled in a current of steam, when the dimethyl ether comes over. The residue is then extracted with ether and the latter distilled off, the monomethyl ether, together with some quinol, remaining behind. These are then separated by cold benzene, in which the methyl ether is readily soluble; after the removal of the benzene this is rectified.[4] It crystallizes in rhombic plates or prismatic tables melting at 53° and boiling at 243°. It is not oxidized by ferric chloride, but reduces silver nitrate solution on warming.

Quinol dimethyl ether, $C_6H_4(OCH_3)_2$, is best obtained by warming 10 pts. of quinol, 12 pts. of caustic potash, and 30 pts. of methyl iodide diluted with double the volume of wood spirit, under an extra pressure of 200 mm. in an apparatus connected with an inverted condenser. On recrystallization from methyl alcohol or ordinary alcohol, it is obtained in splendid plates melting at 56°.[5] It behaves towards ferric chloride and silver nitrate like the preceding compound. When 15 to 20 volumes of ether are added to a concentrated solution of the methyl ether and caustic potash, the phenate, $C_6H_4(OCH_3)OK$, separates

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[1] Wöhler, *Ann. Chem. Pharm.* lxix. 294.
[2] Clemm, *ibid.* cx. 357 ; see also Hesse, *ibid.* cxiv. 300.
[3] Hlasiwetz and Habermann, *ibid.* clxxvii. 338.
[4] Hesse, *ibid*, cc. 254 : Tiemann, *Ber. Deutsch. Chem. Ges.* xiv. 1989.
[5] Mühlhäuser, *Ann. Chem. Pharm.* ccvii. 252.

out as a crystalline powder, or, when the materials are not anhydrous, in crystalline tablets.[1]

Quinol ethyl ether, $C_6H_4(OC_2H_5)OH$, is readily soluble in hot water, and crystallizes in very thin, satin-like needles; it melts at 66° and boils at 246°—247°.[2]

Quinol diethyl ether, $C_6H_4(OC_2H_5)_2$, forms large thin plates, which melt at 72° and are volatile in steam.[3]

Fiala[4] has prepared the following mixed ethers of quinol; these bodies possess an aromatic odour resembling fennel, and have a burning taste:

		Melting Point.
$C_6H_4\left\{\begin{array}{l}OCH_3\\OC_2H_5\end{array}\right.$	crystals.	39°.
$C_6H_4\left\{\begin{array}{l}OCH_3\\OC_3H_7\end{array}\right.$	crystals	26°.
$C_6H_4\left\{\begin{array}{l}OCH_3\\OC_2H_3(CH_3)_2\end{array}\right.$	liquid	—

997 *Arbutin*, $C_{12}H_{16}O_7$.—This glucoside was found by Kawalier in the leaves of the bearberry (*Arbutus* s. *Arctostaphylos uva-ursi*), and he showed that it is decomposed by emulsin into glucose and arctuvin.[5] Strecker, who recognised the latter compound as quinol, proved the composition of arbutin, and also effected its decomposition by boiling with dilute sulphuric acid.[6] He also found it in the leaves of the wintergreen (*Pyrola umbellata*).[7] In order to prepare it, the leaves are boiled with water, lead acetate added to the solution to precipitate tannic acid, &c., and the filtrate treated with sulphuretted hydrogen and evaporated. Arbutin crystallizes from boiling water in long silky needles containing half a molecule of water of crystallization, which is driven off at 100°. It tastes bitter, and gives a light blue colour with ferric chloride. By heating it with acetic anhydride, the pentacetate, $C_{12}H_{11}(C_2H_3O)_5O_7$, which crystallizes from hot alcohol in needles or plates, is obtained.

These different reactions show that arbutin is an ether of

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[1] Michael, *Americ. Chem. Journ.* v. 176.

[2] Hantzsch, *Journ. Prakt. Chem.* [2], xxii. 246; Wichelhaus, *Ber. Deutsch. Chem. Ges.* xii. 1501.

[3] Rakowski, *Neues Handwörterb.* ii. 560.

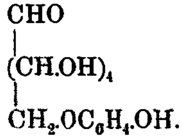
[4] *Monatsb. Chem.* v. 232.

[5] *Ann. Chem. Pharm.* lxxxiv. 356.

[6] *Ibid.* cvii. 228.

[7] Zwenger and Himmelmann, *ibid.* cxxix. 205.

dextrose, and at the same time a phenol: its constitution is therefore expressed by the following formula (Schiff):[1]



$$\begin{array}{l}\mathrm{CHO}\\ |\\ (\mathrm{CH.OH})_4\\ |\\ \mathrm{CH_2.OC_6H_4.OH.}\end{array}$$

Hlasiwetz and Habermann proposed for arbutin the formula $C_{25}H_{34}O_{14}$, because they found that on decomposition it yielded equal molecules of quinol and quinol methyl ether.[2] Arbutin is, however, more probably, a mixture of the glucosides of both compounds,[3] and, indeed, the analyses of different preparations show varying relations. By the fractional crystallization of such a mixture, Schiff succeeded in obtaining a pure normal arbutin crystallizing in needles, 2 to 3 centimetres in length, which, after being dried at 110°—115°, melt at 165°—166°.[4]

On the other hand, he could not then obtain a *methylarbutin*, $C_{12}H_{15}(CH_3)O_7$, free from arbutin. Michael, however, obtained it artificially, by allowing a solution of 11 parts of the above-mentioned potassium compound of methylquinol, and 25 parts of aceto-chlorohydrose, in absolute alcohol to stand for several days (see Phenolglucoside, p. 107). It crystallizes from water in long, silky needles, containing half a molecule of water of crystallization, and melting in the anhydrous state at 168°—169°. Methylarbutin gives no colour with ferric chloride; it is easily decomposed on heating with acids or in presence of emulsin.[5]

Schiff then obtained this compound by heating a solution of ordinary arbutin, methyl iodide, and caustic potash, in methyl alcohol. It contained one molecule of water of crystallization, and melted in the anhydrous state at 175°—176°. He also found that mixtures of both glucosides melt lower than either of them separately, and believes that the true melting-point of pure arbutin is somewhat higher than 190·5°, the temperature which he had previously observed.[6]

Diacetoquinol, $C_6H_4(OC_2H_3O)_2$, is obtained by heating quinol with acetic anhydride or acetyl chloride, and crystallizes in tables

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[1] Schiff, *Ann. Chem. Pharm.* cliv. 237.

[2] *Ibid.* clxxvii. 342.

[3] Fittig, *Org. Chem.* 10 Aufl. 638.

[4] *Ann. Chem. Pharm.* ccvi. 159.

[5] *Americ. Chem. Journ.* v. 176; *Ber. Deutsch. Chem. Ges.* xiv. 2079.

[6] *Ber. Deutsch. Chem. Ges.* xv. 1841; see also *Liebig's Ann.* ccxxi. 365.

or plates, melting at 123°—124°, and readily subliming in needles. It is readily soluble in benzene and ether, and slightly in alcohol and hot water.[1]

Quinol ethylcarbonate, $C_6H_4(O.CO_2C_2H_5)_2$, is obtained by the action of ethyl chlorocarbonate on a mixture of caustic potash and quinol; it crystallizes from absolute alcohol in large needles, which melt at 101°, boil at 310°, and are not attacked by alkalis or acids even on warming.[2]

Acetonequinol, $C_6H_6O_2.C_3H_6O$, is obtained by the direct combination of its constituents and forms beautiful, transparent, monoclinic crystals, which give off acetone in the air and become opaque without falling to powder. This body has an analogous composition to quinhydrone (see p. 164).[3]

Thioquinol, $C_6H_4(SH)_2$, may be obtained by the action of tin and hydrochloric acid on benzenedisulphonyl chloride; it crystallizes in small six-sided plates, melting at 98°. Its lead salt, $C_6H_4S_2Pb$, is a yellowish-red precipitate.[4]

CHLORINE SUBSTITUTION PRODUCTS OF QUINOL.

998 These bodies are not formed by the direct action of chlorine on quinol, because the latter is thereby converted into quinone. They can, however, be obtained by reducing the substitution products of quinone, as well as by treating them with hydrochloric acid.

Chloroquinol, $C_6H_3Cl(OH)_2$, is obtained by treating quinone with concentrated hydrochloric acid (Wöhler)[5], and by the action of sulphurous acid on chloroquinone (Städeler).[6] It is readily soluble in water and crystallizes in prisms melting at 98°.[7]

a-Dichloroquinol, $C_6H_2Cl_2(OH)_2(Cl : Cl = 2 : 5)$, was prepared by Städeler from the corresponding dichloroquinone; it is also obtained by the combination of monochloroquinol with hydro-

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[1] Rakowski, *Neues Handwörterb.* ii. 560; Hesse, *Ann. Chem. Pharm.* cc. 241; Nietzki, *Ber. Deutsch. Chem. Ges.* xi. 470

[2] Bender, *Ber. Deutsch. Chem. Ges.* xiii. 697; Wallach, *Ann. Chem. Pharm.* ccxxvi. 85.

[3] Habermann, *Monatsb. Chem.* v. 329.

[4] Körner and Monselise, *Jahresber.* 1876, 450,

[5] *Ann. Chem. Pharm.* li. 155.

[6] *Ibid.* lxix. 307.

[7] Levy and Schultz, *Ber. Deutsch. Chem. Ges.* xiii. 1427.

chloric acid (Levy and Schultz). It is much more readily soluble in hot water than in cold, and crystallizes in very long needles, or short, thick prisms, melting at 164°.

β-Dichloroquinol (Cl : Cl = 2 : 6), is obtained by reducing β-dichloroquinone. It crystallizes from dilute alcohol in small yellow plates, melting at 157°—158°.[1]

Trichloroquinol, $C_6HCl_3(OH)_2$, is formed by the action of sulphurous acid on trichloroquinone,[2] and, together with trichloroquinone and other products, when benzene is treated with potassium chlorate and dilute sulphuric acid.[3] It is slightly soluble in water, readily in alcohol, and crystallizes in prisms melting at 134°.

Tetrachloroquinol, $C_6Cl_4(OH)_2$, is obtained by the reduction of tetrachloroquinone (Städeler, Gräbe). It forms plates which are insoluble in water, but which readily dissolve in alcohol and alkalis, and reduce silver solution. On heating in a current of air it sublimes in long flat needles, with partial decomposition.

Its dimethyl ether, $C_6Cl_4(OCH_3)_2$, is formed by treating a solution of quinol dimethyl ether in acetic acid with chlorine. It crystallizes in needles, which melt at 153°—154° and sublime without decomposition.[4]

BROMINE SUBSTITUTION PRODUCTS OF QUINOL.

999 These are formed in a similar way to the corresponding chlorine substitution products, but can also be obtained by the direct bromination of quinol.

Bromoquinol, $C_6H_3Br(OH)_2$, is obtained by the combination of quinone and hydrobromic acid,[5] as well as by acting upon an ethereal solution of quinol with a solution of bromine in chloroform.[6] It is very readily soluble in water, and crystallizes from petroleum spirit in lustrous silky plates, melting at 110°—111°.

Dibromoquinol, $C_6H_2Br_2(OH)_2$, is obtained by the action of bromine on a warm solution of quinol in acetic acid,[7] and is also

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[1] Faust, *Ann. Chem. Pharm.* Suppl. vi. 154.

[2] Städeler, Gräbe, *ibid.* cxlvi. 25; Stenhouse, *Journ. Chem. Soc.* xxi. 146.

[3] Krafft, *Ber. Deutsch. Chem. Ges.* x. 797.

[4] Habermann, *ibid.* xi. 1035.

[5] Wichelhaus, *ibid.* xii. 1504.

[6] Sarauw, *Liebig's Ann.* ccix. 105.

[7] Benedikt. *Monatsh. Chem.* i. 345.

formed when quinone (Wichelhaus) or bromoquinone (Sarauw) is heated with hydrobromic acid. It is scarcely soluble in cold water, and crystallizes from a boiling solution in long needles melting at 186°. By mixing solutions of bromine and quinone in chloroform, a compound isomeric with dibromoquinol is obtained, which crystallizes from petroleum spirit in sulphur-coloured needles melting at 86°—87°; on heating with water it quickly decomposes, hydrobromic acid and bromine being formed, but on standing it is gradually converted into dibromoquinol (Sarauw). This peculiar addition product has probably the following constitution, $C_6H_3Br\begin{cases}OH\\OBr.\end{cases}$

Tribromoquinol, $C_6HBr_3(OH)_2$, is formed by the action of hydrobromic acid on dibromoquinol, as well as by that of bromine on quinol or quinone (Sarauw).

$$C_6H_4O_2 + 2Br_2 = C_6H_3Br_3O_2 + HBr.$$

It is very slightly soluble in cold water, readily in hot, and crystallizes in silky needles melting at 136°.

Tetrabromoquinol, $C_6Br_4(OH)_2$, is obtained by the action of sulphurous acid on tetrabromoquinone,[1] or by treating it with hydriodic acid and phosphorus.[2] It is further obtained by the combination of tribromoquinol with hydrobromic acid, and by the action of bromine on a solution of quinol in acetic acid (Sarauw)

NITRO-SUBSTITUTION PRODUCTS OF QUINOL.

1000 *Nitroquinol*, $C_6H_3(NO_2)(OH)_2$, is not known in the free state; but several of its ethers have been obtained by the action of nitric acid on quinol ether.

	Melting Point.
Monomethyl ether, $C_6H_3(NO_2)(OCH_3)OH$, orange yellow needles	83°
Dimethyl ether, $C_6H_3(NO_2)(OCH_3)_2$, golden yellow needles	71·5°
Monoethyl ether, $C_6H_3(NO_2)(OC_2H_5)OH$, deep yellow needles	83°
Diethyl ether, $C_6H_3(NO_2)(OC_2H_5)_2$, golden yellow needles	49°

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[1] Stenhouse, *Ann. Chem. Pharm.* xci. 310.

[2] Stenhouse, *Journ. Chem. Soc.* xxiii. 11.

Dinitroquinol, $2C_6H_2(NO_2)_2(OH)_2 + 3H_2O$, was obtained by Strecker by boiling dinitro-arbutin with dilute sulphuric acid,[1] and by Nietzki by treating the diacetate, described below, with cold caustic soda.[2] It crystallizes from hot water in fine flat needles having a golden lustre, which lose water of crystallization at 100° with disintegration, and then turn brown and melt at 135°—136°. It colours the skin a carmine red. Its yellow solution is coloured first blood-red, and then bluish-violet by the gradual addition of an alkali. Its ammoniacal solution is coloured purple-red on boiling, leaving metallic-green crystals on evaporation.

Its ethers are obtained similarly to those of nitroquinone.[3]

		Melting Point.
Monomethyl ether, $C_6H_2(NO_2)_2(OCH_3)OH$,	greenish needles	102°
Dimethyl ether, $C_6H_2(NO_2)_2(OCH_3)_2$	yellow crystals	169°—170°
Monoethyl ether, $C_6H_2(NO_2)_2(OC_2H_5)OH$,	brownish yellow needles	71°
α-Diethyl ether $C_6H_2(NO_2)_2(OC_2H_5)_2$	lemon yellow plates	176°
β-Diethyl ether $C_6H_2(NO_2)_2(OC_2H_5)_2$	„ „ „	130°

Diacetodinitroquinol, $C_6H_2(NO_2)_2(OC_2H_3O)_2$, is obtained by dissolving quinol diacetate in fuming nitric acid,[4] and crystallizes from alcohol in sulphur-coloured needles melting at 96°.

Trinitroquinol, $C_6H(NO_2)_3(OH)_2$.—The dimethyl ether of this substance is obtained by adding a solution of quinol dimethyl ether in acetic acid to a well-cooled mixture of nitric and sulphuric acids; it crystallizes from alcohol in long, yellow needles which melt at 100°—101° (Habermann).

The diethyl ether is obtained by the nitration of both the dinitroquinol diethyl ethers, and forms long, straw-coloured needles melting at 133° (Nietzki).

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[1] *Ann. Chem. Pharm.* Suppl. cxviii. 293.

[2] *Ber. Deutsch. Chem. Ges.* xi. 470.

[3] Weselsky and Benedikt, *Monatsb. Chem.* ii. 369; Mühlheimer, *Liebig's Ann.* 207, 253; Habermann, *Ber. Deutsch. Chem. Ges.* xi. 1037; Nietzki, *ibid.* xi. 1448; xii. 39; *Liebig's Ann.* 215, 125.

[4] Nietzki, *Ber. Deutsch. Chem. Ges.* xi. 470.

QUINONE, OR BENZOQUINONE, $C_6H_4O_2$.

1001 Woskresensky obtained this body by oxidizing quinic acid with manganese dioxide and sulphuric acid, and named it quinoyl,[1] a name which was changed by Berzelius to that now used. It is also obtained by the oxidation of quercitol, $C_6H_7(OH)_5$, (*vide* p. 193),[2] caffetannic acid, the extract of coffee-beans, the leaves of the coffee shrub, the holly, and other plants,[3] as well as several para-disubstitution products of benzene, such as paradiamidobenzene,[4] paramidophenol,[5] paramidobenzenesulphonic acid (sulphanilic acid),[6] phenolparasulphonic acid,[7] &c. It is also formed by the oxidation of aniline (Hofmann), in which way it is best obtained. The method of preparation is the same as that described under quinol, but another part of potassium bichromate is added to the brown solution, and the whole heated for some hours to about 35°. The cooled solution is then extracted with ether, which on evaporation yields the quinone in golden-yellow plates.[8] It can also be obtained by the direct oxidation of benzene. When 4 parts of this are gently heated with 1 part of chromium oxychloride, CrO_2Cl_2, hydrochloric acid gas is evolved, and a brown precipitate separates out, which probably has the formula, $C_6H_4(OCrOCl)_2$, since it is decomposed by water into chromium trioxide, hydrochloric acid, and quinone, which remains dissolved in the excess of benzene.[9]

Wöhler, who first closely examined the quinone prepared from quinic acid, describes it as follows:[10] "There are probably few substances which have so great a power of crystallization as this. When even small quantities of it are sublimed, crystals are obtained an inch in length. After being melted it solidifies to a crystalline mass. It dissolves in quantity in boiling water with a reddish-yellow colour, and, when this solution is cooled, crystallizes out in long but less transparent prisms, which are

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[1] *Ann. Chem. Pharm.* xxvii. 268.

[2] Prunier, *Compt. Rend.* lxxxii. 1113.

[3] Stenhouse, *Mem. Chem. Soc.* ii. 226; lxxxix. 244.

[4] Hofmann, *Jahresb.* 1863, 415.

[5] Körner, Kekulé's *Org. Chem* iii. 103; Andresen, *Journ. Prakt. Chem.* [2], xxiii. 173.

[6] Ador and Meyer, *Ann. Chem. Pharm* clix. 7.

[7] Schreder, *Ber. Deutsch. Chem. Ges.* viii. 760.

[8] Nietzki, *ibid.* x. 1934.

[9] Etard, *Ann. Chim. Phys.* [5], xxii. 270.

[10] *Ann. Chem. Pharm.* li. 148; lxv. 349.

somewhat darker and of a less beautiful yellow than those obtained by sublimation."

"Its solution stains the skin permanently brown. It is so volatile, that, even at the ordinary temperature, it sublimes from one side of the vessel to the other. Its strong odour, which irritates both the eyes and nose, causes an after-effect similar to that produced by iodine or chlorine."

Quinone is readily soluble in hot alcohol and petroleum spirit, crystallizing from the latter in beautiful yellow prisms,[1] which melt at 115·7°.[2] Hofmann found its vapour density to be 3·72-3·79, by means of which determination its then somewhat doubtful molecular weight was confirmed.[3] Its alkaline solution quickly turns dark brown, and its aqueous solution a dark yellowish-red in the air, and the latter deposits a blackish-brown substance (Wöhler). In presence of sodium acetate this decomposition takes place more rapidly, particularly on warming, the acetate, however, remaining unchanged. At the same time a certain quantity of quinol is obtained, which can be isolated by extracting with ether.[4] That it is easily converted into the latter substance by reducing agents has been already stated. It acts therefore as a strong oxidizing agent, and decomposes hydriodic acid with separation of iodine. It is not poisonous, in spite of its strong smell and its action on the living skin; 0·5 and even 1 grm. given to a dog produced no effect. It could not be found in the urine, and what had become of it could not be ascertained.[5]

To detect quinone dissolved in water, a few drops of a saturated solution of hydrocaerolignone, $C_{12}H_4(OCH_3)_2(OH)_2$, are added. The solution immediately turns a yellowish-red, and then, with a further colouration, deposits steel-blue, iridescent needles of caerolignin, $C_{12}H_4(OCH_3)_4O_2$. In this way 1 part of quinone in 200,000 parts of water can be detected. In more dilute solutions the separation of crystals does not take place, but the colouration is still produced by 1 part of quinone in 1,000,000 parts of water.[6]

Dihydroxyquinone, $C_6H_2(OH)_2O_2$, is not known; its dimethyl ether, $C_6H_2(OCH_3)_2O_2$, is obtained by oxidation of the dimethyl ethers of propylpyrogallol and acetopyrogallol (*vide post*). It

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[1] Hesse, *Ann. Chem. Pharm.* cc. 240.

[2] Hesse, *ibid.* cxiv. 300.

[3] *Ber. Deutsch. Chem. Ges.* iii. 583.

[4] Hesse, *Liebig's Ann.* ccxx. 365.

[5] Wöhler and Frerichs, *Ann. Chem. Pharm.* lxv. 343.

[6] Liebermann, *Ber. Deutsch. Chem. Ges.* x. 1615.

crystallizes in yellow needles, and is converted by reduction into tetrahydroxybenzene dimethyl ether, $C_6H_2(OCH_3)_2(OH)_2$, which forms colourless needles melting at 160°. Equal molecules of the two ethers form a compound, which crystallizes in beautiful red needles[1] (see Quinhydrone).

Trihydroxyquinone, $C_6H(OH)_3O_2$, is obtained when the hydrochloride of amidodi-imidoresorcinol is heated with hydrochloric acid to 140°—150°.

$$C_6H(NH_2)(OH)_2(NH)_2 + 3H_2O = C_6H(OH)_3O_2 + 3NH_3.$$

It forms dark, brass-coloured scales, or an amorphous, almost black powder insoluble in water, scarcely soluble in ether, and slightly soluble in boiling alcohol. It dissolves in alkalis, forming a brown solution, which is precipitated by metallic salts. Thus, by addition of silver nitrate to its alcoholic solution, the silver salt, $C_6H(AgO)_3O_2$, is obtained as a blackish-brown precipitate, which on drying becomes almost black with a shade of green, and by reflected light exhibits a yellow metallic lustre.

Acetyl chloride forms the triacetate, $C_6H(OC_2H_3O)_3O_2$, which crystallizes from glacial acetic acid in dark, ill-defined scales.[2]

CHLORINE SUBSTITUTION PRODUCTS OF QUINONE.

1002 *Monochloroquinone*, $C_6H_3ClO_2$, is obtained by distilling a salt of quinic acid with common salt, manganese dioxide and dilute sulphuric acid,[3] as well as by oxidizing chloroquinol with an ice-cold solution of potassium bichromate in dilute sulphuric acid.[4] It is readily soluble in water, alcohol, and ether, and forms yellowish-red rhombic crystals, smelling like quinone, melting at 57°, and volatilizing at the ordinary temperature.

Paradichloroquinone, $C_6H_2Cl_2O_2(Cl : Cl = 2 : 5)$, was obtained by Städeler, together with the preceding compound; Carius prepared it by the action of chlorous acid on benzene.[5] It is also obtained when α-dichloroquinol is oxidized with dilute nitric acid, or paradichloraniline with a solution of chromic acid (Levy and Schultz), and crystallizes in dark yellow, monoclinic tables melting at 159°. It is volatile in steam, insoluble in

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* xi. 332.
[2] Merz and Zotter, *ibid.* xii. 2043.
[3] Städeler, *ibid.* lxix. 302.
[4] Levy and Schultz, *ibid.* ccx. 144.
[5] *Ann. Chem. Pharm.* cxliii. 316.

water, scarcely soluble in cold alcohol, but readily in boiling alcohol.

Metadichloroquinone (Cl : Cl = 2 : 6) is obtained by the action of cold fuming nitric acid on trichlorophenol,[1] or by passing nitrogen trioxide through its aqueous solution.[2] It is slightly soluble in water and cold alcohol, and crystallizes from boiling alcohol or petroleum spirit in large rhombic straw-coloured prisms, melting at 120°, and subliming readily. It is also obtained by the oxidation of metadichloroparadiamidobenzene.[3]

Trichloroquinone, $C_6HCl_3O_2$.—Woskresensky, by the action of chlorine on quinone, obtained a compound of this composition, which he named chloroquinoyl, but according to his statement, which is supported by the experience since gained concerning chlorinated quinones, this was a mixture. Trichloroquinone was first obtained pure, together with tetrachloroquinone and the above-mentioned compound, by Städeler, by the chlorination of quinic acid. By the action of hydrochloric acid and potassium chlorate on many aromatic substances, a mixture of trichloroquinone and tetrachloroquinone is obtained, as has been shown by Gräbe,[4] whereas it was formerly believed that only the latter compound is produced.

In order to prepare trichloroquinone, Gräbe's process modified by Knapp and Schultz is employed.[5] 1 part of phenol is dissolved in an equal weight of sulphuric acid at 100°. The phenolsulphonic acid thus obtained is brought into a hot aqueous solution of 4 parts of potassium chlorate, and an excess of crude hydrochloric acid added. An energetic reaction soon commences, which is finished after standing twenty-four hours by passing in steam. The mixture of trichloroquinone and tetrachloroquinone is washed with hot water and cold alcohol, then suspended in water and the liquid saturated with sulphur dioxide, and allowed to stand until the crystals have become colourless. Boiling water then only extracts trichloroquinol, while tetrachloroquinol remains behind. By the addition of fuming nitric acid to the hot solution of the former, trichloroquinone separates out. According to Stenhouse, it is better to dissolve in hot water containing sulphuric acid and

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[1] Faust, *Ann. Chem. Pharm.* cxlix. 153.

[2] Weselsky, *Ber. Deutsch. Chem. Ges.* iii. 646.

[3] Levy, *ibid.* xvi. 1444.

[4] *Ann. Chem. Pharm.* cxlvi. 1.

[5] *Ibid.* ccx. 174.

add potassium bichromate to it.[1] The trichloroquinone is then purified by recrystallization from alcohol.

It is also obtained by the action of chromium oxychloride on benzene.[2]

$$4CrO_2Cl_2 + C_6H_6 = C_6HCl_3O_2 + 2Cr_2O_3 + 5HCl.$$

It is further obtained, together with tetrachloroquinone, when bleaching powder is added to a boiling solution of paramidophenol[3] in hydrochloric acid, or by decomposing trichloramidophenol with bromine water.[4] It crystallizes in large yellow plates melting at 165°—166°. It is insoluble in cold water, slightly soluble in cold, and readily in hot alcohol.

1003 *Tetrachloroquinone* or *Chloranil*, $C_6Cl_4O_2$.—Erdmann first obtained this compound by passing chlorine through an alcoholic solution of chlorisatin, and termed it *chloranil*,[5] a name which is still employed. Fritzsche obtained it by the action of hydrochloric acid and potassium chlorate on aniline,[6] and Hofmann, from phenol, quinone, chloraniline, salicylic acid, salicyl aldehyde, isatin, &c.[7] It has since been frequently observed as a final product of the action of the above reagents on aromatic bodies. That the substance thus obtained always contains trichloroquinone has already been stated. It is also obtained when symmetrical tetrachlorobenzene is oxidized with concentrated nitric acid, but is not formed from the isomerides of this compound.[8] Perchlorophenol is similarly converted into chloranil.[9]

Its preparation from phenol has been already described; it is isolated as tetrachloroquinol, and this is oxidized by nitric acid, and repeatedly extracted with boiling alcohol, in order to remove any admixed trichloroquinone. If it be required to convert the trichloroquinone, formed at the same time, into chloranil, the solution must be boiled for a long time with concentrated hydrochloric acid, and the tetrachloroquinol so obtained, oxidized with fuming nitric acid (Knapp and Schultz).

The mixture obtained by the action of hydrochloric acid and potassium chlorate on phenol can, according to Stenhouse, also

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[1] *Journ. Chem. Soc.* xxi. 149.
[2] Carstanjen, *Ber. Deutsch. Chem. Ges.* ii. 633.
[3] Schmitt and Andresen, *Journ. Prakt. Chem.* [2], xxiii. 436.
[4] *Ibid.* xxiv. 434.
[5] *Ann. Chem. Pharm.* xlviii. 309.
[6] *Neues Handwörterbuch*, ii. 561.
[7] *Ann. Chem. Pharm.* lii. 57.
[8] Beilstein and Kurbatow, *ibid.* cxcii 206.
[9] Merz and Weith, *Ber. Deutsch. Chem. Ges.* v. 460.

be converted into chloranil by dissolving it in an equal weight of water, adding half its weight of iodine, and passing in chlorine, until it is only slowly absorbed; the chloranil formed is then distilled off.

Chloranil is employed in the colour industry, and is obtained on the large scale as stated above, or by the oxidation of trichlorophenol with potassium bichromate and sulphuric acid.

Chloranil is insoluble in water, very slightly soluble in cold, only slightly in boiling alcohol, and somewhat more easily in ether. It crystallizes in small gold-coloured plates, or from boiling benzene in light-yellow, transparent prisms;[1] it begins to vapourize at 150° and sublimes rapidly at 210°. It melts at a high temperature and boils with partial decomposition. It is not attacked by concentrated sulphuric acid, nitric acid, or aqua regia, and this explains why it is so frequently obtained as a final product of the action of oxidizing and chlorinating agents on a large number of bodies. By heating it with phosphorous pentachloride to 180°, hexchlorobenzene is obtained (Gräbe):

$$C_6Cl_4O_2 + 2PCl_5 = C_6Cl_6 + 2POCl_3 + Cl_2.$$

By heating with acetyl chloride to 160°—180° it is converted into di-acetotetrachloroquinol:

$$C_6Cl_4O_2 + 2C_2H_3OCl = C_6Cl_4(OC_2H_3O)_2 + Cl_2.$$

It has already been stated, that reducing agents convert it into tetrachloroquinol; this also takes place on boiling with concentrated hydrochloric acid, or still more readily with hydrobromic acid;[2]

$$C_6Cl_4O_2 + 2HBr = C_6Cl_4(OH)_2 + Br_2.$$

By adding chloranil to a dilute solution of acid potassium sulphite, the potassium salt of dichloroquinoldisulphonic acid is formed:[3]

$$C_6Cl_4O_2+3SO_3KH+H_2O = C_6Cl_2(OH)_2(SO_3K)_2+2HCl+SO_4KH.$$

This crystallizes in colourless tables. The free acid is only known in aqueous solution. It, and the solutions of its salts, are coloured indigo-blue by ferric chloride.

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[1] Levy and Schultz, *Liebig's Ann.* ccx. 154.

[2] Levy and Schultz, *Ber. Deutsch. Chem. Ges.* xiii. 1430; Sarauw, *Liebig's Ann.* ccix. 125.

[3] Hesse, *ibid.* cxiv. 324; Greiff, *Jahresb.* 1863, 392.

On treating chloranil with a concentrated solution of acid, or better, normal potassium sulphite, the potassium salt of thiochronic acid is the chief product, the preceding compound being also formed:[1]

$$C_6Cl_4O_2 + 5SO_3K_2 + H_2O = C_6(OH)(SO_4K)(SO_3K)_4 + 4KCl + KOH.$$

It crystallizes from hot water in yellow rhombic prisms containing 4 molecules of water, and its solution is coloured a deep brownish red by ferric chloride. The free acid is only known in aqueous solution, and decomposes when this is gently heated.

On heating the potassium salt with water to 130°—140°, potassium quinoldisulphonate, $C_6H_2(OH)_2(SO_3K)_2 + 4H_2O$, is obtained, together with acid potassium sulphate. The free acid crystallizes in thick tablets, deliquesces in the air, and is coloured blue by ferric chloride (Gräbe).

Hesse obtained an acid isomeric with the above by the action of fuming sulphuric acid on quinic acid. It forms a syrup which readily dissolves in water; its salts are coloured deep blue by ferric chloride.[2]

1004 *Chloranilic Acid* or *Dichlorodihydroxyquinone*, $C_6Cl_2(OH)_2O_2 + H_2O$. Erdmann obtained the potassium salt by dissolving chloranil in dilute caustic potash:

$$C_6Cl_4O_2 + 4KOH = C_6Cl_2(OK)_2O_2 + 2KCl + 4H_2O.$$

Gräbe obtained it as follows from trichloroquinone:

$$2C_6HCl_3O_2 + 3KOH = C_6Cl_2(OK)_2O_2 + C_6HCl_3(OH)_2 + KCl + H_2O.$$

In order to prepare chloranilic acid, 5 parts of chloranil are moistened with alcohol, and a cold solution of 6 parts of caustic potash in 100 parts of water added. When the chloranil is completely dissolved, the potassium salt thus formed is precipitated by the addition of 10 to 15 parts of common salt. The precipitate is redissolved in boiling water and repeatedly purified by precipitation with common salt. It is then dissolved in 100 parts of boiling water, and 10 parts of hydrochloric acid are added to precipitate the free chloranilic acid.[3] It is thus obtained in red crystalline grains, or, if it separates out slowly, in small, yellowish red, lustrous plates. It loses its water of crystallization at 115°, and sublimes, undergoing considerable

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[1] Hesse, *loc. cit.*; Gräbe, *Ann. Chem. Pharm.* cxlvi. 40.
[2] Hesse, *Ann. Chem. Pharm.* cx. 195.
[3] Stenhouse, *Journ. Chem. Soc.* xxiii. 6.

decomposition, at a higher temperature. It dissolves in water forming a violet-red solution; on addition of hydrochloric or sulphuric acid the solution is decolourized, most of the acid being precipitated.

Potassium chloranilate, $C_6Cl_2O_2(OK)_2 + H_2O$, crystallizes in purple prisms or needles, readily soluble in hot water, less so in cold, and still less in water containing free alkali or common salt. On warming it with phosphorus pentachloride, chloranil is formed.[1]

Sodium chloranilate, $C_6Cl_2O_2(ONa)_2 + 4H_2O$, forms dark carmine-red needles. Like the potassium salt, it dissolves in water with an intense violet colour, and detonates on heating.

The ammonium salt resembles the potassium salt; the barium salt is a rust-coloured, and the silver salt a reddish brown precipitate.

Ethyl chloranilate, $C_6Cl_2O_2(OC_2H_5)_2$, is obtained by the action of ethyl iodide on the silver salt, and crystallizes from alcohol in light red, flat prisms, melting at 107° (Stenhouse).

Hydrochloranilic acid or *dichlorotetrahydroxybenzene*, $C_6Cl_2(OH)_4$, is obtained when chloranilic acid is heated to 100° in a sealed tube, with a concentrated solution of sulphurous acid (Koch, Gräbe). On cooling, it separates out in long needles. In the moist state and in alkaline solution it absorbs oxygen, forming chloranilic acid.

When chloranilic acid is treated with only a small quantity of sulphurous acid, the compound, $C_6Cl_2(OH)_2O_2 + C_6Cl_2(OH)_4$, is obtained, which crystallizes in fine, black needles, and belongs to the class of the quinhydrones.

BROMINE AND IODINE SUBSTITUTION PRODUCTS OF QUINONE.

			Melting Point.
Monobromoquinone,[2]	$C_6H_3BrO_2$,	yellow tables or needles	55°—56°
α-Dibromoquinone,[3]	$C_6H_2Br_2O_2$,	small lustrous golden plates	188°
β-Dibromoquinone,[4]	$C_6H_2Br_2O_2$,	lustrous yellow plates	122°
γ-Dibromoquinone,[5]	$C_6H_2Br_2O_2$,	yellow fibrous crystals or needles	76°

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[1] Koch, *Zeitschr. Chem.* 1868, 202.

[2] Saurow, *Liebig's Ann.* ccix. 102, 106.

[3] Saurow; Benedikt, *Monatsh. Chem.* i. 134.

[4] Levy and Schultz, *Liebig's Ann.* ccx. 158.

[5] Böhmer, *Journ. Prakt. Chem.* (2) xxiv. 264.

		Melting Point.
Tribromoquinone,[1] $C_6HBr_3O_2$,	lustrous golden plates	147°
Tetrabromoquinone,[2] $C_6Br_4O_2$,	golden rhombic plates or thick tablets	—
Bromanilic acid,[3] $C_6Br_2(OH)_2O_2$,	reddish scales with a metallic lustre	—

		Melting Point.
Di-iodoquinone,[4] $C_6H_2I_2O_2$,	small golden plates	177°—179°

NITRO-SUBSTITUTION PRODUCTS OF QUINONE.

1005 *Nitroquinone,* $C_6H_3(NO_2)O_2$.—Chromium oxychloride acts on nitrobenzene just as on benzene (p. 155), the body, $C_6H_3(NO_2)(OCrOCl)_2$, which is decomposed by water, being obtained:

$$C_6H_3(NO_2)(OCrOCl)_2 + H_2O = C_6H_3(NO_2)O_2 + Cr_2O_3 + 2HCl.$$

The product is shaken with dilute caustic soda, filtered, and the nitroquinone precipitated from the filtrate by hydrochloric acid. It forms small yellowish brown plates which melt at 232°, and are tolerably soluble in hot water and readily in alcohol.[5]

a-Dinitrodihydroxyquinone or *Nitranilic acid,* $C_6(OH)_2(NO_2)_2O_2$, is obtained by passing nitrogen trioxide into an ethereal solution of quinol kept cool by ice, or better when diacetylquinol is added to a well-cooled mixture of concentrated sulphuric and nitric acids.[6]

Nitranilic acid is insoluble in ether and alcohol, but readily soluble in water, from which it crystallizes in long, golden-yellow prisms containing water, which is given off at 100°; the anhydrous acid detonates at about 170°. It

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[1] Saurow, *loc. cit.*

[2] Stenhouse, *Ann. Chem. Pharm.* xci. 307; *Journ. Chem. Soc.* xxiii. 10; Saurow.

[3] Stenhouse; Saurow, *loc. cit.*

[4] Seifert, *Journ. Prakt. Chem.* (2), xxviii. 437.

[5] Etard, *Ann. Chim. Phys.* (5), xxii. 272.

[6] Nietski, *Ber. Deutsch. Chem. Ges.* x. 2147; xi 1170; xvi. 2092; Nietzki and Benckiser, xviii. 499.

tastes acid and astringent like iron, and forms salts which crystallize well.

Potassium nitranilate, $C_6(OK)_2(NO_2)_2O_2$, is very slightly soluble in cold water, and crystallizes from hot water in light yellow needles with a blue surface lustre, which detonate violently on heating.

β-Dinitrodihydroxyquinone is obtained in small quantity, together with other bodies, when nitrogen trioxide is passed through an ethereal solution of pyrocatechuic acid, $C_6H_3(OH)_2CO_2H$, kept cool by ice. It is readily soluble in water, and slightly in ether; it crystallizes in greenish yellow needles, and is a very unstable substance. Its sodium salt is slightly soluble in cold water, more readily in hot, and forms brass-coloured spangles with a metallic lustre, which detonate violently on heating.[1]

QUINHYDRONES.

Quinhydrone, $C_{12}H_{10}O_4 = C_6H_4O_2 + C_6H_4(OH)_2$.

1006 This compound, which Wöhler described as "green hydroquinone," is formed by the partial reduction of quinone or the cautious oxidation of quinol. He makes the following remarks: "In all cases in which the green compound is obtained, it separates out in the crystalline state, the liquid being momentarily coloured a deep red, and then suddenly becoming full of the most beautiful green metallic prisms, which, even with small quantities, are frequently an inch in length."

"It is most readily obtained by adding ferric chloride to a solution of the colourless hydroquinone."

"It is prepared from quinone by mixing a saturated solution with sulphurous acid, which, in order to obtain large crystals, must be added all at once, but only in such quantity that some quinone still remains unchanged; otherwise the action will proceed further with formation of the colourless hydroquinone."

"The most remarkable method of formation of green hydroquinone is by the mutual action of the colourless compound and quinone; when their solutions are mixed, they instantaneously combine forming the green crystals, no other compound being produced." "Green hydroquinone is one of the most beautiful

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[1] Gruber, *Ber. Deutsch. Chem. Ges.* xii. 514.

substances which organic chemistry has produced. It is very similar to murexide, but excels it in lustre and beauty of colour. In this respect it bears the greatest resemblance to the metallic green of the rose-chafer, or of the feathers of the humming-bird. The crystals are generally very fine, and often very long. Under a high magnifying power the finer ones are seen to be transparent showing a reddish-brown colour. It has a sharp taste and a weak quinone-like odour; it readily fuses to a brown liquid, and at the same time a portion of it sublimes in small green plates, while another portion decomposes with formation of quinone, which sublimes in its characteristic yellow crystals. It is slightly soluble in cold water, while it dissolves in greater quantity in hot water forming a brownish red solution, from which it again crystallizes out on cooling. The green hydroquinone is readily soluble in alcohol and ether with a yellow colour; on evaporation it retains its green metallic lustre, and, in the crystalline condition, presents, especially on white porcelain, a very striking and beautiful appearance."

It crystallizes from hot glacial acetic acid in greenish black tablets or prisms (Hesse).

Quinhydrone is a compound consisting of equal molecules of quinone and quinol. On boiling with water it is decomposed into its constituents, quinone volatilizing and quinol remaining behind. Oxidizing agents convert it into the first and reducing agents into the second. "It dissolves in ammonia with a deep green colour, which in presence of air immediately changes into a dark, brownish red. On evaporation it remains behind as a brown, amorphous mass" (Wöhler).

Quinhydrone dimethyl ether, $C_{18}H_{14}O_6(CH_3)_2 = C_6H_4O_2 + 2C_6H_4(OCH_3)OH$, is formed by the combination of quinone with quinol methyl ether,[1] when the solutions of these in hot petroleum spirit are mixed.[2] On cooling, the compound separates out in beautiful greenish black prisms with a metallic lustre, which become reddish brown in the light. The ether dissolves in warm water with decomposition, and on reduction with sulphurous acid, gives two molecules of quinol methyl ether for each molecule of quinol.

1007 *Chlorine substitution products of quinhydrone* are not formed by the combination of a chlorinated quinol with quinone,

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[1] Wichelhaus, *Ber. Deutsch. Chem. Ges.* xii. 1501; Hesse, *Liebig's Ann.* cc. 254.

[2] Nietzki, *Ber. Deutsch. Chem. Ges.* xii. 1982.

nor of a chlorinated quinone with quinol, quinhydrone being always formed when these are brought together.[1]

$$C_6H_4O_2 + 2C_6H_5ClO_2 = C_{12}H_{10}O_4 + C_6H_4Cl_2O_2.$$
$$C_6H_3ClO_2 + 2C_6H_6O_2 = C_{12}H_{10}O_4 + C_6H_5ClO_2.$$
$$2C_6H_4O_2 + C_6H_4Cl_2O_2 = C_{12}H_{10}O_4 + C_6H_2Cl_2O_2.$$

Chlorinated quinones, on the contrary, combine with chlorinated quinols.

Dichloroquinhydrone or *brown chloroquinol*, $C_{12}H_8Cl_2O_4$, was obtained by Wöhler by the oxidation of chloroquinol with ferric chloride. It is also obtained by the combination of chloroquinone with chloroquinol, and is the first product of the action of hydrochloric acid on quinone (Städeler). It separates out at first as an oil and solidifies after some time to a greenish brown crystalline mass which, when left in a glass tube, sublimes in fine, long, brown needles, which stain the skin a dark purple-red colour.

Tetrachloroquinhydrone or *violet bichloroquinol*, $C_{12}H_6Cl_4O_4 + 2H_2O$, is obtained by warming dichloroquinol with a solution of dichloroquinone, as well as by the oxidation of the former with ferric chloride (Städeler). It crystallizes in small violet prisms, or long, flat, dark green needles, which lose their water of crystallization over sulphuric acid, or at 70°. At 120° they melt and decompose into their constituents. It is insoluble in water, and dissolves in alcohol forming a yellow solution, whilst its solution in ammonia is green.

Hexchloroquinhydrone or *yellow trichloroquinol*, $C_{12}H_4Cl_6O_4$, is formed, according to Woskresensky, by passing chlorine over quinone, or by the oxidation of trichloroquinol (Städeler).[2] It crystallizes in small, yellow, lustrous plates, which are slightly soluble in boiling water and more readily in boiling alcohol. It melts and sublimes a few degrees above 100°, and possesses a penetrating aromatic odour.

By the action of an insufficient quantity of cold nitric acid on trichloroquinol, Gräbe obtained long, black needles, which he considered to be hexchloroquinhydrone, but which are more probably a hydrate of this.

Resorcinolquinone, $C_{12}H_{10}O_4 = C_6H_4O_2 + C_6H_4(OH)_2$, is isomeric with quinhydrone, and is obtained by dissolving equal molecules of resorcinol and quinone in warm benzene. It forms almost black needles, which in transmitted light appear of a

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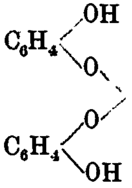
[1] Wichelhaus, *ibid.* xii. 1503.

[2] *Journ. Prakt. Chem.* xviii. 419.

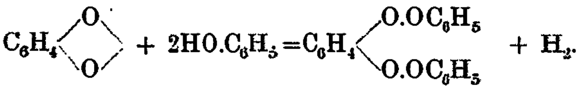
garnet-red colour, and have a green surface lustre. They melt at 90° and are readily soluble in water and alcohol.[1]

Phenoquinone, $C_{18}H_{16}O_4 = C_6H_4O_2 + 2C_6H_5.OH$, was first obtained by Wichelhaus by the oxidation of phenol in aqueous solution; it is also obtained by the direct combination of quinone with phenol,[2] when the solutions of these in hot petroleum ether are mixed.[3] It crystallizes in splendid red needles, the broad faces of which show a green lustre. They have a slightly sharp smell, melt at 71°, and are very volatile. Phenoquinone is soluble in cold water, but more readily in alcohol and ether, as well as in petroleum spirit, by means of which it may be separated from quinone and quinhydrone. It is split up by alkalis or acids into quinone and phenol. On the addition of potash the red needles become blue, and with baryta or ammonia, green.

1008 *Constitution of the Quinhydrones.* Various views have been advanced concerning the constitution of these compounds, which are formed by the direct combination of phenols with quinone. Quinhydrone was first looked upon as a compound of equal molecules of quinone and quinol, and Gräbe gave the following constitutional formula:[4]

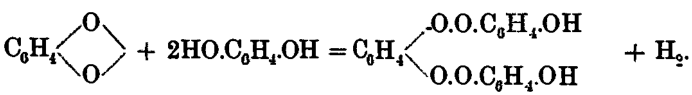


Wichelhaus opposed this view; he explains the formation of phenoquinone according to the following equation:



$$C_6H_4\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle + 2HO.C_6H_5 = C_6H_4\left\langle\begin{matrix}O.OC_6H_5\\O.OC_6H_5\end{matrix}\right. + H_2.$$

Quinhydrone and its methyl ether are formed in a similar manner:



$$C_6H_4\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle + 2HO.C_6H_4.OH = C_6H_4\left\langle\begin{matrix}O.O.C_6H_4.OH\\O.O.C_6H_4.OH\end{matrix}\right. + H_2.$$

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[1] Nietzki, *Ber. Deutsch. Chem. Ges.* xii. 1982.

[2] Wichelhaus. *Ber. Deutsch. Chem. Ges.* v. 248, 346.

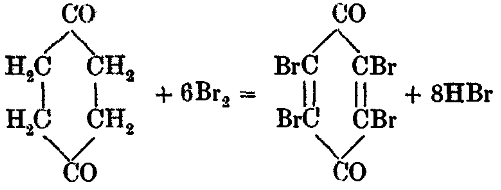
[3] Nietzki, *ibid.* xii. 1981; Hesse, *Liebig's Ann.* cc. 251.

[4] *Ann. Chem. Pharm.* cxlvi. 61.

The hydrogen formed acts as a reducing agent, changing, for example, a portion of the quinone into quinol.[1] Liebermann, however, showed by quantitative researches that quinone is a compound of equal molecules of its constituents;[2] Nietzki then found that quinone can be volumetrically determined by sulphurous acid and iodine solution. He thus obtained the formula, $C_{12}H_{10}O_4 = C_6H_4O_2 + C_6H_6O_2$ for quinhydrone,[3] and $C_{18}H_{16}O_4 = C_6H_4O_2 + 2C_6H_6O$ for phenoquinone.[4] He also found that if phenol and quinone are dissolved in the correct proportions in petroleum spirit, they combine completely to form phenoquinone, an observation which was also made by Hesse. The latter found a further proof of the accuracy of the old formula for quinhydrone in the fact that when it is heated with acetic anhydride, quinone is set free, and 85 to 87 per cent. of diacetoquinol is formed, instead of the theoretical 88·9, while according to the formula of Wichelhaus only 59·5 per cent. should be formed. Finally, he proved that quinhydrone dimethyl ether is a compound of one molecule of quinone with two molecules of quinol methyl ether.[5]

It follows, therefore, that one molecule of quinone combines with one molecule of a phenol, which contains two hydroxyls, and with two molecules of one which contains only one hydroxyl, or with their ethers.

Quinone tetrahydride, $C_6H_8O_2$, is obtained by heating succinosuccinic acid (p. 146), and crystallizes on the gradual evaporation of its aqueous solution in short, flat, lustrous prisms, having a peculiar, faint odour, and melting at 75°. Bromine converts it into bromanil:



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[1] Hesse, *Ber. Deutsch. Chem. Ges.* x. 1781, 2005; xii. 1500.

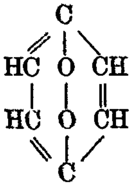
[2] *Ibid.* x. 1614; 2000.

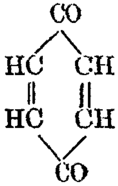
[3] *Ibid.* x. 2003.

[4] *Ibid.* xii. 1279.

[5] *Liebig's Ann.* cc. 248.

1009 *The Constitution of Quinone.*—It has already been stated that the constitution of quinone is expressed by one of the following formulæ (p. 44):

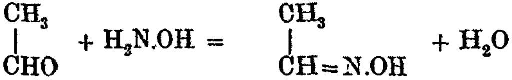




According to the former, quinone would be a peroxide; this theory, which until lately was universally accepted, explains its formation from quinol in a simple manner, as well as the easy conversion of the latter into quinone by oxidation. Gräbe, who first proposed it, has used it, as we have seen, to explain the constitution of the quinhydrones. According to the second formula quinone would be a ketone-like compound; in this case we should expect that it would combine with four atoms of hydrogen to form a body of an alcoholic nature, and that phosphorus pentachloride would convert tetrachloroquinone into the compound C_6Cl_8, and not into hexchlorobenzene.

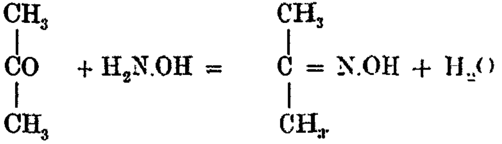
The formation of β-trichloracetylacrylic acid by the action of chlorous acid on quinone (p. 59), as well as the above formation of bromanil from succinosuccinic acid, speak for the second formula, which is rendered very highly probable by the behaviour of quinone towards hydroxylamine. V. Meyer and Janny have found that this converts aldehydes and ketones into oximes, the oxygen of the carbonyl being replaced by the divalent radical oximide, N.OH.

Ethyl Aldehyde. Ethyl Aldoxime.



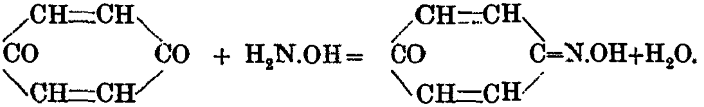
$$\begin{array}{l} CH_3 \\ | \\ CHO \end{array} + H_2N.OH = \begin{array}{l} CH_3 \\ | \\ CH{=}N.OH \end{array} + H_2O$$

Dimethylacetone. Dimethyl Acetoxime.

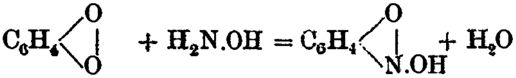


$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + H_2N.OH = \begin{array}{l} CH_3 \\ | \\ C = N.OH + H_2O \\ | \\ CH_3. \end{array}$$

The diketones which contain two carbonyls in adjacent positions thus give di-oximide-compounds. If, however, the carbonyls are not adjacent, only one of them usually enters into the reaction. Now quinone behaves exactly in this manner:


Quinonoxime.

The hydrogen of the hydroxyl group, as in other oximes, can be replaced by metals and radicals.[1] The fact that dimethylketone forms a compound with quinol which corresponds to quinhydrone is in favour of the supposition that quinone is a ketone. On the other hand, it must be remarked that quinone differs from other diketones, in being a powerful oxidizing agent like the peroxides. If it be regarded in this light, the action of hydroxylamine can also be easily explained.[2]


$$C_6H_4\left<\begin{matrix}O\\ |\\ O\end{matrix}\right. + H_2N.OH = C_6H_4\left<\begin{matrix}O\\ |\\ N.OH\end{matrix}\right. + H_2O$$

QUINONOXIMES OR NITROSOPHENOLS.

1010 *Quinonoxime*, $C_6H_4O(NOH)$. Baeyer and Caro first obtained this compound, together with dimethylamine, by boiling nitrosodimethylaniline with caustic soda.[3] They found that it may also be obtained by treating an aqueous solution of phenol and

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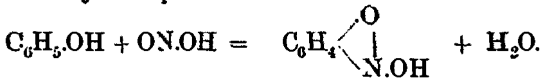
[1] The researches of Meyer and his pupils, which are referred to below, show that not only aldehydes and ketones but also aldehydo-acids, ketonic acids, and ketone-alcohols readily give oximide-compounds, and further, in doubtful cases it can be determined by means of hydroxylamine whether the compound contains a carbonyl group or not. The oximide compounds belonging to the aromatic group will be described in the sequel. In the preceding volumes various nitroso-compounds have been described, obtained by the action of nitrous acid on compounds containing the group CH_2. Among these are nitroso-malonic acid, nitroso-aceto-acetic ether and the nitroso-acetone obtained from it by decomposition. These bodies are likewise oximide-compounds and are now termed isonitroso-compounds. On heating these with concentrated hydrochloric acid they yield hydroxylamine, and they can be prepared by means of this reagent. Thus isonitrosomalonic acid, $C(NOH)(CO_2H)_2$, may be obtained by the action of hydroxylamine on mesoxalic acid, $CO(CO_2H)_2$. To the isonitroso-compounds belong also the nitrolic acids, while the pseudonitrols and the nitroso-amines, which are formed by the action of nitrous acid on the groups CH or NH, contain the monovalent radical nitrosyl, NO. These, like all other nitroso-compounds, give Liebermann's reaction with phenol and sulphuric acid. This reaction is not yielded by the isonitroso-compounds. Cf. *Ber. Deutsch. Chem. Ges.* xv. 1164, 1324, 1525, 2778, 2783, 2786, 3076; xvi. 167, 170, 177, 183, 500, 822, 833, 1616.

[2] L. Claisen, Private Communication.

[3] *Ber. Deutsch. Chem. Ges.* vii. 809.

potassium nitrite with acetic acid,[1] and considered it to be nitrosophenol, $C_6H_4(NO)OH$. Its exact constitution was proved by Goldschmidt, who found that it is formed by the action of hydroxylamine on quinone. In order to prepare it in this way, the free base must not be used, because it reduces the quinone to quinol. The hydrochloride of hydroxylamine does not act in this way; in concentrated solutions, however, it produces such a violent reaction that the mass commences to char, and hence dilute solutions must be employed. This reaction has already been explained; in the formation of quinone-oximes from phenol and nitrous acid, we must assume that the former is oxidized to quinone and the latter reduced to hydroxylamine. If we give to it the second of the proposed formulæ, the reaction may be represented by the equation;



$$C_6H_5.OH + ON.OH = C_6H_4\left\langle\begin{matrix} O \\ | \\ N.OH \end{matrix}\right. + H_2O.$$

Quinonoxime is best obtained by the action of nitrosulphonic acid on phenol. The reagent, which Groves and Stenhouse call nitrosyl sulphate, is prepared by warming 200 cc. of nitric acid, of specific gravity 1·3, with arsenic trioxide to 70°, passing the nitrogen trioxide evolved through an empty flask, and then absorbing it in 250 cc. of concentrated sulphuric acid. Sulphuric acid is then added until the solution contains 15 per cent. of nitrogen trioxide. Somewhat more than the theoretical quantity of this is added to a solution of phenol in 30 parts of water. After twenty minutes the separated crystals must be filtered off, because if allowed to stand they are rendered impure by a tar-like mass which is formed.[2] Quinonoxime crystallizes in light brownish green, thin, rhombic tablets, and is more readily soluble in hot water than in cold, forming a green solution. On rapidly cooling it separates out in small, almost colourless, needles, but on slowly cooling in brownish green plates. It dissolves in alkalis forming a brown solution from which it separates on the addition of acids as an almost white, amorphous precipitate. It is also readily soluble in alcohol, ether and acetone, forming green solutions.

In the moist state the crystals rapidly turn brown, and hence it is best dried on a porous earthenware plate. Quinonoxime is thus obtained as a yellowish powder (Goldschmidt); on

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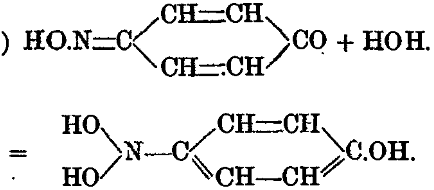
[1] *Ber. Deutsch. Chem. Ges.* vii. 963.

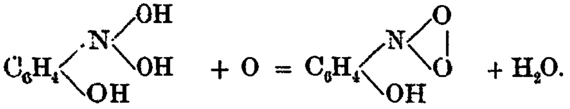
[2] *Journ. Chem. Soc.* 1877, i. 544.

heating to 120°—130° it decomposes with a slight detonation; by dissolving it in phenol and adding a little concentrated sulphuric acid, a dark cherry-red solution is obtained, which on the addition of water and caustic potash is changed into a beautiful blue (p. 176). Hydrochloric acid converts it into chlorophenol. It is oxidized by an alkaline solution of potassium ferricyanide, as well as by nitric acid, into paranitrophenol. As long as it was supposed to be nitrosophenol this reaction was very easily explained, but we must now assume that the quinonoxime first combines with water, and that the compound thus formed is then oxidized;[1]

(1)



(2)



The salts of quinonoxime, which were named *nitrosophenates*, have been examined by ter Meer.[2]

Potassium quinonoximate, $C_6H_4O(NOK)$, is obtained as a beautiful amorphous green precipitate, by mixing an ethereal solution of nitrosophenol with alcoholic potash. It is very readily soluble in water, and crystallizes from acetone or alcohol in thin bluish green tablets; sometimes it is also obtained in red crystals. On heating it detonates.

Sodium quinonoximate, $C_6H_4O(NONa) + 2H_2O$, is a vermilion-coloured amorphous precipitate, which crystallizes from alcohol in beautiful short, red needles, and is readily soluble in water, forming a reddish brown solution.

Silver quinonoximate, $C_6H_4O(NOAg) + H_2O$, is obtained by the addition of silver nitrate to a hot, dilute solution of the sodium salt, in small, dark violet crystals, which under the microscope appear red in transmitted light, and in sunlight show a green reflection.

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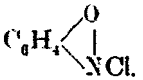
[1] Goldschmidt, *Ber. Deutsch. Chem. Ges.* xvii. 805.

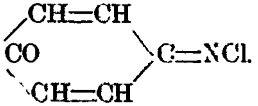
[2] Goldschmidt, *ibid.* ix. 622.

Quinonoxime ethylcarbonate, $C_6H_4O(N.O.CO.OC_2H_5)$, is formed by treating the sodium compound in presence of ether with ethyl chlorocarbonate. It crystallizes in golden-coloured needles melting at 109°, slightly soluble in ether, but readily in alcohol and chloroform.[1]

1011 *Quinone chlorimide*, $C_6H_4O(NCl)$, was obtained by Schmitt and Bennewitz by the action of bleaching powder on a solution of paramidophenol, $C_6H_4(NH_2)OH$, in hydrochloric acid, and was considered to be dichlorazophenol, $C_{12}H_6Cl_2N_2(OH)_2$.[2] Hirsch[3] then showed that it was quinone chlorimide, and gave to it the following constitutional formula:



It is thus quinone in which an oxygen atom is replaced by NCl, and according to the more recent views concerning quinone, its constitution is represented by the following formula:



From this it appears that it stands in close relationship to quinonoxime, from which it is derived by replacement of the hydroxyl by chlorine; it has not, however, been hitherto obtained in this way. Schmitt found that it is also formed by the action of bleaching powder on ethylparamidophenate, $C_6H_4(NH_2)OC_2H_5$.[4]

It is obtained as a crystalline precipitate when a concentrated solution of bleaching powder is added to 100 grms. of a solution of 5 grms. of para-amidophenol hydrochloride. The liquid first assumes a deep violet colour which, on further addition of bleaching powder, becomes gradually paler, until it suddenly changes to yellow when the reaction is complete. The solution is then rendered faintly acid with hydrochloric acid, care being taken to prevent a rise of temperature. The product of the reaction is extracted with ether, the latter distilled off and the residue crystallized from glacial acetic acid (Hirsch).

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[1] Walker, *Ber. Deutsch. Chem. Ges.* xvii. 400.

[2] *Journ. Prakt. Chem.* (2) viii. 1.

[3] *Ber. Deutsch. Chem. Ges.* xiii. 1903.

[4] *Journ. Prakt. Chem.* (2), xix. 315.

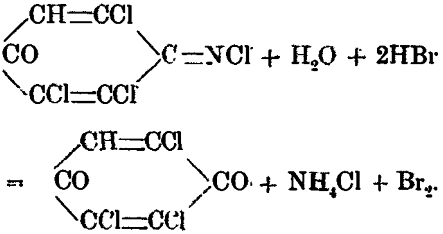
Quinone chlorimide forms golden crystals, which are probably triclinic, melt at 85° and detonate at a higher temperature, but are volatile in steam with partial decomposition. It is scarcely soluble in cold water, but readily in hot water, alcohol and acetic acid. It has a persistent odour, similar to that of quinone, and like this stains the skin a permanent brown. Reducing agents easily reconvert it into paramidophenol, while sulphur dioxide converts it into the sulphonic acids of this. It is converted by strong hydrochloric acid into chlorophenol, and on heating with water to 100° forms ammonium chloride, quinone, and oxidation products of the latter:

$$C_6H_4ONCl + 2H_2O = NH_4Cl + C_6H_4O_2 + O.$$

It dissolves in cold, concentrated sulphuric acid, and in fuming nitric acid without decomposition. On dissolving it in phenol and adding some sulphuric acid, a dark cherry-red coloured solution is obtained, like that produced by quinonoxime, which on addition of water and caustic potash is converted into a splendid blue.[1]

Trichloroquinone chlorimide, $C_6HCl_3O(NCl)$, is obtained in a similar manner to the preceding compound, from trichlorophenol. It is scarcely soluble in cold water, readily in hot, and crystallizes from alcohol in long, yellowish, lustrous prisms, melting at 118°.[2]

Concentrated hydrobromic acid converts it, with separation of bromine, into trichloroquinone.[3]



Quinone dichlorimide, $C_6H_4(NCl)_2$, is obtained by the action of bleaching-powder on a solution of paradiamidobenzene, $C_6H_4(NH_2)_2$, in hydrochloric acid. It is scarcely soluble in cold water, and slightly in boiling water, from which it crystallizes in needles; it is readily dissolved by warm alcohol and acetic acid,

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[1] Schmitt and Andresen, *Journ. Prakt. Chem.* (2), xxiii. 435.
[2] Schmitt and Andresen, *ibid.* (2), xxiv. 426.
[3] *Ibid.* xxviii. 436.

forming solutions which stain the skin brown. On reduction it is reconverted into diamidobenzene.[1]

1012 *Hydroxyquinonoxime* or *mononitrosoresorcinol*, $C_6H_3(OH)O(NOH)$. Bindschedler and Busch first obtained this compound by the action of amyl nitrite on monosodiumresorcinol,[2] and it was then further examined by Fèvre.[3] In order to prepare it, concentrated alcoholic solutions of equal molecules of sodium ethylate and resorcinol are mixed and the calculated quantity of amyl nitrite added, the mixture being kept well agitated. The solid mass which separates out is pulverized and freed from amyl alcohol by washing with water.[4] It crystallizes from dilute alcohol in golden needles, which contain one molecule of water, and on heating become black and decompose without melting.

Its salts are not very characteristic; stannous chloride reduces it to amidoresorcinol, concentrated nitric acid converts it into trinitroresorcinol, and by passing nitrogen trioxide through its ethereal solution dinitroresorcinol is obtained.

It gives colour-reactions with all phenols (p. 177), as well as with amido-compounds. With aniline acetate it forms the compound $C_{18}H_{14}N_2O_2$, which is insoluble in alkalis, and crystallizes from chloroform in small, lustrous steel-blue needles, which dissolve in concentrated hydrochloric acid with a blue, and in sulphuric acid, with a green colour (Fèvre).

Quinonedioxime or *dinitrosoresorcinol*, $C_6H_2O_2(NOH)_2$, is obtained by the action of sodium nitrite on a very dilute solution of resorcinol in acetic acid. After some time the liquid is poured into dilute sulphuric acid, and the compound which separates out purified by crystallization from alcohol.[5] It is more easily obtained by gradually mixing a dilute solution of resorcinol with nitrosyl-sulphate[6] (p. 171).

Dinitrosoresorcinol crystallizes in yellowish brown or green plates which detonate at 115°; it decomposes carbonates, and, to a slight extent, acetates. With the alkali metals it readily forms soluble normal salts and acid ones such as, $C_6H_2O_2(NOH)(NONa)$, which are obtained as slightly soluble, green crystalline powders.

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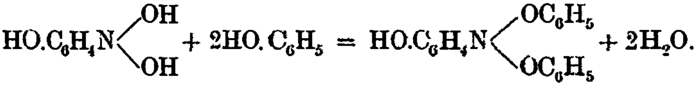
[1] Krause, *Ber. Deutsch. Chem. Ges.* xii. 47; Hirsch, *loc. cit.*
[2] Krause, *Ber. Deutsch. Chem. Ges.* xvii. 1850.
[3] *Ibid.* xvi. 1101.
[4] Walker, *ibid.* xvii. 399.
[5] Fitz, *ibid.* viii. 631.
[6] Stenhouse and Groves, *Journ. Chem. Soc.* xxxvi. 550.

COLOURING-MATTERS FROM QUINONOXIMES AND PHENOLS.

1013 Liebermann observed that a solution of nitrous acid in sulphuric acid gives with different phenols a brown solution, which quickly becomes green and then deep blue. The reagent for the preparation of this colour is obtained by dissolving 5 per cent. of potassium nitrite in concentrated sulphuric acid; the salt is gradually added with continual shaking in order that the nitrous acid may be completely absorbed.

To prepare the phenol colouring-matter, 5 grms. of phenol are mixed with an equal volume of sulphuric acid and 20 cc. of the reagent gradually added, the liquid well agitated, and the temperature not allowed to exceed 40°—50°. After cooling, the solution is poured into a large quantity of cold water, when the colouring-matter separates out as an amorphous, reddish brown powder, which is washed and dried at 130°. It has the composition $C_{18}H_{15}NO_3$, and dissolves in concentrated sulphuric acid and in alkalis with a splendid blue colour.[1] Its formation is explained by the quinonoxime, which is first formed, taking up the elements of water and the compound so obtained uniting with phenol as follows:



$$HO.C_6H_4N\begin{cases}OH\\OH\end{cases} + 2HO.C_6H_5 = HO.C_6H_4N\begin{cases}OC_6H_5\\OC_6H_5\end{cases} + 2H_2O.$$

Together with this compound another body is obtained, which can easily be separated since it is insoluble in ether; it is an oxidation-product, for on allowing the original blue liquid to stand in the air it becomes green, and then only contains the second compound. After precipitation and washing with water, it forms a black mass which dissolves in sulphuric acid with a green, and in alkalis with a brown colour. The latter solution gradually turns violet in the air, but immediately on the addition of a solution of a hypochlorite. The colouring matter dried at 100° has the composition $C_{18}H_{17}NO_5$.[2]

1014 *Azoresorcin*, $C_{12}H_9NO_4$, was discovered by Weselsky, and described as diazo-resorcin, $C_{18}H_{12}N_2O_6$.[3] Since however it is

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[1] *Ber. Deutsch. Chem. Ges.* vii. 247, 1098.

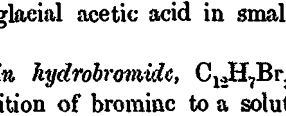
[2] Krämer, *ibid.* xvii. 1875

[3] *Ann. Chem. Pharm.* clxii. 274.

not a diazo-compound, Weselsky and Benedikt decided to call it temporarily "Weselsky's diazoresorcin." Brunner and Krämer, who determined its exact composition, changed the name to azoresorcin, in order to indicate that it only contains one atom of nitrogen in the molecule, and not to make too great a change from the nomenclature which had been in use for twelve years. It would have been better to have given it an entirely new name, since azoresorcin has nothing to do with either the azo-, or diazo-compounds. Azoresorcin[1] is formed by the action of nitrogen trioxide or tetroxide[2] on resorcinol; in order to prepare it Weselsky's reagent is used. This is obtained by saturating well-cooled nitric acid of specific gravity 1·25 with the nitrous gases evolved from starch and nitric acid, 40 to 50 drops of this solution are added to a solution of 4 grms. of resorcinol in 300 cc. of ether. After two days the mother-liquor, containing the two isomeric nitroresorcinols, is poured off from the crystals, which are washed with ether and water, and recrystallized from glacial acetic acid.[3]

Azoresorcin forms small, dark red crystals having a beetle-green lustre, dissolving with difficulty in alcohol with a yellow colour, and readily in alkalis to a splendid violet liquid, which exhibits a blue fluorescence and gives dark violet precipitates with salts of the metals of the earths.

It is formed, like "Liebermann's phenol colour," from nitrosoresorcinol and resorcinol, and has therefore the following constitution:



$$\begin{matrix}HO\\HO\end{matrix}\Big>C_6H_3N\Big<\begin{matrix}O\\O\end{matrix}\Big>C_6H_4.$$

By heating azoresorcin with acetyl chloride, no acetate is obtained, but the compound, $C_6H_3Cl(OH)N(HCl)O_2C_6H_4$, which crystallizes from glacial acetic acid in small, lustrous golden plates, is formed.

Dibromazoresorcin hydrobromide, $C_{12}H_7Br_2NO_4.HBr$, is obtained by the addition of bromine to a solution of azoresorcin in caustic soda, as a brown precipitate, which dissolves in alcohol forming a deep blue solution with a brownish red fluorescence, and remains behind on evaporation as a beetle-green mass.

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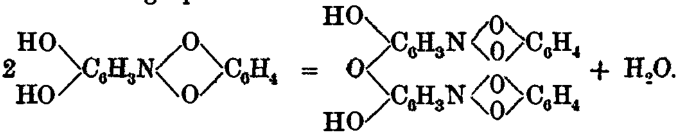
[1] The name azoresorcin is used instead of azoresorcinol to show that it is merely arbitrary and does not express the constitution of the compound.

[2] Weselsky and Benedikt, *Monatsh. Chem.* i. 886.

[3] See also *Monatsh. Chem.* v. 605.

Trinitro-azoresorcin, $C_{12}H_6(NO_2)_3NO_4$, was described by Weselsky as tetrazoresorcin nitrate, $C_{36}H_{12}N_8O_{12}(NO_3)_6$. It is obtained by cautiously warming azoresorcin with ten times its weight of nitric acid of specific gravity 13·7, until an evolution of red vapours commences, when the flame is removed and the solution allowed to stand until a drop of the dark carmine-red liquid gives a brown colouration with ammonia. It is then filtered through glass-wool and the filtrate cooled by ice. Trinitro-azoresorcin separates out in small crystals, with a beetle-green lustre, readily soluble in water and more so in alcohol, forming a beautiful blue liquid; the alcoholic solution decomposes slowly in the cold and rapidly on warming. It dissolves in alkalis with decomposition, forming a brown solution. When heated on platinum foil it detonates (Brunner and Krämer).

1015 *Azoresorufin*, $C_{24}H_{16}N_2O_7$. Weselsky obtained this compound by heating azoresorcin with sulphuric acid to 210°, and named it diazoresorufin, $C_{36}H_{18}N_4O_9$. It is formed according to the following equation:



Brunner and Krämer found that it is also formed when 5 grms. of resorcinol are dissolved in 15 cc. of sulphuric acid, 40 grs. of Liebermann's reagent gradually added, and the splendid blue solution heated to 140°, a violet colour being produced. The liquid is diluted with water, neutralized with carbonate of soda and evaporated. The sodium compound of the azoresorufin is extracted from the residue by alcohol, and forms a solution with a cinnabar-red fluorescence, Glauber's salts and a colouring matter remaining behind. The latter is soluble in water, forming a red solution with a brown fluorescence.

Azoresorufin is also obtained by heating resorcinol with nitroso-resorcinol and sulphuric acid, or by heating the first with nitrobenzene and sulphuric acid to 170°.

It is insoluble in water, slightly soluble in alcohol, and crystallizes from hot hydrochloric acid in small garnet-red prisms. It dissolves in concentrated sulphuric acid with a bluish violet colour; with alkalis, particularly in alcoholic solution, it forms a carmine-red liquid with a splendid cinnabar-red fluorescence. This colour is so intense that azoresorufin may be used as a delicate reagent for alkalis, inasmuch as one drop of a millenormal solution of caustic soda gives the colouration.

Diacetylazorcsorufin, $C_{24}H_{14}N_2O_5(OC_2H_3O)_2$, is obtained by heating azoresorcin with acetic anhydride and anhydrous sodium acetate to 135°; it is a yellowish brown amorphous mass, which on evaporation with hydrochloric acid is coloured beetle-green, the hydrochloride being formed. On heating with alkalis it forms azoresorufin, which is converted by the action of acetic anhydride and sodium acetate into diacetyl azoresorufin ether, $C_{48}H_{28}N_4O_{11}(OC_2H_3O)_2$, crystallizing from glacial acetic acid or benzene in lustrous orange-coloured plates.[1]

If azoresorcin be heated with hydrochloric acid to 100°, the hydrochloride of azoresorufyl chloride, $C_{24}H_{14}N_2O_5Cl_2(HCl)_2$, is formed, crystallizing from an ethereal solution in small red plates with a metallic lustre.

Tetrahydrazoresorufin, $C_{24}H_{20}N_2O_7$. When azoresorcin is warmed with zinc and hydrochloric acid, first a red and then a blue solution is formed; on cooling, dark blue crystals of the hydrochloride, $C_{24}H_{20}N_2O_7(HCl)_2$, having a cupreous lustre, are obtained, which are rapidly converted into azoresorufin by oxidizing agents.

Hydrazoresorufin ether, $C_{48}H_{46}N_4O_{13}$. By the continued action of zinc and hydrochloric acid, the blue solution of the preceding compound is coloured green, and on cooling deposits colourless plates, having the formula $C_{48}H_{46}N_4O_{13}(HCl)_4$, which rapidly oxidize in the air, becoming blue and showing the metallic lustre of sublimed indigo. By rapidly drying the hydrochloride on the water-bath, and dissolving the blue powder thus obtained in alcohol and a few drops of hydrochloric acid, an indigo-blue solution is obtained from which crystals of the composition $C_{43}H_{40}N_4O_{13}(HCl)_3$, resembling potassium permanganate, separate out on cooling. By using acetone instead of alcohol, similar crystals of the composition $C_{48}H_{46}N_4O_{13}(HCl)$ are obtained.

Hexbromazoresorufin hydrobromide, $C_{24}H_{10}Br_6N_2O_7.HBr$, is obtained by the action of bromine on an alkaline solution of azoresorufin as a brownish red, amorphous, precipitate, whose violet alcoholic solution has a splendid bluish red fluorescence.

Another bromine derivative of azoresorufin is the "fluorescent

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[1] Brunner, *Ber. Deutsch. Chem. Ges.* xviii. 580.

resorcinol blue" which is obtained by dissolving azoresorufin in potash, adding bromine and precipitating with hydrochloric acid. The precipitate may be converted into the sodium or ammonium salts, which crystallize in green lustrous needles, slightly soluble in water and absolute alcohol, and more readily in dilute alcohol; the blue solutions possess a splendid red fluorescence. The free colouring matter, obtained by addition of hydrochloric acid, crystallizes from toluene in brown needles; it dyes wool and silk a fast blue with a splendid red fluorescence. By decomposing a dilute, alkaline solution of azoresorcin with bromine, the "non-fluorescent resorcinol blue" is obtained, crystallizing from alcohol in green needles. Its solution is not fluorescent, it dyes wool and silk pure blue, but the colour readily changes on steaming into the reddish blue of the preceding body.[1]

Hexnitro-azoresorufin, $C_{24}H_{10}(NO_2)_6N_2O_7$, is obtained in a similar manner to trinitro-azoresorcin; Weselsky described it as tetrazoresorufin nitrate. It is soluble in alcohol and water with a purple colour, and crystallizes in needles with a beetle-green lustre, which detonate on heating.

Resorcinol blue. When 3 parts of resorcinol are heated with 1 part of sodium nitrite to 130°, an intensely blue mass is formed, an evolution of ammonia accompanied by violent frothing taking place. On dissolving the mass thus obtained in a little water and adding common salt, the sodium compound of the colouring matter is thrown down. This is readily soluble in water, from which it separates out in indistinct crystals, which on drying assume a metallic lustre. Acids precipitate the colouring matter in dark red flocks, which readily dissolve in alcohol, and are reprecipitated by water. It dissolves in concentrated sulphuric acid with a blue colour; its alkaline solution is decolourized by zinc dust, but rapidly becomes blue again in the air.[2] On account of its great similarity to litmus, Traub and Hock, who discovered this colouring matter, named it "lackmoïd."[3]

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[1] Weselsky and Benedikt, *Monatsh. Chem.* v. 605.

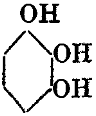
[2] Benedikt and Julius, *Monatsh. Chem.* v. 534.

[3] *Ber. Deutsch. Chem. Ges.* xvii. 2615.

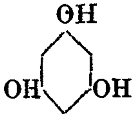
TRIHYDROXYBENZENES.

1016 We are acquainted with the three theoretically possible compounds:

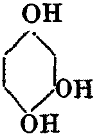
Pyrogallol.



Phloroglucinol.



Hydroxyquinol.



Pyrogallol is obtained by the separation of carbon dioxide from gallic acid, $C_6H_2(OH)_3CO_2H$, which, as will be shown later contains the three hydroxyls in the adjacent position. Hydroxyquinol is obtained from quinol, which, as a para-compound, can only yield one trihydroxybenzene. In phloroglucinol, therefore, the hydroxyls must occupy the symmetrical position, and its general behaviour agrees with this view.

PYROGALLOL, $C_6H_3(OH)_3$.

1017 Scheele, who was the first to obtain pure gallic acid, $C_6H_2(OH)_3CO_2H$, in 1786, showed that on dry distillation it yields a sublimate which, like gallic acid, forms a precipitate with ferrous sulphate. This he thought to be remarkable,[1] and it thus appears that he considered the bodies to be different. Later chemists, nevertheless, considered this sublimate to be pure gallic acid, until Braconnot, in 1831, showed that sublimed is different from ordinary gallic acid,[2] in which conclusion he was confirmed by Pelouze in 1838.[3] It was then called pyrogallic acid, which name is still employed.

In order to prepare pyrogallol in small quantities, gallic acid, dried at 100°, is placed in a tubular retort and heated in an oil bath to 210°—220° but no higher, carbon dioxide being passed through the apparatus; a yield of 30 per cent. is thus obtained. To obtain larger quantities, gallic acid is heated with 2 to 3 parts of water for half an hour in an autoclave to about 210°—220°. A paper ring is placed between the vessel and its cover

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[1] *Opusc.* ii. 226.

[2] *Ann. Chem. Phys.* xlvi. 206.

[3] *Ann. Chem. Phys.* liv. 378.

to allow the carbon dioxide to escape. The solution is boiled with animal charcoal, filtered and concentrated. The pyrogallol which crystallizes out on cooling must be distilled *in vacuo* to render it perfectly pure.[1] The yield is almost theoretical.

Pyrogallol crystallizes in thin plates, or white lustrous needles, melting at 115° and boiling with slight decomposition at 210°. It is readily soluble in water, alcohol and ether, tastes bitter and is poisonous; 2 to 4 grains given to a dog, kill it, producing the same symptoms as phosphorus poisoning.[2] Its alkaline solution rapidly turns brown and black in the air, and then contains carbonic acid, acetic acid, and black humus-like bodies. Oxygen is most rapidly absorbed by it when a solution of 0·25 grms. of pyrogallol in 10 cc. of caustic potash of specific gravity 1·05[3] is used. Its alkaline solution is therefore used in gas analysis (Liebig), but the fact that carbonic oxide is always given off has to be borne in mind,[4] the quantity of this being larger when pure oxygen is absorbed, than when it is absorbed from the air.[5]

Pyrogallol reduces solutions of gold, mercury, and silver. A perfectly pure solution of a ferrous salt produces a white turbidity in a solution of pyrogallol, but if the smallest trace of a ferric salt be present the liquid is coloured blue. Ferric chloride produces a red colour (see pyrogalloquinone). A very delicate reaction of pyrogallol is, that its aqueous solution is coloured brown by nitrous acid: it can hence be employed as a test for the latter compound.[6] Pyrogallol is employed as a developer in photography as it reduces silver salts. Since its price is seven times that of gallic acid, a solution available for dry plate work can be cheaply prepared by heating 10 grms. of gallic acid and 30 grms. of glycerol to 190°—200° as long as carbon dioxide is evolved. The theoretical yield is thus obtained. After cooling, the residue is dissolved in 1 litre of water.[7] Pyrogallol is also employed as a hair dye and for different analytical purposes. It is further made use of in the manufacture of some colouring matters, such as galleïn and coëruleïn.

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[1] De Luynes and Esperandieu, *Ann. Chem. Pharm.* cxxxviii. 60.
[2] Personne, *Zeitschr. Chem.* 1869, 728.
[3] Weyl and Zeitler, *Liebig's Ann.* ccv. 264.
[4] Calvert and Clöez, *Ann. Chem. Pharm.* cxxx. 248.
[5] Boussingault, *ibid.* cxxx. 249.
[6] Schönbein, *Zeitschr. Analyt. Chem.* i. 319.
[7] Thorpe, *Chem. News.* xliii. 109.

1018 *Pyrogallol dimethyl ether*, $C_6H_3(OCH_3)_2OH$, is found in beechwood creasote, and is formed when one molecule of pyrogallol, with two molecules of caustic potash and two molecules of methyl iodide, is dissolved in absolute alcohol and heated to 150°—160°. It crystallizes from boiling water in white prisms, melting at 51°—52° and boiling at 253°. It forms fine, crystalline salts with the alkalis, which do not become black in the air.[1]

The ethyl ethers of pyrogallol are obtained when pyrogallol is heated with caustic potash, ethyl iodide and absolute alcohol to 100°.[2] After evaporating off the alcohol the residue is distilled with steam. The triethyl ether comes over together with some diethyl ether, from which it can be separated by means of caustic potash, in which the first compound is insoluble. In order to separate the residual mono-ethyl ether from any adhering diethyl ether, the latter is extracted with cold benzene.[3]

Pyrogallol mono-ethyl ether, $C_6H_3(OC_2H_5)(OH)_2$, is tolerably soluble in cold, readily in hot water and in alcohol, but very slightly in cold benzene. It crystallizes in needles melting at 95°. Its aqueous solution is coloured bluish violet by ferrous sulphate, and its alkaline solution turns brown in the air.

Pyrogallol diethyl ether, $C_6H_3(OC_2H_5)_2(OH)$, is readily soluble in cold benzene, slightly in cold dilute alcohol, and readily in hot. It forms crystals melting at 79° and boiling at 262°, and its alkaline solution is not coloured brown in the air.

Pyrogallol triethyl ether, $C_6H_3(OC_2H_5)_3$, crystallizes from alcohol in fine needles, melting at 39° and boiling at about 250°.

Triacetopyrogallol, $C_6H_3(OC_2H_3O)_3$, is obtained by the action of acetyl chloride on pyrogallol, and forms crystals which can be sublimed and are almost insoluble in water.[4]

Pyrogalloquinone, $C_{18}H_{16}O_8 = C_6H_4O_2 + 2C_6H_6O_3$, is obtained by the direct combination of pyrogallol with quinone. It dissolves in ammonia with a deep blue colour which soon disappears. According to Wichelhaus it has the formula $C_{18}H_{14}O_8$.[5] (See p. 167).

Purpurogallin, $C_{20}H_{16}O_9$. Girard obtained this compound by oxidizing pyrogallol with silver nitrate or potassium permanganate and sulphuric acid.[6] According to Wichelhaus, who prepared it

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* xi. 333.

[2] Benedikt, *Ber. Deutsch. Chem. Ges.* ix. 125; Hofmann, *ibid.* xi. 798.

[3] Benedikt and Weselsky, *Monatsh. Chem.* ii. 212.

[4] Nachbaur, *Ann. Chem. Pharm.* cvii. 244.

[5] *Ber. Deutsch. Chem. Ges.* v. 846.

[6] *Ibid.* ii. 562.

by the action of chromic acid solution on pyrogallol, it has the formula $C_{18}H_{14}O_9$.[1] This body was then observed by Struve in his investigations on the action of nascent oxygen on pyrogallol. He found that it is formed when a dilute solution of pyrogallol is brought in contact with saliva, malt extract, &c., and allowed to stand in presence of air. It is more readily obtained by using a dilute solution of gum arabic.[2] Loew, who obtained this compound by allowing a solution of pyrogallol and sodium phosphate to stand in the air, believed it to be identical with pyrogalloquinone.[3] Clermont and Chautard, who, like Girard, prepared purpurogallin by the oxidation of pyrogallol with silver nitrate, found the same composition as the latter, and observed that pyrogalloquinone and another body, which has not yet been examined, are also formed. The best method for the preparation of purpurogallin is that of Struve; 10 grms. of pyrogallol are dissolved in 500 cc. of a 10 per cent. solution of gum, and the solution allowed to stand in a large bolt-head for several weeks. By this method a yield amounting to 67 per cent. by weight of the pyrogallol used is obtained.

Purpurogallin crystallizes from alcohol in brown, velvet-like needles, melting at 256°. It forms a sodium salt, $C_{20}H_{12}Na_4O_9$, which crystallizes with difficulty in deliquescent needles, and gives with barium chloride an almost insoluble precipitate of $C_{20}H_{12}Ba_2O_9$. By heating it with acetic anhydride, we obtain the acetate, $C_{20}H_{12}O_9(C_2H_3O)_4$, crystallizing from alcohol in lustrous, brown needles, melting at 186°. By heating with concentrated hydriodic acid, purpurogallin is converted into the hydrocarbon $C_{10}H_{14}$, which boils at 195° and undergoes polymerisation.[4]

Trichloropyrogallol, $C_6Cl_3(OH)_3$, is obtained by passing dry chlorine through a well-cooled mixture of pyrogallol and acetic acid, and crystallizes in fine needles containing 3 molecules of water. On adding baryta water to its ethereal solution a blue colouration is produced.[5]

Tribromopyrogallol, $C_6Br_3(OH)_3$, is formed by triturating a mixture of bromine and pyrogallol, and crystallizes from hot water in lustrous, flat, rhombic needles.[6]

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[1] *Ber. Deutsch. Chem. Ges.* v. 848.

[2] *Ann. Chem. Pharm.* clxiii. 162.

[3] *Journ. Prakt. Chem.* (2), xv. 322.

[4] *Compt. Rend.* xciv. 1189, 1254, 1362.

[5] Webster, *Journ. Chem. Soc.* 1884, i. 205.

[6] Hlasiwetz, *Ann. Chem. Pharm.* cxlii. 250.

Nitropyrogallol, $C_6H_2(NO_2)(OH)_3 + H_2O$, is obtained by passing nitrogen trioxide through a solution of pyrogallol in ten times its quantity of ether until carbon dioxide commences to be evolved. It crystallizes from boiling water in long, thin, brownish-yellow needles or thick rhombic prisms, which become anhydrous at 100°, and melt with decomposition at 205°. Its solution is coloured deep red by lime-water, and green by ferric chloride.

PHLOROGLUCINOL, $C_6H_3(OH)_3 + 2H_2O$.

1019 Hlasiwetz first prepared this body by heating phloretin, $C_{15}H_{14}O_5$, with caustic potash. This substance is thus decomposed into phloretinic acid, $C_6H_4(OH)C_2H_4.CO_2H$, and phloroglucinol, which obtained this name on account of its exceedingly sweet taste.[1] It is also formed from various glucosides, plant-extracts, resins, &c., such as quercetin, maclurin, catechin, kino, gamboge, dragon's blood and others, by fusing them with caustic potash.[2] It is likewise obtained by the action of sodium amalgam or caustic potash on morin,[3] $C_{12}H_8O_6$, which occurs together with maclurin, $C_{13}H_{10}O_6$, in fustic. The latter compound, which is obtained in the impure state as refuse in the preparation of fustic extract, is well adapted for the preparation of phloroglucinol.[4] It is fused with 3 parts of caustic potash and some water until the mass becomes pulpy. After cooling it is dissolved in water, acidified with sulphuric acid, and extracted with ether; on distilling off the latter, the residue is dissolved in water and lead acetate added to precipitate the protocatechuic acid. The solution is then treated with hydrogen sulphide, and the phloroglucinol obtained from the filtrate either by evaporation or by exhaustion with ether (Hlasiwetz and Pfaundler).

It can also be advantageously prepared from resorcinol by fusing this with a tolerably large excess of caustic soda, until the violent evolution of gas, which commences after some time, moderates and the mass has become light chocolate-coloured. The solution is acidified with sulphuric acid, extracted with ether,

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[1] *Ann. Chem. Pharm.* xcvi. 118.

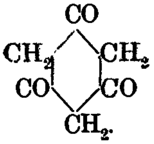
[2] Hlasiwetz, *ibid.* cxii. 98; cxxxiv. 118; cxxxviii. 190; Hlasiwetz and Pfaundler, cxxvii. 357; Hlasiwetz and Barth, cxxxiv. 283; cxxxviii. 68.

[3] *Ibid.* cxliii. 297.

[4] Benedikt, *ibid.* clxxxv. 114.

and the phloroglucinol obtained by evaporation, and recrystallized.[1] According to Tiemann and Will, the adhering resorcinol may be removed by heating the phloroglucinol to 100° and moistening at intervals, the resorcinol being thus sublimed. They also notice the curious facts that ether dissolves phloroglucinol more readily from a neutral than from an acid solution, and that if the solution be saturated with common salt, a large portion of the phloroglucinol separates out.[2] Phloroglucinol is also obtained by fusing benzenetrisulphonic acid with an excess of caustic soda.[3]

Baeyer has recently succeeded in synthesising phloroglucinol;[4] by the action of ethyl malonate, $CH_2(CO.OC_2H_5)_2$, on sodium ethyl malonate he obtained the ethyl ether of phloroglucinol-tricarboxylic acid, $C_6H_3O_3(CO_2.C_2H_5)_3$, which on fusion with caustic potash yields phloroglucinol. From this it would appear that it has the following constitution:



This view is confirmed by the fact that it forms a trioxime, $C_6H_6(N.OH)_3$. On the other hand, phloroglucinol behaves in many reactions as a trihydroxybenzene, and it appears to exist in both forms, one easily changing into the other.[5]

It is readily soluble in water, alcohol, and ether, and crystallizes in small plates or rhombic tablets, which lose their water of crystallization at 100°, and melt at 209°. At a higher temperature it partially sublimes without decomposition. It reduces Fehling's solution; dilute nitric acid converts it into nitrophloroglucinol, while the concentrated acid oxidizes it to oxalic acid. Aqueous ammonia converts it into phloramine, $C_6H_3(OH)_2NH_2$, which will be subsequently described. This reaction is very remarkable, since the other phenols only exchange a hydroxyl group for an amido-group with difficulty. Its aqueous solution is coloured a bluish violet by ferric chloride. As already stated, it is, in presence of hydrochloric acid, a delicate reagent for woody substances, which produce with it a reddish violet

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[1] Barth and Schreder, *Ber. Deutsch. Chem. Ges.* xii. 503.

[2] *Ibid.* xiv. 954.

[3] *Ibid.* xii. 422.

[4] *Ibid.* xviii. 3454; xix. 159.

[5] See also Laar, *ibid.* xviii. 648.

colouration (Vol. III. Pt. II. p. 584). A solution containing 0·01 per cent. of phloroglucinol colours pieces of pine wood, moistened with hydrochloric acid, a distinct red, and even when only 0·001 per cent. is present, the reaction takes place if the wood be allowed to remain in the solution for twenty-four hours. In this way a lignification of the tissue can be recognised in the very earliest stages of vegetable growth. Phloroglucinol is only a weak antiseptic, and, unlike its isomeride pyrogallol, it is not poisonous.[1]

By mixing a very dilute aqueous solution of phloroglucinol and aniline nitrate, or toluidine nitrate, with potassium nitrite, a vermilion-coloured precipitate of azobenzene-phloroglucinol or azotoluene-phloroglucinol,[2] separates out after a short time.

1020 *Phloroglucinol diethyl ether*, $C_6H_3(OC_2H_5)_2OH$, is obtained by saturating an alcoholic solution of phloroglucinol with hydrochloric acid. It crystallizes from hot water in long, lustrous, snow-white crystals, melting at 75°.

Phloroglucinol triethyl ether, $C_6H_3(OC_2H_5)_3$, is obtained when the preceding compound is heated with caustic potash, ethyl iodide, and alcohol. Water precipitates it from its alcoholic solution in fine crystals melting at 43°.[3]

Triacetophloroglucinol, $C_6H_3(OC_2H_3O)_3$, is formed by the action of acetyl chloride on phloroglucinol, and crystallizes from alcohol in small prisms, insoluble in water.[4]

Trichlorophloroglucinol, $C_6Cl_3(OH)_3 + 3H_2O$. When an aqueous solution of phloroglucinol is treated with chlorine, dichloracetic acid is formed, thus affording a proof of its symmetrical structure (p. 181):

$$C_6H_6O_3 + 3H_2O + 6Cl_2 = 3C_2H_2Cl_2O_2 + 6ClH.$$

If, however, the reaction be carried on in absence of water, and if chlorine be passed through a mixture of phloroglucinol and tetrachloromethane surrounded by a freezing mixture, trichlorophloroglucinol is obtained. It is almost insoluble in cold water, crystallizing from warm water or alcohol in fine needles, which lose their water of crystallization over sulphuric acid, melt at 136°, and sublime below this temperature. By the spontaneous evaporation of the alcoholic solution it is obtained in large transparent needles.

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[1] Andreer, *Ber. Deutsch. Chem. Ges.* xvii. Ref. 334.
[2] Weselsky, *ibid.* ix. 216; Weselsky and Benedikt, xii. 226.
[3] Will and Albrecht, *Ann. Chem. Pharm.* xvii. 2107.
[4] Hlasiwetz, *Ibid.* cxix. 201.

By acting on the mixture of phloroglucinol and tetrachloromethane at the ordinary temperature, chlorine substitution-products of acetaldehyde and acetic acid, especially trichloracetic acid, are obtained.[1]

Tribromophloroglucinol, $C_6Br_3(OH)_3 + 3H_2O$, is obtained by the action of bromine water on phloroglucinol, and crystallizes in prisms.[2] Cold nitric acid converts it into tribromodinitropropionic acid:[3]

$$C_6H_3Br_3O_3 + 6NO_2.OH = C_3HBr_3(NO_2)_2O_2 + 3CO_2 + 2NO \\ + N_2O_3 + 4H_2O.$$

By gradually adding 10 parts of bromine to an aqueous solution of 1 part of phloroglucinol, phlorobromine, C_6HBr_9O, is formed, crystallizing from chloroform in lustrous rhombic prisms, melting at 152°. They are not attacked by boiling caustic potash, sodium amalgam or concentrated nitric acid, but dissolve in warm alcohol forming pentabromacetone.[4]

Nitrophloroglucinol, $C_6H_2(NO_2)(OH)_3$, is obtained by dissolving phloroglucinol in warm dilute nitric acid, from which it separates in reddish yellow scales, dissolving in hot water and crystallizing in plates.

Trinitrophloroglucinol, $C_6(NO_2)_3(OH)_3$, is obtained by adding the potassium salt of trinitrosophloroglucinol, which is described below, to a mixture of equal parts of concentrated sulphuric acid, and nitric acid of specific gravity 1·40, in very small quantities at a time with continual agitation. Pieces about as large as a pea kindle on the surface of the liquid and swim about as glowing balls with a hissing noise until they are dissolved. If larger pieces are added, violent explosions may occur.

Trinitrophloroglucinol crystallizes from hot water in yellow hexagonal prisms containing a molecule of water which they lose at 100°. It commences to sublime at 130°, melts at 158°, and explodes when more strongly heated. Like picric acid, it dyes wool and silk, but produces fuller and more beautiful tones. It gives the isopurpuric acid reaction with potassium cyanide, and decomposes carbonates forming three series of explosive salts; of these the most remarkable are:

(1) $C_6(NO_2)_3(OK)_3$ forms orange-red needles, often an inch long, having a diamond-like lustre.

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[1] Webster, *Journ. Chem. Soc.* 1885, i. 423.

[2] Hlasiwetz, *Jahresber.* 1855, 702.

[3] Benedikt, *Ann. Chem. Pharm.* clxxxiv. 255.

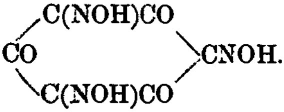
[4] *Ibid.* clxxxix. 165.

(2) $C_6(NO_2)_3(OK)_2OH$ occurs in deep yellow crystals, which have less lustre than those of the normal salt.

(3) $C_6(NO_2)_3OK(OH)_2 + H_2O$ crystallizes in long, very fine, sulphur-yellow needles with a silky lustre.

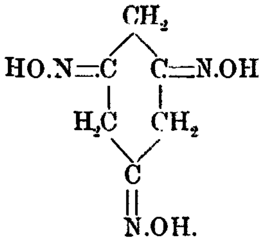
Trinitrosophloroglucinol or *Quinonetrioxime*, $C_6O_3(NOH)_3$. When 10 grms. of phloroglucinol are dissolved in 300 cc. of *water containing 12 grms of acetic anhydride, and a* well-cooled concentrated solution of 16 grams of potassium nitrite is added to this liquid, cooled to 8°—9°, an acid potassium salt of this compound separates out in green crusts. If it be allowed to stand for half an hour and treated with excess of caustic potash and then alcohol, the neutral salt, $C_6(NO)_3(OK)_3$, is precipitated in fine green needles, which are very explosive.

By adding lead acetate to its dilute aqueous solution, a yellow precipitate of the lead salt is obtained, forming, when dry, a cinnamon-brown powder, which explodes on heating with the greatest violence. By decomposing it with dilute sulphuric acid in presence of alcohol and allowing the filtrate to evaporate, trinitrosophloroglucinol is obtained in warty needles.[1] It probably has the following constitution:



According to what has already been said on the constitution of quinonoxime (p. 70), this may also be considered as being derived from benzene, each pair of hydrogen atoms being replaced by the divalent group, —N(OH)—O—.

Phloroglucinoltrioxime, $C_6H_6(NOH)_3$, is obtained by the action of hydroxylamine on phloroglucinol, and forms a sandy powder which is very sparingly soluble in water and alcohol, blackens when heated to 140°, and explodes with a red flame at 155°. It has undoubtedly the following constitution:



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[1] Benedikt, *Ber. Deutsch. Chem. Ges.* xi. 1374.

As already stated, phloroglucinol is also obtained by fusing phenol with caustic soda. According to Gautier the isomeric phenoglucinol, $C_6H_3(OH)_3 + 2H_2O$, is obtained in this way. This crystallizes from water in large prisms melting at 200°·5, possesses a very sweet taste, but only gives a faint violet colour with ferric chloride. According to him, the trihydroxybenzene obtained by fusion of quercitol, is also different from phloroglucinol, and he has named it "querciglucin," $3C_6H_3(OH)_3 + 2H_2O$. It loses its water and melts at 174°, and has a slightly sweet taste. This substance has been found to be simply impure phloroglucinol.[1] Finally he obtained "oenoglucin" by fusing the colouring matter of red wine from Carignane with potash. This substance is very similar to phloroglucinol, but is only coloured a light violet by ferric chloride.[2]

HYDROXYQUINOL, $C_6H_3(OH)_3$.

1021 This compound is obtained, together with diquinol, $C_{12}H_6(OH)_4$, and hexhydroxydiphenyl, $C_{12}H_4(OH)_6$, by fusing quinol with ten times its quantity of caustic soda until the evolution of hydrogen ceases. It crystallizes from ether in microscopic monoclinic plates or tablets, melting at 140°·5. Its aqueous solution becomes rapidly coloured in the air, but more rapidly when a drop of a solution of an alkali is added; it is in this respect as sensitive as a solution of catechol. When applied to the skin it produces a brown colouration, which after some hours turns black. By adding a little ferric chloride to the dilute solution, a brownish green colouration is produced which rapidly disappears; on addition of a little carbonate of soda it becomes a fine dark-blue, and on addition of more, wine-red. Ferrous sulphate gives no colouration, but after the addition of a little carbonate of soda the solution turns violet, and on a further addition becomes intensely blue. Hydroxyquinol dissolves in sulphuric acid forming a green solution, which gradually turns violet, and on heating cherry-red.

When hydroxyquinol undergoes dry distillation, part is volatilized undecomposed, and the remainder is reduced to quinol, the mass becoming charred.[3]

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[1] *Journ. Chem. Soc.* 1886, 232.

[2] *Bull. Soc. Chim.* xxxiii. 583.

[3] Barth and Schreder, *Monatsh. Chem.* iv. 176; v. 489.

Hydroxyquinol triethyl ether, $C_6H_3(OC_2H_5)_3$, is obtained by heating the calcium salt of the corresponding triethoxybenzoic acid, and forms crystals melting at 34°.[1]

Triacetohydroxyquinol, $C_6H_3(OC_2H_3O)_3$, is obtained by heating hydroxyquinol with acetic anhydride and anhydrous sodium acetate. It crystallizes from alcohol in fine, white, bushy needles, melting at 96°·5.

Hydroxyquinhydrone, $C_6H_3(OH)_3 + C_6H_3(O_2)OH$, is formed by the addition of nitric acid to a cold, aqueous solution of hydroxyquinol, in small, dark, grey-blue crystals with a slight surface lustre.

Tribromohydroxyquinone, $C_6Br_3O_2(OH)$, is obtained by triturating a mixture of hydroxyquinol and dry bromine, and separates from chloroform in splendid, orange-red, crystalline granules.

HEXHYDROXYBENZENE, $C_6(OH)_6$.

1022 By the reduction of nitranilic acid (p. 163), diamidotetrahydroxybenzene, $C_6(NH_2)_2(OH)_4$, is formed, as will be afterwards described. By oxidizing the hydrochloride of this compound with strong nitric acid, a colourless solid body is obtained, the analysis of which gave the formula $C_6H_{16}O_{14}$, which at first sight appears very singular. On adding this substance to a solution of stannous chloride, made strongly acid with hydrochloric acid, hexhydroxybenzene separates out after some time in greyish-white needles. It is slightly soluble in cold, more readily in hot water, and is reprecipitated by hydrochloric acid.

It is only slightly soluble in alcohol, ether and benzene, and the solutions turn violet in the air. It reduces silver solution quickly in the cold; on distillation with zinc dust it forms some benzene, together with a solid body, which appears to be diphenyl, $C_{12}H_{10}$.

Hexacetohydroxybenzene, $C_6(OC_2H_3O)_6$, is obtained by heating hexhydroxybenzene with acetic anhydride and sodium acetate. It is a crystalline powder, almost insoluble in alcohol, ether and benzene, and crystallizes from boiling glacial acetic acid in small, beautifully-developed, apparently rhombic prisms, containing acetic acid, which escapes at 150°. It melts at 203°, and on cooling solidifies to a colourless crystalline mass.

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[1] Will and Albrecht, *Ber. Deutsch. Chem. Ges.* xvii. 2108.

Tetrahydroxyquinone, $C_6O_2(OH)_4$.—On decomposing a cold solution of hexhydroxybenzene, which has been saturated while hot with sodium carbonate, the surface is coloured deep yellow, and almost black, stellate needles separate out, having the formula $C_6O_2(OH)_2(ONa)_2$. These crystals have a green metallic lustre, and their formation is hastened by the introduction of air.

The barium salt is a dark red precipitate, which on drying shows a green metallic lustre.

Benzotriquinone, or *triquinoyl*, $C_6O_6 + 8H_2O$.—This is the compound, $C_6H_{16}O_{14}$, mentioned above, which is also obtained by oxidation of the preceding compound, as well as by oxidizing hexhydroxybenzene with nitric acid. It is almost insoluble in cold water and alcohol, and crystallizes from warm dilute nitric acid in colourless, microscopic needles.

Dihydroxybenzodiquinone, or *dihydroxydiquinoyl*, $C_6O_4(OH)_2$, is obtained by warming triquinoyl with aqueous sulphurous acid to 40°—50°, and saturating the yellow solution with carbonate of soda; the sodium salt, $C_6O_4(ONa)_2$, separates out in splendid, lustrous violet needles, which on drying assume a green metallic lustre. Its solution gives a bright vermilion precipitate with barium chloride.

When triquinoyl is heated to 100°, or boiled with water, and caustic potash added to the residue, potassium croconate is obtained:

$$C_6O_6 + H_2O = C_5H_2O_5 + CO_2.$$

This body is also obtained by the action of an excess of caustic potash on tetrahydroxyquinone and dihydroxybenzodiquinone, as well as by boiling diamidotetrahydroxybenzene with caustic potash in presence of air:

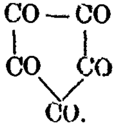
$$C_6H_4O_4(NH_2)_2 + 4KOH + O = C_5K_2O_5 + 2NH_3 \\ + K_2CO_3 + H_2O.$$

This reaction and the properties of hexhydroxybenzene make it appear very probable that the substance in question is identical with the trihydrocarboxylic acid, $C_{10}H_{10}O_{10}$, which Lerch obtained by the action of hydrochloric acid on freshly-prepared potassium carboxide $(COK)_{12}$. By oxidation with nitric acid he obtained oxycarboxylic acid, $C_{10}H_{20}O_{22}$, which is probably triquinoyl, while tetrahydroxyquinone appears to be identical with dihydroxycarboxylic acid, and dihydroxybenzodiquinone with carboxylic acid (Vol. III. Pt. II, p. 634).

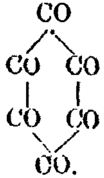
This has been confirmed by further researches, by which it has been shown that rhodizonic acid is identical with carboxylic acid.[1]

Croconic Acid, $C_5O_5H_2$, is dibasic, and forms two series of salts, C_5O_5KNa, $C_5O_5K_2$, C_5O_5KH. The *leuconic acid* obtained by its oxidation has the formula $C_5O_5 + 4H_2O$, and is converted by hydroxylamine into a pentoxime, $C_5(N.OH)_5$, a yellow crystalline body, forming an explosive potassium salt, $C_5H_3K_2N_5O_5$. Leuconic acid, therefore, corresponds to triquinoyl:[2]

Leuconic Acid.



Triquinoyl.



It also follows from the above observations that potassium carboxide has the formula $C_6(OK)_6$, or that this compound is contained in it. Liebig, who prepared it by heating potassium in a current of carbonic oxide, says that the development of the idea that carbonic oxide is a radical has led to most singular and remarkable results.[3] The most remarkable, however, of which Liebig could have no conception, is a direct synthesis of benzene-derivatives from inorganic bodies,[4] which is more simple than any other.

QUERCITOL, $C_6H_7(OH)_5$.

1023 This body was found by Braconnot in the acorn (the fruit of *Quercus racemosa* and *Quercus sessiliflora*), and considered by him to be milk-sugar (*sucre de lait*).[5] Dessaignes found that this "acorn-sugar" (*sucre de glands*) is a distinct compound, and gave to it the name now generally used.[6] He also found it in the rind of the acorn,[7] and the leaves of the fan-palm (*Chamærops humilis*).[8]

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[1] *Ber. Deutsch. Chem. Ges.* xviii. 1833.
[2] Nietzki and Benckiser, *ibid.* xix. 293.
[3] *Ann. Chem. Pharm.* xi. 182.
[4] Nietzki and Benckiser, *Ber. Deutsch. Chem. Ges.* xviii. 449.
[5] *Ann. Chim. Phys.* (3), xxvii. 392.
[6] *Ann. Chem. Pharm.* lxxxi. 103, 251; *Compt. Rend.* xxxiii. 308; 462.
[7] Bottinger, *Liebig's Ann.* ccii. 269.
[8] Hugo Müller, private communication.

In order to prepare it, the cold concentrated extract of the acorn is decomposed with lead acetate to precipitate tannin, colouring matters, &c., and yeast added to the filtrate to remove glucose. The liquid, freed from lead, is evaporated until crystallization commences, and the crystals, to which inorganic salts still adhere, purified by recrystallization from dilute hydrochloric acid.[1]

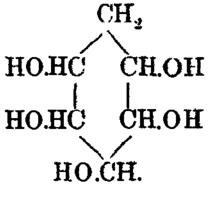
Quercitol has a sweet taste, and is more readily soluble in hot water than in cold, but is insoluble in absolute alcohol or ether. It crystallizes in monoclinic prisms, melting at 225°, and is dextrorotatory.[2] On dry distillation it decomposes with formation of quinol, quinhydrone, and other bodies. These are also formed, together with benzene, phenol, and iodophenol, when it is heated with concentrated hydriodic acid. Volatile iodides are obtained at the same time, which on heating with an excess of hydriodic acid are transformed into hexane (Prunier). Quercitol is also obtained as already stated by the oxidation of quinone (p. 155).

The five hydroxyls of quercitol can be successively replaced by acid radicals. By heating with hydrochloric acid, chlorides are formed, the final product being pentaquercylchloride, $C_6H_7Cl_5$, which crystallizes in needles melting at 102°.

Pentanitroxyquercitol or *nitroquercitol*, $C_6H_7(NO_3)_5$, is obtained by the action of a mixture of concentrated sulphuric and nitric acids, and forms a transparent, resin-like mass, insoluble in water, but readily soluble in alcohol.[3] Various ethereal salts are obtained by heating quercitol with fatty acids or their anhydrides.

Pentacetoquercitol, $C_6H_7(OC_2H_3O)_5$, is obtained by the continued heating of quercitol with acetic anhydride, and is an amorphous mass which is readily soluble in alcohol, slightly in water, and tastes very bitter.[4]

Quercitol probably has the following constitution :—



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[1] Prunier, *Ann. Chim. Phys.* (5), xv. 1.
[2] Berthelot, *Chim. Org.* ii. 218; Prunier, *loc. cit.*
[3] Hofmann, *Ann. Chem. Pharm.* cxc. 282.
[4] For other ethereal salts see Prunier, *loc. cit.*, and Berthelot, *Chim. Org.* and *Ann. Chim. Phys.* (3), liv. 82.

AMIDO-DERIVATIVES OF BENZENE.

AMIDOBENZENE, OR ANILINE, $C_6H_5NH_2$.

1024 By the dry distillation of indigo, Unverdorben in 1826 obtained, together with other products, a peculiar liquid body, which combined with acids to form crystallizable salts, and which he named "crystalline."[1]

Runge, in 1834, found a volatile basic compound in coal-tar oil, which gave an azure-blue colouration with bleaching powder solution, while the solutions of its salts were coloured violet-blue. He accordingly named the new compound "blue-oil" or "kyanol."[2] He also found that it coloured pine-wood and the pith of the elder-tree yellow, and that when a solution of cupric chloride is spread on a porcelain plate heated to 100°, and after it has become dry a drop of kyanol nitrate solution added, a greenish-black spot is obtained.[3]

Fritzsche, in 1840, examined the products which are obtained when indigo is distilled with caustic soda or caustic potash, and found among them a basic oil, which has the formula C_6H_7N, and forms salts which crystallize well. This he named aniline,[4] the word being derived from anil (*nila*, Indian, blue; *anil*, Arabic, the blue), under which designation the Portuguese introduced indigo (*ἰνδικὸν*, *indicum*, the Indian colour), which was known to the Greeks and Romans, into Europe.

In a postscript to this memoir, Erdmann says that aniline is undoubtedly identical with kyanol.

Two years later Zinin found that when an alcoholic solution of nitrobenzide (nitrobenzene) is saturated with ammonia and then treated with sulphuretted hydrogen, an oily, basic liquid, which he named benzidam, is obtained, which forms crystallizable salts and has the formula C_6H_7N.[5] Fritzsche then observed that this substance is simply aniline.

The identity of the three bodies was then experimentally proved by Hofmann,[6] who proposed to name the substance

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[1] *Pogg. Ann.* viii. 397.

[2] *Ibid.* xxxi. 65, 513; xxxii. 331.

[3] Runge was therefore the first to observe the formation of aniline black

[4] *Journ. Prakt. Chem.* xx. 453.

[5] *Ibid.* xxvii. 149.

[6] *Ann. Chem. Pharm.* xlvii. 37.

phenamide, but when aniline was recognized as a compound ammonia this term was altered to phenylamine. Since, however, the aromatic amines differ in many points from those of the fatty bodies, they were called amido-compounds, according to the proposal of Griess, and hence aniline obtained the name amidobenzene (p. 22).

Aniline is not only found in the distillation products of coal,[1] but also in those of bone[2] and peat. In order to prepare it, nitrobenzene is always used. Zinin's method is not generally employed, although it is convenient for the reduction of other nitro-compounds. In the case of nitrobenzene the reaction proceeds as follows:

$$C_6H_5.NO_2 + 3H_2S = C_6H_5.NH_2 + 2H_2O + 3S.$$

Hofmann found that zinc and hydrochloric acid can also be used for the reduction,[3] and Wöhler showed that aniline is obtained when nitrobenzene is treated with caustic soda and arsenic trioxide.[4] In place of the latter grape-sugar may be employed.[5] In the preparation of small quantities it is best to use tin and concentrated hydrochloric acid, or a solution of stannous chloride in hydrochloric acid (Beilstein):

$$C_6H_5.NO_2 + 3SnCl_2 + 6HCl = C_6H_5.NH_2 + 3SnCl_4 + 2H_2O.$$

When all the nitrobenzene has gone into solution, the tin is removed by sulphuretted hydrogen, and the solution of the hydrochloride evaporated to dryness or decomposed by an alkali.

1025 In the manufacture of aniline, iron filings and acetic acid were previously employed as reducing agents according to Béchamp's method. Since 1864 the cheaper hydrochloric acid has been generally used:

$$C_6H_5.NO_2 + 3Fe + 6HCl = C_6H_5.NH_2 + 3FeCl_2 + 2H_2O.$$

The quantity of acetic acid or of hydrochloric acid which is employed is much less than this equation represents. Ferrous chloride in presence of hydrochloric acid acts as a further reducing agent:

$$C_6H_5.NO_2 + 6FeCl_2 + 6HCl = C_6H_5.NH_2 + 3Fe_2Cl_6 + 2H_2O.$$

This reaction goes on as long as free acid is present; this is not long the case, as the aniline which is produced combines to

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[1] Anderson, *Ann. Chem. Pharm.* lxx. 32.

[2] Vohl, *ibid.* cix. 200.

[3] *Ibid.* lv. 200.

[4] *Ibid.* cii. 127.

[5] Vohl, *Jahresb.* 1863, 410.

form the hydrochloride. This, however, in presence of iron and nitrobenzene, behaves exactly like hydrochloric acid, free aniline being formed, which then reacts with the ferric chloride in presence of water, ferric oxide and aniline hydrochloride being produced. According to the theory, therefore, a small amount of acid is sufficient, when enough iron is present, to convert an unlimited amount of nitrobenzene into aniline.

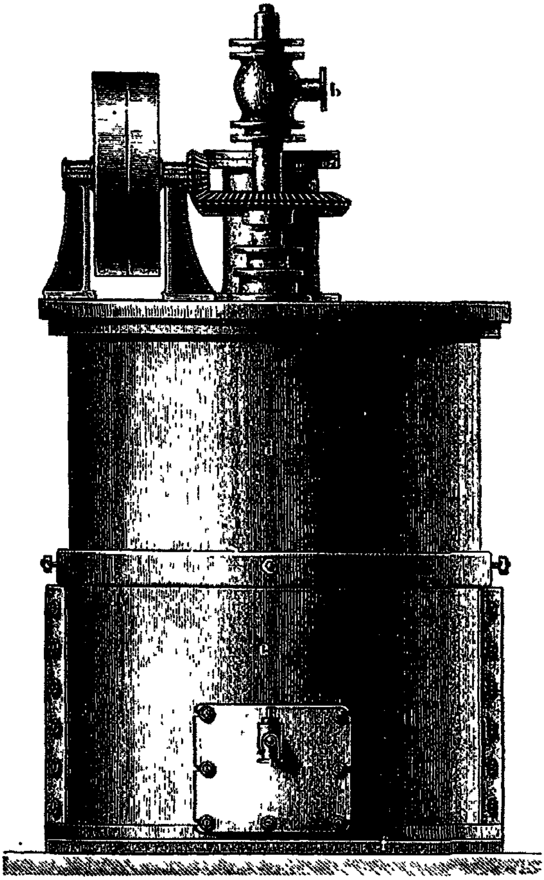

FIG. 11.

The cast-iron apparatus which is generally employed is shown in Fig. 11. It consists of three parts, the lower half being made in two pieces, so that that which is first destroyed by the acid can be easily renewed. In the cover are the necessary openings for the agitator and the condenser, and a manhole for the introduction of the materials, closed by a wooden stopper. In the bottom is an opening through which the iron residues can be removed.

40 parts of water, 25 parts of finely-divided cast-iron filings, and 8 to 10 parts of hydrochloric acid are placed in the vessel, and 100 parts of nitrobenzene (generally 500 kilos) allowed to flow in, the agitator being kept in motion. In order to start the reaction, steam is blown through, and this is kept up during the gradual addition of 75 parts of damp iron filings, which are added as soon as the first violent reaction has ceased, the mixture not being allowed to get cool. If the filings are added too quickly the reaction becomes so violent that some of the aniline is reduced to benzene and ammonia. Finally, from 10 to 20 parts of dry filings are added. Any nitrobenzene which is volatilized during the operation is condensed in a vertical cooler and flows back into the vessel. If all the nitrobenzene has been reduced, the residue consists of aniline, its hydrochloride, and ferric oxide. Milk of lime, or sifted slaked lime, is then added, and the aniline distilled off in a current of high-pressure steam blown through the hollow agitator. The distillate separates into two layers; the lower is aniline, the upper is an aqueous solution of aniline containing 2 to 3 per cent. of the oil, and is used to provide the steam for the next operation. The aniline is then purified by distillation from iron vessels. The iron residues are sent to the blast furnaces.

According to Laurent, small quantities of aniline are formed by heating ammonium phenate to 300° for some time.[1] Berthelot, who repeated this experiment, did not obtain a trace even at 360°;[2] it is obtained, however, together with diphenylamine, by heating phenol with sal-ammoniac and fuming hydrochloric acid to 310°,[3] and also by the continued heating of phenol with ammoniacal zinc chloride to 280°—300°,[4] phenyl ether being formed at the same time.

When pure benzene is used in the preparation of aniline, the aniline obtained is likewise pure, but this is not the case with the "pure" aniline of commerce. In order to obtain perfectly pure aniline from this, it is converted by continued boiling with glacial

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[1] *Compt. Rend.* xvii. 1366.

[2] *Bull. Soc. Chim.* xiii. 314.

[3] Bardy and Dusart, *Compt. Rend.* lxxiv. 188.

[4] Merz and Weith, *Ber. Deutsch. Chem. Ges.* xiii. 1299.

acetic acid into acetanilide, $C_6H_5.NH(C_2H_3O)$ (p. 210), which is purified by distillation, washing with carbon disulphide and recrystallization from hot water until its melting-point reaches 112°, and is then decomposed by caustic soda (Beilstein).

1026 *Properties.*—Aniline is a colourless liquid possessing a peculiar and characteristic odour, and boiling under the normal pressure at 183°·7.[1] It has at 0° a specific gravity of 1·038, and solidifies at a low temperature to a crystalline mass, melting at −8°. Aniline which is not perfectly pure remains liquid even at −20°.[2] On exposure to light and air it becomes brown, and the more impure it is the more rapidly does this colouration take place. It is tolerably soluble in water, 100 parts of the solution containing at the ordinary temperature about 3 parts of aniline; the solubility increases with the temperature. Water also dissolves in aniline, so that 100 parts of aniline dissolve 5 parts of water at the ordinary temperature, and somewhat more at higher temperatures.[3]

It is miscible with alcohol, ether, and benzene in every proportion. The aqueous solution neither colours red litmus paper blue, nor turns turmeric paper brown, but changes the violet colour of the dahlia to green. Although it has such a weak alkaline reaction it precipitates the salts of zinc, aluminium, and iron, and decomposes ammonium salts on heating.

Runge long ago pointed out that an aqueous solution of aniline is coloured blue by a hypochlorite, or if the aniline be not quite pure, bluish violet, the colour of the solution quickly changing to brown. Very dilute solutions either give no colouration or only a very faint one, but on the addition of a few drops of a very dilute solution of ammonium hydrosulphide the liquid becomes rose-red coloured. The limit of this reaction is 1 part of aniline in 250,000 parts of water.[4]

When aniline, or one of its salts, is mixed with concentrated sulphuric acid and a drop of a solution of potassium bichromate added, a pure blue colouration is obtained which soon disappears.[5]

Aniline coagulates albumen and acts as a powerful poison, its action, according to Letheby and Turnbull, being chiefly on the nervous system. According to Grandhomme the first symptom

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[1] Thorpe, *Journ. Chem. Soc.* 1880, i. 221.
[2] Lucius and Hofmann, *Ber. Deutsch. Chem. Ges.* v. 154.
[3] Alexejew, *ibid.* x. 709.
[4] Jacquemin, *ibid.* ix. 1433.
[5] Beissenhirtz, *Ann. Chem. Pharm.* lxxxvii. 376.

observed in slight cases of poisoning, caused by inhaling the vapour, is a blue colour on the edge of the lips, accompanied by a state of mild inebriation; the gait becomes reeling, the speech thick, the head affected, and the face pale, while the appetite fails completely. In such cases aperients, such as Epsom salt, Carlsbad salt, &c. are administered; the use of alcohol aggravates the symptoms. In more severe cases, such as arise, for example, from saturation of the clothes with aniline, the lips become dark blue or even black, and the vertigo so violent that the patient falls. In such cases a stimulus in the form of a cold shower, internal application of ether, &c. must be applied.[1]

Aniline is chiefly used in the colour industry. In the laboratory it is frequently employed as a solvent, since it dissolves many substances—*e.g.* indigo-blue—which are insoluble in the ordinary reagents.

SALTS OF ANILINE.

1027 Although its basic properties are feeble, aniline combines with acids, forming well-crystallizable salts. Hence Unverdorben, as has been already remarked, gave to it the name of crystalline. The salts of aniline have been carefully examined, but we shall here only refer to those which have received technical applications, or are specially characteristic.

Aniline hydrochloride, $C_6H_7N.ClH$, is readily soluble in water, and crystallizes in needles or large plates, which melt at 192°, and sublime unchanged. It is prepared on the large scale, and generally called "aniline salt"; the platinum chloride, $(C_6H_7N.HCl)_2PtCl_4$, crystallizes from hot water in yellow needles.

Aniline sulphate, $(C_6H_7N)_2SO_4H_2$, forms a crystalline powder, readily soluble in water, slightly so in alcohol, and insoluble in ether. This last property is taken advantage of in the separation of aniline from methylaniline.

Aniline nitrate, $C_6H_7N.NO_3H$, crystallizes in large rhombic prisms or needles, which decompose at 190° with formation of nitraniline and other products (Béchamp).

Aniline oxalate, $(C_6H_7N)_2C_2O_4H_2$, is very slightly soluble in cold water, and crystallizes from a hot solution in fine triclinic prisms; it is slightly soluble in alcohol, and insoluble in ether.

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[1] Grandhomme, *loc. cit.*

Aniline phenate, $C_6H_5.NH_2.C_6H_6O$, is formed by heating a mixture of aniline and phenol to boiling for some time, or more slowly when the mixture is allowed to stand in the cold. It forms lustrous tablets, which, after recrystallization from petroleum spirit, melt at 31° and boil at 181°. Its smell resembles that of phenol, but is weaker; it does not attack the skin like the latter.[1]

Aniline, like ammonia, combines with many salts, *e.g.* metallic chlorides, and also with trinitrobenzene. By mixing the warm alcoholic solutions of these, the compound $C_6H_7N.C_6H_3(NO_2)_3$, separates out in orange-red needles, crystallizing from benzene in splendid lustrous plates, which melt at 123°—124° and rapidly give off aniline in the air.[2]

SECONDARY AND TERTIARY ANILINES.

1028 *Methylaniline*, $C_6H_5N(CH_3)H$, is obtained, together with dimethylaniline, by the action of methyl iodide, methyl bromide, or methyl chloride, on aniline,[3] as well as when the latter is heated with methyl nitrate,[4] or when its hydrochloride or hydriodide is heated with methyl alcohol:[5]

$$C_6H_5.NH_2.HCl + CH_3.OH = C_6H_5.N(CH_3)H.HCl + H_2O.$$
$$C_6H_5.NH_2.HCl + 2CH_3.OH = C_6H_5.N(CH_3)_2HCl + 2H_2O.$$

In all cases dimethylaniline is preferably formed, and therefore a portion of the aniline remains unattacked. In order to separate the three bases, dilute sulphuric acid is added as long as aniline sulphate separates out. After the sulphuric acid solution and the free bases have been separated by pressing through a linen cloth, caustic soda is added, and the mixture which separates out dried and treated with acetyl chloride until no further heating takes place; it is then poured into hot water. On cooling, methylacetanilide, $C_6H_5.N(CH_3)C_2H_3O$, separates out in fine, long needles, dimethylaniline hydrochloride remaining in solution. The former is then decomposed by boiling

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[1] Dale and Schorlemmer, *Liebig's Ann.* ccxvii. 387; G. Dyson, *Journ. Chem. Soc.* 1883, i. 466.

[2] Hepp, *Ann. Chem. Pharm.* ccxv. 356.

[3] Hofmann, *ibid.* lxxiv. 150; *Ber. Deutsch. Chem. Ges.* x. 588, 591.

[4] Bardy, *Dingler's Polyt. Journ.* ccxxxiv. 233.

[5] Poisrier and Chappot, *Bull. Soc. Chim.* ii. (6), 502; Reinhardt and Staedel, *Ber. Deutsch. Chem. Ges.* xvi. 29.

with hydrochloric acid (Hofmann). The moderately concentrated solution of the hydrochlorides of the three bases may also be treated with sodium nitrite in the cold, when diazobenzene chloride and nitrosodimethylamine hydrochloride remain in solution, while nitrosomethylaniline, $C_6H_5.N(CH_3)NO$, separates out as an oil, which is extracted with ether and converted into methylaniline by treatment with tin and hydrochloric acid.[1] Pure methylaniline is also obtained by the action of methyl iodide on sodium acetanilide, $C_6H_5N(C_2H_3O)Na$, and the decomposition of the compound thus obtained by caustic potash.[2]

Methylaniline is a liquid resembling aniline, boiling at 192°, and giving no colouration with bleaching powder solution.

Nitrosomethylaniline, $C_6H_5N(CH_3)NO$, is a light yellow oil possessing an aromatic odour. It is not volatile in steam.[3]

1029 *Dimethylaniline*, $C_6H_5.N(CH_3)_2$, is easily obtained pure by heating trimethylphenylammonium iodide[4] in a current of hydrochloric acid, as well as by the dry distillation of its hydroxide. It forms with trinitrobenzene the compound $C_6H_5.N(CH_3)_2,C_6H_3(NO_2)_3$, which crystallizes in fine, lustrous, dark violet needles (Hepp). It is a colourless liquid, boiling at 192°, and solidifying at 0·5°.

It is manufactured on the large scale, and employed for making colours, but the material used for this purpose, as already explained, is not the pure compound, but contains more or less methylaniline, and sometimes aniline. It was first prepared with methyl iodide, which is still used in the colour industry for other purposes, but when the price of iodine rose methyl nitrate was employed as a substitute. By the use of this very explosive substance, however, many fatal accidents were caused, and commercial "methylaniline" was then prepared from aniline hydrochloride and wood-spirit—a method which is still employed. The mixture is heated for some hours in an autoclave (Figs. 12 and 13) to 250°—280°, a mixture of 100 parts of aniline hydrochloride with 50 to 80 parts of methyl alcohol, or 40 parts of aniline hydrochloride, 30 parts of aniline, and 45 parts of methyl alcohol being used. The latter must be pure and quite free from acetone, because this not only diminishes the yield of dimethylaniline, but yields a product which is of little value for the preparation of methyl-violet.[5]

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[1] Nölting and Boasson, *Ber. Deutsch. Chem. Ges.* x. 795.

[2] Hepp, *ibid.* 327.

[3] Fischer, *Liebig's Ann.* cxc. 151.

[4] Merril, *Journ. Prakt. Chem.* (2), xvii. 286.

[5] Krämer and Grodzky, *Ber. Deutsch. Chem. Ges.* xiii. 1006.

In addition to methylaniline and dimethylaniline, the product contains higher boiling bases, such as dimethyltoluidine, $C_6H_4(CH_3)N(CH_3)_2$, dimethylxylidine, $C_6H_3(CH_3)_2N(CH_3)_2$, etc., which are obtained by the entrance of methyl into the benzene nucleus.[1] The portion boiling between 198°—205° forms the technical methylaniline.

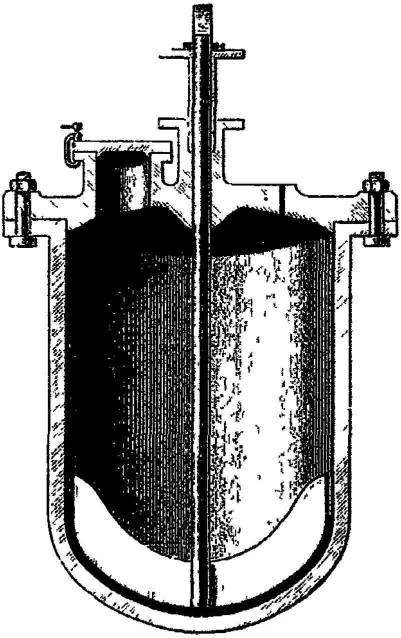

Fig. 12.

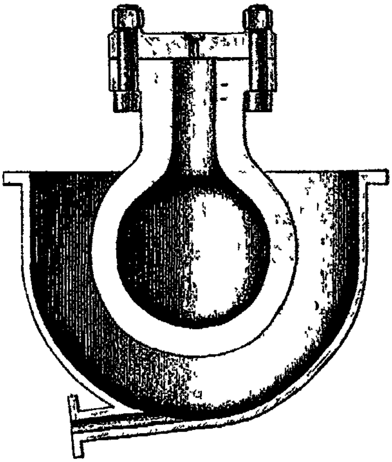

Fig 13.

As methyl chloride is now prepared on the large scale it is used in the manufacture of "methylaniline." A mixture of caustic soda, or milk of lime, and aniline is heated to 100°, and a stream of methyl chloride passed in, the mixture being well agitated (Fig. 14). The proportions of the materials correspond to the following equation:

$$C_6H_5.NH_2 + 2NaOH + 2CH_3Cl = 2NaCl + 2H_2O + C_6H_5.N(CH_3)_2.$$

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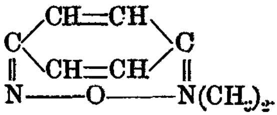
[1] Hofmann and Martius, *Ber. Deutsch. Chem. Ges.* iv. 742; vi. 345.

The pressure must not exceed six atmospheres. The methylaniline is then driven over with steam, and contains about 5 per cent. of monomethylaniline, but no other by-products.

Trimethylphenylammonium iodide, $(CH_3)_3C_6H_5.NI$, is a crystalline body which is formed by a violent reaction when methyl iodide and dimethylaniline are brought together. The hydroxide, obtained by means of silver oxide, is crystalline and very corrosive, and tastes very bitter. It is very deliquescent, but its salts crystallize well, the picrate being very slightly soluble in water.[1]

Paranitrosodimethylaniline, $C_6H_4(NO)N(CH_3)_2$, is obtained by the action of amyl nitrite, or sodium nitrate, on dimethylaniline hydrochloride.[2] It is prepared on the large scale as follows: 10 parts of dimethylaniline are dissolved in 50 parts of concentrated hydrochloric acid and 200 parts of water, and the cold solution gradually mixed with a solution of 5·7 parts of sodium nitrite in 200 parts of water. The hydrochloride is thus obtained, crystallizing in small sulphur-yellow needles. By decomposition with potassium carbonate the free base is obtained, which crystallizes from ether in large green plates. On boiling with caustic potash it splits up completely into dimethylaniline and nitrosophenol, or quinonoxime, $C_6H_4O(NOH)$.

It has therefore the following constitution:



The foregoing decomposition is especially adapted for the preparation of pure dimethylaniline;[3] nitrosodimethylaniline is also employed in the manufacture of colouring matters, such as methylene blue.

		Boiling-point.
Ethylaniline,	$C_6H_5N(C_2H_5)H$.	. 204°
Ethylmethylaniline,	$C_6H_5.N(C_2H_5)(CH_3)$	. 201°
Diethylaniline,	$C_6H_5.N(C_2H_5)_2$ . .	. 213°·5.

Hofmann has prepared several aniline derivatives containing other alcohol radicals.[4]

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[1] Lauth, *Bull. Soc. Chim.* vii. 448.

[2] Baeyer and Caro, *Ber. Deutsch. Chem. Ges.* vii. 963; Schraube, *ibid.* viii. 616; Wurster, *ibid.* xii. 523; Meldola, *Journ. Chem. Soc.* 1881, i. 37.

[3] Baeyer and Caro, *Ber. Deutsch. Chem. Ges.* vii. 963.

[4] *Ann. Chem. Pharm.* lxxiv.

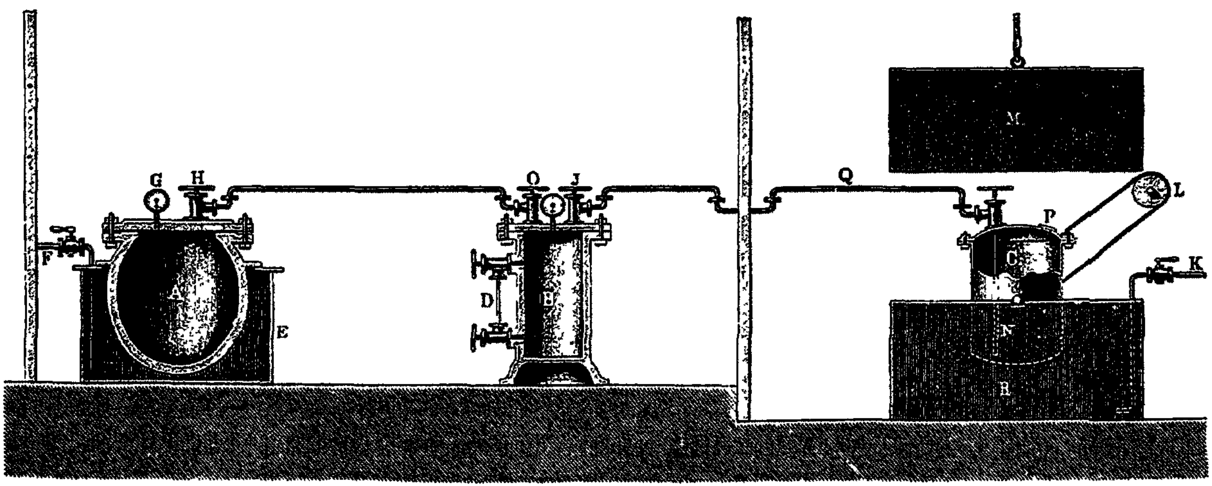
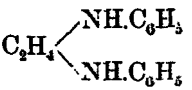


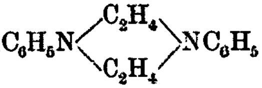
FIG. 14.

A. Autoclave for the preparation of the methyl chloride, with manometer G. and tap H; it is placed in a steam chest E, which is heated by the pipe F. B. Receiver, in which the methyl chloride is condensed by its own pressure, with manometer, gauge, D, and taps O and J. C. Autoclave in which the methylation takes place; it is placed in a water bath, R, which is heated by steam from K. Q N. Delivery tube. P. Screw valve by which the pressure can be lessened. L. Shaft for moving the agitator. M. Lid to cover the autoclave during the operation.

By the action of ethylene bromide on aniline he obtained the following compounds:[1]

Melting-point.

Ethylene-aniline,

$C_2H_4\langle{NH.C_6H_5 \atop NH.C_6H_5}$
small lustrous plates 63°

Diethylene-aniline,

$C_6H_5N\langle{C_2H_4 \atop C_2H_4}\rangle NC_6H_5$
needles . . 157°

Hydroxyethylaniline, $C_6H_5.NH.C_2H_4.OH$, is obtained by warming aniline with ethylene oxide, and is an oily liquid, which boils at about 280°, and gives a green colouration with bleaching-powder solution. Its salts are very soluble and crystallize with difficulty.[2]

Hydroxyethylmethylaniline or *methylphenylethylalkine*, $C_6H_5N(CH_3)C_2H_4OH$, is obtained by the continued heating of methylaniline with ethylene chlorhydrin. It is a liquid possessing a weak smell similar to that of aniline, and distilling under diminished pressure without decomposition. On continued standing in the air it is converted into a fine, blue, thick, syrupy liquid, which dissolves in water and still more readily in alcohol. Its salts are readily soluble and very deliquescent.[3]

Phenyltaurine, $C_6H_5.NH.C_2H_4.SO_3H$, is obtained when the aniline salt of chlorisethionic acid, $C_2H_4Cl.SO_3H$ (Vol. III. Part II. p. 55), is heated with aniline. It crystallizes from hot water in fine thin plates which have a silky lustre and an acid re action and taste. It gives an intense violet colouration with bleaching-powder solution, and on warming its solution with ferric chloride it is coloured green and then gradually indigo-blue.[4]

1030 *Phenylaniline* or *diphenylamine*, $(C_6H_5)_2NH$.—Hofmann first obtained this compound by the dry distillation of aniline blue,[5] and then of aniline and related bodies. It is more simply obtained by heating aniline hydrochloride with aniline:[6]

$$C_6H_5.NH_2 + C_6H_5.NH_2.ClH = (C_6H_5)_2NH.ClH + NH_3.$$

It is prepared in this way on the large scale, by heating 6 parts aniline and 7 parts aniline hydrochloride under a pressure of four to five atmospheres, and at a temperature of 250° for twenty-four

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[1] *Jahresb. Chem.* 1858, 352; 1859, 388; Gretillat, *ibid.* 1873, 698; Morley, *Ber. Deutsch. Chem. Ges.* xii. 1794.

[2] Demole, *Ann. Chem. Pharm.* clxxiii. 126.

[3] Laun, *Ber. Deutsch. Chem. Ges.* xvii. 675.

[4] James, *Journ. Chem. Soc.* 1885, i. 367.

[5] *Ann. Chem. Pharm.* cxxxii. 160.

[6] De Laire, Girard and Chapoteaut, *ibid.* cxl. 344.

hours. From time to time the ammonia formed must be allowed to escape to prevent a transformation of the diphenylamine into aniline. The product is treated with warm hydrochloric acid, and then a large quantity of water is added to dissolve the aniline hydrochloride. Free diphenylamine separates out, and may be purified by distillation.

It is almost insoluble in water, readily soluble in alcohol and ether, and crystallizes in small monoclinic plates, which have an agreeable odour of flowers, and melt at 54°. It boils at 310°, and is a weak base, its salts being decomposed by water. A deep blue colouration is produced by dissolving it in hydrochloric acid and adding nitric acid drop by drop; this also takes place when its solution in pure sulphuric acid is mixed with sulphuric acid containing nitrous acid, and for this reason it is employed as a test for nitrous acid.[1]

Of its numerous substitution products only the following will be mentioned here:

Hexnitrodiphenylamine or *dipicrylamine*, $(C_6H_2(NO_2)_3)_2NH.$, is obtained by the action of nitric acid on diphenylamine and methyldiphenylamine.[2] It is almost insoluble in water, but dissolves somewhat more readily in alcohol, and crystallizes from hot glacial acetic acid in light yellow prisms, melting at 238°. The hydrogen of the imido-group can be replaced by metals; the ammonium salt, $C_{12}H_4(NO_2)_6N(NH_4)$, occurs in commerce under the name *Aurantia;* it forms reddish-brown crystals, and dyes wool and silk a beautiful orange. Goods dyed with this colouring matter produce an irritation of the skin and exanthema in certain individuals, while on others even concentrated solutions produce no effect. Martius has never observed these poisonous effects, and considers that they arise from an impurity.[3]

Methyldiphenylamine, $(C_6H_5)_2NCH_3$, is obtained when diphenylamine is heated with methyl iodide, as well as by the action of wood-spirit on diphenylamine at 250°—300°.[4] On the large scale it is prepared by heating a mixture of 100 parts of diphenylamine, 68 parts of hydrochloric acid of specific gravity 1·17, and 24 parts of methyl alcohol for about ten hours, under a pressure of fifteen atmospheres, to 200°—250°.

The base is separated from the product by caustic soda, distilled, and shaken with double its volume of concentrated hydro-

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[1] E. Kopp, *Ber. Deutsch. Chem. Ges.* v. 284.

[2] Gnehm, *ibid.* vii. 1399; ix. 1245; Mertens, xi. 845.

[3] *Ber. Deutsch. Chem. Ges.* ix. 1247.

[4] Bardy, *ibid.* iii. 833.

chloric acid, when the diphenylamine hydrochloride separates out in the solid form, while the salt of the methyl compound remains liquid, and by treatment with a large quantity of water is decomposed.[1]

Methyldiphenylamine is a liquid boiling at 282°. Oxidizing agents give various colour reactions with it; with dilute sulphuric acid a solution is obtained which is very similar to that of potassium permanganate. It is employed in the preparation of blue colouring matters.

Triphenylamine, $(C_6H_5)_3N$.—Potassium dissolves in aniline with elimination of hydrogen, and formation of the compounds, $C_6H_5.NHK$ and $C_6H_5.NK_2$, inasmuch as by the action of bromobenzene a mixture of diphenylamine and triphenylamine is obtained. Fused diphenylamine likewise dissolves potassium, the product thus obtained yielding triphenylamine when treated with bromobenzene. It crystallizes from ether in splendid, vitreous, monoclinic pyramids, melting at 127°. Its solution in glacial acetic acid is coloured green by a little nitric acid, but violet, and then blue by sulphuric acid.[2] It does not combine with acids, and forms no compound with picric acid.

Parahydroxydiphenylamine, $C_6H_5.NH.C_6H_4OH$, is obtained by heating quinol with aniline and calcium chloride to 250° for ten hours. It is scarcely soluble in cold, slightly soluble in hot water and petroleum spirit, but readily dissolves in alcohol and benzene, from which it crystallizes in small plates, melting at 70°, and solidifying to a scaly mass; it boils above 340° without decomposition. As it is at the same time a phenol and an amido-base it forms compounds with bases as well as with acids.

By heating it with methyl iodide and caustic potash, the methyl ether of methylhydroxydiphenylamine, $C_6H_5(NCH_3)C_6H_4.OCH_3$, is obtained as a yellow oily liquid, boiling at 313°, and smelling like the violet or geranium.

Metahydroxydiphenylamine is obtained in an analogous manner to the para-compound from resorcinol, and crystallizes in small plates having a pearly lustre, and melting at 81°·5.

Both compounds are reduced to diphenylamine by heating with zinc dust, while by continued heating with aniline, calcium chloride, and zinc chloride, they are converted into diphenyldiamidobenzenes, $C_6H_4(NHC_6H_5)_2$, which will be subsequently described.[3]

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[1] Girard, *Bull. Soc. Chim.* xxiii. 2.

[2] Merz and Weith, *Ber. Deutsch. Chem. Ges.* vi. 1514.

[3] Calm, *ibid.* xvi. 2786; Calm and Philip, *ibid.* xvii. 2431.

ANILIDES.

1031 These bodies are obtained by replacing the hydrogen of the amido-group by acid radicals. They are formed by the action of aniline on the ethers, anhydrides, and chlorides of the acids, and also by heating salts of aniline. If more than one hydrogen atom in aniline be replaced by halogens or nitroxyls, and its basicity thus weakened, or entirely destroyed, no anilide is formed on heating with a strong acid, such as acetic acid, and even acetic anhydride has often no action. An anilide is, however, nearly always obtained by heating with an acid chloride in a sealed tube.

When aniline is treated with an acid chloride, aniline hydrochloride is formed, and, being a solid, readily incloses some free aniline, thus rendering the action of the chloride incomplete. It is therefore better, especially in the preparation of acetyl derivatives, to dissolve the aniline, or substituted aniline, in a molecule of the acid, and then to add a molecule of the chloride.

The anilides are decomposed by boiling with caustic soda into the acid and aniline. In the case of the higher substituted anilides it is often better to effect the decomposition by heating with alcoholic ammonia, or hydrochloric acid in a sealed tube. It is, however, more convenient to heat with concentrated sulphuric acid to 100°, almost all anilides being in this way readily decomposed. The acid is then diluted with water and neutralized with an alkali, the substituted aniline being extracted with ether, chloroform, &c., or obtained by distillation.

The anilides are generally slightly soluble in cold water, crystallize well, and are, by reason of their chemical indifference and stability, peculiarly adapted for the preparation of substituted anilines, which cannot be obtained by the direct action of halogens or nitric acid, since these act too violently upon aniline. Acetanilide is generally employed in the preparation of substitution products of aniline.

Formanilide, $C_6H_5.N(CHO)H$, was obtained by Gerhardt, together with oxanilide, aniline, carbon dioxide and water, by heating normal aniline oxalate.[2] According to Hofmann, the

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[1] Beilstein, *Org. Chem.* 891.

[2] *Ann. Chem. Pharm.* lx. 310.

chief product is oxanilide, but when acid aniline oxalate is rapidly distilled, formanilide is almost exclusively formed:

$$C_6H_5.NH_2 + C_2H_2O_4 = C_6H_5.N(CHO)H + CO_2 + H_2O.$$

At the same time by-products are obtained in small quantity.[1] Pure formanilide is easily obtained when ethyl formate is digested with aniline.[2]

Formanilide is tolerably soluble in cold, and somewhat more readily in hot water, and crystallizes on spontaneous evaporation of its solution in long, flat, four-sided prisms, melting at 46°.

Diphenylformamide, $(C_6H_5)_2N(CHO)$, is obtained as a by-product in the preparation of diphenylamine-blue, which is formed by heating diphenylamine with oxalic acid. It is also obtained from formic acid and diphenylamine. It is insoluble in water, and crystallizes from alcohol in splendid orthorhombic crystals, which melt at 73°—74°.[3]

Thioformanilide, $C_6H_5.N(CHS)H$, is obtained by the direct combination of sulphuretted hydrogen with phenyl carbamine,[4] as well as by the action of phosphorus pentasulphide on formanilide.[5] It crystallizes from boiling water in long white needles, which melt at 137°·5, and have an intensely bitter taste.

1032 *Acetanilide* or *phenylacetamide*, $C_6H_5.N(C_2H_3O)H$.—Gerhardt prepared this substance by the action of acetyl chloride or acetic anhydride on aniline.[6] In order to obtain it, aniline is boiled with glacial acetic acid for one or two days, and the acetanilide isolated from the product by fractional distillation.[7] It can be further purified by recrystallization from benzene. It is moderately soluble in ether and alcohol, and slightly in water, from which it crystallizes in lustrous tablets, consisting of small rhombic plates. It melts at 112°, and boils at 295°. On heating it for a long time with sodium ethylate in a sealed tube to 170°—200°, it forms ethylaniline, but when the mixture is distilled from a retort, ethyl alcohol and sodium acetanilide are formed.[8]

Sodium acetanilide, $C_6H_5.N(C_2H_3O)Na$, is also obtained by adding sodium to a solution of acetanilide in xylene;[9] it is a crystalline powder, or a radiating crystalline mass.

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[1] *Ann. Chem Pharm.* cxlii. 121.
[2] Hofmann, *Jahresb.* 1865, 410.
[3] Girard and Willm, *ibid.* viii. 1195.
[4] Hofmann, *ibid.* x. 1095.
[5] *Ibid.* xi. 338.
[6] *Ann. Chem. Pharm.* lxxxvii. 164.
[7] Williams, *ibid.* cxxxi. 288.
[8] Seifert, *Ber. Deutsch. Chem. Ges.* xviii. 1355, 1358.
[9] Bunge, *Ann. Chem. Pharm. Suppl.* vii. 122.

Mercuric acetanilide, $(C_6H_5.NC_2H_3O)_2Hg$, is obtained by heating acetanilide with mercuric oxide; it crystallizes from alcohol in small needles.[1]

Acetanilide hydrochloride, $C_6H_5NH(C_2H_3O)HCl$, is formed by passing hydrochloric acid through a solution of acetanilide in acetone. It crystallizes in pliable needles, which are decomposed by water into their components, and are gradually converted into aniline hydrochloride and acetic acid in the air.[2]

When acetanilide is heated with zinc chloride for several hours to 250°—260°, *Flavaniline*, $C_6H_{14}N_2.ClH$, a beautiful yellow colouring matter, is obtained, having a splendid moss-green fluorescence, which shows brilliantly on silk.[3] This body will be more fully described later on.

Di-acetanilide, $C_6H_5.N(C_2H_3O)_2$, is formed by heating glacial acetic acid with phenyl mustard oil to 130°—140°:

$$C_6H_5.NCS + 2C_2H_3O.OH = C_6H_5N(C_2H_3O)_2 + H_2S + CO_2.$$

It resembles acetanilide in its properties, and melts at 111°.[4]

Acetylmethylanilide, $C_6H_5.N(CH_3)C_2H_3O$, crystallizes from hot water in splendid long needles, which melt at 99°·5 and boil at 245°.[5]

Diphenylacetamide, $(C_6H_5)_2N(C_2H_3O)$, crystallizes from petroleum spirit in large tablets having a pearly lustre, and melting at 99°·5.[6]

Thiacetanilide, $CH_3.CS.NH(C_6H_5)$, is obtained by heating acetanilide with phosphorus pentasulphide. It crystallizes from boiling water in splendid yellowish needles, melting at 75°,[7] and is soluble in caustic soda, forming a sodium salt which can be obtained in compact crystals. By the action of methyl iodide a compound is obtained which has the composition of methylthiacetanilide, but which is entirely different from the substance obtained by the action of phosphorus pentasulphide on methyl acetanilide, and is therefore named methylisothiacetanilide. It is decomposed by hydrochloric acid with formation of methylthiacetate and aniline, from which it follows that the methyl is combined with the sulphur, and that in the formation of the

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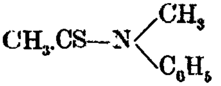
[1] Pfaff and Oppenheim, *Ber. Deutsch. Chem. Ges.* vii. 624.
[2] Nölting and Weingärtner, *ibid.* xviii. 1340.
[3] Fischer and Rudolph. *ibid.* xv. 1500.
[4] Hofmann, *ibid.* iii. 770.
[5] Hofmann, *ibid.* x. 599.
[6] Merz and Weith, *ibid.* vi. 1511.
[7] Hofmann, *ibid.* xi. 338.

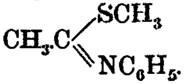
isothiacetanilide a molecular change has taken place. The constitution of these isomeric compounds is shown by the following formulæ:

Methylthiacetanilide.



$$CH_3.CS-N\Big\langle\begin{matrix}CH_3\\C_6H_5\end{matrix}$$

Methylisothiacetanilide.

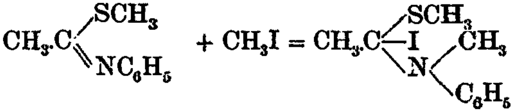


$$CH_3.C\Big\langle\begin{matrix}SCH_3\\NC_6H_5.\end{matrix}$$

Methylthiacetanilide, $CH_3.CS.N(CH_3)C_6H_5$, crystallizes from chloroform in monoclinic tablets, melting at 58°—59°. It is insoluble in water and alkalis, and boils, with slight decomposition, at 290°.[1]

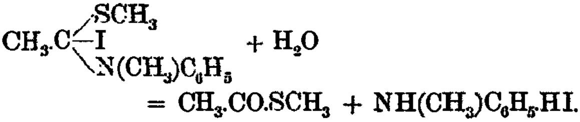
Methylisothiacetanilide, $CH_3.C(SCH_3)NC_6H_5$, is readily obtained by the action of methyl iodide on an alkaline solution of thiacetanilide.[2] It is an oily liquid, boiling at 244°—245°.[3] On heating it with methyl iodide to 100°, a crystalline mass is obtained, which is decomposed by water with formation of methyl thiacetate and methylaniline hydriodide, the following reactions probably taking place:[4]

(1)



$$CH_3.C\Big\langle\begin{matrix}SCH_3\\NC_6H_5\end{matrix} + CH_3I = CH_3.C\Big\langle\begin{matrix}SCH_3\\I\\N\Big\langle\begin{matrix}CH_3\\C_6H_5\end{matrix}\end{matrix}$$

(2)



$$CH_3.C\Big\langle\begin{matrix}SCH_3\\I\\N(CH_3)C_6H_5\end{matrix} + H_2O$$
$$= CH_3.CO.SCH_3 + NH(CH_3)C_6H_5.HI.$$

Ethylisothiacetanilide, $CH_3C(SC_2H_5)NC_6H_5$, is formed when alcoholic solutions of sodium ethylate and thiacetanilide are mixed (Wallach). It is a liquid which is heavier than water, boiling at 255°—257° (Wallach and Bleibtreu). On passing hydrochloric acid through its ethereal solution, a white mass separates out, which is very soluble in water, and forms with platinum chloride the slightly soluble double salt $(C_{10}H_{13}N.S.HCl)_2$-$PtCl_4$.

Wallach and Bleibtreu have also prepared several other isothiacetanilides.

1033 *Glycolylanilide*, $C_6H_5.NH(CO.CH_2.OH)$, is obtained by heating glycolide with aniline to 130°. It is moderately soluble

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[1] Wallach, *Ber. Deutsch. Chem. Ges.* xiii. 528.

[2] Wallach, *ibid.* xi. 1595.

[3] Wallach and Bleibtreu, *ibid.* xii. 1061.

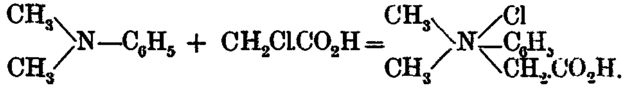
[4] Wallach, *ibid.* xiii. 529.

in cold and very readily in hot water, from which it crystallizes in long prismatic needles, melting at 108°.[1]

Phenylglycocoll or *phenylamido-acetic acid*, $(C_6H_5)NH.CH_2.CO_2H$, is isomeric with the preceding compound. It is obtained by heating chloracetic acid with aniline and water, and is tolerably soluble in the latter. It forms imperfect crystals, melting at 126°—127°, and does not dissolve freshly precipitated mercuric oxide, or silver oxide, but, on the other hand, forms a salt with copper hydroxide, which crystallizes in small dark green plates. In other respects it behaves very similarly to amido-acetic acid.[2]

Several homologues of phenylamido-acetic acid are known.

Phenyl betaïne.—The chloride of this body is obtained by heating dimethylaniline with chloracetic acid:



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle N-C_6H_5 + CH_2ClCO_2H = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle N\left\langle\begin{matrix}Cl\\C_6H_5\\CH_2.CO_2H.\end{matrix}\right.$$

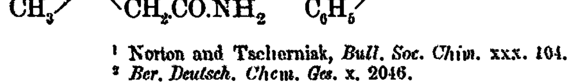
Ether precipitates it from its concentrated aqueous solution in long white needles. Its ethyl ether is obtained in a similar manner to ethyl chloracetate. With moist silver oxide both compounds give the corresponding strongly alkaline, and deliquescent hydroxides.[3]

By heating the ethyl ether for a long time to 130°, and warming the residue with concentrated hydrochloric acid, phenylmethylglycocoll hydrochloride is obtained:

$$\begin{aligned}&C_6H_5N(CH_3)_2Cl.CH_2.CO_2.C_2H_5\\&= C_6H_5N(CH_3)CH_2.CO_2.C_2H_5 + CH_3Cl.\\&C_6H_5N(CH_3)CH_2.CO_2.C_2H_5 + 2ClH\\&= C_6H_5N(CH_3)CH_2.CO_2H,ClH + C_2H_5Cl.\end{aligned}$$

It crystallizes in prisms, which are readily soluble in water, and slightly in alcohol; on continued heating with water it decomposes into carbon dioxide and dimethylaniline hydrochloride.

Phenyl betaïnamide.—The chloride of this body is formed by heating an alcoholic solution of chloracetamide and dimethylaniline. It forms colourless crystals, which on heating to 110°—120° decompose into methyl chloride and methylphenylglycolamide:



$$\left.\begin{matrix}CH_3\\C_6H_5\\CH_3\end{matrix}\right\rangle N\left\langle\begin{matrix}Cl\\ \\CH_2.CO.NH_2\end{matrix}\right. = \left.\begin{matrix}CH_3\\C_6H_5\end{matrix}\right\rangle N-CH_2.CO.NH_2 + CH_3Cl.$$

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[1] Norton and Tscherniak, *Bull. Soc. Chim.* xxx. 104.

[2] *Ber. Deutsch. Chem. Ges.* x. 2046.

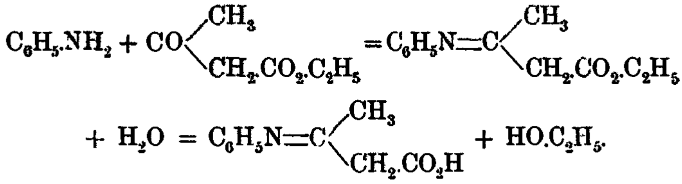
[3] Zimmermann, *Ber. Deutsch. Chem. Ges.* xii. 2206.

Methylphenylglycolamide is also obtained when methylaniline is heated with chloracetamide. It is slightly soluble in cold, more readily in hot water and alcohol, and crystallizes in small plates or prisms, having a satin-like lustre, and melting at 163°.[1]

Phenylimido-acids are obtained by the action of aniline on ketonic acids, the oxygen of the ketone being replaced by the divalent group C_6H_5N.

Anilpyrotartaric acid or *phenyl-a-imidopropionic acid*, $CH_3.C(NC_6H_5)CO_2H$, is obtained by mixing ethereal solutions of pyrotartaric acid and aniline, the mixture being kept cool.[2] It forms small crystals, which melt at 122° with evolution of carbon dioxide. On boiling it with water, carbon dioxide, aniline, and aniluvitonic acid, $C_{11}H_9NO_2$,[3] which will be described later on, are formed.

Anilacetic acid or *phenyl-β-imidobutyric acid*, $CH_3.C(C_6H_5N)CH_2.CO_2H$, is obtained by heating aniline with aceto-acetic ether to 150°—160°:



$$C_6H_5.NH_2 + CO\left\langle\begin{matrix}CH_3\\ CH_2.CO_2.C_2H_5\end{matrix}\right. = C_6H_5N{=}C\left\langle\begin{matrix}CH_3\\ CH_2.CO_2.C_2H_5\end{matrix}\right.$$

$$+ H_2O = C_6H_5N{=}C\left\langle\begin{matrix}CH_3\\ CH_2.CO_2H\end{matrix}\right. + HO.C_2H_5.$$

It forms crystals which are tolerably soluble in water, and very readily in alcohol and benzene. It is coloured dark violet by ferric chloride, and combines with acids and bases.[4]

Oxanilide, $C_2O_2(NH.C_6H_5)_2$, is obtained by heating aniline oxalate to 160°—180° till no more gas is evolved; the formanilide produced at the same time can be removed by washing with cold alcohol.[5] It is also formed when cyananiline is evaporated with dilute hydrochloric acid.[6] Oxanilide is insoluble in water, ether, and cold alcohol, slightly soluble in boiling alcohol, and more readily in benzene, from which it crystallizes in white pearly scales, which melt at 245°, solidifying on cooling to a radiating mass. It boils at 320°, but sublimes at a lower temperature in small iridescent plates; its vapour has a penetrating odour similar to that of benzoic acid.

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[1] Silberstein, *Ber. Deutsch. Chem. Ges.* xvii. 2660.

[2] Böttinger, *Ann. Chem. Pharm.* clxxxviii. 336.

[3] *Ibid.* cxci. 321.

[4] Knorr, *Ber. Deutsch. Chem. Ges.* xvii. 540.

[5] Gerhardt, *Ann. Chem. Pharm.* lx. 308.

[6] Hofmann, *ibid.* lxxiii. 180.

Thioxanilide, $C_2S_2(NH.C_6H_5)_2$.—When oxanilide is warmed with phosphorus pentachloride and the product then treated with sulphuretted hydrogen, thioxanilide is obtained, together with an intensely red-coloured body, which is removed by dissolving the product in caustic soda and passing in carbon dioxide; the sulphuretted anilide separates out in splendid plates similar to those of mosaic gold, and melts at 133°.[1]

Oxanilic acid, $NH(C_6H_5)C_2O_2.OH$, is obtained by strongly heating aniline with a large excess of oxalic acid for ten minutes.[2] The fused mass is extracted with water, the solution boiled with lime, and the filtrate after being acidified with sulphuric acid extracted with ether.[3] The residue remaining after distilling off the ether is then recrystallized from boiling water. It is thus obtained in satin-like needles containing a molecule of water; it crystallizes from benzene in long, fine, lustrous needles, melting at 150°.[4] It forms crystallizable salts.

Ethyl oxanilate, $NH(C_6H_5)C_2O_2.OC_2H_5$, is obtained by the continued heating of ethyl oxalate and aniline. It crystallizes from alcohol in tablets or prisms, melting at 66°—67°. On adding ammonia to its alcoholic solution, phenyl oxamide, $(C_6H_5)H.N.C_2O_2.NH_2$, is precipitated (Klinger). This is also obtained by the action of hydrochloric acid on cyananiline. It separates from its hot alcoholic or aqueous solution in snow-white, hair-like flakes with a silky lustre, which melt at 224° and are easily sublimed; "the sublimate is as light and mobile as precipitated silica" (Hofmann).

Malonanilic acid, $NH(C_6H_5)CO.CH_2.CO_2H$.—By heating equal molecules of malonamide and aniline to 200°—220°, phenyl malonamide, $NH(C_6H_5)CO.CH_2.CO.NH_2$, is obtained, crystallizing from hot water in fine, matted needles, melting at 163°, and yielding the calcium salt of malonanilic acid on boiling with milk of lime.[5] It is also formed by heating malonic acid with aniline,[6] and by the following remarkable reaction. On passing carbon dioxide through sodium acetanilide, sodium acetylphenylcarbonate is obtained as a crystalline powder,

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[1] Wallach and Pirath, *Ber. Deutsch. Chem. Ges.* xii. 1063; Wallach, *ibid.* xiii. 527.

[2] Gerhardt and Laurent, *Ann. Chem. Pharm.* lxviii. 15.

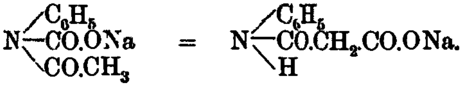
[3] Claus, *Zeitschr. Chem.* 1868, 158.

[4] Klinger, *Ann. Chem. Pharm.* clxxxiv. 265.

[5] Freund, *Ber. Deutsch. Chem. Ges.* xvii. 133.

[6] Rügheimer, *ibid.* xvii. 235.

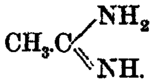
which on heating to 130°—140° undergoes an intermolecular change:



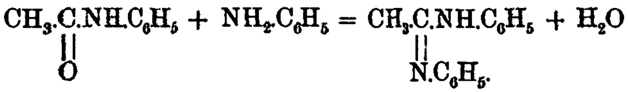
Malonanilic acid crystallizes from warm water in oblique, lustrous prisms, which melt at 132°, and completely decompose, on continued heating, into carbon dioxide and acetanilide.[1]

Anilides of the homologues of malonic, malic, and tartaric acids, &c. are also known.

PHENYLAMIDINES.

1034 Wallach[2] designated by the term amidines a series of bases which are obtained from the acid-amides by replacing the oxygen atom by the group NR, in which R signifies a monad radical or hydrogen. The simplest amidine is acetdiamine, which has already been described as acetamide 

The phenylated amidines are obtained by treating a mixture of aniline and an anilide with phosphorus trichloride, which acts as a dehydrating agent;[3] when acetanilide is employed ethenyldiphenylamidine is obtained:



$$CH_3.\underset{\underset{O}{\parallel}}{C}.NH.C_6H_5 + NH_2.C_6H_5 = CH_3.\underset{\underset{N.C_6H_5.}{\parallel}}{C}.NH.C_6H_5 + H_2O$$

Lippmann obtained this compound by the action of phosphorus pentachloride on acetanilide.[4] According to Wallach and Hoffman[5] the following reactions take place:

$$(1)\ CH_3CO.NH.C_6H_5 + PCl_5 = CH_3.CCl_2.NH.C_6H_5 + POCl_3.$$

$$(2)\ CH_3.CCl_2.NH.C_6H_5 + NH_2.C_6H_5 = CH_3.C(NC_6H_5)NH.C_6H_5 + 2HCl.$$

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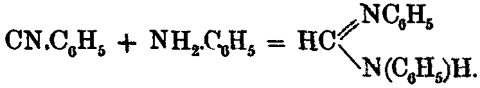
[1] Seifert, *Ber. Deutsch. Chem. Ges.* xviii. 1358.
[2] Wallach, *ibid.* viii. 1575.
[3] Hofmann, *Zeitschr. Chem.* 1866, 161.
[4] *Ber. Deutsch. Chem. Ges.* vii. 541.
[5] *Ibid.* viii. 1567.

The phenylated amidines are monacid bases, which are scarcely soluble in water but take up its elements when boiled with dilute alcohol, decomposing into aniline and an anilide.

On heating those amidines which contain the group NH with carbon disulphide, a thio-anilide is formed, together with thiocyanic acid, which combines with a part of the amidine (Bernthsen):—

$$CH_3.C(NH)NH.C_6H_5 + CS_2 = CH_3.CS.NH.C_6H_5 + CNSH.$$

Methenyldiphenylamidine, $CH(NC_6H_5)NH.C_6H_5$.—Hofmann first obtained this compound by heating chloroform with aniline to 180°—190°, and named it formyldiphenyldiamine.[1] Ethyl orthoformate can be employed instead of chloroform.[2] It is likewise obtained when formic acid is boiled with aniline, or when the latter is heated with phenyl carbamine:[3]

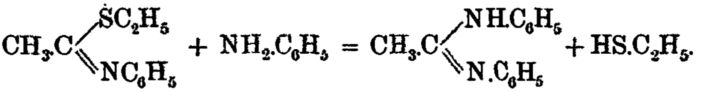


$$CN.C_6H_5 + NH_2.C_6H_5 = HC\begin{cases} NC_6H_5 \\ N(C_6H_5)H. \end{cases}$$

It crystallizes from hot alcohol or benzene in long needles, melting at 135°—136°, and volatilizing at a higher temperature with partial decomposition. On heating it to 140°—150° in a stream of sulphuretted hydrogen, it decomposes into aniline and thioformanilide.[4]

Ethenylphenylamidine, $CH_3.C(NH)NH.C_6H_5$, is prepared by heating aniline hydrochloride and acetonitril to 170°. It is an oily liquid having an alkaline reaction, and is decomposed on heating.[5]

Ethenyldiphenylamidine, $CH_3.C(NC_6H_5)NH.C_6H_5$.—The formation of this compound has already been explained. It is also obtained when acetanilide hydrochloride (p. 211) is heated to 250°, or when aniline hydrochloride is heated with acetonitrile to 230°—240° (Bernthsen), as well as by the action of aniline on the isothiacetanilides:[6]



$$CH_3.C\begin{cases} SC_2H_5 \\ NC_6H_5 \end{cases} + NH_2.C_6H_5 = CH_3.C\begin{cases} NH.C_6H_5 \\ N.C_6H_5 \end{cases} + HS.C_2H_5.$$

In order to prepare it, 2 parts of phosphorus trichloride are gradually added to a well-cooled mixture of 1 part of acetic

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[1] *Jahresb.* 1858. 354.

[2] Wichelhaus, *Ber. Deutsch. Chem. Ges.* ii. 116.

[3] Wolth, *ibid.* ix. 454.

[4] Bernthsen, *Liebig's Ann.* cxcii. 35.

[5] *Ibid.* clxxxiv. 358.

[6] Wallach and Bleibtreu, *Ber. Deutsch. Chem. Ges.* xii. 1063.

acid and 3 parts of aniline, and the whole heated for some hours to 160°. The resinous mass thus obtained is dissolved in boiling water, the cooled filtrate treated with caustic soda, and the precipitate recrystallized from alcohol.[1]

It forms small needles, melting at 131°—132°,[2] and having a neutral reaction. The hydrochloride, $C_{14}H_{14}N_2.HCl$, crystallizes in small tablets. The nitrate, $C_{14}H_{14}N_2.HNO_3$, is very characteristic, and first forms an oily liquid, which soon solidifies to a crystalline mass.

Ethenylisodiphenylamidine, $CH_3.C(NH)N(C_6H_5)_2$, is obtained by heating diphenylamine and acetonitrile to 140°—150°. It forms monoclinic crystals, melting at 62°—63°, and is a strong base.[3]

Isopentenyldiphenylamidine, $(CH_3)_2C_2H_3.C(NC_6H_5)NH.C_6H_5$, is a crystalline body, melting at 111°, and obtained by Hofmann from valerianic acid.

CYANOGEN COMPOUNDS OF BENZENE.

1035 *Phenyl carbamine*, $C_6H_5.NC$.—When chloroform is gradually added to a saturated alcoholic solution of caustic potash mixed with aniline, an energetic reaction is set up, and the carbamine, which is also called phenyl isocyanide, is formed. On distillation it passes over together with aniline; this is removed by oxalic acid, and the residual brown oil dried over potash and rectified.

Phenyl carbamine is a mobile liquid which appears green by transmitted, and blue by reflected light; it possesses the unpleasant, penetrating smell of carbamine, and its vapour produces on the tongue a characteristic bitter taste, and in the throat a sticky sensation. When it is distilled a portion boils constantly at 167°, the thermometer then rises rapidly to 230° and it is converted into an odourless liquid, which solidifies on cooling to a splendid crystalline mass.[4]

On heating phenyl carbamine to 200°—220°, a crystalline body, probably identical with the preceding compound, is obtained, while another portion of the carbamine is converted into the

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[1] Hofmann, *Jahresb.* 1865, 414.
[2] Biedermann, *Ber. Deutsch. Chem. Ges.* vii. 540.
[3] Bernthsen, *Liebig's Ann.* cxcii. 25.
[4] Hofmann, *Ann. Chem. Pharm.* cxliv. 117.

isomeric benzonitrile, $C_6H_5.CN$.[1] The aqueous mineral acids readily decompose phenyl carbamine, forming aniline and formic acid; formanilide occurs in this reaction as an intermediate product. It combines with sulphuretted hydrogen to form thioformanilide.

Phenyl isocyanate or *phenylcarbimide*, $CO.N{-}C_6H_5$. Hofmann obtained this body, which was formerly called anilocyanic acid, or carbanil, by distilling diphenylcarbamide with phosphorus pentoxide; he then found that it is better to use phenyl urethane:[2]

$$CO\left\{\begin{matrix}N(C_6H_5)H\\OC_2H_5\end{matrix}\right. = CO.NC_6H_5 + HO.C_2H_5.$$

It is still more readily prepared by the action of carbonyl chloride on diphenyl urea or aniline hydrochloride:[3]

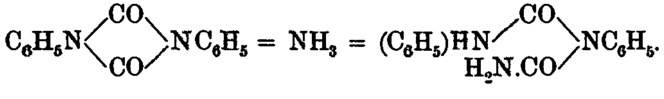
$$C_6H_5.NH_2 + COCl_2 = C_6H_5.NCO + 2HCl.$$

In this manner it can be readily prepared on the large scale.[4]

It is a colourless liquid, the vapour of which has a very penetrating odour and produces a flow of tears. It readily unites with the alcohols to form ethers of carbanilic acid.

Phenylcarbimide hydrochloride, $CO(C_6H_5)NHCl$, is obtained by passing hydrochloric acid through pure phenyl isocyanate, heat being evolved. It is a crystalline mass, melting at 45°.[5]

Phenyl di-isocyanate, $(CO)_2(NC_6H_5)_2$, is obtained in a remarkable manner when the preceding compound is treated with a drop of triethylphosphino. If, however, the isocyanate be present in great excess, crystals appear after some time and gradually increase in number, but the liquid does not become solid even when allowed to stand for months.[6] It crystallizes from hot ether in thin iridescent plates, which melt at 175°, and on strongly heating are reconverted into the monomolecular compound.[7] By treatment with alcoholic ammonia it is converted into β-diphenylbiuret:



$$C_6H_5N\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_6H_5 = NH_3 = (C_6H_5)HN\left\langle\begin{matrix}CO\\H_2N.CO\end{matrix}\right\rangle NC_6H_5.$$

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[1] Weith, *Ber. Deutsch. Chem. Ges.* vi. 213.

[2] Hofmann, *Ann. Chem. Pharm.* lxxiv. 9 and 33; *Jahresber.* 1858, 348; *Ber. Deutsch. Chem. Ges.* iii. 654.

[3] Hentschel, *Ber. Deutsch. Chem. Ges.* xvii. 1284.

[4] *Ibid.* xviii. Ref. 12.

[5] *Ibid.* xviii. 1178.

[6] Hofmann, *ibid.* xviii. 764.

[7] *Ber. Deutsch. Chem. Ges.* iii. 735; iv. 246.

This body crystallizes in prisms, which melt at 164°, and are decomposed by hydrochloric acid with formation of phenyl isocyanate and ammonia.

a-Diphenylbiuret, $NH(CON.H.C_6H_5)_2$, is obtained by heating biuret or ethyl allophanate (Vol. III., Part I., p. 373) with aniline. It forms crystals which are slightly soluble in alcohol, melt at 210°, and are converted by dry hydrochloric acid into aniline, cyanic acid, and phenyl isocyanate.[1]

Phenyl isocyanurate, $(CO)_3(NC_6H_5)_3$, is formed when an alcoholic solution of phenyl isocyanuramide is boiled for a short time with hydrochloric acid, or by heating 5 parts of phenyl isocyanate with 3 parts of potassium acetate for three hours to 100°, while if 10 parts of isocyanate are employed the complete polymerization only occurs at 188°—200° (Hofmann). Phenyl isocyanurate crystallizes from hot alcohol in prisms, melting at 270°.

Phenyl cyanurate, $(CN)_3(OC_6H_5)_3$, is formed on passing cyanogen chloride through an alcoholic solution of sodium phenate. It is insoluble in water and crystallizes from alcohol in long, fine needles, melting at 224°.[2]

1036 *Phenylcyanamide* or *cyananilide*, $C_6H_5NH(CN)$.—Cahours and Cloëz obtained this substance by passing cyanogen chloride through an ethereal solution of aniline.[3] It is also obtained by the action of lead oxide on an alcoholic, or better, alkaline solution of phenyl thio-carbamide.[4] On evaporating the alcoholic solution it remains behind as a tenacious mass, which becomes crystalline in moist air or on continued contact with alcohol, and then crystallizes from ether in needles containing three molecules of water, and melting at 36°—37°. When water is added to its alcoholic solution, it combines to form phenyl urea, and on passing sulphuretted hydrogen through its solution in benzene, phenyl thio-carbamide is formed.[5]

Phenyl cyanuramide or *triphenylmelamine*, $(C_6H_5.NH)_3(CN)_3$, is formed from the preceding compound on standing, or more rapidly on heating, and crystallizes from alcohol in fine prisms, melting at 162°—163°. On adding platinum chloride to its

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* iv. 265; Peitzsch and Salomon, *Journ. Prakt. Chem.* [2], vii. 477.

[2] Hofmann and Olshausen, *Ber. Deutsch. Chem. Ges.* iii. 257.

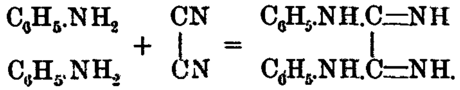
[3] *Ann. Chem. Pharm.* xc. 91.

[4] Hofmann, *Ber. Deutsch. Chem. Ges.* iii. 266; Rathke, *ibid.* xii. 733; Feuerlein, *ibid.* xii. 1602; Berger, *Monatsh. Chem.* v. 217.

[5] Weith, *ibid.* ix. 820.

solution, a crystalline precipitate of $(CN)_2(C_6H_5.NH)_2PtCl_6H_2$ is formed.[1]

Cyananiline, $C_{14}H_{14}N_4$, is obtained when cyanogen is passed through an alcoholic solution of aniline:



$$\begin{array}{l} C_6H_5.NH_2 \\ C_6H_5.NH_2 \end{array} + \begin{array}{c} CN \\ | \\ CN \end{array} = \begin{array}{l} C_6H_5.NH.C{=}NH \\ \qquad\qquad\quad | \\ C_6H_5.NH.C{=}NH. \end{array}$$

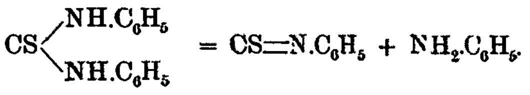
It is insoluble in water, slightly soluble in alcohol, and crystallizes in small lustrous plates showing a play of colours; they melt at 210°—220°, and are decomposed at a higher temperature.[2] As a diacid base it forms salts with acids, but they are rather unstable; when heated with aqueous mineral acids it is converted into oxanilide and oxamide.

Phenyl thiocyanate, $C_6H_5.S.CN$, is formed by the action of thiocyanic acid on diazobenzene sulphate, or by passing cyanogen chloride through alcoholic lead thiophenate:—

$$(C_6H_5S)_2Pb + 2CNCl = 2C_6H_5S.CN + PbCl_2.$$

It is a colourless liquid boiling at 231°, which on standing becomes yellow. An alcoholic solution of potassium hydrosulphide decomposes it into thiophenol and potassium thiocyanate.[3]

Phenyl thiocarbimide or *phenyl mustard oil*, $C_6H_5.N.CS$.—Hofmann obtained this body by the distillation of diphenylthiocarbamide (sulphocarbanilide) with phosphorus pentoxide, and named it sulphocarbanil or phenyl sulphocyanide.[4] It may be more simply obtained by heating the thio-carbamide with concentrated hydrochloric acid:[5]



$$CS\begin{array}{l} \diagup NH.C_6H_5 \\ \diagdown NH.C_6H_5 \end{array} = CS{=}N.C_6H_5 + NH_2.C_6H_5.$$

It is also formed by the action of thiocarbonyl chloride, $CSCl_2$, on aniline,[6] as well as by the direct combination of sulphur with phenyl carbamine,[7] and when phenyl isocyanate is heated with phosphorus pentasulphide.[8]

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* iii 267.

[2] Hofmann. *Ann. Chem. Pharm.* lxvi. 129 ; lxxiii. 180.

[3] Billeter, *Ber. Deutsch. Chem. Ges.* vii. 1753.

[4] *Jahresb.* 1858, 349.

[5] Merz and Weith. *Zeitschr. Chem.* 1869, 589.

[6] Rathke, *Ber. Deutsch. Chem. Ges.* iii. 861.

[7] Weith, *ibid.* vi. 211.

[8] Michael and Palmer, *Amer. Chem. Journ.* vi. 257.

It is a liquid having a smell similar to that of ordinary mustard oil, boils at 222°, and combines with ammonia and the amines to form ureas. It also combines with alcohols, forming ethers of thiocarbanilic acid (p. 224).

When chlorine is passed through its solution in chloroform, isocyanphenyl chloride, $C_6H_5.N.CCl_2$, is obtained as a heavy, yellow liquid, boiling at 211°—212°. It possesses a very unpleasant pungent odour, and its vapour attacks the eyes and mucous membrane. Dry silver oxide acts on it violently with partial carbonization and formation of phenylcarbimide.[1]

PHENYLCARBAMIDES.

1037 *Phenyl urea* or *carbanilamide*, $H(C_6H_5)N.CO.NH_2$.—Hofmann obtained this substance by passing the vapour of cyanic acid through cold aniline, and also by the action of ammonia on phenylcarbimide, $C_6H_5N(CO)$. It is, however, most readily prepared by mixing a solution of aniline hydrochloride or sulphate with potassium cyanate, the phenyl urea soon separating out.[2] It is also obtained by heating urea with the theoretical quantity of aniline in a sealed tube to 150°—170.[3] It crystallizes from hot water in monoclinic needles, melting at 147°.[4] It does not combine with nitric or oxalic acids.

Symmetrical diphenyl urea or *carbanilide*, $CO(NH.C_6H_5)_2$, is formed by the combination of aniline with phenylcarbimide, or by the action of water on the latter, as well as on heating phenyl urea, or when aniline is treated with carbonyl chloride, &c.[5]

To prepare it, one part of urea is heated with three parts of aniline to 150°—170°,[6] or equal molecules of phenyl urea and aniline are heated to 180°—190°.[7]

It is scarcely soluble in water, readily in alcohol and ether, and crystallizes in prisms, melting at 235° (Weith). On heating

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[1] Sell and Zierold, *Ber. Deutsch. Chem. Ges.* vii. 1228.

[2] *Ann. Chem. Pharm.* liii. 57; lvii. 265; lxx. 130; lxxiv. 14; Weith, *Ber. Deutsch. Chem. Ges.* ix. 820.

[3] Fleischer, *ibid.* ix. 820.

[4] Steiner, *ibid.* viii. 518.

[5] Hofmann, *Ann. Chem. Pharm.* lxx. 138; lxxiv. 15.

[6] Baeyer, *ibid.* cxxxi. 252.

[7] Weith, *Ber. Deutsch. Chem. Ges.* ix. 821.

it with alcoholic ammonia to 140°—150°, it decomposes into aniline and urea.[1]

Asymmetrical diphenyl urea, $(C_6H_5)_2N.CO(NH_2)$.—When the vapour of carbonyl chloride is passed through a solution of diphenylamine in chloroform, diphenylamine hydrochloride separates out, and the solution contains the chloride of diphenyl urea, $(C_6H_5)_2N.COCl$, which crystallizes from alcohol in beautiful small plates, melting at 85°. By the action of alcoholic ammonia it is converted into the urea, which crystallizes in long needles, melting at 189°. On distillation with caustic potash, it decomposes into diphenylamine, ammonia, and carbon dioxide, and on dry distillation, into cyanic acid and diphenylamine.[2]

Triphenyl urea, $(C_6H_5)_2N.CO.N(C_6H_5)H$, is obtained by the action of aniline on the diphenyl urea chloride described above, and crystallizes from alcohol in needles, melting at 136° (Michler).

Tetraphenyl urea, $CO(N(C_6H_5)_2)_2$, is formed when the chloride is heated for some minutes with diphenylamine and zinc dust.[3] It is readily soluble in boiling alcohol and forms small crystals, melting at 183°.

Carbanilic acid, $CO\begin{cases} NH(C_6H_5) \\ OH \end{cases}$, is not known in the free state; its ethers, the phenyl urethanes (Vol. III., Part I., p. 165), are obtained by the action of aniline on the ethers of chloroformic acid.

Ethyl carbanilate, $CO(OC_2H_5)(NHC_6H_5)$, crystallizes from hot water in long needles melting at 51°; it boils at 237°—238°, a small quantity decomposing into phenylcarbimide and alcohol,[4] while in the cold these combine to form the original compound.

Phenyl carbanilate, $CO(OC_6H_5)NH(C_6H_5)$, is formed by the action of phenol on phenyl isocyanate and phenyl di-isocyanate.[5] It is more readily obtained, and at a lower temperature, when aluminium chloride is added to the mixture;[6] it is readily soluble in alcohol, slightly in water, and crystallizes in needles melting at 121°.[7]

[1] Claus, *Ber. Deutsch. Chem. Ges.* ix. 693.
[2] Michler, *ibid.* ix. 396; 715.
[3] Michler and Zimmerman, *ibid.* xii. 1166.
[4] Wilm and Wischin, *Ann. Chem. Pharm.* cxlvii. 157.
[5] Hofmann, *Ber. Deutsch. Chem. Ges.* iv. 249.
[6] Leuckart, *ibid.* xviii. 873.
[7] Gumpert, *Journ. Prakt. Chem.* [2], xxxi. 119.

1038 *Phenyl thio-carbamide*, $H(C_6H_5)N.CS.NH_2$, is formed by the action of ammonia on phenyl mustard oil,[1] and by heating ammonium thiocyanate with aniline hydrochloride.[2] It is slightly soluble in cold, more readily in boiling water, and still more readily in alcohol; it has a bitter taste, and crystallizes in needles melting at 154°.

Ethyl phenyl thio-carbamide, $H(C_6H_5)N.CS.N(C_2H_5)H$, is obtained by the action of ethylamine on phenyl mustard oil, or of aniline on ethyl mustard oil, and forms monoclinic crystals melting at 99·5°.[3]

Diphenyl thio-carbamide or *thiocarbanilide*, $CS(NH.C_6H_5)_2$, is formed, together with ammonia thiocyanate, when aniline thiocyanate is distilled:[4]

$$2C_6H_5.NH_2.CNSH = CS(NH.C_6H_5)_2 + CNS(NH_4).$$

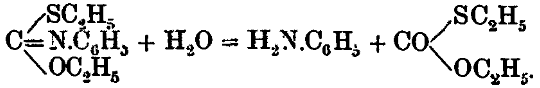
It is likewise obtained by boiling an alcoholic solution of carbon disulphide with aniline, the sulphuretted hydrogen formed being removed by the addition of caustic potash.[5]

Diphenyl thio-carbamide is scarcely soluble in water, readily in alcohol, and crystallizes in small plates melting at 144°.

On heating it with alcoholic ammonia to 100°, it is decomposed into phenyl thio-carbamide and aniline.[6]

Thiocarbanilic acid, $CS\left\{\begin{matrix}NH(C_6H_5)\\ OH\end{matrix}\right.$, is not known in the free state; its ethyl ether, or phenyl thio-urethane, is obtained by heating phenyl mustard oil with alcohol,[7] as well as by treating it at the ordinary temperature with alcoholic potash.[8] Ethyl thiocarbanilate forms triclinic prisms melting at 71°—72°.

It behaves as a mercaptan; by the action of ethyl iodide on its silver salt, phenyl urethane ethyl ether is obtained, which forms beautiful crystals, melting at 29·5°—30·5°. On heating with dilute sulphuric acid to 180°—200°, it is split up into aniline and ethyl thioxycarbonate, from which it follows that it has the following constitution:—



$$C\begin{matrix}\diagup SC_2H_5\\ =N.C_6H_5\\ \diagdown OC_2H_5\end{matrix} + H_2O = H_2N.C_6H_5 + CO\begin{matrix}\diagup SC_2H_5\\ \diagdown OC_2H_5.\end{matrix}$$

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[1] Hofmann, *Jahresb.* 1858, 349.

[2] Schiff, *Ann. Chem. Pharm.* cxlviii. 338; Clermont, *Ber. Deutsch. Chem. Ges.* ix. 446; x. 494.

[3] Weith, *Ber. Deutsch. Chem. Ges.* viii. 1524.

[4] Hofmann, *Ann. Chem. Pharm.* lxx. 142.

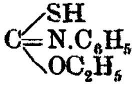
[5] Weith, *Ber. Deutsch. Chem. Ges.* vi. 967.

[6] Gerhardt, *ibid.* xvii. 3043.

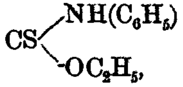
[7] Hofmann, *ibid.* ii. 120; iii. 772.

[8] R. Schiff, *ibid.* ix. 1316.

From this we may further conclude that of the following formulæ,



$$C\begin{matrix}\diagup SH\\ =N.C_6H_5\\ \diagdown OC_2H_5\end{matrix}$$



$$CS\begin{matrix}\diagup NH(C_6H_5)\\ \diagdown OC_2H_5,\end{matrix}$$

the first, and not the second, which is generally accepted, represents the constitution of phenyl urethane. It is also possible, however, that the second represents the compound in the free state, and that on the formation of a salt, an intermolecular rearrangement takes place.[1]

PHENYLGUANIDINES.

1039 *Phenylguanidine*, $C(NH)\left\{\begin{matrix}NH_2\\ NH(C_6H_5)\end{matrix}\right.$, is obtained by the action of alcoholic ammonia on phenyl thiocarbamide, and is a solid body which on standing decomposes into ammonia and phenylcyanamide.[2]

Diphenylguanidine or *melaniline*, $C(NH)(NH.C_6H_5)_2$.—Hofmann obtained this substance by passing cyanogen chloride through aniline.[3] Cyananilide and aniline hydrochloride are first formed and then react on each other:—

$$CN.NH.C_6H_5 + NH_2.C_6H_5.HCl = C(NH)(NH.C_6H_5)_2HCl.$$

It is, therefore, also obtained by heating the alcoholic solutions of these two compounds,[4] as well as by the action of lead oxide on a solution of thiocarbanilide in alcoholic ammonia.[5] In order to prepare it, the thiocarbanilide is first treated with concentrated caustic potash, concentrated solution of ammonia and washed litharge are then added, and the whole digested on the water bath, the liquid decanted off, and the melaniline extracted from the residue by hydrochloric acid.[6] It crystallizes from alcohol in monoclinic needles melting at 147°, and is a monacid base forming salts which crystallize well. On heating it under pressure with concentrated hydrochloric acid, it forms carbon dioxide, ammonia, and aniline.

[1] Liebermann, *Ann. Chem. Pharm.* ccvii. 142.
[2] Feuerlein, *Ber. Deutsch. Chem. Ges.* xii. 1602.
[3] *Ann. Chem. Pharm.* lxvii. 129.
[4] Cahours and Cloëz, *ibid.* xc. 93.
[5] Hofmann, *Ber. Deutsch. Chem. Ges.* ii. 460; Schröder and Weith, *ibid.* vii. 937.
[6] Rathke, *ibid.* xii. 772.

a-Triphenylguanidine, $C(NC_6H_5)(NH.C_6H_5)_2$, is best obtained by decomposing a boiling alcoholic solution of equal molecules of thiocarbanilide and aniline with lead oxide.[1]

It crystallizes from alcohol in hexagonal rhombic prisms, melting at 143°, and combines with acids to form crystalline salts.

β-Triphenylguanidine, $C(NH)\left\{\begin{array}{l}N(C_6H_5)_2\\NH(C_6H_5)\end{array}\right.$, is obtained when cyananilide and diphenylamine hydrochloride are heated to 100°—125°. It crystallizes from alcohol in large, strongly refractive tablets, melting at 131°. The hydrochloride, $C_{19}H_{17}N_3HCl + H_2O$, forms thick tablets or prisms.[2] When it is heated with concentrated hydrochloric acid to 260°—270°, it takes up water, and splits up into carbon dioxide, ammonia, aniline, and diphenylamine, while the *a*-compound, under the same conditions, only yields carbon dioxide and aniline.

Tetraphenylguanidine, $C(NH)(N(C_6H_5)_2)_2$, is formed by passing cyanogen chloride into diphenylamine heated to 150°—170°. It crystallizes from petroleum ether in rhombic prisms, melting at 130°—131°, and is a monacid base, most of its salts being only slightly soluble in water. Concentrated hydrochloric acid decomposes it at 330°—340°, forming carbon dioxide, ammonia, and diphenylamine.[3]

HALOGEN SUBSTITUTION PRODUCTS OF ANILINE.

1040 In 1842 Fritzsche found that three of the hydrogen atoms in aniline can be replaced by bromine, the tribromaniline which was thus formed being called by him bromaniloïd.[4] This compound was investigated three years later by Hofmann, who observed that, unlike aniline, it does not combine with acids, the basic character of the aniline having been neutralized by the presence of the electronegative element. He therefore endeavoured to obtain compounds in which only one or two of the hydrogen atoms had been replaced by a halogen. The action of chlorine did not yield the desired result, as this substance acts very violently on aniline, forming resinous products, among which, however, he was able to recognize

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[1] Hofmann, *Ber. Deutsch. Chem. Ges* ii. 458.
[2] Weith and Schröder, *ibid.* viii. 294.
[3] Weith, *ibid.* vii. 843.
[4] *Journ. Prakt. Chem.* xxviii. 204.

trichloraniline. He was more successful when he started with isatin, $C_8H_5NO_2$, which is an oxidation product of indigo, and yields aniline on distillation with caustic potash. When the substitution products of this substance, which had previously been prepared by Laurent, were heated with caustic potash he obtained the bases monochloraniline and monobromaniline, and also dibromaniline, the basic properties of which are much feebler than those of the monosubstitution products.[1]

It has been stated in the introduction that these important researches were chiefly instrumental in securing universal recognition for the substitution theory. Hofmann himself says that it undoubtedly follows from the facts observed by him, that chlorine or bromine can take the part of hydrogen in organic compounds, that these preserve their electronegative character in the new compounds, and impress it the more strongly upon them the greater the number of hydrogen atoms replaced by halogens.

Liebig adds in a note: "The author seems to me to have definitely proved by this research that the chemical nature of a compound does not in any way depend upon the nature of the elements contained in it, as is assumed by the electrochemical theory, but entirely on their arrangement."

Aniline forms a large number of halogen substitution products, which are prepared by the following methods:—

1. An anilide, generally acetanilide, is treated with chlorine or bromine, the action proceeding much more quietly and smoothly than with aniline or its salts. The substituted anilides are then decomposed by being heated with an alkali or fuming hydrochloric acid. In many cases it is better to decompose the anilide by strong sulphuric acid; the solution is diluted with water, neutralized with caustic soda, and the substituted aniline extracted with ether. Iodine and chloride of iodine act upon aniline or the anilides with formation of iodine substitution products.

2. Substituted anilines are also readily obtained by the reduction of the substituted nitrobenzenes with tin and hydrochloric acid or stannous chloride.

As already mentioned, the replacement of hydrogen by a halogen weakens the basic character of the aniline. In all cases the presence of the amido-group can readily be proved by the action of acetyl chloride, which forms substituted anilides.

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[1] *Ann. Chem. Pharm.* liii. 1.

CHLORANILINES.

1041 *Orthochloraniline*, $C_6H_4Cl.NH_2$, is obtained by reducing orthochloronitrobenzene, and is a liquid which does not solidify at −14°, and boils at 207°. The hydrochloride, $C_6H_4Cl.NH_2.ClH$, crystallizes in large rhombic tablets. The picrate is almost insoluble in cold water, and only slightly soluble in hot water; it is much less soluble in alcohol than the picrate of the para-compound. This property is made use of in the separation of the two chloranilines. As it is very difficult to obtain orthochloronitrobenzene free from parachloronitrobenzene, a mixture of the choranilines is obtained on reduction, which can readily be separated by means of picric acid. Another method of separation depends upon the fact that orthochloraniline is a much weaker base than parachloraniline. When, therefore, the equivalent quantity of sulphuric acid is added to the mixture of the two bases and the whole distilled with water the sulphate of orthochloraniline completely decomposes, and the base passes over mixed with only a little parachloraniline.[1]

Metachloraniline may be obtained by reducing metachloronitrobenzene with stannous chloride (Beilstein and Kurbatow). It is a liquid boiling at 230°, and is as strong a base as the ortho-compound, its salts being only partially decomposed on boiling with water.

Parachloraniline.—Hofmann first obtained this compound by distilling chlorisatin with caustic potash, it is also formed by the action of chlorine on acetanilide,[2] but it is best prepared by reducing parachloronitrobenzene with stannous chloride (Beilstein and Kurbatow).

It is very slightly soluble in boiling water, but readily in alcohol, and forms diamond-like crystals, very similar to regular octahedra, but which belong to the rhombic system,[3] and melt at 70°—71°. It can be distinguished from parabromaniline, which is very similar to it, as it boils without decomposition at 230°—231°.

Parachloraniline is a powerful base, but its salts have an acid reaction. It does not decompose the salts of aluminium and zinc.

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[1] Beilstein and Kurbatow, *Ann. Chem. Pharm.* clxxvi. 36.
[2] Mills, *Jahresber.* 1860, 349.
[3] Groth, *Ber. Deutsch. Chem. Ges.* iii. 453.

Parachloraniline hydrochloride, $C_6H_4Cl.NH_2.HCl$, crystallizes in large, monoclinic prisms. The platinum chloride forms small plates, soluble in water, alcohol, and even a mixture of the latter with ether (Hofmann).

DICHLORANILINES, $C_6H_3Cl_2.NH_2$.[1]

1042 These may be distinguished according to the position of the chlorine atoms as ortho-, meta-, and para-compounds; in the following tables this is expressed by the numbers, the amido-group being assumed to have position 1.

Orthodichloranilines.

			Melting-point.	Boiling-point.
(*a*) Asymmetric	(3 : 4)	broad needles . .	71·5°	272°
(*b*) Adjacent	(2 : 3)	needles	23-24°	252°

Metadichloranilines.

Asymmetric	(2 : 4)[2]	long needles . . .	63°	245°
Symmetric	(3 : 5)	needles	50·5°	259—260°
Adjacent	(2 : 6)	needles	39°	—
Paradichloraniline	(2 : 5)	thick needles .	50°	251°

TRICHLORANILINES, $C_6H_2Cl_3.NH_2$.[3]

Asymmetric	(2 : 4 : 5)[4]	needles	95—96°	270°
Symmetric	(2 : 4 : 6)	long needles . .	77·5°	262°
Adjacent	(2 : 3 : 4)	needles	67·5°	292°

The second of these was first prepared by Hofmann.

TETRACHLORANILINES, $C_6HCl_4.NH_2$.

Asymmetric	(2 : 3 : 4 : 6)[5]	needles . . .	88°	—
Symmetric	(2 : 3 : 5 : 6)[6]	needles . . .	90°	—
Adjacent	(2 : 3 : 4 : 5)[7]	broad needles .	118	—

Pentachloraniline,[8] $C_6Cl_5.NH_2$, crystals.

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[1] Beilstein and Kurbatow, *loc. cit.*

[2] Beilstein and Kurbatow, *Ann. Chem. Pharm.* clxxxii, 95; Witt, *Ber. Deutsch. Chem. Ges.* vii. 1602.

[3] Beilstein and Kurbatow.

[4] Lesimple, *Ann. Chem. Pharm.* cxxxvii. 125.

[5] Beilstein and Kurbatow.

[6] Lesimple, *Zeitschr. Chem.* 1868, 227.

[7] Beilstein and Kurbatow.

[8] Jungfleisch, *Jahresber.* 1868, 354.

BROMANILINES.

1043 These are best obtained from the three nitrobromobenzenes.

Orthobromaniline is insoluble in water, but readily dissolves in alcohol. It crystallizes in colourless needles, melts at 31°·5, and boils without decomposition at 229°.

Metabromaniline forms a colourless, crystalline mass melting at 18°—18°·5, and boiling at 251°.[2]

Parabromaniline was, as already explained, first obtained by Hofmann. It is also obtained by the action of bromine on aniline,[3] or better, acetanilide,[4] and forms large, well-formed crystals, similar to regular octahedra, but belonging to the rhombic system,[5] which melt at 66·4°.[6] On heating more strongly the liquid suddenly becomes a deep violet colour, and between 190° and 270° a liquid distils over, while a residue is left which forms a splendid blue solution in alcohol. The distillate shows similar phenomena when redistilled, and can be split up by fractionation into aniline, ordinary dibromaniline, and tribromaniline.[7]

Parabromaniline hydrochloride, $C_6H_4Br.NH_2.HCl$, is isomorphous with choraniline hydrochloride (Hofmann).

DIBROMANILINES, $C_6H_3Br_2.NH_2$.

			Melting-point.
Orthodibromaniline	(3 : 4)[8]	white crystals	80·4°
Metadibromanilines.			
(*a*) Asymmetric	(2 : 4)[9]	small long plates	79·5°
(*b*) Symmetric	(3 : 5)[10]	needles	56·5°
Paradibromaniline	(2 : 5)[11]	prisms	51°—52°

a-Metadibromaniline was first obtained by Hofmann. It is also obtained by the action of bromine on ortho- and paracetanilide. Its hydrochloride forms arborescent crystals.

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[1] Fittig and Mager, *Ber. Deutsch. Chem. Ges.* vii. 1179.

[2] *Ibid.* viii. 364.

[3] Kekulé, *Zeitschr. Chem.* 1866, 687.

[4] Mills, *ibid.* 1860, 834.

[5] Azruni, *Ann. Chem. Pharm.* clxxxviii. 23.

[6] Körner, *Jahresber.* 1875, 342.

[7] Fittig and Büchner, *Ann. Chem. Pharm.* clxxxviii. 23.

[8] Körner, *Jahresber.* 1875, 342.

[9] Hofmann, *loc. cit.*; Griess, *Ann. Chem. Pharm.* cxxi. 266; Körner, *loc. cit.*; Wurster, *Ber. Deutsch. Chem. Ges.* vi. 1486; Meyer and Stüber, *Ann. Chem. Pharm.* clxv. 169.

[10] Körner.

[11] Meyer and Stüber.

TRIBROMANILINES, $C_6H_2Br_3.NH_2$.

	Melting-point.
Symmetric (2 : 4 : 6)[1] long needles	118°
Adjacent (3 : 4 : 5)[2] crystals	—

The first of these is also called ordinary tribromaniline, because it is obtained by the direct bromination of aniline. Unlike the isomeric compound, which is obtained by the reduction of the corresponding nitrobromobenzene, it does not combine with acids. This compound does not melt even at 130°, and decomposes when more strongly heated.

	Melting-point.
Tetrabromaniline, $C_6HBr_4.NH_2$ (2 : 3 : 4 : 6)[3] needles	115·3°
Pentabromaniline, $C_6Br_5.NH_2$.[4] lustrous needles . .	222°.

IODANILINES.

1044 *Meta-iodaniline*, $C_6H_4I.NH_2$.—Griess obtained this substance by reducing metanitro-iodobenzene; it crystallizes in small plates melting at 25°.[5]

Para-iodaniline. While chlorine and bromine readily form substitution products, iodine does not act directly on most carbon compounds. Aniline is among the exceptions to this rule, and is readily converted by iodine into iodaniline hydriodide.[6] The base may be obtained by the reduction of paranitro-iodobenzene.[7] To prepare it, acetanilide is dissolved in glacial acetic acid and the equivalent quantity of iodine chloride added, para-iodacetanilide, which crystallizes in rhombic tablets, being formed. This is then boiled with concentrated hydrochloric acid, and the solution decomposed with ammonia.[8]

Para-iodaniline crystallizes in needles or prisms melting at 60°. It precipitates aluminium salts, but not those of zinc or iron. On heating it with ethyl iodide, ethylaniline, diethylaniline, and free iodine are obtained. Its hydrochloride crystallizes from hot water in plates, or broad thin needles.

[1] Körner; Fittig and Büchner, *Ann. Chem. Pharm.* clxxxviii. 962; Wurster and Nölting, *Ber. Deutsch. Chem. Ges.* vii. 1564.

[2] Körner.

[3] Wurster and Nölting; Körner.

[4] Körner.

[5] Griess, *Zeitschr. Chem.* 1866, 218.

[6] Hofmann, *Ann. Chem. Pharm.* lxvii. 61; Mills, *ibid.* clxxvi. 354.

[7] Griess, *Zeitschr. Chem.* 1866, 218; Kekulé, *ibid.* 687.

[8] Michael and Norton, *Ber. Deutsch. Chem. Ges.* xi. 108.

Metadi-iodaniline, $C_6H_3I_2.NH_2(2:4)$.—When hot solutions of aniline and mercuric chloride are mixed, mercuric phenylammonium chloride, $N(C_6H_5.HHg)Cl$, separates out as a yellow amorphous precipitate, which is converted into di-iodaniline by an alcoholic solution of iodine.[1] This compound may also be obtained by passing the vapour of two molecules of iodine chloride into a solution of aniline in acetic acid.[2] It crystallizes in needles melting at 95°—96°, and forms salts which are decomposed by cold water. It is converted by the diazo-reaction into metadi-iodobenzene.

Tri-iodaniline, $C_6H_2I_3.NH_2$, is obtained by passing three molecules of iodine chloride into a solution of aniline in hydrochloric acid. It crystallizes from boiling alcohol in long needles melting at 185·5°.[3]

NITRO-SUBSTITUTION PRODUCTS OF ANILINE.

1045 Hofmann and Muspratt found that when ordinary dinitrobenzene (metadinitrobenzene) is treated with alcoholic ammonium sulphide, only one nitroxyl is reduced, and nitraniline, $C_6H_4(NO_2)NH_2$, is formed.[4] This is also the case with the two isomeric dinitrobenzenes.[5] The nitranilines are also obtained when the monochloronitrobenzenes, or the corresponding bromo- or iodo-compounds, are heated with ammonia:

$$C_6H_4Cl(NO_2) + 2NH_3 = C_6H_4(NH_2)NO_2 + NH_4Cl.$$

This reaction takes place most readily with the ortho-compounds. The substituted nitrobenzenes containing more than one halogen are still more readily attacked by ammonia, but only one halogen atom is replaced by the amido-group.

Nitro-substitution products of aniline are also obtained by heating the methyl- or ethyl-ethers of the nitrophenols with ammonia:

$$C_6H_4(NO_2)OCH_3 + NH_3 = C_6H_4(NO_2)NH_2 + HO.CH_3.$$

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[1] Rudolph, *Ber. Deutsch. Chem. Ges.* xi. 78.

[2] Michael and Norton, *loc. cit.*

[3] Stenhouse, *Journ. Chem. Soc.* xvii. 329; Michael and Norton.

[4] *Ann. Chem. Pharm.* lvii. 201.

[5] Zincke and Rinne, *Ber. Deutsch. Chem. Ges.* vii. 869 and 1372.

The basic character of aniline is weakened much more by the introduction of nitroxyl than by that of a halogen atom; hence the mononitranilines are very weak bases, while the dinitranilines do not combine with acids, and trinitraniline behaves as an acid-amide, being decomposed by alkalis with formation of ammonia and trinitrophenol (picric acid), on account of which reaction it was first named picramide.

NITRANILINES, $C_6H_4(NO_2)NH_2$.

1046 *Orthonitraniline* may be obtained by the methods given above from orthodinitrobenzene, orthonitrobromobenzene,[1] and orthonitranisol.[2] It is best obtained from sulphanilic acid or anilineparasulphonic acid, $C_6H_4(NH_2)SO_3H$, by converting its sodium salt into sodium acetanilidesulphonate by means of acetic anhydride. This is dissolved in 5 parts of sulphuric acid, well cooled, and heated with the calculated quantity of nitric acid. The solution is poured on to ice, neutralized with lime, and the filtrate evaporated to a small bulk and boiled with dilute sulphuric acid in order to remove the acetyl group. Potassium nitranilinesulphonate is prepared from this, and is then decomposed by heating with concentrated hydrochloric acid to 170°—180°; orthonitraniline separates out from the solution thus obtained on addition of ammonia.[3] It crystallizes in orange-yellow needles melting at 71°·5, which dissolve in hot water and volatilize when the solution is boiled. Its yellow salts are very unstable.

Metanitraniline is best obtained by mixing 10 parts of metadinitrobenzene, 30 parts of 90 per cent. alcohol, and 5 parts of concentrated ammonia, and passing sulphuretted hydrogen through the mixture, which is warmed from time to time, until 5 parts by weight have been absorbed. The solution is then precipitated with water, the precipitate boiled with dilute hydrochloric acid, and the filtrate re-precipitated with ammonia, the metanitraniline being crystallized from boiling water.[4] It crystallizes in long yellow needles melting at 114°, and subliming in small plates at 100°.[5] It has a sweet

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[1] Walker and Zincke, *Ber. Deutsch. Chem. Ges.* v. 114.
[2] Salkowski, *Ann. Chem. Pharm.* clxxiv. 278.
[3] Nietzki and Benckiser, *Ber. Deutsch. Chem. Ges.* xviii. 294.
[4] Beilstein and Kurbatow, *Ann. Chem. Pharm.* clxxvi. 44.
[5] Hübner, *Ber. Deutsch. Chem. Ges.* x. 1716.

burning taste, boils at 285°, and does not precipitate metallic salts. Its salts are much more stable than those of the ortho-compound, but are decomposed by aniline. It is not attacked by boiling caustic soda.[1]

Paranitraniline is obtained in a similar manner to the ortho-compound from the corresponding para-compounds, as well as, together with the former, by the nitration of the anilides.[2]

To prepare it, 1 part of acetanilide is dissolved in 3 parts of cooled nitric acid of sp. gr. 1·5, the solution precipitated with ice-water, and the paranitracetanilide filtered off. The filtrate contains orthonitracetanilide, which can be extracted with chloroform; both anilides are then decomposed with boiling hydrochloric acid.[3] According to Nölting and Collin, acetanilide is dissolved in 4 parts of sulphuric acid, and to this solution, which is kept cold by a freezing mixture of ice and salt, the calculated quantity of 85 per cent. nitric acid is gradually added, the para-compound being formed, together with a little orthonitracetanilide.[4] If aniline be dissolved in concentrated sulphuric acid, well cooled, and then treated with nitric acid largely diluted with sulphuric acid, all three nitranilines are formed. In order to separate them, the solution is precipitated by ice-water, neutralized with carbonate of soda, and distilled, the ortho- and meta-compound being found in the distillate, while the para-compound remains behind.[5]

It crystallizes from hot water in long, yellow, monoclinic needles, which are almost tasteless, and melt at 147°. It is a very weak base, and on boiling with concentrated caustic soda forms paranitrophenol (Wagner). Its salts are less stable than those of the meta-compound, but more so than those of orthonitraniline.[6]

DINITRANILINES, $C_6H_3(NO_2)_2NH_2$.

			Melting-point.
Asymmetrical	(2 : 4)[7]	yellow monoclinic needles having a bluish lustre	182°
Adjacent	(2 : 6)[8]	long yellow needles	138°

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[1] Wagner, *Ber. Deutsch. Chem. Ges.* vii. 77.

[2] Arppe, *Ann. Chem. Pharm.* xciii. 357 ; Hofmann, *Jahresb.* 1860, 349.

[3] Grethen, *Ber. Deutsch. Chem. Ges.* ix. 775 ; Beilstein and Kurbatow, *Liebig's Ann.* cxcvii. 83 ; Witt, *Ber. Deutsch. Chem. Ges.* viii 144.

[4] *Ibid.* xvii. 261.

[5] Hübner, *ibid.* x. 1716.

[6] Lellmann, *ibid.* xvii. 2719.

[7] Gottlieb, *Ann. Chem. Pharm.* lxxxv. 24 ; Rudnew, *Zeitsch. Chem.* 1871, 202 ; Engelhardt and Latschinow, *ibid.* 1870, 233 ; Clemm, *Journ. Prakt. Chem.* [2]. i. 145 ; Salkowski, *Ann. Chem. Pharm.* clxxiv. 263 ; Schaumann, *Ber. Deutsch. Chem. Ges.* xii. 1345.

[8] Salkowski, Körner.

TRINITRANILINE, $C_6H_2(NO_2)_3NH_2$ (2 : 4 : 6).

This compound, which is also named picramide, is obtained by the action of ammonia on ethyl picrate and chlorotrinitrobenzene.[1] It crystallizes from glacial acetic acid in dark yellow monoclinic tablets with a violet lustre, melting at 188°.

Like picric acid, it combines with benzene to form $C_6H_2(NO_2)_3NH_2 + C_6H_6$, crystallizing in broad, light yellow transparent prisms, which rapidly lose benzene in the air. It also combines with other hydrocarbons and with amido-bases.

Picramide-aniline, $C_6H_2(NO_2)_3NH_2 + C_6H_5NH_2$, crystallizes in thick, black, lustrous prisms or very long needles with a dark purple reflection, which form a blood-red powder, and melt at 123°—125°.

Picramide-dimethylaniline, $C_6H_2(NO_2)_3NH_2 + C_6H_5.N(CH_3)_2$, forms dark blue, lustrous crystals melting at 139°—141°.

Both these compounds decompose in the air, picramide being left behind.[2]

CHLORONITRANILINES, $C_6H_3Cl(NO_2)NH_2$.

1047 These compounds are obtained by the nitration of the monochloracetanilides, as well as by heating the dichloronitrobenzenes with ammonia. The following are known (the first of the subjoined numbers gives the position of the chlorine, and the second that of the nitroxyl, the amido-group occupying position 1):

			Melting-point.
Orthochlorometanitraniline	(2 : 5)[3]	yellow needles .	117°—118°
Orthochloroparanitraniline	(2 : 4)[4]	light yellow needles	104°—105°
Metachlororthonitraniline	(3 : 6)[5]	yellow needles .	124°—125°
Metachloroparanitraniline	(3 : 4)[6]	small yellow plates	156°—157°
Parachlororthonitraniline	(4 : 2)[7]	orange red needles	115°

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[1] Pisani, *Ann. Chem. Pharm.* xcii. 326.

[2] Mertens, *Ber. Deutsch. Chem. Ges.* xi. 843; Hepp, *Ann. Chem. Pharm.* ccxv. 358.

[3] Beilstein and Kurbatow, *Ann. Chem. Pharm.* clxxxii. 98.

[4] *Ibid.*

[5] Korner, *loc. cit.*; Laubenheimer, *Ber. Deutsch. Chem. Ges.* ix. 1826.

[6] *Ibid.*

[7] Korner.

BROMONITRANILINES, $C_6H_3Br(NO_2)NH_2$.

			Melting-point.
Orthobromoparanitraniline	(2 : 4)[1]	yellow needles	104·5°
Metabromorthonitraniline	(3 : 6)[2]	reddish yellow needles	151·4°
Parabromorthonitraniline	(4 : 2)[3]	orange-yellow needles	111·4°

IODONITRANILINES.

			Melting-point.
Ortho-iodoparanitraniline	(2 : 4)[4]	long needles	105·5°
Meta-iodorthonitraniline	(3 : 6)[5]	steel-blue plates	—
Para-iodorthonitraniline	(4 : 2)[6]	orange-yellow needles	122°

Besides these substitution products of aniline, many others can be prepared containing several halogens, and also nitroxyl.

AMIDOBENZENESULPHONIC ACIDS,
$C_6H_4(NH_2)SO_3H$.

1048 Gerhardt, by heating formanilide, oxanilide, or aniline with sulphuric acid, obtained an acid which he called sulphanilic acid.[7] Laurent considered that he had obtained this compound by the reduction of his nitrobenzenesulphonic acid, but Schmitt showed that this was a different substance.[8] Limpricht, who first prepared the three nitrobenzenesulphonic acids in the pure state, found that they are readily converted into the amido-acids by treating their ammonium salts with concentrated ammonia and passing in hydrogen sulphide as long as heat is evolved. The solution is then evaporated until all the ammonium sulphide is driven off, filtered from the precipitated sulphur, and acidified with hydrochloric acid. The amido-acid,

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[1] Körner; Hübner, *Ber. Deutsch. Chem. Ges.* x. 1709.

[2] Körner; Wurster, *ibid.* vi. 1542.

[3] Körner; Meyer and Wurster, *Ann. Chem. Pharm.* clxxi. 59.

[4] Michael and Norton, *Ber. Deutsch. Chem. Ges.* xi. 113.

[5] Körner.

[6] Michael and Norton.

[7] *Ann. Chem. Pharm.* lx. 308.

[8] *Ibid.* cxx. 164.

which separates out after long standing, is purified by recrystallization from hot water.[1]

Orthamidobenzenesulphonic acid has been carefully examined by Limpricht and Berndsen.[2] It is obtained by converting nitrometabromobenzenesulphonic acid into the amido-acid and heating this with hydriodic acid and phosphorus.[3] It is scarcely soluble in cold water, somewhat more readily in hot, and crystallizes in anhydrous dull-white rhombohedral forms, or sometimes in thick rhombic plates, mixed with transparent, four-sided, pointed prisms, containing half a molecule of water.

Metamidobenzenesulphonic acid has also been examined by Berndsen;[4] it crystallizes in long, fine, anhydrous needles, or, on gradual evaporation of its solution, in transparent monoclinic prisms, which contain 1·5 molecules of water. It is prepared on the large scale from the crude metanitro-acid, and is employed in the manufacture of colours.

Paramidobenzenesulphonic acid is formed by the above reactions, and also on heating aniline ethylsulphate,[5] and aniline parabenzenesulphate, which decomposes into phenol and sulphanilic acid.[6]

According to Schmitt it is prepared by pouring 2 parts of fuming sulphuric acid into 1 part of aniline, warming the mixture to 180° till sulphur dioxide begins to escape, allowing it to cool, and then pouring it into water. The acid separates out as a crystalline mass, which can be purified by recrystallization from hot water. It is employed in the coal-tar colour industry, and is prepared on the large scale by heating 3 parts of concentrated sulphuric acid with 1 part of aniline to 195°; if fuming sulphuric acid be used, the reaction proceeds more rapidly, but the mixture must not be so strongly heated (Busch and Bindschedler).

Sulphanilic acid is slightly soluble in cold, readily in hot water, and crystallizes in rhombic tablets which contain 1 molecule of water, and rapidly effloresce in the air. Dilute chromic acid oxidizes it to quinone.

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[1] *Ann. Chem. Pharm.* clxxvii. 79.
[2] *Ibid.* clxxvii. 18.
[3] *Ibid.* clxxxvi. 128.
[4] *Ibid.* clxxvii. 82.
[5] Limpricht, *Ber. Deutsch. Chem. Ges.* vii. 1349.
[6] Pratesi and Kopp, *ibid.* iv. 978.

DIAMIDOBENZENES OR PHENYLENEDIAMINES, $C_6H_4(NH_2)_2$.

1049 Zinin first obtained the meta-compound of this group in an impure state by the continued action of ammonium sulphide on ordinary dinitrobenzene, and called it "semibenzedam,"[1] while Gerhardt gave to it the name of azophenylamine. Hofmann first obtained it pure by reducing dinitrobenzene with iron and acetic acid, and described it as α-phenylenediamine, to distinguish it from β-phenylenediamine, which he had obtained from paranitraniline.[2] Besides their preparation from dinitrobenzene and nitraniline, the three diamidobenzenes can be obtained from the six diamidobenzoic acids, $C_6H_3(NH_2)_2CO_2H$, by the elimination of carbon dioxide, as shown by Griess, who first prepared the ortho-compound in this way.[3]

ORTHODIAMIDOBENZENE.

This body may be obtained by the above-mentioned reactions,[4] and also by the action of sodium amalgam and water on parabromonitraniline.[5] It crystallizes from hot water in colourless or slightly reddish tablets, and from chloroform in quadratic plates; it melts at 102°—103° (Hübner), and boils at 252° (Griess).

On throwing a crystal into water it acquires an extremely rapid rotation in dissolving, which is still more striking than that which is exhibited by camphor. Its isomerides and homologues behave in a similar manner.[6]

Orthodiamidobenzene hydrochloride, $C_6H_4(NH_3Cl)_2$, is readily soluble in water, and crystallizes in groups of radiating needles. On adding ferric chloride to its solution, ruby-red needles separate out[7] having the formula $C_{24}H_{18}N_6O(ClH)_2 + 5H_2O$.[8]

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[1] *Journ. Prakt. Chem.* xxxiii. 34.

[2] *Jahresb.* 1863, 421.

[3] *Ber. Deutsch. Chem. Ges.* v. 201.

[4] Zincke and Sintenis, *Ber. Deutsch. Chem. Ges.* vi. 123; Zincke and Rinne, *ibid.* vii. 1374.

[5] Meyer and Wurster, *Ann. Chem. Pharm.* clxxi. 63; Hübner, *ibid.* ccix. 360.

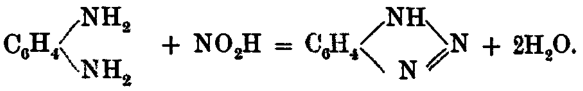
[6] Gattermann, *Ber. Deutsch. Chem. Ges.* xviii. 1484.

[7] Griess.

[8] Rudolph, *Ber. Deutsch. Chem. Ges.* xii. 2211.

On treating an alcoholic solution of the base with a drop of a solution of phenanthraquinone, $C_{14}H_8O_2$, in hot glacial acetic acid, and boiling for a short time, a bright yellow precipitate of diphenylenequinoxaline, $C_{20}H_{12}N_2$, separates out, consisting of small needles, which are coloured deep-red by concentrated hydrochloric acid. In this way 0·5 mgms. of orthodiamidobenzene can be detected. Orthodiamidotoluene behaves in a similar manner.[1]

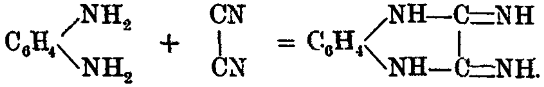
On adding a dilute solution of potassium nitrite to a very dilute solution of orthodiamidobenzene sulphate, *amido-azophenylene* separates out as any oily liquid, which soon solidifies:



$$C_6H_4\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right. + NO_2H = C_6H_4\left\langle\begin{array}{l}NH\\N\end{array}\right\rangle N + 2H_2O.$$

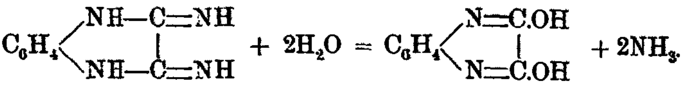
This body crystallizes from a mixture of benzene and toluene in needles, with a pearly lustre, which melt at 98°·5 and are not acted on by ferric chloride.[2]

Dicyanorthodiamidobenzene, $C_8H_8N_4$, is obtained by passing cyanogen through a concentrated alcoholic solution of orthodiamidobenzene:



$$C_6H_4\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right. + \begin{array}{c}CN\\|\\CN\end{array} = C_6H_4\left\langle\begin{array}{l}NH-C{=}NH\\ \qquad\;|\\NH-C{=}NH.\end{array}\right.$$

It crystallizes from hot water in pale yellow rhombic tablets readily soluble in alcohol, which sublime when cautiously heated, but do not melt even at 280°.[3] On heating it with hydrochloric acid to 150° the following reaction takes place:



$$C_6H_4\left\langle\begin{array}{l}NH-C{=}NH\\ \qquad\;|\\NH-C{=}NH\end{array}\right. + 2H_2O = C_6H_4\left\langle\begin{array}{l}N{=}C.OH\\ \quad\;\;|\\N{=}C.OH\end{array}\right. + 2NH_3.$$

The dioxyquinoxyline formed will be described later on.

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[1] Hinsberg, *Ber. Deutsch. Chem. Ges.* xviii. 1228.
[2] Ladenburg, *ibid.* ix. 221.
[3] Bladin, *ibid.* xviii. 672.

METADIAMIDOBENZENE.

1050 This compound is obtained by reducing metanitraniline, metadinitrobenzene,[1] bromodinitrobenzene,[2] and β-dinitrobenzoic acid, with elimination of carbon dioxide in the latter case.[3] It is also obtained by heating δ-diamidobenzoic acid with baryta,[4] and was found by Hofmann in aniline oil.[5] It is prepared from its hydrochloride by heating with caustic baryta. It generally remains liquid for a long time, but solidifies gradually, or, when a crystal of the base is thrown in, suddenly to a crystalline mass, which is scarcely soluble in water but readily in alcohol. It melts at 63°, boils at 287°, and has an alkaline reaction.

Metadiamidobenzene hydrochloride, $C_6H_4(NH_3Cl)_2$, is obtained by the evaporation of its aqueous solution in concentrically arranged crystals. It is employed in the manufacture of colouring matters, for which it is prepared by adding tin to a mixture of hydrochloric acid and dinitrobenzene; zinc is gradually added to the solution to precipitate the metallic tin and so bring it into action again. After the dinitrobenzene has dissolved, the metadiamidobenzene hydrochloride is precipitated by concentrated hydrochloric acid. It is also obtained on the manufacturing scale by reducing dinitrobenzene with iron and hydrochloric acid, the solution thus obtained being directly employed for the preparation of colouring matters.

On adding potassium nitrite to the neutral solution of the hydrochloride, a yellow to brown colouration is produced according to the degree of concentration; this reaction is so delicate that even less than 0·1 mgrm. of nitrous acid in 1 litre of water can be detected by means of it.[6] The substance formed is triamido-azobenzene or phenylene brown.

Tetramethylmetadiamidobenzene, $C_6H_4.N_2(CH_3)_4$, is obtained by heating metadiamidobenzene with methyl alcohol and hydrochloric acid to 180°—190°, and decomposing the product with caustic soda.

It is an oily liquid, boiling at 256°, and having a peculiar smell. With methyl iodide it forms the compound $C_6H_4N_2(CH_3)_5I$, which can be obtained in splendid crystals by evaporating the

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[1] Hofmann, *Jahresb. Chem.* 1861, 512; 1863, 422; Gerdemann, *Zeitschr. Chem.* 1865, 51.

[2] Zincke and Sintenis, *Ber. Deutsch. Chem. Ges.* v. 792.

[3] Wurster, *ibid.* vii. 149.

[4] Ambühl and Wurster, *ibid.* vii. 214.

[5] *Ibid.* vii. 812.

[6] Griess, *ibid.* xi. 624.

aqueous solution; this body is both an ammonium iodide and an amidobase, and therefore combines with acids.[1]

Nitrosotetramethylmetadiamidobenzene, $C_6H_3(NO)N_2(CH_3)_4$, is obtained by adding sodium nitrite to a solution of the tetramethyl-base in hydrochloric acid. The hydrochloride, $C_6H_3(NO)N_2(CH_3)_4ClH$, thus obtained crystallizes in lustrous, deep garnet-red, almost black, needles, which dissolve in water with a fine wine-red colour. On adding caustic soda the solution becomes orange-yellow, with formation of the free nitro-base which may be extracted with ether, and is thus obtained as a deep brown oil, which gradually solidifies. It forms colouring matters of various shades with phenols and amido-bases.[2]

Hexmethylorthodiphenylammonium iodide, $C_6H_4N_2(CH_3)_6I_2$, was obtained by Hofmann, together with the preceding compound, as a final product of the alternate treatment of metadiamidobenzene with methyl iodide and silver oxide; it forms small plates readily soluble in water.[3]

Diphenylmetadiamidobenzene, $C_6H_4(NH.C_6H_5)_2$, is obtained by heating resorcinol with aniline, calcium chloride and a little zinc chloride. It readily dissolves in benzene and hot alcohol, and crystallizes in flat needles melting at 95°. Its hydrochloride, $C_6H_4(NH.C_6H_5)_2(ClH)_2$, forms deliquescent needles. Nitric acid added to its solution in concentrated sulphuric acid produces a yellowish green colouration which soon changes to a bluish violet.[4]

Metaphenylene-oxamic acid, $C_6H_4(NH_2)NH.C_2O_2\,OH$, is formed when metadiamidophenol is added to a boiling solution of oxalic acid; it is slightly soluble in water, and crystallizes in bushy needles, which melt at a very high temperature, undergoing considerable carbonization.[5]

PARADIAMIDOBENZENE.

1051 This is obtained in a similar manner to its isomerides.[6] It is best prepared by the reduction of paranitracetanilide with tin and hydrochloric acid.[7]

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[1] Wurster and Morley, *Ber. Deutsch. Chem. Ges.* xii. 1814.

[2] Witt, *ibid.* xviii. 877.

[3] Hofmann, *Jahresber.* 1863, 422.

[4] Calm, *Ber. Deutsch. Chem. Ges.* xvi. 2792.

[5] Klasemann, *ibid.* vii. 1261.

[6] Hofmann, *loc. cit.*; Zincke and Rinne, *Ber. Deutsch. Chem. Ges.* vii. 871; Martins and Griess, *Zeitschr. Chem.* 1866, 136; Griess, *Ber. Deutsch. Chem. Ges.* v. 201.

[7] Horbrecker, *Ber. Deutsch. Chem. Ges.* v. 920.

To prepare the free base, the hydrochloride is distilled with anhydrous sodium carbonate.[1] It is slightly soluble in water, more readily in alcohol and ether, crystallizing from the latter in tablets melting at 140°; it sublimes in small plates, and boils at 267°. It is distinguished from its isomerides by the fact that on heating with manganese dioxide and dilute sulphuric acid it is oxidized to quinone.

Paradiamidobenzene hydrochloride, $C_6H_4(NH_3.Cl)_2$, is readily soluble in water and crystallizes in tablets which are scarcely soluble in hydrochloric acid. Bleaching powder precipitates quinone-dichlorimide from its solution (p. 174).

Dimethylparadiamidobenzene, $C_6H_4(NH_2)N(CH_3)_2$, is obtained by the reduction of nitrodimethylaniline or nitrosodimethylaniline.[2] It dissolves readily in water, melts at 41°, and boils at 257°. It is employed for the manufacture of colouring matters, and as a reagent for the detection of sulphuretted hydrogen. The sulphate, which is employed for this purpose, may be readily prepared from *Helianthin*, $C_6H_4N(CH_3)_2.N_2.C_6H_4.SO_3NH_4$, a commercial azo-colour, by heating it with ammonium sulphide on the water-bath until the orange colour disappears. In this way it is decomposed into the ammonium salt of sulphanilic acid and the free base; this is extracted with ether, the solution shaken with lead hydroxide suspended in water, and an ethereal solution of sulphuric acid added to the filtrate. The ether is then poured off from the pulpy mass, and the residue warmed on the water-bath with 4 to 5 parts of absolute alcohol until the salt separates out in fine needles. It is then washed with alcohol on to a filter pump and dried. On treating it with a hydrochloric acid solution of sulphuretted hydrogen, a splendid blue colour is obtained, methylene blue being formed.[3]

Tetramethylparadiamidobenzene, $C_6H_4(N(CH_3)_2)_2$, is obtained by heating the preceding compound with hydrochloric acid and methyl alcohol to 170°—180°, and then gradually to 200°. It is slightly soluble in cold, more readily in hot water, and readily in alcohol, crystallizing in small, lustrous, colourless or yellowish tablets melting at 51°, and boiling at 260°. Its aqueous solution becomes deep violet-blue in the air, and its salts are also coloured on addition of oxidizing agents, while its acetic acid

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[1] Biedermann and Ledoux, *Ber. Deutsch. Chem. Ges.* vii. 1531.

[2] Schraube, *ibid.* viii. 619; Weber, *ibid.* x. 762; Wurster, *ibid.* xii. 522 and 528.

[3] E. Fischer, *ibid.* xvi. 2234.

solution is converted by sodium nitrite into nitrosotrimethylparadiamidobenzene, $C_6H_4N_2(CH_3)_3NO$, which crystallizes from water in small greenish yellow plates, melting at 98°—99°, and giving Liebermann's reaction. Tin and hydrochloric acid convert it into trimethylparadiamidobenzene, $C_6H_4N_2(CH_3)_3H$, an oily liquid, the salts of which give a splendid reddish-violet colouration with weak oxidizing agents.

On adding potassium ferricyanide to a solution of the sulphate of the tetramethyl-base, small blue needles are precipitated, possessing a cupreous lustre similar to that of indigo; these are a ferrocyanide, $C_{10}H_{14}N_2.Fe_2(CN)_6H_4$.

The tetramethyl-base combines with methyl iodide to form the compound $C_6H_4N_2(CH_3)_5I$, which crystallizes in small plates.[1]

Hexmethylparadiphenylammonium iodide, $C_6H_4N_2(CH_3)_6I_2$, Hofmann obtained this compound by the alternate action of methyl iodide and silver oxide on paradiamidobenzene; it crystallizes in small plates (Hofmann).

Ethylparadiamidobenzene, $C_6H_4(NH_2)NH(C_2H_5)$, and *Diethylparadiamidobenzene*, $C_6H_4(NH_2)N(C_2H_5)_2$, may be obtained from ethylaniline and diethylaniline by the nitroso-reaction, and likewise give colouring matters.[2]

Diphenylparadiamidobenzene, $C_6H_4(NH.C_6H_5)_2$, is obtained by heating quinol with aniline, calcium chloride and a little zinc chloride, and crystallizes in lustrous plates melting at 152°. Its solution in concentrated sulphuric acid is coloured cherry red to magenta red by nitric acid.[3]

Acetylparadiamidobenzene or *Amido-acetanilide*, $C_6H_4(NH_2)(NH.C_2H_3O)$, may be obtained by the reduction of nitroacetanilide with iron and acetic acid, and crystallizes from hot water in clusters of long, thin needles melting at 161°. It is a monacid base, and forms crystalline salts.[4]

Amidodiphenylamine, $NH(C_6H_5)C_6H_4.NH_2$, is obtained by the action of acetic acid and zinc dust on nitrodiphenylamine, phenylamido-azobenzene, $C_6H_5.N_2.C_6H_4.NH(C_6H_5)$, and phenylamido-azosulphonic acid, the potassium salt of which is known in commerce under the name *Tropaeolin* OO. The product is extracted with water, saturated with caustic potash, and extracted with ether. On shaking the ethereal solution with

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[1] Wurster, *loc. cit.*; Wurster and Schobig, *Ber. Deutsch. Chem. Ges.* xii. 1807.

[2] Oehler, *ibid.* xiv. 553; Nietzki, *ibid.* xvi. 470.

[3] Calm, *ibid.* xvi. 2805.

[4] Nietzki, *ibid.* xvii. 343.

dilute sulphuric acid, amidodiphenylamine sulphate separates out in small fine plates with a silver lustre.

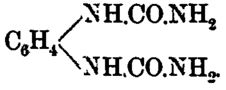
On adding ammonia to the hot aqueous solution of the salt, and allowing it to cool, the base crystallizes out in small lustrous plates which melt at 61°, and are coloured green by the air. Ferric chloride added to solutions of its salts, produces a red colouration which soon changes into green, while on strongly concentrating the solution a green precipitate is obtained, which dissolves in concentrated sulphuric acid with a carmine-red colour.[1]

Diamidodiphenylamine, $NH(C_6H_4.NH_2)_2$, is formed, together with paradiamidobenzene, when aniline-black is boiled with tin and hydrochloric acid, or with hydriodic acid and phosphorus.[2] It crystallizes from hot water in small, feather-like plates which melt at 158°; and yields a diazo-compound which is converted by boiling alcohol into diphenylamine. On oxidation it yields quinone, and ferric chloride colours its solution dark green.

Diphenylamine gives two dinitro-compounds, one of which is yellow and yields diamidodiphenylamine on reduction, while the isomeric one is red and yields an oily base (Nietzki and Witt).

CARBAMIDE-DERIVATIVES OF THE DIAMIDO-BENZENES.[3]

1052 On treating solutions of the diamido-benzene hydrochlorides with a solution of potassium cyanate, phenylene-carbamides are obtained:



$$C_6H_4\begin{cases} NH.CO.NH_2 \\ NH.CO.NH_2. \end{cases}$$

Orthophenylene dicarbamide is readily soluble in water and alcohol, and crystallizes in delicate needles, which melt at 290° and sublime in small plates showing a play of colours.

Metaphenylene dicarbamide is only slightly soluble in hot water, and less so in alcohol; it forms crystals which melt above 300° and sublime, with considerable decomposition, in stellate-grouped needles.[4]

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[1] Nietzki and Witt, *Ber. Deutsch. Chem. Ges.* xii. 1399.

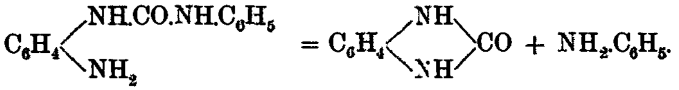
[2] Nietzki, *ibid.* xi. 1097.

[3] Lellmann, *Ann. Chem. Pharm.* ccxxi. 1; Lellmann and Würthner, *ibid.* ccxxviii. 199.

[4] Warder, *Ber. Deutsch. Chem. Ges.* viii. 1180.

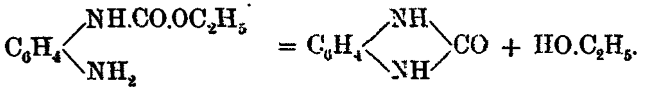
Paraphenylene dicarbamide forms small plates with a silver lustre, which are extremely difficult to dissolve in the ordinary solvents, and on heating decompose with carbonization.

The diamidobenzenes combine with phenylisocyanate to form compounds which decompose on heating into aniline and phenylene carbamides:



$$C_6H_4\begin{cases}NH.CO.NH.C_6H_5\\NH_2\end{cases} = C_6H_4\begin{cases}NH\\NH\end{cases}CO + NH_2.C_6H_5.$$

Orthophenylene carbamide is also obtained by heating orthonitraniline with ethyl chlorocarbonate and converting the nitrophenyl urethane formed, by means of tin and hydrochloric acid, into the amido-compound, which crystallizes in long needles, melting at 86° and decomposing on strongly heating.



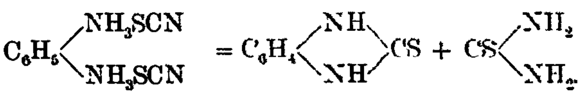
$$C_6H_4\begin{cases}NH.CO.OC_2H_5\\NH_2\end{cases} = C_6H_4\begin{cases}NH\\NH\end{cases}CO + HO.C_2H_5.$$

Orthophenylene carbamide crystallizes from hot water, in which it is only slightly soluble, and from alcohol in bright, lustrous plates, which become coloured brown and melt at 305°.[1]

Metaphenylene carbamide is also obtained by the action of carbonyl chloride on metadiamidobenzene. It is a white amorphous insoluble powder, which commences to char at 300° without melting. On heating with hydrochloric acid to 160°—170°, it decomposes into carbon dioxide and metadiamidobenzene.[2]

Paraphenylene carbamide is a brown, insoluble powder which carbonizes on heating.

On mixing solutions of the diamidobenzene hydrochlorides with ammonium thiocyanate, thiocyanates of these bases are obtained; those of the meta- and para-compounds are converted on heating into the isomeric phenylene-dithiocarbamides, while that of the ortho-compound is converted into phenylene-monothiocarbamide:



$$C_6H_5\begin{cases}NH_3SCN\\NH_3SCN\end{cases} = C_6H_4\begin{cases}NH\\NH\end{cases}CS + CS\begin{cases}NH_2\\NH_2.\end{cases}$$

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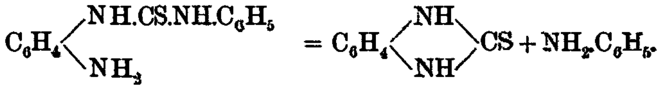
[1] Rudolph, *Ber. Deutsch. Chem. Ges.* xii. 1295.
[2] Wichler and Zimmermann, *ibid.* xiv. 2177.

The diamidobenzenes also combine with phenyl mustard oil forming amidodiphenyl-thiocarbamides, of which the meta-compound melts on heating without decomposition, while the two isomerides lose aniline without melting:



$$C_6H_4\left\langle\begin{array}{l}NH.CS.NH.C_6H_5\\NH_2\end{array}\right. = C_6H_4\left\langle\begin{array}{c}NH\\NH\end{array}\right\rangle CS + NH_2.C_6H_5.$$

This is therefore an example of condensation taking place in the para-series.

Orthophenylene thiocarbamide is slightly soluble in water, readily in alcohol, and crystallizes from ammonia in large, colourless plates, which blacken and melt at about 290°, giving off a vapour which condenses forming plates exhibiting a play of colours, and produces on inhalation an intensely bitter taste.

Orthamidodiphenyl thiocarbamide forms colourless, lustrous prisms, which are readily soluble in alcohol and glacial acetic acid, with difficulty in benzene, and insoluble in ether.

Metaphenylene dithiocarbamide is only slightly soluble in the ordinary reagents; it is more readily soluble in alkalis, and is precipitated by acids in microscopic plates, melting at 215°.

Metamidodiphenyl thiocarbamide forms a yellow, amorphous powder, or colourless prisms, melting at 147°—148°, and solidifying to a vitreous mass.

Paraphenylene thiocarbamide forms light brown, almost insoluble microscopic plates, melting at 270°—271°.

Paraphenylene dithiocarbamide is insoluble in water, slightly soluble in alcohol, and crystallizes from aqueous ammonia in small needles, melting at 218°.

Paramidodiphenyl thiocarbamide crystallizes from alcohol in red prisms, which begin to fuse at 163° with separation of aniline, this being formed in much larger quantity at 185°.

TRIAMIDOBENZENES, $C_6H_3(NH_2)_3$.

1053 Two of these are known at present:

a-Triamidobenzene (1 : 2 : 3), is obtained by the dry distillation of triamidobenzoic acid, and is a red or brown crystalline mass, melting at 103°, and boiling at 330°. It is a diacid base and forms crystallizable salts. If it be dissolved in concentrated sulphuric acid and a trace of nitric acid added, the liquid is coloured a greenish blue and then a fine dark blue.[1]

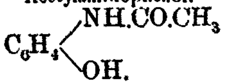
β-Triamidobenzene, (1 : 2 : 4), is formed by the reduction of the asymmetrical dinitraniline,[2] as well as by the action of tin and hydrochloric acid on dinitro-azobenzeneparasulphonic acid, $C_6H_3(NO_2)_2N{=}NC_6H_4SO_3H$.[3] It is a crystalline mass which soon turns red, melts at 132°—133°, and boils at about 340°. Like the preceding compound it is a diacid base; its dilute solutions are coloured emerald green by ferric chloride or potassium dichromate.

AMIDOPHENOLS, $C_6H_4(NH_2)OH$.

1054 These compounds are obtained by the reduction of the nitrophenols as well as by heating amidosalicylic acid, $C_6H_3(NH_2)(OH)COOH$, and its isomerides with caustic baryta. They are weak bases; their halogen substitution products, on the other hand, behave like phenol, their acid character increasing with the number of hydrogen atoms replaced. The replacement of hydrogen by nitroxyl acts still more strongly in this way.

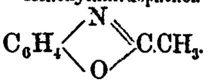
In these compounds, as in other amido-derivatives, hydrogen can be replaced by acid radicals. It is a characteristic property of ortho-amidophenol that its acid derivatives, like those of many other ortho-amido-compounds, readily lose water and form anhydro-compounds:

Acetylamidophenol.



$$C_6H_4\begin{cases}NH.CO.CH_3\\OH.\end{cases}$$

Ethenylamidophenol.



Ortho-amidophenol was discovered by Hofmann, who obtained it by the action of sodium sulphide on orthonitrophenol;[4] the reduction may be more readily effected by tin and hydrochloric acid.[5] It crystallizes in small rhombic plates with a pearly lustre, which melt at 170° but sublime at a lower temperature. Its hydrochloride is readily soluble in water and crystallizes in long needles.

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[1] Salkowski, *Ann. Chem. Pharm.* clxiii. 23.

[2] *Ibid.* clxxiv. 265.

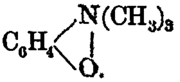
[3] Janowsky, *Monatsh. Chem.* v. 159.

[4] *Ann. Chem. Pharm.* ciii. 351.

[5] Cook and Schmitt, *Kekulé's Lehrb.* iii. 61; *Ber. Deutsch. Chem. Ges.* i. 67.

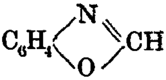
Methylortho-amidophenate or *Ortho-anisidine*, $C_6H_4(NH_2)OCH_3$, is formed by the reduction of orthonitranisol, $C_6H_4(NO_2)OCH_3$,[1] and is a mobile, strongly refractive liquid, having a peculiar odour, and boiling at 226°·5. It forms salts which crystallize well. Methyl iodide acts violently upon it; if the two substances be mixed and kept cool by a freezing mixture, methylortho-anisidine, $C_6H_4(NH.CH_3)OCH_3$, is formed as a liquid boiling at 218°—220°.[2]

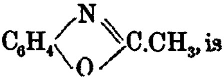
Trimethylortho-amidophenol or *Trimethylhydroxyphenylammonium hydroxide*, $HO.C_6H_4N(CH_3)_3OH$, is obtained by treating a solution of ortho-amidophenol hydrochloride in methyl alcohol with 3 parts of methyl iodide, adding a considerable excess of caustic potash and allowing the whole to stand, with repeated additions of potash, until an acid reaction is no longer produced.[3] The hydriodide thus obtained is decomposed by freshly precipitated silver oxide. The base is readily soluble in water and alcohol, but not in ether, and crystallizes in white prisms which have an intensely bitter taste. On heating to 105° it forms the anhydride:



$$C_6H_4\begin{cases}N(CH_3)_3\\ \mid \\ O.\end{cases}$$

On distillation it is converted into the isomeric orthodimethylamido-anisol, $CH_3O.C_6H_4N(CH_3)_2$, a basic, strongly refractive liquid, boiling at 210°—212° (Griess, Mühlhäuser). The corresponding orthodimethylamidophenol, $HO.C_6H_4.N(CH_3)_2$, is formed, together with methyl chloride, by the dry distillation of trimethylamidophenol hydrochloride, and crystallizes in rhombic prisms, which melt at 45° and form an amorphous hydrochloride.

Methenylamidophenol,  $C_6H_4\begin{cases}N\\O\end{cases}CH$, is prepared by heating ortho-amidophenol with formic acid. It crystallizes in prisms, melting at 30°·5, and boiling at 182°·5.[4]

Ethenylamidophenol,  $C_6H_4\begin{cases}N\\O\end{cases}C.CH_3$, is obtained by heating ortho-amidophenol with acetic anhydride, and is a basic liquid boiling at 200°—201°. It is converted by heating with dilute

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[1] Mühlhäuser, *Liebig's Ann.* ccvii. 235.
[2] *Ibid.*
[3] Griess, *Ber. Deutsch. Chem. Ges.* xiii. 246.
[4] Ladenburg, *ibid.* x. 1124.

acids into *acetylamidophenol*, $HO.C_6H_4.NH(CO.CH_3)$,[1] which is also formed by the action of tin and acetic acid on orthonitrophenol.[2] It crystallizes from dilute alcohol in small plates, melting at 201°.

1055 *Metamidophenol* is not known in the free state, as it is a very unstable substance. Its hydrochloride is obtained by the reduction of metanitrophenol with tin and hydrochloric acid; it forms hard, colourless granules, an aqueous solution of which soon decomposes and becomes brown.[3]

Paramidophenol. Fritsche obtained this compound by the action of acetic acid and iron filings on paranitrophenol.[4] It is best prepared by reducing the latter compound with tin and hydrochloric acid.[5] It crystallizes in small colourless plates, which rapidly turn brown and melt, with decomposition, at 184°.[6] Its alkaline solution becomes coloured violet in the air, and it is readily converted into quinone by oxidizing agents.[7] The hydrochloride crystallizes in prisms, which readily dissolve in water, forming a solution which is coloured first violet and then green by bleaching powder (Lossen).

Methylparamidophenate or *Paranisidine*, $C_6H_4(NH_2)OCH_3$, has been prepared by the reduction of paranitranisol,[8] and forms large rhombic tablets, melting at 55°·5—56°·5,[9] and boiling at 245°—246°.[10] Its hydrochloride crystallizes in long needles, and gives a violet colouration with ferric chloride.

Trimethylparamidophenol, $HO.C_6H_3N(CH_3)_3OH$, is obtained in a similar manner to the ortho-compound, and crystallizes in small plates or prisms. On distillation it is converted into *paradimethylamido-anisol*, $CH_3O.C_6H_4N(CH_3)_2$, which crystallizes from alcohol in small rhombic plates (Griess).

1056 *α-Nitramidophenol*, $C_6H_3(NO_2)NH_2(OH)$, is formed by the reduction of α-dinitrophenol. It crystallizes with one molecule of water in orange-red prisms, which lose their water of crystallization on heating, and then melt at 142°—143°.[11]

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[1] *Ber. Deutsch. Chem. Ges.* ix. 1524.

[2] Morse, *ibid.* xi. 232.

[3] Bantlin, *ibid.* xi. 2099.

[4] *Ann. Chem. Pharm.* cx. 166.

[5] Cook and Schmitt, *Kekulé's Lehrb.* iii. 62.

[6] Lossen, *Ann. Chem. Pharm.* clxxv. 296.

[7] Körner, *Jahresb.* 1867, xxiii. and clxxiii.; Schmitt, *Journ. Prakt. Chem.* [2], xix. 317; Andresen, *ibid.* xxiii. 173.

[8] Cahours, *Ann. Chem. Pharm.* lxxiv. 300; Brunck, *Zeitsch. Chem.* 1867, 205.

[9] Lossen, *Ann. Chem. Pharm.* clxxv. 324.

[10] Salkowski, *Ber. Deutsch. Chem. Ges.* vii. 1009.

[11] Stuckenberg, *Liebig's Ann.* ccv. 66.

β-Nitramidophenol crystallizes in red needles, melting at 110°—111° (Stuckenberg).

γ-Nitramidophenol is obtained by boiling nitrometadiamidobenzene with caustic potash, and crystallizes in yellowish red plates, melting at 133°—134°.[1]

α-Dinitramidophenol or *Picramic acid*, $C_6H_2(NO_2)_2NH_2(OH)$. By the action of milk of lime or baryta on a mixture of ferrous sulphate and picric acid (carbazotic acid), Wöhler obtained a blood-red solution, and found that it contained the salts of a peculiar crystalline acid, which he called "reduced carbazotic acid,"[2] while Berzelius named it "nitrohaematic acid."[3] Girard, by treating picric acid with ammonium sulphide, obtained a similar compound, and named it picramic acid;[4] Pugh then showed that this is identical with Wöhler's acid, and that it is also formed by the action of stannous chloride on picric acid.[5] It may also be obtained by nitrating *α*-nitramidophenol (Stuckenberg). In order to prepare it, an alcoholic solution of picric acid is evaporated with an excess of ammonium sulphide, the residue extracted with water, and the filtrate decomposed by acetic acid.[6]

Picramic acid ($OH : NO_2 : NH_2 : NO_2 = 1 : 2 : 4 : 6$), crystallizes in dark red needles or monoclinic prisms, melting at 165°, and forming orange-red solutions in water and alcohol, which are rendered more deeply coloured by alkalis.

Potassium picramate, $C_6H_2(NO_2)_2NH_2(OK)$, crystallizes in long, red, rhombic tablets.

Ammonium picramate, $C_6H_2(NO_2)_2NH_2(ONH_4)$, forms dark, orange-red rhombohedra.

Silver picramate, $C_6H_2(NO_2)_2(NH_2)(OAg)$, is an amorphous, red precipitate.

Methyl picramate or *Dinitranisidine*, $C_6H_2(NO_2)_2NH_2(OCH_3)$. Cahours prepared this compound by the action of alcoholic ammonium sulphide on methyl picrate. It crystallizes from hot alcohol in dark violet needles, and, like picramic acid, combines with acids to form unstable salts.

β-Dinitramidophenol, ($OH : NO_2 : NH_2 : NO_2 = 1 : 4 : 6 : 2$). This compound, which is also known as *isopicramic acid*, is prepared by heating a solution of benzoylamidosalicylic acid, $C_6H_3(NH.C_7H_5)(OH)CO_2H$, in glacial acetic acid with nitric

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[1] Barbaglia, *Ber. Deutsch. Chem. Ges.* vii. 1257.

[2] *Pogg. Ann.* xiii. 488.

[3] *Lehrb.* iv. 675.

[4] *Ann. Chem. Pharm.* lxxxviii. 281; *Jahresb.* 1855, 535.

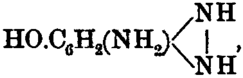
[5] *Ann. Chem. Pharm.* xcvi. 83.

[6] Lea, *Chem. News*, iv. 193; Petersen, *Zeitsch. Chem.* 1868, 377.

acid; carbon dioxide is thus eliminated with formation of benzoylisopicramic acid, which is then decomposed, by heating with hydrochloric acid, into benzoic acid and isopicramic acid. This crystallizes from hot water in lustrous yellow plates or needles, which become brown on drying, dissolve in alcohol or water with a cherry-red colour, and melt with decomposition at 170°.

Potassium isopicramate, $C_6H_2(NO_2)_2NH_2(OK)$, is readily soluble in water, and crystallizes in dark blue needles.[1]

Diamidophenol, $C_6H_3(NH_2)_2OH$, is formed by the reduction of *a*-dinitrophenol,[2] and is scarcely known in the free state, as it is very readily decomposed. Its salts crystallize well; their aqueous solutions rapidly turn brown in the air, and are coloured an intense dark red by ferric chloride or potassium dichromate.

Triamidophenol, $C_6H_2(NH_2)_3OH$. By the action of iodide of phosphorus and water on picric acid, Lautemann obtained a salt which he named picrammonium iodide, $C_6H_3(NH_3I)_3$.[3] Heintzel, however, found[4] that by the reduction of picric acid with tin and hydrochloric acid, the hydrochloride of triamidophenol, $C_6H_2(OH)(NH_3Cl)_3$, is formed, and that Lautemann's compound is the corresponding hydriodide. Gauhe[5] denied this, but Heintzel then proved[6] that triamidophenol, and not triamidobenzene, is obtained by the reduction of picric acid. It is also formed by the action of tin and hydrochloric acid on picramide,[7] one amido-group being replaced by hydroxyl. It is very unstable in the free state, and its salts also readily oxidize. Its dilute solution is coloured a deep blue by ferric chloride, amidodi-imidophenol,  $HO.C_6H_2(NH_2)\left\langle\begin{array}{l}NH\\ |\\ NH\end{array}\right.$, being formed. This is a monacid base, the hydrochloride of which crystallizes in brown needles with a blue lustre (Heintzel).

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[1] Dabney, *Amer. Chem. Journ.* v. 20.

[2] Gauhe, *Ann. Chem. Pharm.* cxlvii. 66; Stuckelberg, *ibid.* ccv. 66; Hemilian, *Ber. Deutsch. Chem. Ges.* viii. 768.

[3] *Ann. Chem. Pharm.* cxxv. 1.

[4] *Zeitsch. Chem.* 1867, 338.

[5] *Ibid.* 1868, 90.

[6] *Ber. Deutsch. Chem. Ges.* i. 111.

[7] Hepp, *Ann. Chem. Pharm.* ccxv. 350.

AMIDODIHYDROXYBENZENES.

1057 *Amidocatechol*, $C_6H_3(NH_2)(OH)_2$, is obtained by the reduction of nitrocatechol with tin and hydrochloric acid; its hydrochloride forms long, dark coloured needles. When the free base is separated by an alkali it immediately oxidizes in the air and dissolves with a dark violet colour.[1]

Amidoresorcinol, $C_6H_3(NH_2)(OH)_2$, is formed by the action of tin and hydrochloric acid on nitroresorcinol[2] and phenylazoresorcinol, $C_6H_5.N_2.C_6H_3(OH)_2$.[3] The hydrochloride, $C_6H_7NO_2.HCl + 2H_2O$, crystallizes in large oblique prisms or flat plates, which appear colourless when the light passes through the broad faces, but olive-brown when it passes through the narrow ones. They become coloured green in the air; when caustic soda is added to the solution a deep blue colouration is produced, which then becomes green and finally yellowish brown. Ferric chloride produces a deep brown colouration, and then an almost black precipitate.

Diamidoresorcinol, $C_6H_2(NH_2)_2(OH)_2$, has been prepared from dinitrosoresorcinol[4] (p. 143), and from phenyldisazoresorcinol, $(C_6H_5N_2)_2C_6H_2(OH)_2$.[5] The hydrochloride, $C_6H_8N_2O_2(HCl)_2$, is rather unstable; the sulphate, $2C_6H_8N_2O_2.SO_4H_2 + 3H_2O$, forms slightly soluble needles. The free base, which is separated by alkalis, rapidly decomposes and becomes brown; if, however, the salt be suspended in chloroform, shaken with a few drops of caustic soda solution, and then largely diluted with water, it is coloured bright blue. Ferric chloride produces the same colouration, which, however, soon changes into a dirty brown.

Triamidoresorcinol, $C_6H(NH_2)_3(OH)_2$, is prepared from trinitroresorcinol, and is very unstable in the free state. The hydrochloride, $C_6H_9N_3O_2(HCl)_3 + H_2O$, crystallizes in needles, which dissolve very readily in water, and are reprecipitated by hydrochloric acid. They decompose in the air, and become coloured red.

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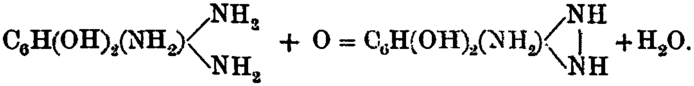
[1] Benedikt, *Ber. Deutsch. Chem. Ges.* xi. 363.
[2] Weselsky, *Ann. Chem. Pharm.* clxiv. 6.
[3] Meyer and Kreis, *Ber. Deutsch. Chem. Ges.* xvi. 1330.
[4] Fitz, *ibid.* viii. 633.
[5] Liebermann and Kostanecki, *ibid.* xvii. 881.

Amidodi-imidoresorcinol, $C_6H_7N_3O_2 + H_2O$, is obtained by the oxidation of the preceding compound, either by passing air through its concentrated solution, or by the addition of ferric chloride:



$$C_6H(OH)_2(NH_2)\left\langle\begin{matrix}NH_2\\ NH_2\end{matrix}\right. + O = C_6H(OH)_2(NH_2)\left\langle\begin{matrix}NH\\ |\\ NH\end{matrix}\right. + H_2O.$$

Ammonia precipitates the compound in green needles, having a metallic lustre, which are insoluble in alcohol and dissolve in caustic potash with a deep blue colour. The hydrochloride crystallizes in splendid red needles, being only very slightly soluble in water, and reprecipitated by hydrochloric acid.[1] When it is heated with an acid to 170°, trihydroxyquinone (p. 157) is formed.

Phloramine, $C_6H_3(NH_2)(OH)_2(1:3:5)$, is formed when phloroglucinol is dissolved in ammonia. This reaction is very remarkable, as in other phenols the hydroxyl can only be replaced by the amido-group with great difficulty. It crystallizes from warm water in small micaceous plates, which in the damp state rapidly become brown, but when dry do not change. In this it differs from amidoresorcinol, which contains the hydroxyls in the same positions. Phloramine has a slightly astringent taste, gives no colouration with ferric chloride, and only reduces silver solution when warmed; most of its salts crystallize well.

Phloramine hydrochloride, $C_6H_7NO_2.HCl + H_2O$, forms needles or small plates; the nitrate, $C_6H_7NO_2.HNO_3$, crystallizes in bronze-coloured, and the sulphate $(C_6H_7NO_2)_2.H_2SO_4 + 2H_2O$, in yellow, needles.[2]

Amidodimethylquinol, $C_6H_3(NH_2)(OCH_3)_2$, is formed by the action of tin and hydrochloric acid on nitrodimethylquinol;[3] it is, however, much more readily prepared by gradually adding sodium amalgam to an alcoholic solution of this containing acetic acid.[4]

It crystallizes from hot water in small plates with a pearly lustre; it separates from hot benzene in brown crystals, and from petroleum spirit in scales with a silver lustre, which in thick layers show a brown reflection. It readily decomposes

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[1] Schreder, *Ann. Chem. Pharm.* clviii. 250.

[2] Hlasiwetz, *ibid.* cxix. 202.

[3] Mühlhäuser, *ibid.* ccvii. 254; Margatti, *Ber. Deutsch. Chem. Ges.* xiv. 71.

[4] Baessler, *ibid.* xvii. 2118.

even in vacuo and changes into a black mass. Its hydrochloride crystallizes in white, efflorescent needles.

The aqueous solution of the base reduces silver solution, a mirror being formed; on heating it with ferric chloride, small greenish plates separate out, which dissolve in water with a red colour.

Dimethylquinoltrimethylammonium iodide, $C_6H_2(OCH_3)_2N(CH_3)_3I$, is formed when the base is heated to 150° with methyl iodide and a little wood spirit. It crystallizes in fine white needles, which melt at 202°, and dissolve readily in water, but with some difficulty in alcohol. Moist silver oxide converts it into the hydroxide, which has a strong alkaline reaction, is exceedingly soluble in water, and crystallizes in transparent needles; the chloride forms white, readily soluble needles, which melt at 172° (Baessler).

Diamidodimethylquinol, $C_6H_2(NH_2)_2(OCH_3)_2$, is prepared by reducing the corresponding nitro-compound, dissolved in acetic acid, with tin and hydrochloric acid. The hydrochloride crystallizes in long, lustrous needles, which melt at 169°, and when dried at 100° have the composition $C_8H_{12}N_2O_2.HCl$.[1]

AMIDOTRIHYDROXYBENZENES.

1058 *Amidopyrogallol*, $C_6H_2(NH_2)(OH)_3$, is obtained by the action of tin and hydrochloric acid on nitropyrogallol. The hydrochloride forms brown needles, which become a greyish black on standing; its solution soon becomes dark and deposits a flocculent blue precipitate; if, however, it be rapidly evaporated, a dark blue mass separates out, and the concentrated liquid then deposits aggregates of short dark prisms, which dissolve in water with a deep bluish violet colour. These become black on standing, and then only partially dissolve in water with a brown colour. When a freshly prepared solution of the hydrochloride is shaken up with caustic soda, a deep blue colouration, which remains for some time, is produced.[2]

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[1] Kariof, *Ber. Deutsch. Chem. Ges.* xiii. 1676.

[2] Barth, *Monatsh. Chem.* i. 882.

AMIDOTETRAHYDROXYBENZENES.

1059 *Amidonitrotetrahydroxybenzene*, $C_6(NO_2)(NH_2)(OH)_4$, is prepared by reducing the potassium salt of nitranilic acid (p. 163) with a solution of stannous chloride in hydrochloric acid; it separates out in long, brownish violet needles. Its solution in caustic potash or potassium carbonate rapidly blackens in the air, the corresponding quinone being formed.

Diamidotetrahydroxybenzene, $C_6(NH_2)_2(OH)_4$. In order to obtain this substance the method described for the preparation of the preceding compound is followed, and, after this has separated out, zinc is added until the solution becomes colourless. The hydrochloride of the base, $C_6(NH_2.HCl)_2(OH)_4$, is then precipitated in long needles by a stream of hydrochloric acid gas. The base, which is separated by caustic soda, rapidly decomposes and becomes brown; nitric acid oxidizes it to triquinoyl (p. 193).

AMIDO-DERIVATIVES OF QUINONE.

1060 *Dichlorodiamidoquinone* or *Chloranilamide*, $C_6Cl_2(NH_2)_2O_2$, is formed by the action of alcoholic ammonia on chloranil.[1] It forms a dark red crystalline powder with a semi-metallic lustre, sublimes when heated, and is insoluble in water, alcohol, ether, and ammonia. It dissolves in alcoholic potash with a violet-red colour, but is decomposed when the solution is boiled, chloranilic acid and ammonia being formed. Its violet-red solution in sulphuric acid is coloured blue by a little water; when more is added the colour changes to wine-red and the compound is precipitated.

Amidonitrodihydroxyquinone, $C_6(NO_2)(NH_2)O_2(OH)_2$. When the solution of amidonitrotetrahydroxybenzene in potassium carbonate is sufficiently concentrated, the salt, $C_6(NO_2)(NH_2)O_2(OK)_2$, separates out in black needles which have a cupreous lustre. The black solution of this compound is turned yellow by hydrochloric acid, and on standing deposits small orange-red prisms of the compound $C_6(NO_2)(NH_2)O_2(OH)OK$.

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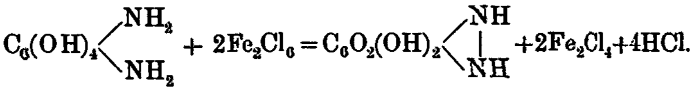
[1] Laurent, *Berz. Jahresb.* xxv. 850; Knapp and Schultz, *Ann. Chem. Pharm.* ccx. 180.

Di-imidodihydroxyquinone, $C_6(NH_2)O_2(OH)_2$, is obtained in small, almost black plates with a green lustre, by the addition of ferric chloride or some other oxidizing agent to a solution of diamidotetrahydroxybenzene hydrochloride:



$$C_6(OH)_4\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right. + 2Fe_2Cl_6 = C_6O_2(OH)_2\left<\begin{matrix}NH\\|\\NH\end{matrix}\right. + 2Fe_2Cl_4 + 4HCl.$$

It is scarcely soluble in the ordinary solvents, but imparts a yellowish red colour to them. It forms a brown solution in sulphuric acid, but is partially decomposed; nitric acid oxidizes it to triquinoyl.[1]

Dianilidoquinone or *Quinonanilide*, $C_6H_2(NH.C_6H_5)_2O_2$, is formed when quinone is boiled with aniline and alcohol;[2] in this reaction quinol and a brownish red substance, insoluble in water, are formed:[3]

$$3C_6H_4O_2 + 2NH_2.C_6H_5 = C_6H_2(NH.C_6H_5)_2O_2 + 2C_6H_4(OH)_2.$$

It crystallizes in small, reddish brown plates with a metallic lustre, which form a magenta-coloured solution in sulphuric acid.

Chlorodianilidoquinone, $C_6HCl(NH.C_6H_5)_2O_2$, is prepared from trichloroquinone, and forms small brown plates with a metallic lustre, which form a blue solution in sulphuric acid.[4]

Dichloranilidoquinone, $C_6Cl_2(NH.C_6H_5)_2O_2$. This compound, which has also been called *chloranil-anilide*, is obtained by boiling chloranil with aniline and alcohol (Hofmann, Knapp, and Schultz). It is insoluble in water, scarcely soluble in alcohol, but somewhat more readily in boiling benzene and glacial acetic acid, from which it crystallizes in small, square, brownish black plates, which form a bluish violet solution in sulphuric acid.

By the action of aniline on an alcoholic solution of trichloroquinone chlorimide, $C_6HCl_3O(NCl)$, a compound is obtained which is probably identical with dichloranilidoquinone. It crystallizes from hot benzene in small, yellowish brown plates with a slight metallic lustre, which form a deep blue solution in sulphuric acid.[5]

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[1] Nietzki, *Ber. Deutsch. Chem. Ges.* xvi. 2092; Nietzki and Benckiser, *ibid.* xviii. 499.

[2] Hofmann, *Jahresb. Chem.* 1863, 415; Wichelhaus, *Ber. Deutsch. Chem. Ges.* v. 851.

[3] Knapp and Schultz, *Ann. Chem. Pharm.* ccx. 178.

[4] Neuhöfer and Schultz, *Ber. Deutsch. Chem. Ges.* x. 1793; Knapp and Schultz.

[5] Schmitt and Andresen, *Journ. Prakt. Chem.* [2], xxiv. 426.

The three preceding compounds are converted by reduction into the corresponding quinol derivatives, which rapidly oxidize again in the air.

1061 *Trichloroquinonedimethylanilenimide*, $C_{14}H_{11}Cl_3N_2O$.—Schmitt and Andresen give this name to a compound which is obtained by adding dimethylaniline to a warm alcoholic solution of trichloroquinone chlorimide:

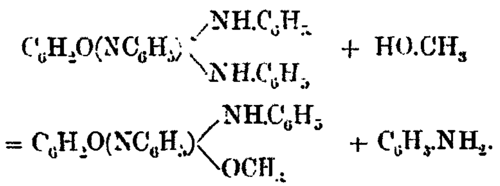
$$C_6HCl_3O.NCl + C_6H_5.N(CH_3)_2 = C_6HCl_3O.NC_6H_4.N(CH_3)_2 + HCl.$$

The liquid becomes coloured a deep blue, and after some hours deposits needles an inch in length, which appear golden green when the beam of light falls in one plane with the longer axis, and deep red when it is perpendicular to this axis. They give a sky-blue streak and are very elastic and tough, and therefore difficult to pulverize. Hot water is coloured blue by them, but only a trace dissolves; they are slightly soluble in cold alcohol, more readily in hot, and easily in ether and benzene, forming a greenish blue solution.

This compound is converted by reduction into *trichlorodimethylanilenamidophenol*, $C_6HCl_3(OH)NH.C_6H_4.N(CH_3)_2$, which crystallizes from hot alcohol in fine white prisms, fusing at 138°—139° to a deep blue liquid. As it is a phenol it dissolves in alkalis forming solutions which rapidly absorb oxygen, the quinonimide being re-formed. On the other hand it gives stable, crystalline salts with acids.

Dianilidoquinonanilide, $C_6H_2(NH.C_6H_5)_2O(NC_6H_5)$, is obtained by heating a solution of 1 part of quinone and 2 parts of aniline in 20 parts of hot glacial acetic acid for a short time on the water bath. The anilide separates out on cooling in brownish red needles which melt at 202°—203° and form a blood-red solution in sulphuric acid. It forms salts which are very soluble, and therefore difficult to obtain pure.

Anilidohydroxyquinonanilide, $C_6H_2O(NC_6H_5)(NH.C_6H_5)OH$.—The methyl ether of this compound is formed when the preceding compound is warmed with methyl alcohol and sulphuric acid:



$$C_6H_2O(NC_6H_5)\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. + HO.CH_3$$
$$= C_6H_2O(NC_6H_5)\left\langle\begin{matrix}NH.C_6H_5\\OCH_3\end{matrix}\right. + C_6H_5.NH_2.$$

It crystallizes in large, brownish red plates, which melt at 188°—189°, and form soluble blue salts. The platinum chloride is deposited from its solution in small, dark, lustrous plates; the picrate forms small, brownish violet, lustrous crystals.

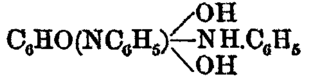
The ethyl ether crystallizes in small red plates or prisms, melting at 134°.

When the ether is decomposed with very dilute alcoholic potash, the free anilidohydroxyquinonanilide is obtained. It crystallizes in scales with a metallic lustre, which form a green powder, slightly soluble in alcohol and readily in acetic acid. It forms very soluble salts; those of potassium and sodium crystallizing in small brown needles with a silky lustre.

Anilidohydroxyquinone, $C_6H_2O_2(NH.C_6H_5)OH$, is prepared by heating the above compound with dilute caustic potash until the dark red solution becomes brighter. It is set free by acids as a blue crystalline precipitate, which dissolves readily in hot alcohol and glacial acetic acid, and forms a brown solution in sulphuric acid, from which it is reprecipitated by water. It forms soluble alkaline salts.

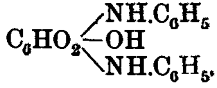
When dianilidoquinonanilide is heated with alcoholic potash, the compound $C_{18}H_{14}N_2O_3$ is formed; this crystallizes in small red needles melting at 191°—192°, is readily soluble in alcohol and benzene, dissolves in sulphuric acid with a green colour, and forms metallic salts. Its constitution is expressed by one of the following formulæ:[1]

Anilidodihydroxyquinonanilide.



$$C_6HO(NC_6H_5)\left\langle\begin{matrix}OH\\NH.C_6H_5\\OH\end{matrix}\right.$$

Dianilidohydroxyquinone.



$$C_6HO_2\left\langle\begin{matrix}NH.C_6H_5\\OH\\NH.C_6H_5.\end{matrix}\right.$$

Dihydroxyanilidoquinone, $C_6H_2(NH.C_6H_4.OH)_2O_2$, is formed when quinone is added to a hot solution of paramidophenol in hydrochloric acid. It crystallizes in small, violet-brown, lustrous plates, which are insoluble in the ordinary solvents, but dissolve readily in alkalis.

Orthamidophenol does not give an analogous compound, but is oxidized by the quinone:

$$4C_6H_7NO + 5C_6H_4O_2 = C_{24}H_{18}N_4O_4 + 5C_6H_4(OH)_2.$$

In order to prepare the condensation product which is formed in this reaction, 4—4·5 parts of quinone are added to a hot, con-

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[1] *Zincke, Ber. Deutsch. Chem. Ges.* xviii. 785.

centrated, alcoholic solution of ortho-amidophenol. It separates out on cooling in small violet needles, melting at 250°, and subliming at a higher temperature in small, red, lustrous needles, which are slightly soluble in alcohol and benzene, and more readily in aniline. It dissolves in acids with a deep red colour.

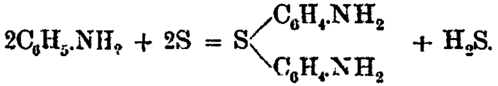
The hydrochloride, $C_{24}H_{18}N_4O_4(HCl)_2$, crystallizes in arborescent needles with a beetle-green lustre, and readily forms double salts with several metallic chlorides. The sulphate is a green crystalline powder, the oxalate crystallizes in green, and the picrate in steel-blue needles with a green reflection.

When the base is boiled with acetic anhydride, the compound $C_{24}H_{16}(C_2H_3O)_2N_4O_4$ is formed; this crystallizes in yellowish brown needles or small plates, melting at 285°.

Ortho-amidophenol methyl ether, $NH_2.C_6H_4.O\ CH_3$, reacts with quinone in an analogous manner to aniline and paramidophenol, *orthodimethoxyanilidoquinone*, $C_6H_2(NH.C_6H_4.OCH_3)_2O_2$, being formed; this substance crystallizes in reddish violet needles melting at 230°, and forms a beautiful blue solution in sulphuric acid. Quinone, on the other hand, does not act upon acetylortho-amidophenol, $C_6H_4(OH)NH(C_2H_3O)$, and from this it follows that both the hydroxyl and the amido-group take part in the formation of the base from ortho-amidophenol.[1]

THIO-AMIDO-COMPOUNDS.

1062 *Thio-aniline* or *Diamidophenyl sulphide*, $S(C_6H_4.NH_2)_2$, is obtained by heating aniline to 150°—160° with sulphur:



$$2C_6H_5.NH_2 + 2S = S\begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{cases} + H_2S.$$

The reaction proceeds more rapidly if litharge be gradually added to take up the sulphuretted hydrogen which is formed.[2]

Thio-aniline may also be prepared by dissolving phenyl sulphide in concentrated nitric acid and reducing the nitro-compound thus formed.[3] It is slightly soluble in hot water, readily in alcohol and ether, and crystallizes in long, thin, odourless needles, melting at 105°.

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[1] Zincke and Hebebrand, *Ann. Chem. Pharm*, ccxxvi. 60.
[2] Merz and Weith, *Ber. Deutsch. Chem. Ges.* iv. 384.
[3] Krafft, *ibid.* vii. 384.

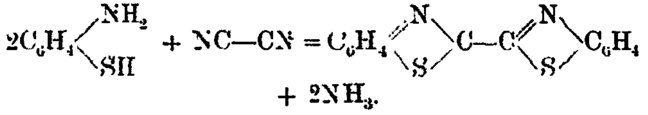
Thio-aniline hydrochloride, $C_{12}H_{12}N_2S(HCl)_2 + 2H_2O$, is readily soluble in water, slightly in hydrochloric acid and alcohol, and crystallizes in lustrous prisms or needles.

Thio-aniline sulphate, $C_{12}H_{12}N_2S,SO_4H_2 + H_2O$, is slightly soluble in cold water, more readily in hot, and almost insoluble in alcohol; it forms short prisms or pointed needles.

Thio-aniline oxalate, $C_{12}H_{12}N_2S,C_2H_2O_4$, crystallizes in fine needles, which are only slightly soluble in hot water.

The solutions of these salts have an acid reaction, and, even when very dilute, colour pine wood a fine orange. Ferric chloride produces a deep violet or blue colouration on warming. When thio-aniline is heated with concentrated sulphuric acid, a colourless solution is obtained, which soon becomes deep blue, and finally violet. If the blue liquid be poured into water, a splendid red solution is formed.

Ortho-amidothiophenol, $C_6H_4(NH_2)SH$, is obtained by the action of tin and hydrochloric acid on orthonitrobenzenesulphonic chloride.[1] It boils at 234°, and solidifies in the cold to needles melting at 26°. When cyanogen is passed through its alcoholic solution, *oxalamidothiophenol* is formed:



This compound may also be prepared by adding phosphorus oxychloride to a solution of anhydrous oxalic acid in ortho-amidothiophenol, or, together with sixty per cent of other products which have not yet been investigated, by heating acetanilide with sulphur for some time; in spite of the small yield this is the best method of preparation. Oxalamidothiophenol crystallizes in lustrous plates, which melt at about 300°, and are almost unaffected by the ordinary solvents. It distils almost without decomposition; when heated to 200° with caustic potash it decomposes completely into oxalic acid and ortho-amidothiophenol, so that the latter is most readily prepared from acetanilide.[2]

Metamidothiophenol is obtained by the reduction of metanitrobenzenesulphonic chloride. It is an oily liquid, smelling of mushrooms;[3] its hydrochloride, $C_6H_4(SH)NH_2.ClH$, is readily

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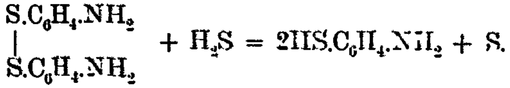
[1] Hofmann, *Ber. Deutsch. Chem. Ges.* xiii. 19.
[2] *Ibid.* xiii. 1223.
[3] Glutz and Schranck, *Journ. Prakt. Chem.* [2], ii. 223.

soluble in water and crystallizes in lustrous, warty masses, melting at 232°, and subliming at higher temperatures.[1]

Orthodiamidophenyl disulphide, $S_2(C_6H_4.NH_2)_2$, is formed by the oxidation of ortho-amidothiophenol in the air, or more rapidly by the addition of ferric chloride to its solution in hydrochloric acid. It is insoluble in water, and crystallizes from hot alcohol in small plates melting at 93°. Its hydrochloride forms small plates, which are scarcely soluble in hydrochloric acid, even when very dilute. When sulphuretted hydrogen is passed through a solution of the base, amidothiophenol is regenerated (Hofmann):



$$\begin{array}{l} S.C_6H_4.NH_2 \\ | \\ S.C_6H_4.NH_2 \end{array} + H_2S = 2HS.C_6H_4.NH_2 + S.$$

Paradiamidophenyl disulphide, $S_2(C_6H_4.NH_2)_2$.—When acetanilide is heated to 100° with chloride of sulphur, two compounds are formed, dithio-acetanilide, $S_2(C_6H_4.NH.C_2H_3O)_2$, and trithio-acetanilide, $S_3(C_6H_4.NH.C_2H_3O)_2$, both of which crystallize from glacial acetic acid in small plates. When the former is heated with dilute sulphuric acid, the sulphate of paradiamidophenyl disulphide, $S_2(C_6H_4.NH_2)_2SO_4H_2 + 2H_2O$, is obtained; it crystallizes in very fine needles, and when treated with an alkali yields the free base. This is slightly soluble in hot water, and crystallizes in long, thin, greenish needles, which have a vitreous lustre, and melt at 78°—79°.

Schmidt calls this compound pseudothio-aniline, and gives the name dithio-aniline to an isomeric resinous substance, which is prepared by the action of bromide of sulphur on aniline, and possesses basic properties.[2]

1063 *Thiodiphenylamine*, $S(C_6H_4)_2NH$, is obtained by heating diphenylamine with sulphur to 250°—300°. It crystallizes from hot alcohol in yellowish, lustrous plates, melting at 180°, distilling at a higher temperature almost without decomposition, and solidifying to a coarse radiating mass.[3] Moderately concentrated nitric acid converts it into nitrodiphenylamine sulphoxide, $SO(C_{12}H_7.NO_2)NH$. This substance has not yet been obtained pure, but the following compound has been obtained from it:

Amidothiodiphenylamine, $S(C_{12}H_7.NH_2)NH$, may be prepared either by reducing the nitro-compound with stannous chloride

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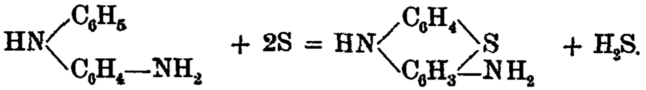
[1] Biedermann, *Ber. Deutsch. Chem. Ges.* viii. 1674.
[2] *Ibid.* xi. 1168.
[3] Bernthsen, *ibid.* xvi. 2896.

and hydrochloric acid in presence of metallic tin, or by heating amidodiphenylamine with sulphur:



$$HN\begin{matrix}\diagup C_6H_5\\ \diagdown C_6H_4-NH_2\end{matrix} + 2S = HN\begin{matrix}\diagup C_6H_4\diagdown\\ \diagdown C_6H_3\diagup\end{matrix}S \quad\begin{matrix}\\ -NH_2\end{matrix} + H_2S.$$

It is slightly soluble in hot water, readily in alcohol, and crystallizes in small plates with a satin lustre.

Ferric chloride oxidizes its solution in hydrochloric acid to imidothiodiphenylimide, $C_{12}H_8N_2S$, a violet-red colouring matter, which will be subsequently described. Alcoholic ammonium sulphide reduces it again to amidothiodiphenylamine, which is most readily purified in this manner.[1]

Fuming nitric acid converts thiodiphenylamine into two isomeric dinitrodiphenylamine sulphoxides, $SO(C_6H_3.NO_2)_2NH$.[2]

a-Dinitrodiphenylamine sulphoxide soon separates out from the solution in small, bright yellow crystals, almost insoluble in alcohol, and only slightly soluble in glacial acetic acid; it crystallizes from hot aniline in small yellowish red needles or prisms.

β-Dinitrodiphenylamine sulphoxide is precipitated by water from the nitric acid solution, and after being boiled with alcohol forms a fine, bright yellow powder.

Both these compounds are reduced by tin and hydrochloric acid to the corresponding diamidothiodiphenylamines, $S(C_6H_3.NH_2)_2NH$, the oxygen of the sulphoxide being eliminated; these compounds and the colouring matters which are readily obtained from them by oxidation will be subsequently described. Owing to this formation of colouring matters, even fractions of a milligramme of thiodiphenylamine can be detected with ease. The substance to be tested is dissolved in a few drops of glacial acetic acid, treated with fuming nitric acid and diluted with water. The nitro-compound which is precipitated is then boiled with an acid solution of stannous chloride, the tin precipitated from the colourless solution by zinc, and an excess of ammonia added; the solution on standing in the air soon becomes coloured a deep violet. If ferric chloride be added instead of ammonia, a deep violet colouration is produced if the solution be dilute, while if it be concentrated a reddish violet precipitate is thrown down.

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[1] Bernthsen, *Ber. Deutsch. Chem. Ges.* xvii. 2857.

[2] *Ibid.* xvii. 611.

Methylthiodiphenylamine, $S(C_6H_4)_2NCH_3$, is obtained by heating thiodiphenylamine with methyl iodide and wood spirit, and crystallizes from hot alcohol in splendid long prisms, melting at 99°·3. Potassium permanganate, added to its boiling aqueous solution, oxidizes it to *methyldiphenylamine sulphone*, $SO_2(C_6H_4)_2NCH_3$, crystallizing in masses of small needles, and melting at about 222°. Like other sulphones it has neither acid nor basic properties; it forms a deep blue solution in boiling sulphuric acid, which becomes a brownish violet on dilution with water.

Dinitromethyldiphenylamine sulphoxide, $SO(C_6H_3.NO_2)_2NCH_3$, is formed by the action of fuming nitric acid on the preceding compound. It is more soluble in glacial acetic acid than the dinitrodiphenylamine sulphoxides, but, unlike these, is insoluble in dilute alkalis, the hydrogen of the imido-group, which is replaceable by metals, being absent. On reduction it is converted into *diamidomethylthiodiphenylamine*, $S(C_6H_3.NH_2)_2NCH_3$, which rapidly oxidizes to a very unstable bluish green colouring matter.[1]

Ethylthiodiphenylamine, $S(C_6H_4)_2NC_2H_5$, crystallizes from alcohol in long, thin, white prisms, melting at 102°.

Acetylthiodiphenylamine, $S(C_6H_4)_2NC_2H_3O$, is obtained in thick, colourless crystals by heating thiodiphenylamine with acetic anhydride; it is slightly soluble in alcohol and is deposited from its solution in long, thin, glittering prisms.

DIAZO-DERIVATIVES OF BENZENE.

1064 The formation and constitution of these important compounds have been discussed in the Introduction. They are much used in the laboratory, as well as in colour works, for the preparation of substitution-products, azo-colours, &c. For these purposes it is generally unnecessary to prepare the pure diazo-salt, a solution of it being all that is required. A solution of the chloride is obtained by adding sodium nitrite to a cooled, dilute solution of one molecule of aniline and two of hydrochloric acid, which is well stirred during the addition. The end of the reaction is recognised by the evolution of free nitrous acid, which may be detected by its smell, or by holding some paper soaked

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[1] *Ber. Deutsch. Chem. Ges.* xvii. 2854.

in potassium iodide and starch over the liquid. In this way either sodium nitrite or aniline in solution can be roughly estimated.[1]

When the solution is treated with strong hydrochloric acid and heated, a mixture of phenol and chlorobenzene is formed.[2] If, however, the solution be heated nearly to boiling, and then a solution of cuprous chloride in hydrochloric acid added, pure chlorobenzene is obtained.[3] In a similar manner Sandmeyer has replaced the amido-groups of metanitraniline, orthamidophenol, paradiamidobenzene, and metadiamidobenzene directly by chlorine.[4]

A solution of diazobenzene nitrate or sulphate is often used instead of the chloride, and is obtained in a similar manner. When a solution of the sulphate is boiled, pure phenol is formed, and by means of this reaction many amido-bases can be completely converted into phenols.[5]

Diazobenzene chloride, $C_6H_5N_2Cl$, is only known in solution; when hydrochloric acid and stannic chloride are added to a concentrated solution, the double salt, $(C_6H_5N_2Cl)_2SnCl_4$, separates out in small, white, indistinct plates, which are only very slightly soluble in alcohol and ether, but readily in lukewarm water, from which they are reprecipitated by concentrated hydrochloric acid. The dry compound decomposes on heating with vigorous decrepitation; on boiling with water it yields phenol. When allowed to stand in the air for a considerable time, the compound undergoes a decomposition in which the greater portion of it is apparently converted into paradiphenol, $OH.C_6H_4.C_6H_4.OH$.[6]

Diazobenzene bromide, $C_6H_5N_2Br$, is prepared by the addition of bromine to an ethereal solution of diazo-amidobenzene:

$$C_6H_5N{=\!=}N{-}NH.C_6H_5 + 3Br_2 = C_6H_5N{=\!=}NBr \\ + C_6H_2Br_3.NH_2 + 2HBr.$$

The tribromaniline remains in solution, while the bromide separates out in small plates with a mother-of-pearl lustre, which are very explosive in the dry state. By shaking its aqueous solution with silver chloride, a solution of pure diazobenzene chloride is obtained.

Diazobenzene perbromide, $C_6H_5NBr{-}NBr_2$, is formed when a solution of the nitrate is treated with hydrobromic acid and

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[1] Nietzki, *Ber. Deutsch. Chem. Ges.* xvii. 1351.
[2] Gasiorowsky and Wayss, *ibid.* xviii. 337.
[3] Sandmeyer, *ibid.* xvii. 1633.
[4] *Ibid.* xvii. 2650.
[5] V. Meyer, *ibid.* viii. 1074.
[6] Griess, *ibid.* xviii. 965.

bromine. It separates out as a brown oil, which, after being washed with ether, solidifies in large yellow plates. It is tolerably stable in the dry state, but on standing in contact with water or ether, in which it is insoluble, or with alcohol, in which it dissolves to a slight extent, it rapidly decomposes. On heating it detonates violently; when it is heated with anhydrous carbonate of soda, or boiled with absolute alcohol, bromobenzene is formed. This can also be obtained from aniline by means of the diazo-reaction in the following manner; a solution of 12·5 grms. of copper sulphate, 36 grms. of potassium bromide, and 11 grms. of sulphuric acid, sp. gr. 1·8, in 80 grms. of water is heated with 20 grms. of copper filings until the colour has nearly disappeared; 9·3 grms. of aniline are then added, the whole heated nearly to boiling, and a solution of 7 grms. of sodium nitrite added gradually. In this way 9 grms. of bromobenzene are obtained (Sandmeyer).

1065 *Diazobenzene nitrate*, $C_6H_5.N_2.NO_3$, was first obtained by Griess, and used as a starting-point for other diazobenzene compounds.[1] In order to prepare it, the nitrous gases evolved from a mixture of arsenic trioxide and nitric acid are led slowly into a well-cooled paste of aniline nitrate and water, until the addition of caustic potash to a small portion ceases to set free aniline. It is then filtered from a brown resinous body which is generally formed, and the diazobenzene nitrate precipitated in long, white needles by the addition of alcohol and ether to the filtrate. It is readily soluble in water and slightly in alcohol, but is insoluble in ether; in the dry state it explodes when gently heated, or on percussion, even more violently than fulminating mercury or iodide of nitrogen.

If its cold, saturated solution be allowed to drop into concentrated ammonia, diazo-amidobenzene, an amorphous brownish red body, $C_{18}H_{24}N_2O$ and a compound, which has the formula $C_{12}H_{13}N_5O$, are formed. This last compound may be obtained in yellow prisms by the spontaneous evaporation of its deep yellow solution, and explodes even more readily and with greater violence than the nitrate. On boiling with hydrochloric acid it decomposes with formation of phenol and aniline:

$$C_{12}H_{13}N_5O = C_6H_6O + C_6H_7N + 2N_2.$$

Acid diazobenzene sulphate, $C_6H_5.N_2.SO_4H$, is obtained by the addition of dilute sulphuric acid to an aqueous solution of the

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[1] *Ann. Chem. Pharm.* cxxxvii. 39.

nitrate. The nitric acid and excess of sulphuric acid are removed by washing with alcohol and ether, and the solution is then allowed to evaporate over sulphuric acid; a little phenol and free sulphuric are thus formed and must be removed by absolute alcohol. The crystals are then dissolved in the smallest possible quantity of water, treated with alcohol and ether, and the aqueous layer again allowed to evaporate.

Acid diazobenzene sulphate crystallizes in white prisms which decompose and deliquesce in the air. It detonates at about 100°.

Diazobenzene platinichloride, $C_6H_5N_2PtCl_6$, is formed when an acid solution of platinum chloride is added to the solution of a diazobenzene salt; it crystallizes in fine, yellow prisms, slightly soluble in water and insoluble in alcohol. When it is ignited with carbonate of soda, chlorobenzene is obtained.

This reaction is used to replace the amido-group by chlorine, but this may be more simply effected by Sandmeyer's method.

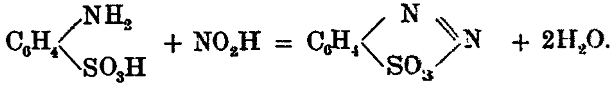
Diazobenzene aurichloride, $C_6H_5N_2AuCl_4$, crystallizes from warm alcohol in splendid small plates with a golden lustre, which are insoluble in water.

Diazobenzene cyanide, $C_6H_5N_2CN + HCN$, is obtained by the addition of the sulphate to a cooled solution of potassium cyanide, and crystallizes in orange-yellow prisms, which melt at 69° and are very unstable.[1]

Diazobenzene picrate, $C_6H_5N_2OC_6H_2(NO_2)_3$, is a yellow, crystalline precipitate, insoluble in water, alcohol, ether and benzene.[2]

Potassium diazobenzenesulphonate, $C_6H_5N_2SO_3K$, is prepared by adding diazobenzene nitrate to a cooled, slightly alkaline solution of potassium sulphite and then treating with caustic potash; this precipitates the compound in yellow crystals which detonate violently when heated. Like all the diazo-compounds, it gives Liebermann's reaction (p. 176) with phenol and sulphuric acid.[3] On reduction it is converted into potassium phenylhydrazinesulphonate, $C_6H_5.N_2H_2.SO_3K$.

1066 *Diazobenzenesulphonic acids* are obtained by the action of nitrous acid on the anilinesulphonic acids according to the following equation;



$$C_6H_4\begin{cases}NH_2\\SO_3H\end{cases} + NO_2H = C_6H_4\begin{cases}N\\SO_3\end{cases}N + 2H_2O.$$

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[1] Gabriel, *Ber. Deutsch. Chem. Ges.* xii. 1638.

[2] Baeyer and Jäger, *ibid.* viii. 893.

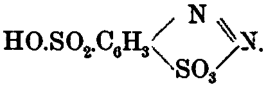
[3] Fischer, *Liebig's Ann.* exc. 73.

As may be seen from this formula, they are not true acids, but must be considered as salts of diazobenzene.

Metadiazobenzenesulphonic acid forms small, reddish yellow prisms, which readily dissolve in cold water, but are decomposed by water at 60° with formation of metaphenolsulphonic acid. It is not attacked by boiling absolute alcohol, and in the dry state detonates violently when heated.[1]

Paradiazobenzenesulphonic acid was first obtained by Schmitt.[2] To prepare it, rather more than the calculated quantity of sodium nitrite is added to a solution of sulphanilic acid (paramidobenzenesulphonic acid) in dilute caustic soda, and the mixture poured into cooled, dilute sulphuric acid. The diazo-compound separates out in white crystals,[3] which are insoluble in cold water, and readily soluble in water at 60°—70°, but are decomposed by it at higher temperatures with formation of paraphenolsulphonic acid, while boiling alcohol converts them into benzenesulphonic acid. Gaseous ammonia decomposes the diazo-compound with explosive violence; it is not attacked by phosphorus pentachloride even at 100°.[4]

Diazobenzenedisulphonic acids are formed by the action of nitrous acid on the amidobenzenedisulphonic acids.[5] They are monobasic acids of the following constitution:



$$HO.SO_2.C_6H_3\left\langle\begin{matrix} N \\ SO_3 \end{matrix}\right\rangle N.$$

Diazobenzene potassoxide, $C_6H_5N_2OK$, is obtained, according to Griess, by gradually adding a cold saturated solution of diazobenzene nitrate to a large excess of concentrated caustic potash and evaporating the yellow liquid, which has a peculiar aromatic odour, until it solidifies as a crystalline mass. It is then well pressed between porous plates, extracted with alcohol, the solution evaporated, and the residue again pressed, dried over sulphuric acid and washed with ether to remove a brownish red decomposition product. In order to obtain it perfectly pure, ether is added to its solution in a little absolute alcohol; the diazobenzene potassium is thus precipitated in small white plates which have an alkaline reaction and absorb carbon dioxide very readily. It detonates feebly at 130°, and decomposes in aqueous

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[1] Berndsen, *Liebig's Ann.* clxxvii. 88.
[2] *Ibid.* cxx. 144.
[3] Fischer, *ibid.* cxc. 76.
[4] Laar, *Journ. Prakt. Chem.* [2], xx. 263.
[5] Drebes, *Ber. Deutsch. Chem. Ges.* ix. 553; Heinzelmann, *Liebig's Ann.* clxxxviii. 157, cxc. 223; Zander, *ibid.* cxcviii. 5 and 24.

solution, slowly in the cold, more rapidly on heating, with separation of a brownish red substance.

Diazobenzene argentoxide, $C_6H_5N_2OAg$, is obtained as a greyish white precipitate by mixing a solution of the potassium compound with a silver solution. It can be preserved without undergoing any change, and detonates violently on heating.

Griess has prepared several other compounds of diazobenzene with the metals.[1]

Diazobenzene hydroxide, $C_6H_5N_2OH$.—Griess prepared this compound by the addition of an equivalent of acetic acid to an aqueous solution of diazobenzene potassoxide. He looked upon it as free diazobenzene, $C_6H_4N_2$, and assumed the existence of this group of atoms in its derivatives, giving, *e.g.* to the nitrate, the formula $C_6H_4N_2.NO_3H$. It is a thick yellow oil, which has an aromatic odour, begins to evolve nitrogen a few minutes after it has been isolated, and soon changes to a brownish red elastic substance; with larger quantities the spontaneous decomposition proceeds with explosive violence. The formula given for this substance is deduced from the fact that when freshly prepared it combines with caustic potash, nitric acid, &c., to form the diazo-derivatives which have just been described.

1067 *Diazo-amidobenzene*, $C_6H_5N{=}N.NH.C_6H_5$.—Griess obtained this compound by passing nitrous acid into an alcoholic solution of aniline.[2] He also prepared it by the action of aniline on diazobenzene nitrate:[3]

$$C_6H_5.N_2.NO_3 + 2C_6H_5.NH_2 = C_6H_5.N_2.NH.C_6H_5 \\ + C_6H_5.NH_2.NO_3H.$$

In order to prepare it, a solution of pure potassium nitrite of sp. gr. 1·5, cooled to 5°, is gradually allowed to run on to pure dry aniline hydrochloride, and the residue washed with cold water,[4] or two molecules of aniline are dissolved in ether, exactly a molecule of amyl nitrite added, and the mixture allowed to evaporate over sulphuric acid.[5]

R. Fischer adds one molecule of sodium nitrite to a well-cooled aqueous solution of two molecules of aniline and three molecules of hydrochloric acid, and then a concentrated solution of two molecules of sodium acetate, when the diazo-amidobenzene separates out as a crystalline precipitate.[6]

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[1] *Ann. Chem. Pharm.* cxxxvii. 57.

[2] *Ibid.* xxi. 258.

[3] *Ibid.* cxxxvii. 58; see also Kekulé, *Lehrb.* ii. 726.

[4] Martius, *Zeitschrift, Chem.* [2], 381; Sarauw, *Ber. Deutsch. Chem. Ges.* xiv. 2442.

[5] V. Meyer, *ibid.* viii. 1074.

[6] *Ibid.* xvii. 641.

Diazo-amidobenzene is insoluble in water, slightly soluble in cold, more readily in hot alcohol, and crystallizes in golden-yellow plates, or from benzene in large flat prisms, fusing at 91° to a reddish brown oil which detonates at a higher temperature. On warming with strong hydrochloric acid it decomposes into nitrogen, aniline, and phenol.

It forms no salts with acids, but chloroplatinic acid produces a precipitate of $(C_{12}H_{11}N_3)_2PtCl_6$, in small red needles or prisms, which readily decompose. Diazo-amidobenzene, in presence of salts of aniline, is, as already explained, readily converted into amido-azobenzene, $C_6H_5.N_2.C_6H_4.NH_2$.

Diazobenzene-amidobromobenzene, $C_6H_5.N_2.NH.C_6H_4Br$.—Griess obtained this compound by the action of parabromaniline on diazobenzene nitrate; it crystallizes in yellow needles or small plates.[1] When he treated aniline with diazobromobenzene nitrate he did not obtain the isomeric compound $C_6H_4Br.N_2.NH.C_6H_5$, but the same substance as before.[2] A similar result was obtained in the preparation of other diazo-compounds; whether a molecular change takes place, or whether, as Griess assumes, the diazo-amido-compounds have a different constitution from that which is generally assigned to them, has not yet been determined. He gives the following formula to diazo-amidobenzene:

$$C_6H_4=NH=NH=NH=C_6H_4.$$

Diazobenzene-ethylamine, $C_6H_5.N_2.NH(C_2H_5)$, is obtained by the action of ethylamine on an aqueous solution of diazobenzene nitrate; it is an oily liquid, very similar to the following compound, which has been more carefully examined.

Diazobenzenedimethylamine, $C_6H_5.N_2.N(CH_3)_2$, is a yellowish oil having a peculiar aromatic odour, and can be distilled in small quantities without decomposition, but in large quantities decomposes with a tolerably violent explosion, forming dimethylamine. It is a weak base, and forms salts which are slowly decomposed by water in the cold, more rapidly on heating:

$$C_6H_5.N_2.N(CH_3)_2 + H_2O = C_6H_5.OH + N_2 + N(CH_3)_2H.$$

The alcoholic solutions of both these compounds yield amido-azobenzene when treated with a salt of aniline, ethylamine or dimethylamine being formed at the same time.[3]

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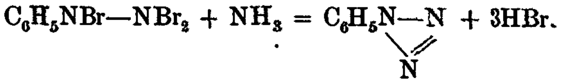
[1] *Ann. Chem. Pharm.* cxxxvii. 60.

[2] *Ber. Deutsch. Chem. Ges.* vii. 1618.

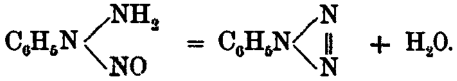
[3] Baeyer and Jäger, *ibid.* viii. 148.

Diazobenzenimide, $C_6H_5N_3$.—Griess first obtained this compound by the action of aqueous ammonia on diazobenzene perbromide :[1]



$$C_6H_5NBr{-}NBr_2 + NH_3 = \underset{\diagdown\; N \;\diagup\!\!\diagup}{C_6H_5N{-}N} + 3HBr.$$

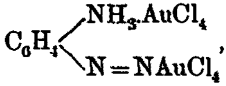
It is also obtained by the action of hydroxylamine on an alkaline solution of diazobenzene sulphate (Fischer), as well as by the decomposition of nitrosophenylhydrazine, which will be subsequently described :



$$C_6H_5N\left\langle\begin{matrix}NH_2\\ NO\end{matrix}\right. = C_6H_5N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + H_2O.$$

To prepare it, crude phenylhydrazine hydrochloride is dissolved in 15 parts of water, an excess of sodium nitrite gradually added, and the mixture heated to boiling in an apparatus connected with an inverted condenser until the gentle evolution of gas ceases.[2]

Diazobenzenimide is a yellowish, oily liquid having a stupefying, ammoniacal and aromatic odour. It is insoluble in water, and can be distilled with steam, or in a vacuum, but explodes on distillation under the ordinary pressure.

Amidodiazobenzene-compounds.—By passing nitrous acid through a solution of paradiamidobenzene hydrochloride and adding gold chloride, a precipitate of paramidodiazobenzene aurichloride,  $C_6H_4\left\langle\begin{matrix}NH_2.AuCl_4\\ N{=}NAuCl_4\end{matrix}\right.$, is obtained, from which other salts of paramidodiazobenzene can be prepared; these have not yet been described.[3]

The two other diamidobenzenes are not converted into diazo-compounds by nitrous acid. Metadiamidobenzene yields triamido-azobenzene, $C_6H_4(NH_2)N_2.C_6H_3(NH_2)_2$, while orthodiamidobenzene is converted into the following compound :

Azo-imidobenzene, $C_6H_5N_3$.—Ladenburg obtained this compound by adding potassium nitrite to a solution of orthodiamidobenzene sulphate, and named it amido-azophenylene.[4]

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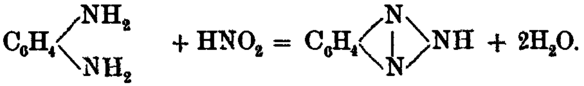
[1] *Ann. Chem. Pharm.* cxxxvii. 65.
[2] *Ibid.* cxc. 92, 96.
[3] Griess, *Ber. Deutsch. Chem. Ges.* xvii. 603.
[4] Ladenburg, *ibid.* ix. 222 ; xvii. 147.

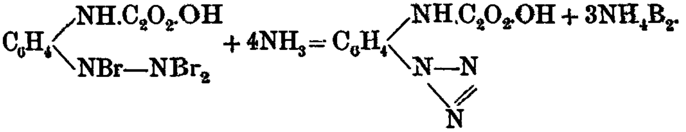
Its formation is expressed by the following equation:



$$C_6H_4\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + HNO_2 = C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle NH + 2H_2O.$$

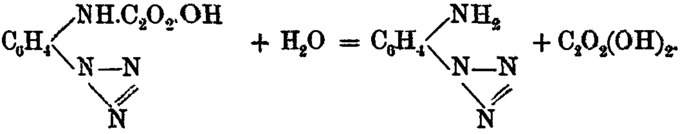
It crystallizes from benzene in needles having a mother-of-pearl lustre, and melting at 98°·5.

Metamidodiazobenzenimide, $C_6H_4(N_3)NH_2$.—This interesting base was obtained by Griess, who converted metaphenylene oxamic acid (p. 241) into the diazo-chloride by means of sodium nitrite and hydrochloric acid, and from this prepared the perbromide, which gives the following reaction with ammonia:



$$C_6H_4\left\langle\begin{matrix}NH.C_2O_2.OH\\NBr-NBr_2\end{matrix}\right. + 4NH_3 = C_6H_4\left\langle\begin{matrix}NH.C_2O_2.OH\\ \underset{\diagdown\,/\!\!/\atop N}{N-N}\end{matrix}\right. + 3NH_4B_2.$$

The new acid is almost insoluble in cold water, and crystallizes in white needles. On boiling with concentrated caustic potash it decomposes according to the equation:



$$C_6H_4\left\langle\begin{matrix}NH.C_2O_2.OH\\ \underset{\diagdown\,/\!\!/\atop N}{N-N}\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}NH_2\\ \underset{\diagdown\,/\!\!/\atop N}{N-N}\end{matrix}\right. + C_2O_2(OH)_2.$$

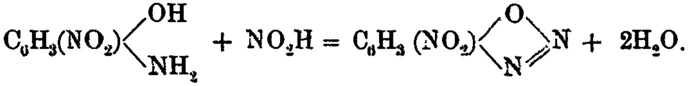
Amidodiazobenzenimide is a yellowish, oily liquid, having a slight smell resembling bitter almonds, is volatile in steam, but detonates on heating. It tastes at first as sweet as sugar, and then extremely bitter. It forms salts which crystallize well.

Amidodiazobenzenimide hydrochloride, $C_6H_4(N_3)NH_3Cl$, crystallizes from hot water in small, white, pointed rhombic plates; platinum chloride precipitates the double salt from its dilute solution in small, greyish yellow needles.

The hydrochloric acid solution of the base gives with nitrous acid a diazo-compound which has the formula $C_6H_4(N_3)N_2Cl$, and combines with phenols and amido-compounds to form azo-compounds, which are colouring matters possessing very remarkable properties.[1]

[1] *Ber. Deutsch. Chem. Ges.* xviii. 963.

1068 *Diazohydroxybenzene compounds* are obtained by treating alcoholic solutions of the salts of the amidophenols with nitrogen trioxide. They are decomposed by hydriodic acid in the cold with formation of the iodophenols. Alcoholic solutions of the substituted amido-phenols are not converted by nitrous acid into diazohydroxybenzene salts, but into anhydrides of the substituted diazophenols:



$$C_6H_3(NO_2)\left\langle\begin{matrix}OH\\NH_2\end{matrix}\right. + NO_2H = C_6H_3(NO_2)\left\langle\begin{matrix}O\\N\end{matrix}\right\rangle N + 2H_2O.$$

When, on the contrary, the ethers of these amidophenols are employed, the formation of such anhydrides is impossible, and they behave like the amidophenols or aniline.

Orthodiazophenol chloride, $C_6H_4(OH)N_2Cl$, is obtained by treating ortho-amidophenol hydrochloride with absolute alcohol saturated with nitrogen trioxide, the mixture being cooled by ice-water. An indigo-blue solution is first formed, and soon changes to brown. On addition of ether the chloride is precipitated and crystallizes in beautiful rhombohedra, which are readily soluble in alcohol and become milk-white in the air, losing their water of crystallization. It forms a platinum chloride which crystallizes well and yields orthochlorophenol on heating.[1]

Paradiazophenol chloride, $C_6H_4(OH)N_2Cl$, is obtained in a similar manner to the preceding compound, from paramidophenol hydrochloride, and crystallizes in long needles, slightly soluble in alcohol (Schmitt). The platinum chloride, $[C_6H_4(OH)N_2]_2PtCl_6$, on ignition yields parachlorophenol, and quinol is obtained by heating the chloride with concentrated hydrochloric acid.[2]

Paradiazophenol nitrate is formed in a peculiar manner by passing nitrogen trioxide through a well-cooled ethereal solution of phenol:

$$C_6H_5(OH) + 2N_2O_3 = C_6H_4(OH)N_2.NO_3 + NO_2H.$$

The free nitric acid formed converts a portion of the phenol into ortho- and metanitrophenol.[3] The nitrate is also obtained when nitrogen trioxide is passed through an ethereal solution of nitrosophenol.[4] It is readily soluble in alcohol, insoluble in

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[1] Schmitt, *Ber. Deutsch. Chem. Ges.* i. 67.

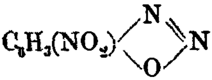
[2] Weselsky and Schuler, *ibid.* ix. 1160.

[3] Weselsky, *ibid.* viii. 98.

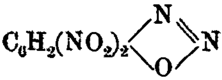
[4] Jäger, *ibid.* viii. 891.

ether, and crystallizes in light brown needles which are very explosive and fire like gunpowder, leaving a large residue of carbon. By dissolving it in dilute sulphuric acid, and adding alcohol and then ether, the sulphate is obtained as a splendid crystalline mass. This is not explosive, and is converted by barium chloride into diazophenol chloride, which is identical with that obtained from paramidophenol (Weselsky and Schuler).

Paradiazo-anisol nitrate, $C_6H_4(OCH_3)N_2.NO_3$, is obtained when nitrogen trioxide is passed through water containing nitrate of anisidine (methylparamidophenyl ether) in suspension. It forms colourless crystals which explode on percussion, and gradually decompose on boiling with water, more rapidly on heating to 140°, with formation of quinol.[1]



Diazonitrophenol anhydride, $C_6H_3(NO_2){<}\genfrac{}{}{0pt}{}{N}{O}{>}N$. Griess obtained this compound by passing nitrogen trioxide through an ethereal solution of paramido-orthonitrophenol. It is a brownish yellow, granular mass, which is slightly soluble in hot water, and explodes at 100° with extreme violence.[2] Its methyl ether, diazonitranisol, is only known as the nitrate, $C_6H_3(NO_2)(OCH_3)N_2.NO_3$, and may be obtained from nitranisidine nitrate; it crystallizes in small plates.[3]



Diazodinitrophenol anhydride, $C_6H_2(NO_2)_2{<}\genfrac{}{}{0pt}{}{N}{O}{>}N$, was prepared by Griess from amidodinitrophenol; it crystallizes from alcohol in small plates, which explode violently on heating.[4]

Diazo-amidonitranisol, $C_6H_3(NO_2)(OCH_3)N_2.NH.C_6H_3(NO_2)OCH_3$. Griess obtained this compound by passing nitrogen trioxide through an alcoholic solution of nitranisidine. It forms yellow microscopic needles, insoluble in water, and only soluble in hot alcohol.[5]

Diazonitrodihydroxyquinone. When amidonitrotetrahydroxybenzene (p. 255) is made into a paste with dilute hydrochloric acid, well cooled with ice, and a solution of sodium nitrite added drop by drop, nitric oxide is evolved and a clear solution is obtained, which after some time solidifies to a pulpy mass, consisting of long, golden-yellow needles, having the composition

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[1] Salkowski, *Ber. Deutsch. Chem. Ges.* vii. 1009.

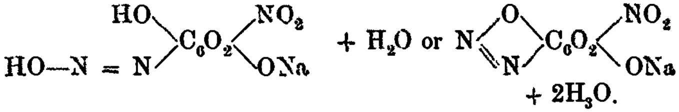
[2] *Ann. Chem. Pharm.* cxiii. 212.

[3] *Jahresb. Chem.* 1866, 459.

[4] *Ann. Chem. Pharm.* cxiii. 205.

[5] *Ibid.* cxxi. 278.

$C_6H_4NaN_3O_8$. This compound is also obtained by dissolving amidonitrotetrahydroxybenzene in cold dilute nitric acid, and partially neutralizing the golden-yellow solution with carbonate of soda. Its constitution is expressed by one of the following formulæ:



It is readily soluble in water and is reprecipitated by alcohol. It can be recrystallized from water at 50°, but decomposes on boiling with a violent evolution of gas. In the dry state it explodes with great violence.

When potassium nitrite is used in its preparation, the less soluble potassium salt is obtained, which is much more explosive, while the silver salt, obtained in small yellow plates by precipitating the sodium salt with silver nitrate, explodes by pressure or percussion with almost greater violence than silver fulminate.[1]

HYDRAZINE DERIVATIVES OF BENZENE.

1069 These bodies, as well as those of the fatty series, were discovered and carefully examined by E. Fischer.[2] The yellow diazobenzene potassium sulphonate, $C_6H_5N{=}NSO_3K$, is formed, as already explained, by the action of a weak alkaline solution of potassium sulphite on diazobenzene nitrate. This is converted by reducing agents into the white phenylhydrazine potassium sulphonate, which is also obtained by acting on diazobenzene nitrate with an excess of acid potassium sulphite:

$$C_6H_5N{=}N.NO_3 + 3SO_3KH = C_6H_5.NH{-}NH.SO_3K + SO_4KH + NO_3K + SO_2.$$

On boiling this salt with hydrochloric acid, phenylhydrazine hydrochloride is obtained:

$$C_6H_5.NH{-}NH.SO_3K + HCl + H_2O = C_6H_5.NH{-}NH_2.HCl + SO_4KH.$$

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[1] Nietzki and Benckiser, *Ber. Deutsch. Chem. Ges.* xviii. 499.
[2] *Liebig's Ann.* cxc. 67.

Phenylhydrazine is also obtained, together with aniline, when an alcoholic solution of diazo-amidobenzene is treated with zinc dust and acetic acid:

$$C_6H_5N_2.NH.C_6H_5 + 4H = C_6H_5.N_2H_3 + NH_2.C_6H_5.$$

Phenylhydrazine, $C_6H_5.N_2H_3$, may be readily prepared in the following manner: 20 parts of aniline are dissolved in 50 parts of hydrochloric acid of sp. gr. 1·19, and 80 parts of water; the calculated amount of sodium nitrite, dissolved in twice its quantity of water, is then added to the cold solution, which is slightly acidified with hydrochloric acid, and the mixture poured into an excess of an ice-cold solution of sodium sulphite; the following reaction takes place:

$$C_6H_5N_2Cl + 2SO_3Na_2 + H_2O = C_6H_5.N_2H_2.SO_3Na + SO_4NaH.$$

There is always a certain quantity of the yellow diazobenzene-salt formed, most of which is reduced by the sulphur dioxide evolved on neutralizing the solution with hydrochloric acid. The warm solution is afterwards treated with acetic acid and zinc dust, to convert the remainder into the white salt. A third of its volume of concentrated hydrochloric acid is then added to the hot filtrate; phenylhydrazine hydrochloride separates out on cooling, and a further quantity may be obtained by concentrating the mother-liquor. This is decomposed with caustic soda, when most of the phenylhydrazine is precipitated as an oil, that remaining in solution being extracted with ether. The crude phenylhydrazine is dried over fused potash and purified by fractional distillation; the portion distilling between 225°—235° is sufficiently pure for the preparation of all its derivatives.

Phenylhydrazine may be more readily prepared by the method of Meyer and Lecco:[1] 10 grms. of aniline are dissolved in 200 grms. of concentrated hydrochloric acid, and to this solution, which is kept cool, a cold solution of 7·5 grms. of sodium nitrite in 50 parts of water is gradually added, and then a solution of 45 grms. of stannous chloride in 45 grms. of concentrated hydrochloric acid, the liquid forming a crystalline pulpy mass of phenylhydrazine hydrochloride:

$$C_6H_5N{=}NCl + 4HCl + 2SnCl_2 = C_6H_5.NH{-}NH_2.HCl + 2SnCl_4.$$

Phenylhydrazine is a colourless oily liquid having a faint aromatic odour. It boils at 233°—234°, and solidifies at a low

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[1] *Ber. Deutsch. Chem. Ges.* xvi. 2976.

temperature in tablets, melting at 23°. It is very readily oxidized, and absorbs oxygen from the air, becoming red to dark brown; it reduces Fehling's solution in the cold with evolution of nitrogen and separation of cuprous oxide, aniline and benzene being formed. "This property can be employed as a delicate reaction for all primary hydrazines, and also, indirectly, for the diazo-compounds; in order to detect the latter in an aqueous solution, it is treated with acid potassium sulphite in excess, heated to boiling, neutralized with caustic potash, and tested with copper solution. The salts of the hydrazinesulphonic acid, which are formed in the liquid from the diazo-compounds, without exception produce the immediate precipitation of cuprous oxide; if the presence of hydroxylamine, which is readily formed by the reduction of nitrous acid, is to be feared, the alkaline solution must be boiled for some time in order to destroy it" (Fischer). On adding mercuric oxide to an ethereal solution of phenylhydrazine, nitrogen is evolved and aniline and benzene formed, as well as a considerable quantity of mercury diphenyl $(C_6H_5)_2Hg$.[1]

While ethylhydrazine is a strong diacid base, phenylhydrazine only combines with one equivalent of an acid, and is consesequently a weaker base. This is easily explained, since phenylhydrazine stands in the same relation to ethylhydrazine as aniline to ethylamine.

Phenylhydrazine hydrochloride, $C_6H_5.N_2H_3.HCl$, which, as already described, is employed as a reagent, may be obtained perfectly pure by dissolving the base, freed from ammonia by distillation, in ten parts of alcohol, neutralizing with concentrated hydrochloric acid, and washing the separated crystals with alcohol and ether until they are perfectly colourless. Phenylhydrazine hydrochloride crystallizes from hot water in small, thin, lustrous plates, which sublime on cautious heating; it is almost completely precipitated from its aqueous solution by concentrated hydrochloric acid, by which means phenylhydrazine can be separated from aniline and several other amido-bases. It reduces the salts of silver, mercury, gold and platinum in the cold.

Phenylhydrazine sulphate, $(C_6H_5.N_2H_3)_2H_2SO_4$, forms small plates, readily soluble in hot water, and slightly soluble in alcohol.

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[1] Fischer and Ehrhard, *Ann. Chem. Pharm.* cxcix. 332.

Phenylhydrazine oxalate, $(C_6H_5.N_2H_3)_2H_2C_2O_4$, crystallizes from hot water in small plates, which are slightly soluble in cold water.

Phenylhydrazine picrate, $C_6H_5.N_2H_3(OH)C_6H_2(NO_2)_3$, crystallizes in fine yellow needles, slightly soluble in water, readily in alcohol, and deflagrates explosively on heating.

1070 *Nitrosophenylhydrazine*, $C_6H_5N(NO)NH_2$, is obtained by adding sodium nitrite to a well-cooled dilute solution of phenylhydrazine hydrochloride; the yellow flocks which separate are dissolved in ether, and the compound is precipitated in small yellow plates by the addition of petroleum spirit. It is a very unstable body. The extremely poisonous action of its vapour is remarkable, the action being similar to that of amyl nitrite, but more intense. If even a small quantity of the vapour be inhaled, determination of blood to the head, violent headache, and nausea are produced. On warming with dilute caustic potash, it is completely converted into diazobenzene-imide (p. 270). The latter compound is also obtained, together with aniline, by mixing the aqueous solutions of diazobenzene nitrate and phenylhydrazine hydrochloride.

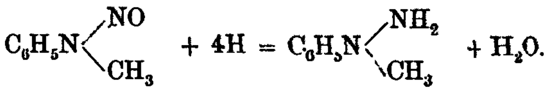
Phenylhydrazinesulphonic acid, $C_6H_5.NH.NHSO_3H$, is only known as the potassium salt, the formation of which has been already described; it is also obtained, together with the hydrazine sulphate, by heating the base with potassium disulphate to 80°:

$$4C_6H_5.N_2H_3 + 2K_2S_2O_7 = 2C_6H_5.N_2H_2SO_3K + (C_6H_5N_2H_3)_2SO_4H_2 + K_2SO_4.$$

It forms colourless scales, soluble with difficulty in cold water. By the action of mercuric oxide, or potassium dichromate, on its hot aqueous solution, it is oxidized to yellow diazobenzene potassium sulphonate, $C_6H_5.N_2.SO_3K$.

The salts of phenylhydrazine in aqueous solution are converted by mercuric oxide into diazobenzene salts; aniline and diazobenzene-imide being, however, simultaneously formed, as may be readily understood.

Methylphenylhydrazine, $C_6H_5N(CH_3)NH_2$, is obtained by reducing nitrosomethylaniline in alcoholic solution with zinc-dust and acetic acid.



$$C_6H_5N\begin{cases}NO\\CH_3\end{cases} + 4H = C_6H_5N\begin{cases}NH_2\\CH_3\end{cases} + H_2O.$$

It is a liquid, boiling at 220°—224°, and reduces Fehling's solution on warming, methylaniline and free nitrogen being formed.

Dimethyldiphenyltetrazone, $C_{14}H_{16}N_4$, is formed when methylphenylhydrazine is dissolved in chloroform and mercuric oxide gradually added, the mixture being kept cool:

$$\begin{array}{l} C_6H_5N(CH_3)-NH_2 \\ C_6H_5N(CH_3)-NH_2 \end{array} + 2HgO = \begin{array}{r} C_6H_5N(CH_3)N \\ \| \\ C_6H_5N(CH_3)N \end{array} + 2Hg + 2H_2O.$$

The compound crystallizes in small plates, slightly soluble in cold alcohol and ether, readily in chloroform, and melts at 133° with evolution of gas. It can be boiled with water without undergoing decomposition; on adding hydrochloric acid to the alcoholic solution, the tetrazone decomposes into nitrogen and methylaniline, and on adding iodine to its solution in chloroform, dimethyldiphenyltetrazone iodide, $C_{14}H_{16}N_4I_4$, is formed as a black crystalline precipitate, which deflagrates in the dry state spontaneously, and when suspended in carbon bisulphide and shaken with silver-dust is reconverted into the original compound.

1071 *Ethylphenylhydrazine compounds.* On heating phenylhydrazine with ethyl bromide, a mixture of the hydrobromides of different ethylated bases is obtained, as:

Asymmetric ethylphenylhydrazine, $C_6H_5.N(C_2H_5)NH_2$.
Symmetric ethylphenylhydrazine, $C_6H_5NH-NH(C_2H_5)$;

together with compounds containing more ethyl groups, and *diethylphenylhydrazonium bromide*, $H_2N-N.C_6H_5(C_2H_5)_2.Br$.[1]

On dissolving the product of the reaction in water, decomposing with caustic soda, and extracting with ether, the ethyl bases, together with the unattacked phenylhydrazine, go into solution. On adding concentrated hydrochloric acid, after the evaporation of the ether, the hydrazine hydrochloride separates out. The solution is then again made alkaline, the bases extracted with ether, and the liquid treated with mercuric oxide; the asymmetric ethylphenylhydrazine is thus converted into the non-volatile tetrazone, and the symmetric compound into the volatile azophenylethyl, $C_6H_5N{=}NC_2H_5$, which will be subsequently described.

Symmetric ethylphenylhydrazine or *Hydrazophenylethyl* may be obtained in the pure state by the action of sodium amalgam

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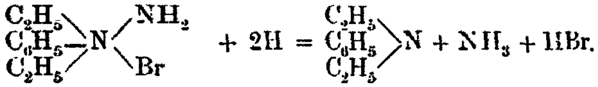
[1] Fischer and Ehrhard, *Liebig's Ann.* cxcix. 325.

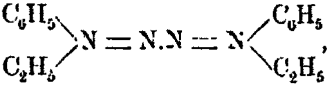
on an alcoholic solution of azophenylethyl. It is an oily liquid, which can be distilled without decomposition. It reduces Fehling's solution in the cold, and is oxidized by the oxygen of the air. By the continued action of acetic acid and zinc-dust it is gradually split up into aniline and ethylamine.

Asymmetric ethylphenylhydrazine may be prepared pure by the action of zinc-dust and acetic acid on nitroso-ethylaniline. It is an oily liquid, which can be boiled without decomposition, and reduces Fehling's solution on warming. It combines with ethyl bromide to form diethylphenylhydrazonium bromide, which is readily soluble in water but is precipitated by concentrated caustic soda. It forms rhombic crystals, and is converted by moist silver oxide into the strongly alkaline hydroxide $NH_2-N(C_6H_5)(C_2H_5)_2OH$.

On adding zinc-dust and hydrochloric acid to a warm aqueous solution of the bromide it is decomposed into diethylaniline, ammonia, and hydrobromic acid:[1]



$$\begin{matrix}C_2H_5\\C_6H_5\\C_2H_5\end{matrix}\!\!>\!N\!<\!\!\begin{matrix}NH_2\\Br\end{matrix} + 2H = \begin{matrix}C_2H_5\\C_6H_5\\C_2H_5\end{matrix}\!\!>\!N + NH_3 + HBr.$$

Diethyldiphenyltetrazone,  $\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\!\!>\!N=N.N=N\!<\!\!\begin{matrix}C_6H_5\\C_2H_5\end{matrix}$, crystallizes from alcohol in monoclinic prisms, which melt at 108° with evolution of gas.

Diphenylhydrazine, $(C_6H_5)_2N-NH_2$, is obtained by reducing nitrosodiphenylamine with acetic acid and zinc-dust. It is a yellow oily liquid, which on distillation partially decomposes into diphenylamine, ammonia, and resinous products. It is almost insoluble in water, and for this reason scarcely acts on Fehling's solution even on boiling. On the other hand it is readily oxidized by mercuric oxide, ferric chloride, &c., free nitrogen, diphenylamine, and a bluish violet colouring matter which contains nitrogen, being obtained, especially if the mixture be not cooled. When, however, it is shaken with a very dilute neutral and well-cooled solution of ferric chloride, the following compound is obtained as chief product, together with the above:

Tetraphenyltetrazone, $(C_6H_5)_2N=N.N=N(C_6H_5)_2$, separates

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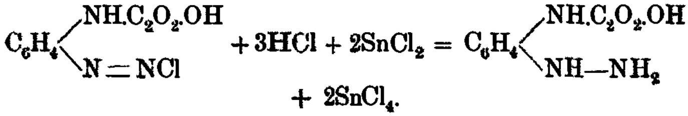
[1] Fischer, *Ber. Deutsch. Chem. Ges.* xvii. 2841.

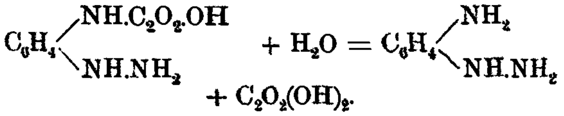
from carbon disulphide in colourless crystals, melting at 123° without decomposition.

Metamidophenylhydrazine, $H_2N.C_6H_4.NH.NH_2$. When the diazochloride obtained from phenylene-oxamic acid (p. 271) is treated with a solution of stannous chloride in hydrochloric acid, the following reaction occurs:



$$C_6H_4\left\langle\begin{array}{l}NH.C_2O_2.OH\\N=NCl\end{array}\right. + 3HCl + 2SnCl_2 = C_6H_4\left\langle\begin{array}{l}NH.C_2O_2.OH\\NH{-}NH_2\end{array}\right. + 2SnCl_4.$$

The new acid separates out in white crystalline grains, which are almost insoluble in alcohol, ether, and boiling water. On boiling it with strong hydrochloric acid, amidophenylhydrazine hydrochloride is obtained:



$$C_6H_4\left\langle\begin{array}{l}NH.C_2O_2.OH\\NH.NH_2\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}NH_2\\NH.NH_2\end{array}\right. + C_2O_2(OH)_2.$$

On adding strong caustic potash to the solution and concentrating on the water bath, the base separates out. At the ordinary temperature it forms a varnish-like mass, converted on warming into an oil, which is almost odourless and has a very bitter taste. It is slightly soluble in water, readily in alcohol and ether, and is very easily oxidizable, reducing Fehling's solution immediately with evolution of gas.

Its salts crystallize well; the hydrochloride is precipitated by hydrochloric acid from a concentrated solution in small pointed plates. Gold chloride and platinum chloride are immediately reduced by it.[1]

Dicyanphenylhydrazine, $C_8H_8N_4$. This substance, together with the isomeric dicyanorthodiamido-benzene (p. 239), is obtained by passing cyanogen through an aqueous solution of phenylhydrazine. It is scarcely soluble in cold water, readily in dilute hydrochloric acid and alcohol, and melts above 160° with decomposition (E. Fischer). On heating with acetic anhydride, the compound $C_{10}H_8N_4$ is obtained; it is very slightly soluble in water, and crystallizes from alcohol in hard prisms; its formation is explained by the following equation:

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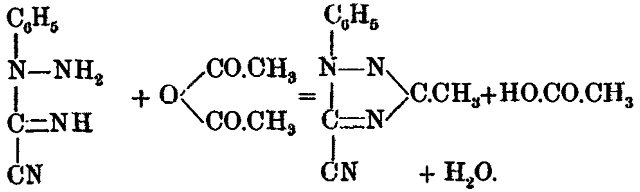
[1] Griess, *Ber. Deutsch. Chem. Ges.* xviii. 964.



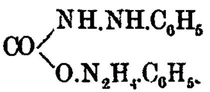
Its constitution is deduced from the fact that on heating with alcoholic potash it is converted into the acid $C_6H_5N_3(C_2H_3)C.CO_2H$, which is slightly soluble in cold, readily in hot water and alcohol, and is converted on heating into the basic compound $C_6H_5N_3(C_2H_3)CH$ with evolution of carbon dioxide; the latter is a yellowish oily liquid, possessing a peculiar aromatic odour, and boiling at 240°.[1]

ACID DERIVATIVES OF PHENYLHYDRAZINE OR PHENYLHYDRAZIDES.

1072 The hydrogen in phenylhydrazine can be replaced by acid radicals, just as in ammonia, the amines, and the amido-bases. Phenylhydrazine also combines directly with carbon dioxide and carbon disulphide, forming compounds analogous to ammonium carbamate, &c.

Acetylphenylhydrazide, $C_6H_5.N_2H_2.C_2H_3O$, is readily formed by the action of acetic anhydride on phenylhydrazine, as well as by boiling the latter with glacial acetic acid. It crystallizes from hot water in hexagonal prisms or tablets having a silky lustre, and melting at 128°·5. On dissolving it in chloroform and adding mercuric oxide, it is oxidized to an oily liquid, which has a penetrating odour, and is probably acetyldiazobenzene $C_6H_5N{=}NC_2H_3O$.[2]

Oxalyldiphenyldihydrazide, $(C_6H_5.N_2H_2)_2C_2O_2$, is obtained by heating phenylhydrazine with ethyl oxalate; it forms a foliated crystalline mass, melting at 277°—278°, and distilling at a higher temperature almost undecomposed.

Phenylhydrazine phenylcarbazide,  $CO\begin{cases}NH.NH.C_6H_5\\O.N_2H_4.C_6H_5\end{cases}$ may be obtained by passing carbon dioxide through a well-cooled emulsion of 1 part of phenylhydrazine with 10 parts of water. It

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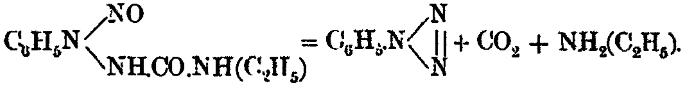
[1] Bladin, *Ber. Deutsch. Chem. Ges.* xviii. 1544.

[2] Fischer, *Liebig's Ann.* cxc. 129.

forms a fine, soft crystalline mass, which deliquesces in the air, giving off carbon dioxide.

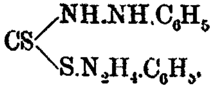
Phenylsemicarbazide, $C_6H_5.NH-NH.CO.NH_2$. This compound urea is formed on mixing solutions of potassium cyanate and phenylhydrazine hydrochloride; it crystallizes from hot water in white plates, melting at 170°.

Ethylphenylsemicarbazide, $C_6H_5.NH.-NH.CO.NH(C_2H_5)$, is obtained by the direct combination of ethyl isocyanate with phenylhydrazine, and crystallizes from hot, dilute alcohol in transparent, monoclinic tablets, melting at 151°. Its aqueous solution gives a bluish-black colouration and a precipitate of the same colour with Fehling's solution, the reaction being very delicate. This colour is rapidly converted into yellow in a closed vessel, but on shaking the liquid in the air it reappears. On gently warming, complete decomposition takes place with separation of cuprous oxide. Nitrous acid converts it into nitrosophenylethylsemicarbazide, the fine yellow needles of which decompose on boiling with alkalis into carbon dioxide, diazobenzene-imide and ethylamine;[1]



$$C_6H_5N\left\langle\begin{matrix}NO\\NH.CO.NH(C_2H_5)\end{matrix}\right. = C_6H_5N\left\langle\begin{matrix}N\\ \|\\N\end{matrix}\right. + CO_2 + NH_2(C_2H_5).$$

Phenylhydrazine phenylthiocarbazide



$$CS\left\langle\begin{matrix}NH.NH.C_6H_5\\S.N_2H_4.C_6H_5,\end{matrix}\right.$$

is formed by the addition of carbon disulphide to an ethereal solution of phenylhydrazine, and crystallizes in hexagonal tablets or prisms, melting at 96°—97°. On dissolving it in weak caustic potash and adding dilute sulphuric acid, phenylthiocarbazic acid, $C_6H_5.N_2H_2.CS.SH$, separates out in lustrous plates, which decompose on heating, forming carbon disulphide, sulphuretted hydrogen, ammonia, and the following compound.

Diphenylthiocarbazide, $(C_6H_5.N_2H_2)_2CS$, crystallizes from hot alcohol in hard, colourless, three-sided prisms, which form a dark red solution in warm caustic potash. On the addition of an acid, blue-black flocks separate out, which are converted by precipitation with alcohol from solution in warm chloroform into blue-black microscopic needles, which seem to be isomeric with diphenylthiocarbazide. Its solution, which has a slight alkaline reaction, dyes wool and silk red; the solution of the colouring

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[1] Fischer, *Liebig's Ann.* cxc. 109.

matter in chloroform is distinguished by its fine dichroism. The colour, which is dark red when seen in thick layers, is converted on dilution into a vivid green, which is so intense that the formation of this body, together with the copper test, can be employed as a delicate reaction for phenylhydrazine.

Diphenylthiosemicarbazide, $C_6H_5.N_2H_2.CS.NH(C_6H_5)$, is formed when alcoholic solutions of phenyl mustard oil and phenylhydrazine are mixed; it crystallizes from hot alcohol in prisms, melting at 177°.

COMPOUNDS OF PHENYLHYDRAZINE WITH ALDEHYDES AND KETONES.

1073 These compounds are readily formed with elimination of water according to the following equations:

Ethidenephenylhydrazine.

$$C_6H_5.N_2H_3 + CHO.CH_3 = C_6H_5.N_2H = CH.CH_3 + H_2O.$$

Propidenephenylhydrazine.

$$C_6H_5.N_2H_3 + CO(CH_3)_2 = C_6H_5.N_2H = C(CH_3)_2 + H_2O.$$

On heating with hydrochloric acid, the original substances are again formed. The hydrazine compounds of the aldehydes and ketones of the fatty series are oily liquids; other aldehydes and ketones, on the contrary, form crystalline compounds, which are so characteristic that phenylhydrazine can be employed for detecting even small quantities of them.[1]

The combination of the bodies is usually best brought about in an acetic acid solution; the reagent, which ought always to be freshly prepared, is obtained by dissolving 1 part of pure phenylhydrazine hydrochloride and 1·5 parts of crystallized sodium acetate in 10 parts of water. An excess of this is added to the aqueous solution to be tested for an aldehyde or ketone; if any be present, the condensation-product soon separates out as an oily or crystalline precipitate. Free mineral acids, which hinder or retard the reaction, are neutralized by a previous addition of sodium carbonate. Special care must be taken that no nitrous acid is present, because this gives rise to diazobenzene-imide or other products; it can be readily removed, however, by warming with urea.

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[1] Fischer, *Ber. Deutsch. Chem. Ges.* xvii. 572.

The aldehydo- and ketonic acids likewise form very characteristic compounds with phenylhydrazine.

Acetonephenylhydrazine or *Propidenephenylhydrazine*, $C_6H_5.N_2H{=}C(CH_3)_2$, is an oily liquid which boils at 165° under a pressure of 91 mm. On adding sodium nitrite to its solution in dilute sulphuric acid, it decomposes into diazobenzene-imide and acetone.[1]

$$C_6H_5N_2H{=}C(CH_3)_2 + NO.OH = C_6H_5N_3 + CO(CH_3)_2 + H_2O.$$

Oenantholphenylhydrazine, $C_6H_5.N_2H = CH.C_6H_{13}$, is a yellowish oil, boiling at 240° under a pressure of 77 mm. (Reisenegger).

Glyoxalphenylhydrazine, $C_6H_5.N_2H = CH.CH = N_2H.C_6H_5$, is almost insoluble in water, very dilute acids and alkalis. It crystallizes from alcohol in small plates melting at 169° to 170°. By means of this compound the smallest quantity of the very soluble and non-volatile glyoxal can be readily detected.

Phenylhydrazine glyoxylic acid, $C_6H_5N_2H = CH.CO_2H$, crystallizes from hot water in fine, yellow needles, which are coloured brown at 130°, and decomposed at 137° with evolution of gas. It is readily soluble in alkalis, from solution in which it is precipitated by acids, and by this means it can be separated from the hydrazine compounds of the aldehydes and ketones, as well as from the scarcely soluble phenylhydrazine oxalate.

Phenylhydrazidacetic acid, $C_6H_5.N_2H_2.CH_2.CO_2H$, is obtained by the action of sodium amalgam and water on the preceding compound, and crystallizes from hot alcohol in splendid plates having a silver lustre and melting at 157° with decomposition. Ammoniacal copper solution[2] reconverts it into phenylhydrazine glyoxylic acid.

Phenylhydrazine mesoxalic acid, $C_6H_5.N_2H{=}C(CO_2H)_2$, crystallizes in fine, yellow needles melting between 158°—164°, and decomposing almost completely at a higher temperature (Elbers).

Phenylhydrazine pyroracemic acid, $C_6H_5.N_2H{=}C(CH_3)CO_2H$. Phenylhydrazine and pyroracemic acid combine with such violence that complete decomposition of the products ensues. To obtain the compound, the solutions must be diluted with ether and gradually mixed in the cold.

Phenylhydrazine pyroracemic acid crystallizes from boiling alcohol in hard, light yellow, lustrous needles, which melt at

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[1] Reisenegger, *Ber. Deutsch. Chem. Ges.* xvi. 661.
[2] Elbers, *Ann. Chem. Pharm.* ccxxvii. 354.

169° with evolution of gas, and decompose at a higher temperature into carbon dioxide and ethidene phenylhydrazine. While the ketone phenylhydrazines are readily decomposed on heating with acids, phenylhydrazine pyroracemic acid can be boiled with dilute hydrochloric or sulphuric acids without undergoing any change. On heating it with alcoholic sulphuric acid, the ethyl ether, $C_6H_5.N_2H{=}C(CH_3)CO_2.C_2H_5$, is obtained melting at 114°—115°.

Phenylhydrazine glyoxylic acid behaves in a similar manner towards acids, while the analogous phenylhydrazine laevulinic acid, $C_6H_5N_2H{=}C(CH_3)CH_2.CH_2.CO_2H$, is readily decomposed by them.

The formation of phenylhydrazine pyroracemic acid takes place so readily in aqueous, acetic acid, and weak hydrochloric acid solutions, that by this reaction pyroracemic acid can be readily detected in very dilute solutions, and in solutions containing other bodies. The test is best applied in a weak hydrochloric acid solution; after a short time a voluminous crystalline precipitate is produced, which is filtered off and recrystallized from hot water or alcohol; it is then only necessary to dry the substance and determine the melting-point, in order to detect pyroracemic acid very rapidly and with great certainty.

Phenylhydrazidopropionic acid, $C_6H_5.N_2H_2.CH(CH_3)CO_2H$, is obtained, together with aniline, by the action of sodium amalgam and water on the preceding compound; it crystallizes from boiling alcohol in very fine white needles, which melt with evolution of gas at 152°—153°. Ammoniacal copper solution reconverts it into phenylhydrazine pyroracemic acid.[1]

Phenylhydrazine aceto-acetic acid, $C_6H_5.N_2H{=}C(CH_3)CH_2.CO_2H$, is not known in the free state; its ethyl ether is readily formed when phenylhydrazine is treated with aceto-acetic ether; its exact description has not yet been given. On heating it to 100°, alcohol is eliminated and oxymethylquinizine, $C_{10}H_{10}N_2O$, formed; this is prepared on the large scale and employed in the manufacture of oxydimethylquinizine, or *antipyrine*, $C_{10}H_9N_2(CH_3)O$. The latter, which is obtained by the action of methyl iodide, is frequently used in place of quinine on account of its powerful antipyretic action. These compounds belong to the quinoline group, and will be subsequently described.

Furfurphenylhydrazine, $C_6H_5.N_2H{=}CH.C_4H_3O$, separates out at first as a yellowish oil, which soon solidifies to a crystalline

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[1] Fischer and Jourdan, *Ber. Deutsch. Chem. Ges.* xvi. 2241.

mass. On dissolving it in ether and adding petroleum spirit, small yellowish plates are obtained, melting at 97°—98°. By means of this reaction 1 part of furfurol can be detected in 10,000 parts of water; by dissolving it in 1,000 parts of water and bringing a drop of the solution under the microscope together with a drop of the above-mentioned reagent, a turbidity is immediately obtained, followed by the formation of the characteristically grouped plates.

The aromatic aldehydes and ketones behave like furfurol; their phenylhydrazine compounds will be described under their respective headings.

Phenylhydrazine also forms compounds with those sugars which reduce alkaline copper solution and are either aldehydes or ketones (Vol. III. Pt. II., p. 495). The reaction does not, however, proceed so simply as with the ordinary aldehydes and ketones.[1]

Phenylglucosazone, $C_{18}H_{22}N_4O_4$, is formed when dextrose is warmed on the water-bath with the hydrazine solution; it forms fine, yellow needles, almost insoluble in water, but readily soluble in boiling alcohol. They fuse at 204°—205°, forming a dark-red liquid, a small quantity of gas being evolved. The compound is formed according to the following equation:

$$C_6H_{12}O_6 + 2N_2C_6H_8 = C_{18}H_{22}N_4O_4 + 2H_2O + H_2.$$

No free hydrogen is, however, evolved, a simultaneous reduction probably taking place, and the yield is, therefore, far below the theoretical, being equal in the most favourable case to the quantity of dextrose employed.

The same compound is obtained from laevulose and therefore from invert-sugar, as well as, more slowly, from cane-sugar, which is inverted by the hydrazine solution.

Phenylgalactosazone, $C_{18}H_{22}N_4O_4$, is prepared from galactose, and is very similar to the preceding compound, but melts at 182° without any evolution of gas.

Phenyl-lactosazone, $C_{24}H_{32}N_4O_9$. While cane-sugar only reacts with phenylhydrazine after inversion, milk-sugar does so directly. The compound obtained is tolerably soluble in hot water and crystallizes in yellow needles, melting at 200° with decomposition.

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[1] E. Fischer, *Ber. Deutsch. Chem. Ges.* xvii. 579.

Phenylmaltosazone, $C_{24}H_{32}N_4O_9$, is obtained from maltose, and crystallizes from hot water in fine, yellow needles, melting at 190°—191°.

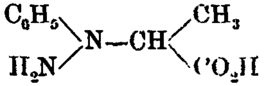
Sorbin also forms a hydrazine compound, while inosite and trehalose do not.

COMPOUNDS OF PHENYLHYDRAZINE WITH THE CYANHYDRINS.[1]

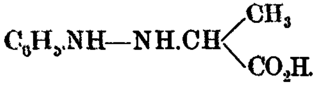
1074 Phenylhydrazine not only forms compounds with aldehydes and ketones, but also with the cyanhydrins, or nitrils of the lactic acid group, which are obtained by the combination of the former with hydrocyanic acid.

a-Phenylhydrazidopropionitril, $C_6H_5.N_2H_2.CH(CH_3)CN$, is formed by the continued heating of ethidene cyanhydrin (lactonitril) with phenylhydrazine to 100°. It separates from hot petroleum spirit in colourless crystals, which are scarcely soluble in water, but dissolve readily in alcohol, and melt at 58°. On heating with alkalis or dilute acids it is split up into hydrocyanic acid and ethidene phenylhydrazine. Cold concentrated hydrochloric acid converts it into

a-Phenylhydrazopropionamide, $C_6H_5\,N_2H_2.CH(CH_3)CO.NH_2$, which forms hard, readily soluble crystals, melting at 124°. On boiling with caustic soda it forms α-phenylhydrazidopropionic acid, $C_6H_5.N_2H_2.CH(CH_3)CO_2H$, which is slightly soluble in cold water, readily in alcohol, and crystallizes from hot dilute alcohol in lustrous white needles, melting at 187°. If the solution of the nitril in absolute alcohol be saturated with hydrochloric acid, the ethyl ether, $C_6H_5.N_2H_2.CH(CH_3)CO_2.C_2H_5$, is obtained in crystals, readily soluble in alcohol, and melting at 116°. When the acid is boiled with tin and hydrochloric acid it splits up into ammonia and α-anilidopropionic acid, thus indicating its constitution, which is expressed by the first of the following formulæ, while the second probably represents that of the phenylhydrazidopropionic acid obtained from pyroracemic acid:



$$\left.\begin{matrix}C_6H_5\\H_2N\end{matrix}\right\rangle N—CH\left\langle\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$$



$$C_6H_5.NH—NH.CH\left\langle\begin{matrix}CH_3\\CO_2H.\end{matrix}\right.$$

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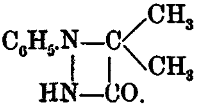
[1] Reissert, *ibid.* xvii. 1451.

a-Phenylhydrazido-isobutyronitril, $C_6H_5.N_2H_2.C(CH_3)_2CN$, is formed when the acetone cyanhydrin obtained by the action of nascent hydrocyanic acid on acetone dissolved in ether, is heated with phenylhydrazine. It is insoluble in water and crystallizes from petroleum spirit in needles melting at 70°. Cold concentrated hydrochloric acid has no action on this compound; when it is carefully dissolved in sulphuric acid and gently warmed, it yields the anhydride of *a*-phenylhydrazidobutyric acid, which forms white crystals, melting at 175°, readily soluble in acids and gradually in boiling caustic soda. On the addition of acids to the alkaline solution, the anhydride again separates out; it has the following constitution:



AZO-DERIVATIVES OF BENZENE.

1075 *Azophenylethyl*, $C_6H_5.N_2.C_2H_5$, is formed, as already mentioned, by the oxidation of the symmetric ethylphenylhydrazine (p. 278), and is a yellow oil which has a piercing odour, volatilizes with steam, and distils at 175°—185° with slight decomposition.

Azophenylnitro-ethyl, $C_6H_5.N_2.C_2H_4(NO_2)$, is formed by the action of sodium nitro-ethane on diazobenzene nitrate[1] and crystallizes from hot alcohol in small rectangular plates melting at 136°—137° with decomposition. If it be triturated with alcoholic potash, the potassium salt, $C_8H_7N_3O_2K_2 + 4H_2O$, is obtained; it crystallizes in small orange-coloured plates and is decomposed by hydrochloric acid with re-formation of azophenylnitro-ethyl.

Azophenylnitro-propyl, $C_6H_5.N_2.CH(NO_2)CH_2.CH_3$, has been obtained from potassium nitropropane and diazobenzene nitrate; it crystallizes in broad, deep orange-coloured needles, readily soluble in alkalis.[2]

Azophenylnitro-isopropyl, $C_6H_5.N_2.C(NO_2)(CH_3)_2$, is obtained in a similar manner from nitro-isopropane, and is a non-volatile, golden-yellow oil, which is insoluble in alkalis, and forms no metallic compounds.[3] The constitutions of azophenylnitro-ethyl

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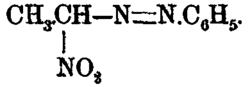
[1] Meyer and Ambühl, *Ber. Deutsch. Chem. Ges.* viii. 751, 1073.

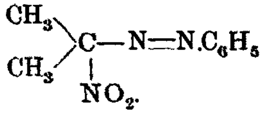
[2] Meyer, *ibid.* ix. 386.

[3] *Ibid.* viii. 1076.

and of the isopropyl-compound are expressed by the following formulæ:



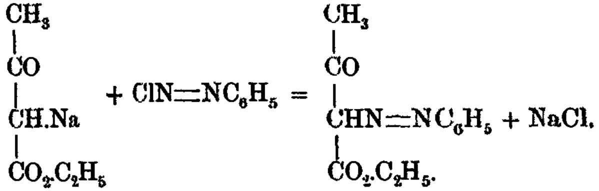
$$\begin{array}{l} CH_3.CH\text{—}N{=}N.C_6H_5. \\ \quad | \\ \quad NO_3 \end{array}$$



$$\begin{array}{l} CH_3\diagdown \\ \qquad\quad C\text{—}N{=}N.C_6H_5 \\ CH_3\diagup\ | \\ \qquad\quad NO_2. \end{array}$$

The fact that the latter forms no metallic compounds is readily explicable (Vol. III., Part I., p. 188), while the behaviour of the former as a dibasic acid is very singular. Several salts have been prepared, all containing two equivalents of a metal. They are probably to be looked upon as basic salts, the formula of the potassium compound being $C_8H_8N_3O_2K + KOH + 3H_2O$. It is, however, remarkable that the normal salts have not been obtained.

Azobenzene aceto-acetic acid, $C_6H_5.N_2.CH(CO.CH_3)CO_2H$. The ethyl ether of this compound is formed by the action of diazobenzene nitrate on a solution of aceto-acetic acid in caustic potash.[1] In order to prepare it, sodium is dissolved in alcohol, the necessary amount of aceto-acetic ether added, and the cooled mixture treated with an aqueous solution of diazobenzene chloride:[2]



$$\begin{array}{lcl} CH_3 & & CH_3 \\ | & & | \\ CO & & CO \\ | & + ClN{=}NC_6H_5 = & | \\ CH.Na & & CHN{=}NC_6H_5 + NaCl. \\ | & & | \\ CO_2.C_2H_5 & & CO_2.C_2H_5. \end{array}$$

The ether is very readily saponified by warming with alkalis. The addition of hydrochloric acid to the solution separates the free acid, which crystallizes from alcohol in small, golden-yellow plates, melting at 154°—155°. The potassium salt, $C_{10}H_9N_2O_3K$, forms small, light-yellow plates with a satin lustre.

Azobenzene aceto-acetic ether, $C_6H_5N_2.CH(CO.CH_3)CO_2C_2H_5$, crystallizes from alcohol in hard, lustrous, honey-yellow prisms, melting at 75° (Richter and Münzer).

Azobenzene dimethylketone, $C_6H_5.N_2.CH_2.CO.CH_3$, is formed by warming the ether with alcoholic soda, as well as by heating the

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[1] *Ber. Deutsch. Chem. Ges.* x. 2075; Züblin, *ibid.* xi. 1417.
[2] Richter and Münzer, *ibid.* xvii. 1926.

free acid to 178°—180°. It crystallizes from warm alcohol in lustrous, leather-yellow prisms, and from hot water in fine, light-yellow needles, which melt at 148°—149°, and have a peculiar odour rendered specially noticeable on warming.

Nitro-azobenzene aceto-acetic acid, $C_6H_4(NO_2).N_2.CH.(CO.CH_3)CO_2H$. The ethyl ether is obtained by adding a dilute solution of sodium nitrite to a well-cooled solution of orthonitraniline in hydrochloric acid, allowing the mixture to stand for a considerable time and then adding an alkaline solution of aceto-acetic ether. It crystallizes from alcohol in splendid golden-lustrous plates, melting at 92°—93°. On heating it with caustic potash the potassium salt is formed; this is decomposed by hydrochloric acid with formation of the free acid, which crystallizes from hot alcohol in small, yellowish-brown plates resembling mosaic gold, and forms yellow salts.

On heating with ammonia and ferrous sulphate, it is converted into *amido-azobenzene aceto-acetic acid*, $C_6H_4(NH_2)N_2CH(CO.CH_3)CO_2H$, crystallizing from acetic acid in small, orange-red tablets with a satin lustre, which melt at 157°, with evolution of gas and partial blackening, and are changed by continued heating at 100° into a black syrupy mass.

Nitro-azobenzene dimethylketone, $C_6H_4(NO_2).N_2.CH_2.CO.CH_3$, is obtained by treating the ethyl ether with warm caustic soda, or by heating the acid. It is best prepared by passing nitrous fumes into a solution of orthonitraniline, dissolving the white needles of orthonitrodiazobenzene nitrate thus obtained in water, and adding an alkaline solution of aceto-acetic ether without cooling. The product is freed from the nitro-azobenzene aceto-acetic ether, which is formed, by alcoholic potash, and the ketone is recrystallized from hot water or alcohol. It crystallizes in long, sulphur-yellow needles with a silky lustre, which melt at 123°—124°.[1]

1076 *Azobenzene*, $C_6H_5N{=}NC_6H_5$. Mitscherlich obtained this compound by distilling nitrobenzene with alcoholic potash, and named it nitrogen benzide.[2] Zinin then showed that the first product of this reaction is azohydroxybenzene, $C_{12}H_{10}N_2O$, which decomposes on distillation with formation of azobenzene, aniline, and other products.[3] Azobenzene is also formed, together with combustible gases, aniline, etc., by heating nitrobenzene with

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[1] Bamberger, *Ber. Deutsch. Chem. Ges.* xvii. 2415.

[2] *Pogg. Ann.* xxxii. 224.

[3] *Journ. Prakt. Chem.* xxxvi. 93.

aniline,[1] or by treating it with acetic acid and an excess of iron.[2] Alexejew has not been able to obtain it by this last method.[3] According to him and Werigo,[4] azobenzene is readily obtained by acting upon an alcoholic solution of nitrobenzene with sodium amalgam, or with zinc dust and caustic soda:[5]

$$\begin{array}{c} C_6H_5.NO_2 \\ C_6H_5.NO_2 \end{array} + 8H = \begin{array}{c} C_6H_5.N \\ \| \\ C_6H_5.N \end{array} + 4H_2O.$$

It is also formed when nitrosobenzene is heated with aniline nitrate:[6]

$$C_6H_5.NH_2 + C_6H_5.NO = C_6H_5N{=}NC_6H_5 + H_2O.$$

It may also be obtained by the oxidation of aniline hydrochloride with potassium permanganate (Glaser),[7] ammonia and oxalic acid being also formed if the oxidation be carried on in an alkaline solution.[8]

Schmidt has obtained it by the action of bleaching powder on a solution of aniline in chloroform.[9]

In order to prepare it, caustic soda and zinc dust are added to an alcoholic solution of nitrobenzene, and, when the reaction is over, nitrogen trioxide passed in to oxidize the hydrazobenzene, $C_{12}H_{12}N_2$, which is always formed (Alexejew). Azobenzene crystallizes from alcohol or petroleum spirit in yellowish-red plates which melt at 68° and have a faint odour of roses. It boils at 293°, and its vapour has a sp. gr. of 6·5.[10] On the spontaneous evaporation of its solution in benzene, the compound $C_{12}H_{10}N_2 + C_6H_6$ separates out in long, thick, yellowish-red prisms, which effloresce in the air.[11] If hydrochloric acid gas be passed into a solution of azobenzene in carbon disulphide, a yellow crystalline compound, $(C_{12}H_{10}N_2)_2 3HCl$, is formed; the analogous hydrobromic acid compound is a carmine-red crystalline mass. Bromine, gradually added to a solution of azobenzene in chloroform, forms the addition product

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[1] Merz and Coray, *Ber. Deutsch. Chem. Ges.* iv. 651.
[2] Noble, *Ann. Chem. Pharm.* xcviii. 253.
[3] *Bull. Soc. Chim.* [2], i. 234.
[4] *Ann. Chem. Pharm.* cxxxv. 176.
[5] Alexejew, *Beilst. Org. Chim.* 971.
[6] Baeyer, *Ber. Deutsch. Chem. Ges.* vii. 1638.
[7] *Ann. Chem. Pharm.* cxlii. 365.
[8] Hoogewerff and Dorp, *Ber. Deutsch. Chem. Ges.* x. 1936.
[9] *Journ. Prakt. Chem.* [2], xviii. 196.
[10] Hofmann, *Ann. Chem. Pharm.* cxiv. 362.
[11] Schmidt, *Ber. Deutsch. Chem. Ges.* v. 1106.

$C_{12}H_{10}N_2Br_6$, which separates out in large dark-red prisms. All these compounds decompose in the air, leaving a residue of azobenzene.[1]

1077 *Substitution-products of azobenzene.* These are either formed by direct substitution, or by the oxidation of the corresponding hydrazo-compounds.

			Melting-point.
Metadichlorazobenzene,[2]	$C_{12}H_8Cl_2N_2$	orange-red needles	101°
Paradichlorazobenzene,[3]		yellow needles with a silky lustre .	183°—184°
Metadibromazobenzene,[4]	$C_{12}H_8Br_2N_2$	hair-like needles .	125·5°
Paradibromazobenzene,[5]		large yellow needles	205°
Metadi-iodazobenzene,[4]	$C_{12}H_8I_2N_2$	orange-red needles	150°
Paradi-iodazobenzene,[4]		red scales	237°

Mononitro-azobenzene, $C_{12}H_9(NO_2)N_2$, is obtained by treating azobenzene with fuming nitric acid.[6] It crystallizes from alcohol in small yellow needles, melting at 137°. It is reduced by ammonium sulphide to amido-azobenzene, but is split up by the continued action of tin and hydrochloric acid into aniline and paradiamidobenzene.[7]

Paradinitro-azobenzene, $C_{12}H_8(NO_2)_2N_2$, is formed by the action of warm nitric acid, and can readily be separated from the preceding compound, since it is almost insoluble in cold acetone. It crystallizes from glacial acetic acid in fine orange-red needles, melting at 206°, and is slightly soluble in alcohol and ether. Ammonium sulphide reduces it in the cold to dinitrohydrazobenzene, on warming to diamidohydrazobenzene, while it is split up by the continued action of tin and hydrochloric acid into two molecules of paradiamidobenzene.

Metadinitro-azobenzene is a red oil, which is formed together with the para-compound, and was not further investigated by Gerhardt and Laurent. It dissolves readily in alcohol, ether

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[1] Worigo, *Ann. Chem. Pharm.* clxv. 189.
[2] Laubenheimer, *Ber. Deutsch. Chem. Ges.* viii. 1625.
[3] Heumann, *ibid.* v. 913.
[4] Gabriel, *ibid.* ix. 1407.
[5] Werigo, *Ann. Chem. Pharm.* cxxxv. 178.
[6] Laurent and Gerhardt, *ibid.* lxxv. 73.
[7] Janovsky and Erb, *Ber. Deutsch. Chem. Ges.* xviii. 1133.

and acetone, and solidifies, after standing for some weeks at 15°, to an orange-red crystalline magma. On heating with tin and hydrochloric acid it splits up into two molecules of metadiamidobenzene (Janovsky and Erb).

α-Trinitro-azobenzene, $C_{12}H_7(NO_2)_3N_2$, is obtained by the action of cold, fuming nitric acid on paradinitro-azobenzene. It crystallizes from acetone in chamois-coloured needles with a silky lustre, and from alcohol in long, sulphur-yellow needles, fusing at 169° to a red liquid, which detonates violently on further heating.

β-Trinitro-azobenzene is formed by the action of the warm acid, and forms crystals with a silky lustre, less soluble in alcohol than the α-compound, and melting at 180°.

γ-Trinitro-azobenzene, $C_6H_5.N_2.C_6H_2(NO_2)_3$. Fischer obtained this compound by the action of yellow mercuric oxide on a warm alcoholic solution of trinitrohydrazobenzene. It crystallizes in fine, dark-red prisms, melting at 142°.[1]

Azobenzenenitrolic acid, $C_{12}H_{10}N_3O$, is formed by adding aqueous ammonium sulphide to a hot alcoholic solution of nitro-azobenzene, until the colour becomes olive-brown and a permanent precipitate is formed. The compound separates out on cooling in yellow flocks, crystallizing from alcohol in small, brownish-red needles. It forms a deep blue solution in cold alcoholic potash, and in warm caustic potash solution, and is reprecipitated by carbon dioxide. An alcoholic solution of potassium ferricyanide oxidizes it again to nitro-azobenzene.

Nitro-azobenzenenitrolic acid, $C_{12}H_9(NO_2)N_3O$, is obtained in a similar mannner to the preceding compound, paradinitro-azobenzene being employed, and crystallizes from acetone in lustrous, amber-coloured, monoclinic prisms, which have a blue fluorescence, and melt at 218°. It readily dissolves in aqueous alkalis and baryta water, forming splendid blue solutions.

Metadinitro-azobenzene gives an oily nitrolic acid, which also dissolves in alkalis with a blue colour.

Janovsky and Erb consider that the following formulæ express the constitutions of these acids:

$$\begin{array}{lll} C_6H_5.N{=}NC_6H_4N.OH & \qquad & NO_2.C_6H_4.N{=}NC_6H_4N.OH \\ \qquad\qquad\qquad | & & \qquad\qquad\qquad\qquad | \\ C_6H_5N{=}NC_6H_4N.OH & & NO_2.C_6H_4.N{=}NC_6H_4N.OH. \end{array}$$

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[1] *Ann. Chem. Pharm.* cxc. 133.

1078 *Azobenzenesulphonic acid*, $C_{12}H_9N_2SO_3H + 3H_2O$. Griess obtained this compound by dissolving azobenzene in 5 parts of fuming sulphuric acid heated to 130°.[1] It is scarcely soluble in dilute mineral acids, slightly in alcohol and ether, tolerably in cold, and very readily in hot water, crystallizing in large, deep orange-red plates, which lose their water of crystallization above 100°, and melt at 127°.[2] It forms salts which crystallize well and are only slightly soluble.

Potassium azobenzenesulphonate, $C_{12}H_9N_2SO_3K$, is formed when a solution of any potassium salt, except the sulphate, is treated with a hot solution of the acid, and separates out on cooling in large, yellowish red plates.

Azobenzenesulphonic acid is, therefore, a very strong acid, decomposing even chlorides and nitrates.

Azobenzenesulphonic chloride, $C_{12}H_9N_2SO_2Cl$, forms orange-yellow warty masses, insoluble in water, and only slowly decomposed by boiling water.[3]

Azobenzenesulphonamide, $C_{12}H_9N_2SO_2.NH_2$, is a powder, slightly soluble in boiling alcohol.

Azobenzenedisulphonic acids, $C_{12}H_8N_2(SO_3H)_2$. By dissolving azobenzene in 5 to 8 parts of fuming sulphuric acid heated to 130°, and then keeping the temperature for two hours at 150°—170°, two isomeric acids are formed, and can be separated by means of their potassium salts.[4]

a-Azobenzenedisulphonic acid crystallizes with one molecule of water in deliquescent, red, concentrically grouped needles; the potassium salt, $2C_{12}H_8N_2(SO_3K)_2 + 5H_2O$, forms red prisms, slightly soluble in cold, readily in hot water.

The *chloride*, $C_{12}H_8N_2(SO_4Cl)_2$, crystallizes from ether in small, brownish-red needles, melting at 220°—222°; and the *amide*, $C_{12}H_8N_2(SO_2.NH_2)_2$, forms yellowish-red needles or small plates which do not melt below 300°.

If the hot, concentrated solution of the potassium salt be treated with stannous chloride, *a-hydrazobenzenedisulphonic acid*, $C_{12}H_{10}N_2(SO_3H)_2$, is formed, and crystallizes in transparent, lustrous tablets, containing water of crystallization.

β-Azobenzenedisulphonic acid forms a syrup; its potassium salt, $2C_{12}H_8N_2(SO_3K)_2 + 5H_2O$, is exceptionally soluble in water, and crystallizes from alcohol in deep-yellow needles.

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[1] *Ann. Chem. Pharm.* cliv. 208.

[2] Janovsky, *Monatsh. Chem.* ii. 221.

[3] Skandarow, *Zeitschr. Chem.* 1870, 613.

[4] Limpricht, *Ber. Deutsch. Chem. Ges.* xiv. 1356.

The *chloride* crystallizes from ether in fine, red needles, melting at 123°—125°, and the *amide* forms yellowish needles, melting at 258°.

No β-hydrazobenzenedisulphonic acid could be obtained by treating the potassium salt with tin and hydrochloric acid.

Meta-azobenzenedisulphonic acid. Claus and Moser obtained this compound by the action of sodium amalgam on a solution of sodium metanitrobenzenesulphonate;[1] it may be more readily obtained by using zinc dust and caustic potash.[2] The free acid crystallizes in pale-yellow, deliquescent, monoclinic prisms, containing three molecules of water; it forms yellow to dark-red salts.

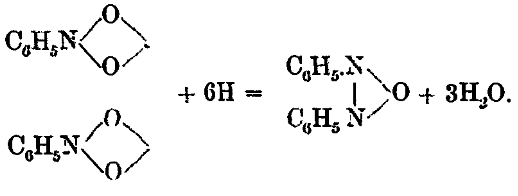
The potassium salt crystallizes in yellowish-red needles, which are sometimes anhydrous and sometimes contain water.

The *chloride* separates from ether in ruby-red needles, and melts at 166°, while the *amide* crystallizes from alcohol in yellow needles, melting at 295°.

On reduction the acid yields *metahydrazobenzenedisulphonic acid*, $C_{12}H_{10}N_2(SO_3H)_2$, crystallizing in fine, colourless, monoclinic prisms, scarcely soluble in alcohol and ether, slightly in cold, and somewhat more readily in warm water.

Para-azobenzenedisulphonic acid is formed by the oxidation of sulphanilic acid with potassium permanganate in the cold. The potassium salt, $2C_{12}H_8N_2(SO_3K)_2 + 5H_2O$, is thus obtained in red crystals, slightly soluble in water.[3] The amide crystallizes from hot water in yellow tablets, melting at 176° (Marenholz and Gilbert).

1079 *Azoxybenzene*, $C_{12}H_{10}N_2O$, is, as already mentioned, the first product of the action of caustic potash or sodium amalgam, in presence of alcohol, on nitrobenzene:



It is also obtained by oxidizing azobenzene, dissolved in acetic acid, with chromic acid,[4] as well as, together with azobenzene, by

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[1] *Ber. Deutsch. Chem. Ges.* xi. 762.

[2] Marenholz and Gilbert, *Ann. Chem. Pharm.* ccii. 331.

[3] Laar, *Journ. Prakt. Chem.* [2], xx. 264.

[4] Petriew, *ibid.* vi. 557.

the action of potassium permanganate on aniline hydrochloride (Glaser).

Methyl alcohol is used in its preparation instead of ethyl alcohol, as the oxidation products of the latter seem to take part in the reaction and form black masses, which were found by Mitscherlich and Zinin to consist of the salts of coloured acids.

Ten parts of sodium are dissolved in 250 parts of methyl alcohol, the solution mixed with 30 parts of pure nitrobenzene, and the whole allowed to boil gently for 5 to 6 hours, in an apparatus connected with an inverted condenser. The liquid becomes coloured brownish-red, but, if pure nitrobenzene has been used, remains perfectly clear, the reaction proceeding according to the following equation:

$$4C_6H_5NO_2 + 3CH_3ONa = 2C_{12}H_{10}N_2O + 3HCO_2Na + 3H_2O.$$

The alcohol is then distilled off, the residue of sodium formate and azoxybenzene extracted with water, and the azoxybenzene allowed to crystallize out; the yield amounts to 90 to 92 per cent. of the theoretical.[1]

Alexejew obtained it by the action of sodium amalgam on an alcoholic solution of nitrobenzene, kept acid by acetic acid. According to Moltschanowsky, 87 per cent. of the theoretical yield is obtained.[2]

Azoxybenzene is insoluble in water, but readily soluble in alcohol, and crystallizes in long, yellow, rhombic needles, or, on the gradual evaporation of its ethereal solution, in prisms an inch in length. It fuses at 36° to a yellow, strongly refractive liquid, which solidifies on cooling in a radiating mass (Zinin). If small quantities are carefully heated, it volatilizes undecomposed; when larger quantities are distilled, a portion decomposes into azobenzene and aniline, carbonized products being formed. By the addition of three parts of iron filings, the yield of azobenzene is increased to 72·5 per cent., aniline and decomposition products being also obtained. This behaviour adapts it for the preparation of azobenzene.[3] While azoxybenzene in alkaline solution is reduced by sodium amalgam to azobenzene and hydrazobenzene, the greater portion of it is converted by stannous chloride, in an acid alcoholic solution, into aniline (Schmidt and Schultz). On heating with concentrated sul-

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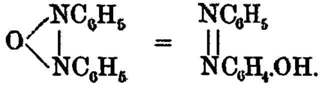
[1] Klinger, *Ber. Deutsch. Chem. Ges.* xv. 865. See also Moltschanowsky, *ibid.* xvi. 81.

[2] *Ibid.* xv. 1575.

[3] Schmidt and Schultz, *Liebig's Ann.* ccvii. 329.

phuric acid it is converted into the isomeric hydroxyazobenzene:[1]



$$O\left\langle\begin{matrix}NC_6H_5\\ |\\ NC_6H_5\end{matrix}\right. = \begin{matrix}NC_6H_5\\ \|\\ NC_6H_4.OH.\end{matrix}$$

Substitution products of Azoxybenzene. The halogen compounds are obtained from the substitution products of nitrobenzene, just as azoxybenzene is obtained from nitrobenzene. They are converted by reduction into substituted hydrazobenzenes, and these again by oxidation into substituted azobenzenes. The nitro-compounds are formed by the nitration of azoxybenzene.

			Melting-point.
Metadichlorazoxybenzene,[2]	$C_{12}H_8Cl_2N_2O$	flat long ochre-coloured needles	97°
Paradichlorazoxybenzene,[3]		light yellow needles . .	155°
Metadibromazoxybenzene,[4]	$C_{12}H_8Br_2N_2O$	light yellow broad prisms	111—111·5°
Paradibromazoxybenzene,[5]		small yellow plates . . .	175°
Metadi-iodazoxybenzene,[6]	$C_{12}H_8I_2N_2O$	flat yellow needles . .	—
Paradi-iodazoxybenzene,[6]		light yellow plates . .	199—199·5°
Orthonitro-azoxybenzene,[7]	$C_{12}H_9(NO_2)N_2O$	yellow prisms or needles . .	49°
Paranitro-azoxybenzene,[7]		light yellow hair-like needles .	153°

Meta-azoxybenzenedisulphonic acid, $C_{12}H_8(SO_3H)_2N_2O$, is formed by heating metanitrobenzenesulphonic acid with alcoholic potash. It is readily soluble in water and alcohol, and forms microscopic yellow needles melting at 125°. Sodium amalgam reduces it to meta-azobenzenedisulphonic acid, and stannous chloride to the hydrazo-compound.[8]

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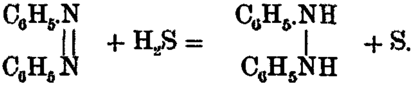
[1] Wallach and Belli, *Ber. Deutsch. Chem. Ges.* xiii. 525; Wilsing, *Ann. Chem. Pharm.* ccxv. 218.
[2] Laubenheimer, *Ber. Deutsch. Chem. Ges.* viii. 1623.
[3] *Ibid.*
[4] Gabriel, *ibid.* ix. 1405.
[5] Hofmann and Geyger, *ibid.* v. 919; Werigo, *Ann. Chem. Pharm.* clxv. 198.
[6] Gabriel.
[7] Zinin, *Ann. Chem. Pharm.* cxiv. 218.
[8] Brunnemann, *ibid.* ccii. 340.

1080 *Hydrazobenzene*, $C_{12}H_{12}N_2$. Hofmann obtained this compound in 1863 by the reduction of azobenzene with ammonium sulphide:[1]



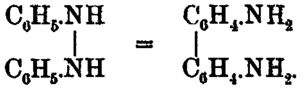
$$\begin{array}{l} C_6H_5.N \\ \quad\ \ \| \\ C_6H_5N \end{array} + H_2S = \begin{array}{l} C_6H_5.NH \\ \quad\ \ | \\ C_6H_5NH \end{array} + S.$$

In order to prepare it, an alcoholic solution of azobenzene or azoxybenzene is boiled with zinc-dust until it has become colourless, filtered, and precipitated with water (Alexejew). It is slightly soluble in water, readily in alcohol, and crystallizes in colourless tablets, smelling like camphor, and melting at 136°. On distillation it decomposes into aniline and azobenzene:

$$2C_{12}H_{12}N_2 = C_{12}H_{10}N_2 + 2C_6H_7N.$$

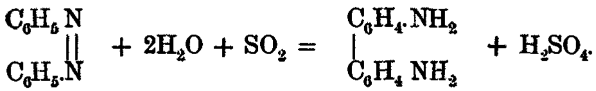
On oxidation it is readily reconverted into azobenzene; in the damp state, therefore, it becomes coloured in the air, and its alcoholic solution readily absorbs oxygen.

Hydrochloric or sulphuric acid converts it into benzidine:



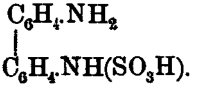
$$\begin{array}{l} C_6H_5.NH \\ \quad\ \ | \\ C_6H_5.NH \end{array} = \begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2. \end{array}$$

The product thus obtained is a mixture of two isomeric diamidodiphenylenes. It is also formed by passing sulphur dioxide through an alcoholic solution of azobenzene:



$$\begin{array}{l} C_6H_5\,N \\ \quad\ \ \| \\ C_6H_5.N \end{array} + 2H_2O + SO_2 = \begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4\,NH_2 \end{array} + H_2SO_4.$$

When azobenzene is heated with a considerable excess of acid ammonium sulphite and alcohol, the ammonium salt of amidodiphenylsulphamic acid is obtained; this is converted by sulphuric acid into benzidine, and has, therefore, the following constitution:[2]



$$\begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH(SO_3H). \end{array}$$

These compounds will be described under diphenyl.

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[1] *Jahresb.* 1863, 424.

[2] Spiegel, *Ber. Deutsch. Chem. Ges.* xviii. 1479.

Diacetylhydrazobenzene, $C_{12}H_{10}(NC_2H_3O)_2$, is formed by boiling hydrazobenzene with acetic anhydride, and forms large, thick, yellow, rhombic crystals, slightly soluble in cold water, more readily in hot, and readily in alcohol (Schmidt and Schultz).

Substitution products of hydrazobenzene are obtained by the reduction of the substituted azobenzenes or azoxybenzenes, as well as from the substituted nitrobenzenes. Monosubstitution products have not yet been obtained.

			Melting-point.
Metadichlorohydrazobenzene,[1]	$C_{12}H_{10}Cl_2N_2$	crystals resembling gypsum	94°
Paradichlorohydrazobenzene,[2]		crystals	122°
Metadibromohydrazobenzene,[3]	$C_{12}H_{10}Br_2N_2$	short thick prisms	107—109°
Paradibromohydrazobenzene,[4]		fine needles . . .	130°
Metadi-iodohydrazobenzene,[5]	$C_{12}H_{10}I_2N_2$	spherical aggregation of crystals .	89—90°
Paradi-iodohydrazobenzene,[5]		flat needles . . .	—
Dinitrohydrazobenzene,[6]	$C_{12}H_{10}(NO_2)_2N_2$	yellow needles . .	220°

Trinitrohydrazobenzene, $C_{12}H_9(NO_2)_3N_2$. Fischer obtained this compound by the action of picryl chloride on phenylhydrazine:

$$C_6H_5NH-NH_2 + C_6H_2Cl(NO_2)_3 = C_6H_5NH-NH.C_6H_2(NO_2)_3 + HCl.$$

It crystallizes from glacial acetic acid or acetone in short, dark-red prisms, which melt at 181° with evolution of gas, and deflagrate when more strongly heated. Mercuric oxide converts it, in alcoholic solution, into γ-trinitro-azobenzene (p. 293).[7]

a-Diamidohydrazobenzene, $C_{12}H_{10}(NH_2)_2N_2$. Gerhardt and Laurent prepared this substance by boiling paradinitro-azobenzene with alcoholic ammonium sulphide; they gave to it the

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[1] Laubenheimer, *ibid.* viii. 1621.

[2] Hofmann, *ibid.* v. 918; Calm and Heumann, *ibid.* xiii. 1181.

[3] Gabriel, *ibid.* ix. 1405.

[4] Werigo, *Ann. Chem. Pharm.* clxv. 192; Calm and Heumann.

[5] Gabriel.

[6] Julie Lermontow, *Ber. Deutsch. Chem. Ges.* v. 231.

[7] *Ann. Chem. Pharm.* cxc. 132.

formula, $C_{12}H_2(NH_2)_2N_2$, and named it dipheuine. Julie Lermontow subsequently showed that when dinitro-azobenzene is treated with ammonium sulphide in the cold, dinitrohydrazobenzene is formed, and that this is converted into diamidohydrazobenzene by warming with the sulphide. It is slightly soluble in cold, more readily in hot water, and forms a yellow crystalline powder, melting at 145°. It is converted into paradiamidobenzene by heating to 100° in a sealed tube with ammonium sulphide, and into quinone by oxidation with manganese dioxide and sulphuric acid. Its hydrochloride, $C_{12}H_{10}N_2(NH_3Cl)_2$, crystallizes in red scales, slightly soluble in water.

β-Diamidohydrazobenzene. Haarhaus obtained this compound by the action of sodium amalgam on an alcoholic solution of metanitraniline, and named it hydrazo-aniline.[1] It may be readily prepared by the reduction of metanitraniline with zinc dust and alcoholic potash,[2] and is slightly soluble in water, readily in alcohol, and crystallizes in golden-yellow needles, melting slightly higher than 140°. On heating to 100° with ammonium sulphide it is converted into paradiamidobenzene (Lermontow). Its hydrochloride crystallizes in small golden-yellow plates.

HYDROXY- AND AMIDO-DERIVATIVES OF AZO-BENZENE.

THE AZO-DYES.

1081 All azo-compounds are coloured, but only those which contain an amido- or hydroxyl-group are dyes. In 1876 the only azo-dyes in use were amido-azobenzene, or aniline yellow, and triamido-azobenzene, or phenylene brown. Since that time, however, a large number of azo-dyes has been discovered through the labours of Caro, Griess, Poirrier, Witt, and others, and, owing to their simple formation from the numerous amido-compounds and phenols, they have come into very general use.

The simplest compound of this class is aniline yellow or amido-azobenzene, obtained by the action of aniline on diazobenzene chloride; diazo-amidobenzene is first formed, and is converted, in presence of aniline, into amido-azobenzene:

$$C_6H_5N{=}N.NH.C_6H_5 = C_6H_5N{=}N.C_6H_4.NH_2.$$

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[1] *Ann. Chem. Pharm.* cxxxv. 164.

[2] Limpricht, *Ber. Deutsch. Chem. Ges.* xviii. 1403.

When potassium phenate is added to diazobenzene nitrate, hydroxyazobenzene is directly obtained:

$$C_6H_5N{=}N.NO_3 + C_6H_5.OK = C_6H_5N{=}NC_6H_4.OH + KNO_3.$$

The formation of an intermediate diazohydroxy- or diazo-amido-compound has not been observed in the preparation of this and other azo-dyes. Among the diamido-compounds only those of the meta-series form colouring matters. Metadiamidobenzene combines with diazobenzene chloride, diamido-azobenzene or chrysoïdine being formed:

$$C_6H_5N{=}NCl + C_6H_4(NH_2)_2 = C_6H_5N{=}NC_6H_3(NH_2)_2 + HCl.$$

Metadihydroxybenzene or resorcinol yields metadihydroxyazobenzene, $C_6H_5N{=}C_6H_3(OH)_2$.

According to Witt's proposal, the dyes obtained from meta-diamido-compounds are called *chrysoïdines*, and those obtained from metadihydroxy-compounds, *chrysoïns*.[1] The colour of these compounds is darker the higher the molecular weight; thus amido-azobenzene is yellow, diamido-azobenzene orange, and triamido-azobenzene brown.

If paradiazobenzenesulphonic acid be used instead of a diazo-salt, the sulphonic acids of the azo-dyes are obtained; these are called *tropaeolins*, because the shades of colour which they produce resemble those of the flowers of *Tropaeolum majus*. They are distinguished in trade according to their shades as *Tropaeolin Y* (yellow), *Tropaeolin O* (orange), and the deeper, redder ones as *OO*, *OOO*, etc.[2]

These sulphonic acids may also be obtained by the action of sulphuric acid on the azo-dyes.

When nitrogen trioxide is passed into an alcoholic solution of amido-azobenzene hydrochloride, a diazo-compound

$$C_6H_5N{=}NC_6H_4N{=}NCl,$$

is formed, and this is converted by aniline into an amido-azo-compound, $C_6H_5N{=}NC_6H_4N{=}NC_6H_4.NH_2$, which is a colouring matter. Similar reactions with other amido- and hydroxy-compounds, as well as with their sulphonic acids, lead to the building up of very complicated azo-dyes.[3]

Among these numerous compounds those derived from naphthalene are of special importance, but only those of the benzene group will be described at present.

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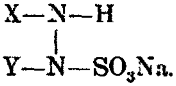
[1] *Ber. Deutsch. Chem. Ges.* x. 654.

[2] Witt, *ibid.* xii. 258.

[3] Caro and Schraube, *ibid.* x. 2230.

At first only the *water soluble* sulphonic acids were commercially employed as dyes, since the application of the *spirit soluble* colouring matters was prevented by practical difficulties; these have now been overcome, it having been found that the azo-compounds combine with acid sodium or ammonium sulphite to form soluble compounds, decomposed by steaming or by the action of alkalis, and that the dye can thus be fixed directly on the fibre.[1]

The sulphonic acids give analogous compounds, which form yellow solutions when the azo-dye has a red colour, and red solutions when they are derived from blue colouring matters. All these sulphite-compounds are characterized by a great power of crystallization, and their crystals possess in greater or less degree a dark colour and metallic lustre; since, as already mentioned, they readily decompose with formation of the original colouring matter, they do not correspond to the amidodiphenylsulphamic acids (p. 298), but are addition-products of the general formula:[2]



$$\begin{array}{l} X—N—H \\ \quad\;\; | \\ Y—N—SO_3Na. \end{array}$$

1082 *Hydroxyazobenzene*, $C_6H_5.N_2.C_6H_4.OH$. Griess obtained this substance, together with phenolbidiazobenzene (p. 304), by the action of barium carbonate on diazobenzene nitrate, and named it phenoldiazobenzene.[3] He then found that the same compound is formed when azobenzenesulphonic acid is fused with caustic potash,[4] while Kekulé and Hidegh prepared it by the action of potassium phenate on diazobenzene nitrate.[5] It may also be obtained by heating the isomeric azoxybenzene with sulphuric acid (Wallach and Belli).[6] To prepare it, 30 grms. of potassium nitrite dissolved in 4 litres of water are added to 20 grms. of phenol and 20 grms. of aniline nitrate dissolved in 2 litres of water, the mixture allowed to stand for two hours, and the precipitate filtered off. On treatment with ammonia a resinous substance remains undissolved and is separated by filtration, the filtrate being then precipitated with hydrochloric acid.[7]

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[1] Caro and Schraube, *Ber. Deutsch. Chem. Ges.* xvii. ref. 452, xviii. ref. 10 and 89.

[2] Spiegel, *ibid.* xviii. 1479.

[3] *Ann. Chem. Pharm.* cxxxvii. 84.

[4] *Ibid.* cliv. 208.

[5] *Ber. Deutsch. Chem. Ges.* iii. 324.

[6] *Ibid.* xiii. 525.

[7] Mazzara, *Jahresb.* 1879, 465.

Hydroxyazobenzene is slightly soluble in water, readily in alcohol, and crystallizes in yellowish-red rhombic prisms, melting at 152°—154°. It readily dissolves in alkalis and forms metallic salts. The silver compound is a yellow precipitate which detonates at 100°.

a-Hydroxyazobenzenesulphonic acid, $C_6H_4(SO_3H)N_2C_6H_4.OH$, is formed when hydroxyazobenzene,[1] or more simply azoxybenzene,[2] is heated to 100°—110° with 5 parts of fuming sulphuric acid until a small portion is completely soluble in water. On dilution with water the monosulphonic acid separates out after twenty-four hours, while the di- tri- and tetrasulphonic acids remain in solution.

It forms small, reddish plates with a metallic lustre, which are readily soluble in water and alcohol. The potassium salt, $C_6H_4(SO_3K)N_2C_6H_4.OH + H_2O$, crystallizes in small, yellowish-red, lustrous plates or flat needles, tolerably soluble in cold, readily in hot water. When it is reduced with stannous chloride no aniline is formed, whence it follows that the sulpho-group and the hydroxyl are not situated in the same benzene nucleus.

β-Hydroxyazobenzenesulphonic acid, $C_6H_4(SO_3H)N_2C_6H_4.OH$, is obtained by dissolving 1 part of phenol in 10 parts of a 10 per cent. solution of caustic potash, and adding the corresponding amount of diazosulphanilic acid. The yellowish-red solution is saturated after some time with acetic acid, the potassium salt, $C_6H_4(SO_3K)N_2C_6H_4.OH$, being thus precipitated in small, anhydrous, lustrous plates,[3] which are still less soluble than those of the isomeric compound (Wilsing). The acid, which is obtained from the salt, crystallizes in yellowish-red prisms, having a blue surface lustre, which are readily soluble in pure water, but only slightly in acidulated water. It is split up by the action of tin and hydrochloric acid into sulphanilic acid and paramidophenol.

The sodium salt, $C_6H_4(SO_3Na)N_2C_6H_4.OH$, occurs in commerce under the name of *Tropaeolin Y*, as a pale yellow powder, which has not much value as a dye.

γ-Hydroxyazobenzenesulphonic acid, $C_6H_4(SO_3H)N_2C_6H_4.OH$. Griess obtained this substance by the action of metadiazobenzenesulphonic acid on an alkaline solution of phenol. It is readily soluble in water and crystallizes in long, narrow, pentagonal plates having a violet surface lustre. Tin and hydrochloric

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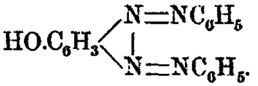
[1] Tschirwinsky, *Ber. Deutsch. Chem. Ges.* vi. 560.
[2] Wilsing. *Ann. Chem. Pharm.* ccxv. 228.
[3] Griess, *Ber. Deutsch. Chem. Ges.* xi. 2191.

acid decompose it into metamidobenzenesulphonic acid and paramidophenol. The potassium salt, $C_{12}H_9N_2SO_3K$, crystallizes in long needles.

δ-Hydroxyazobenzenesulphonic acid, $C_6H_5N_2C_6H_3(SO_3H)OH$, is obtained by the action of diazobenzene nitrate on an alkaline solution of phenolorthosulphonic acid, and is precipitated by strong hydrochloric acid from a concentrated aqueous solution, in small, lustrous yellow plates. On the gradual evaporation of its solution it is also deposited in large, cherry-red, rhombic tablets or prisms. On reduction it yields aniline and amidophenolsulphonic acid.

The potassium salt, $C_{12}H_9N_2SO_3K$, forms small, narrow, lustrous plates or needles (Griess).

Phenolbidiazobenzene, $C_{18}H_{14}N_4O$. This name has been given by Griess to a compound which he obtained, together with hydroxyazobenzene, by the action of barium carbonate on diazobenzene nitrate. It is also formed by treating diazobenzene chloride with caustic soda, or by adding diazobenzene nitrate to an alkaline solution of hydroxyazobenzene,[1] and crystallizes from hot alcohol in brownish red needles or small plates, which melt at 131° and have a metallic lustre. It is split up by the action of tin and hydrochloric acid into aniline and diamidophenol,[2] $C_6H_3(NH_2)_2OH$ (4 : 2 : 1). It must therefore have the following constitution :—



$$HO.C_6H_3\left\langle\begin{matrix}N{=}NC_6H_5\\ |\\ N{=}NC_6H_5.\end{matrix}\right.$$

Caro and Schraube[3] obtained an isomeric compound by the action of potassium phenate on the diazo-compound of amidoazobenzene, concerning which they only state that it is split up by nascent hydrogen into aniline, paradiamidobenzene, and paramidophenol :

$$C_6H_5N{=}NC_6H_4N{=}NC_6H_4OH.$$

1083 *Dihydroxyazobenzenes*, $C_{12}H_8N_2(OH)_2$. According to theory twelve isomerides can exist, six containing the hydroxyls in the same benzene nucleus, and six containing one hydroxyl in each nucleus. The latter, termed azophenols, are obtained by fusing the nitrophenols with caustic potash.[4]

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[1] Griess, *Ber. Deutsch. Chem. Ges.* ix. 627.
[2] Percy Frankland, *Journ. Chem. Soc.* 1880, i. 751.
[3] *Ber. Deutsch. Chem. Ges.* x. 2230.
[4] Benedikt and Weselsky, *Ann. Chem. Pharm.* cxcvi. 339.

Ortho-azophenol, $C_6H_4(OH)N_2C_6H_4.OH$, crystallizes in small, golden, lustrous plates, melting at 171°, and subliming without decomposition. It is insoluble in water, slightly soluble in alcohol and readily in ether; it forms a yellow solution in the alkalis.

Para-azophenol is formed by adding a solution of potassium phenate to diazoparaphenol nitrate, as well as by the action of caustic potash on nitrosophenol.[1] It is slightly soluble in water, readily in alcohol, and forms light-brown triclinic prisms, melting with decomposition at about 204°.

Metadihydroxyazobenzene, Phenylazoresorcinol, or *Resorcinolazobenzene*, $C_6H_5N_2C_6H_3(OH)_2$, is obtained by the action of diazobenzene nitrate on an alkaline solution of resorcinol; it crystallizes in red needles, which melt at 168°, and are readily soluble in alcohol and alkalis.[2]

Dihydroxyazobenzenesulphonic acid, $C_6H_4(SO_3H)N_2C_6H_3(OH)_2$, is formed by the action of fuming sulphuric acid on the preceding compound, as well as by that of paradiazobenzenesulphonic acid on an alkaline solution of resorcinol.[3] It is slightly soluble in cold, somewhat more readily in hot water and in alcohol, and crystallizes in small, ruby-red, pointed rhombic plates with a steel-blue surface-lustre. It is split up by the action of tin and hydrochloric acid into sulphanilic acid and amidoresorcinol.

The acid potassium salt, $C_6H_4(SO_3K)N_2C_6H_3(OH)_2$, crystallizes in small, yellowish-red, rhombic plates; both it and the corresponding sodium salt occur in commerce under the names *Tropaeolin O* or *R*, *Chrysoïn*, &c.; it is chiefly used, in combination with other dyes, for olive-greens, chestnut-browns, &c.

Phenyldisazoresorcinol, or *Resorcinoldisazobenzene*,

$$(C_6H_5N_2)_2C_6H_2(OH)_2,$$

is obtained in the preparation of phenylazoresorcinol; it is only slightly soluble in alcohol, and crystallizes in broad, red needles, which melt at 220°—222° and form a brownish-yellow solution in alkalis or sulphuric acid. On reduction with tin and hydrochloric acid it yields diamidoresorcinol and aniline (Liebermann and Kostanecki).

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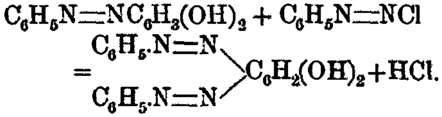
[1] Jaeger, *Ber. Deutsch. Chem. Ges.* viii. 1499.

[2] Baeyer and Jaeger, *ibid.* ix. 151; Typke, *ibid.* x. 1576; Liebermann and Kostanecki, *ibid.* xvii. 880.

[3] Griess, *ibid.* xi. 2195.

a-Resorcinoldisazobenzene is formed, together with the *β*- compound, by the action of diazobenzene chloride on an alkaline solution of phenylazoresorcinol:



$$C_6H_5N{=}NC_6H_3(OH)_2 + C_6H_5N{=}NCl = \begin{matrix} C_6H_5.N{=}N \\ C_6H_5.N{=}N \end{matrix}\!\!>C_6H_2(OH)_2 + HCl.$$

It is slightly soluble in alcohol and ether, more readily in chloroform, and crystallizes in brownish red, matted needles melting at 213°-215°; it forms a bordeaux-red solution in caustic soda, and colours sulphuric acid a pure red.

β-Resorcinoldisazobenzene is a red crystalline powder, insoluble in caustic soda; it dissolves in alcoholic potash with a brownish red, and in sulphuric acid with an indigo-blue colour.[1]

Benzenedisazobenzeneresorcinol, or *Azo-azobenzeneresorcinol*, $C_6H_4N{=}NC_6H_4N{=}NC_6H_2(OH)_2$, is obtained in two isomeric modifications by dissolving equal molecules of amido-azobenzene and resorcinol in alcohol, adding sufficient acetic acid, and treating the well-cooled liquid with an aqueous solution of one molecule of sodium nitrite, the mixture being well agitated. The *a*-compound is a brownish red crystalline powder, soluble in alcohol, and melting at 183°-184°. It dissolves in aqueous alkalis and in concentrated sulphuric acid with a carmine-red colour.

The *β*-compound is also a brownish red powder, which takes a metallic lustre when rubbed, melts at 215°, and is insoluble in alcohol and aqueous alkalis; it dissolves in alcoholic potash with a bluish violet, and in sulphuric acid with a pure deep blue colour (Wallach and Fischer).

1084 *Amido-azobenzene*, $C_6H_5N{=}NC_6H_4.NH_2$. In the year 1863 the firm of Simpson, Maule, and Nicholson brought into the market a new dye called *aniline-yellow*, obtained by the action of nitrous acid on aniline.[2] Martius and Griess found that this was the oxalate of a base, which they named amidodiphenylimide, $C_{12}H_{11}N_3$.[3] At the same time Kekulé showed that this body is formed by a molecular change from the isomeric diazo-amidobenzene when the latter is allowed to stand in contact with an aniline salt, and must therefore be considered as amidoazobenzene;[4] this observation was confirmed by Schmidt, who

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[1] Wallach and Fischer, *Ber. Deutsch. Chem. Ges.* xv. 2816.

[2] Mène, *Jahresb.* 1861. 496.

[3] *Zeitsch. Chem.* 1866, 132.

[4] *Ibid.* 1866, 689.

obtained the same substance by the reduction of nitro-azobenzene.[1] It is also formed by heating an aniline salt with sodium stannate.[2] To prepare it, 2 parts of aniline hydrochloride are gradually mixed with an aqueous solution of 1 part of sodium nitrite, the temperature not being allowed to rise above 60°. After some time an excess of hydrochloric acid is added, and then water, the amido-azobenzene separating out, while the excess of aniline remains in solution and may be recovered.[3]

Amido-azobenzene is scarcely soluble in water, but readily in alcohol, and crystallizes in yellow rhombic needles or prisms, melting at 127°·4. It boils above 300° without decomposition, is oxidized by manganese dioxide and sulphuric acid to quinone, and reduced by nascent hydrogen with formation of aniline and paramidobenzene; its constitution is, therefore, represented by the following formula:

Amido-azobenzene is a weak monacid base, and its salts are readily decomposed by water.

Amido-azobenzene hydrochloride, $C_{12}H_{11}N_3.ClH$, crystallizes from a slightly acid, boiling, saturated solution in lustrous, bluish violet needles or scales. This salt, or the oxalate, forms the commercial aniline-yellow; it dyes wool and silk a fine yellow, but, as it is volatile in steam, is not much employed for dyeing goods; it is, however, used for the preparation of other dyes.

Amido-azobenzenesulphonic acid, $C_6H_4(SO_3H)N{=}NC_6H_4.NH_2$, is obtained from sulphanilic acid by converting this into paradiazobenzenesulphonic acid by means of sodium nitrite and hydrochloric acid, adding aniline, removing the excess of the latter by hydrochloric acid, and precipitating the sulphonic acid with common salt. It is also prepared by treating amido-azobenzene with strongly fuming sulphuric acid, and washing the product until it is free from sulphuric acid.[4] The substance thus obtained, which contains the disulphonic acid,[5] occurs commercially as a paste, under the names *Acid-yellow* or *Echtgelb*,

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[1] *Ber. Deutsch. Chem. Ges.* v. 480.

[2] Schiff, *Ann. Chem. Pharm.* cxxvii. 346.

[3] Grässler, *Dingl. Polyt. Journ.* ccxxxii. 192: Thomas and Witt, *Jour. Chem. Soc.* 1883, i. 112.

[4] Grässler, *Chem. Ind.* ii. 48, 346: iii. 171.

[5] Nietzki, *Ber. Deutsch. Chem. Ges.* xiii. 800.

and is used as a yellow dye for wool and silk; it is also employed in the preparation of Biebrich scarlet, a colouring matter which will be described under naphthalene.

Methylamido-azobenzene, $C_6H_5.N_2.C_6H_4N(CH_3)H$, is obtained by heating amido-azobenzene with methyl iodide; it crystallizes in brick-red needles melting at 180°; its hydrochloride forms violet needles.[1]

Dimethylamido-azobenzene, $C_6H_5.N_2.C_6H_4N(CH_3)_2$. Griess obtained this substance by the action of dimethylaniline on a diazo-salt.[2] It is also formed when equal molecules of the hydrochlorides of aniline and dimethylaniline are dissolved in water and treated with an alkaline solution of sodium nitrite:[3]

$$C_6H_5.NH_3Cl + C_6H_5.N(CH_3)_2HCl + NaNO_2 + NaHO = C_6H_5.N_2.C_6H_4N(CH_3)_2 + 2NaCl + 3H_2O.$$

It may also be prepared by the action of methyl iodide on the preceding compound; it crystallizes in small yellow plates melting at 115°, and its hydrochloride forms purple-red, hair-like needles.

The corresponding sulphonic acid, $C_6H_4(SO_3H)N_2C_6H_4N(CH_3)_2$, is obtained by the action of dimethylaniline on paradiazobenzenesulphonic acid, as well as by dissolving dimethylamido-azobenzene in fuming sulphuric acid containing 30 per cent. of sulphur trioxide, allowing the solution to stand for twenty-four hours and precipitating with water (Möhlau). Hydrochloric acid precipitates it from a boiling alkaline solution in microscopic needles, which soon change into small, strongly-lustrous, violet plates or prisms (Griess). It forms a solution in concentrated sulphuric acid with a yellowish-brown colour, which on dilution becomes a splendid red.

The ammonium salt occurs in commerce under the names *Golden-orange*, *Helianthin*, *Tropaeolin D*, and *Orange III.*, and is used for dyeing wool and silk. Its aqueous solution, even when dilute, has a dark, reddish yellow colour, which is changed by the slightest quantity of free acid into a light red; it is therefore used instead of litmus in titrations, its solution being much more stable and more sensitive towards acids.[4]

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[1] Berju, *Ber. Deutsch. Chem. Ges.* xvii. 1400.
[2] *Ibid.* x. 528.
[3] Möhlau, *Ber. Deutsch. Chem. Ges.* xvii. 1490.
[4] Lunge, xi. 1941.

Phenylamido-azobenzene, $C_6H_5N_2C_6H_4NH(C_6H_5)$, is formed by the action of diphenylamine on diazobenzene chloride in alcoholic solution. It is readily soluble in alcohol and ether, and crystallizes in small, golden-yellow, lustrous plates or fine prisms, melting at 82°. An alcoholic solution is first coloured a splendid violet by acids, and then deposits the salts in grey crystals. This compound dissolves in concentrated sulphuric acid with a green colour, which is converted into indigo-blue, and then into reddish violet by the addition of water.

Phenylamido-azobenzenesulphonic acid, $C_6H_4(SO_3H)N_2C_6H_4NH(C_6H_5)$, is obtained by acting on paradiazobenzenesulphonic acid with diphenylamine, and crystallizes in grey, hair-like needles with a steel-blue lustre; it is only slightly soluble in water, forming a light-red solution, but somewhat more readily in alcohol and acetic acid. The potassium salt, $C_{18}H_{14}N_3SO_3K$, occurs in commerce as *Tropaeolin OO, Orange IV*, or *Orange N*. It is only slightly soluble in cold, but readily in hot water, and crystallizes in flat, dichroic needles, generally arranged in the shape of a fan, which appear light- and dark-golden-yellow, and are often an inch long.[1] Small quantities of the mineral acids diminish its solubility; its slightly acid solution dyes silk and wool a fiery golden-yellow. This tropaeolin is, like helianthin, an excellent indicator for titrations, since its solution is coloured red by the slightest excess of a free acid, while carbon dioxide and sulphuretted hydrogen produce no change.[2]

1085 *Asymmetric diamido-azobenzene*, $C_6H_5N_2C_6H_3(NH_2)_2$, was prepared almost simultaneously by Caro and Witt;[3] it is obtained by the action of metadiamidobenzene on diazobenzene chloride; it is slightly soluble in water, readily in alcohol, ether, &c., crystallizes in fine yellow needles, melting at 117°·5, and is split up by reduction with stannous chloride into aniline and 1 : 2 : 4 triamidobenzene. Its constitution is, therefore, expressed by the following formula:

It is a monacid base; its hydrochloride, $C_{12}H_{12}N_4.HCl$, occurs in commerce under the name of *Chrysoïdin*, and forms lustrous

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[1] Witt, *Ber. Deutsch. Chem. Ges.* xii. 258.

[2] v. Miller, *ibid.* xi. 460; Danilewski, *ibid.* xiv. 115; Tropaeolin OOO or naphtholazobenzene-sulphonic acid, $C_{10}H_6(OH)N_2.C_6H_4.SO_3H$, behaves in a precisely opposite manner, since it is turned red by alkalis, and is a most delicate reagent for these.

[3] *Ber. Deutsch. Chem. Ges.* x. 388.

needles, greenish black by reflected light and deep-red by transmitted light, which form a brownish red solution in water.

Chrysoïdin dyes wool and silk orange-red; it absorbs the chemically active rays of the spectrum to a very large extent, and is therefore used, dissolved in dilute shellac varnish, by photographers for covering the window of the dark room; it is, however, gradually decomposed by the action of the light.

Diamidodisazobenzene, $C_6H_5N_2.C_6H_2(NH_2)_2.N_2.C_6H_5$, is formed by the action of chrysoïdin on diazobenzene nitrate, and crystallizes from chloroform in dark-red lustrous needles or small plates, which melt at 250° and detonate when more strongly heated. It is a weak monacid base and forms salts which are decomposed by water.[1]

Paradiamido-azobenzene or *Parazo-aniline*,

$$NH_2.C_6H_4.N_2.C_6H_4.NH_2.$$

In order to prepare this compound, an alkaline solution of paranitracetanilide is treated with ammonia, zinc dust and a little platinum chloride; after some days, para-azoxyacetanilide, $N_2(C_6H_4.NH.C_2H_3O)_2O$, separates out, and on evaporation of the mother liquor, paradiamidobenzene and para-azo-acetanilide $N_2(C_6H_4.NH.C_2H_3O)_2$, are obtained; the former of these is removed by dilute hydrochloric acid and the latter then converted into parazo-aniline by heating with hydrochloric acid.[2]

This is also formed by reducing paranitracetanilide with iron and acetic acid, and then diazotizing. On adding aniline to the neutral solution thus obtained, a bright-yellow diazo-amido-compound separates out, and is converted by heating with aniline and aniline hydrochloride into acetyldiamido-azobenzene, $NH_2.C_6H_4.N_2.C_6H_4.N(C_2H_3O)H$; this is then decomposed by heating with dilute sulphuric acid.[3]

Parazo-aniline crystallizes from dilute alcohol in long, flat, golden-yellow needles, melting at 235°. On gradually adding hydrochloric acid to the alcoholic solution, the colour is first changed to a dark-green, which is then converted into red; this is caused by the formation of a normal and an acid salt, the former of which, $C_{12}H_{12}N_4(HCl)_4$, crystallizes in almost black needles with a green surface lustre.

Paramidobenzene-azodimethylaniline,

$$C_6H_4(NH_2)N_2C_6H_4N(CH_3)_2.$$

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[1] Griess, *Ber. Deutsch. Chem. Ges.* xvi. 2028.
[2] Mixter, *Americ Chem. Journ.* v. 1 and 282.
[3] Nietzki, *Ber. Deutsch. Chem. Ges.* xvii. 343.

Meldola has given this name to a base which is obtained by adding an aqueous solution of diazoparanitrobenzene chloride to a well-cooled solution of dimethylaniline hydrochloride; the hydrochloride of paranitrobenzene-azodimethylaniline is thus formed, and crystallizes in long red needles with a splendid blue metallic lustre. On treatment with ammonia this yields the free base, which separates from solution in hot alcohol in reddish-brown, microscopic needles, melts at 229°—230°, and is reduced by ammonium sulphide to the amido-compound. This crystallizes from dilute alcohol in small brick-red needles having a feeble metallic lustre, and melting at 182°—183°; its salts readily dissolve in water forming red solutions. Its alcoholic solution is coloured green by acetic and oxalic acids, and red by the addition of water. On heating the base with aniline and aniline hydrochloride, a violet dye, which is one of the indulines (p. 313), is obtained.

Nitrous acid converts the base into a diazo-compound, the very dilute, neutral or slightly ammoniacal solution of which assumes a splendid blue colour in the air; this soon disappears, brown flocks being deposited. Traces of nitrous acid can be detected by means of this reaction more readily and with greater certainty than by metadiamidobenzene (p. 240), since 1 part of sodium nitrite in 64,000 parts of water gives a distinct colouration.

If the base be dissolved in hydrochloric acid and treated with zinc dust, dimethyldiamidobenzene is obtained.[1]

1086 *Azylines.* Lippmann and Fleissner[2] have given this name to a group of compounds obtained by the action of nitrogen dioxide on tertiary amido-compounds:

$$2C_6H_5N(CH_3)_2 + 2NO = (CH_3)_2N.C_6H_4N{=}NC_6H_4N(CH_3)_2 + H_2O + O.$$

No oxygen is set free but resinous oxidation products are formed.

Nölting obtained the same compound by treating a well-cooled solution of dimethylparadiamidobenzene in hydrochloric acid with sodium nitrite and, after some time, adding a solution of dimethylaniline in glacial acetic acid:

$$(CH_3)_2NC_6H_4{=}NCl + C_6H_5N(CH_3)_2 = (CH_3)_2NC_6H_4N{=}NC_6H_4N(CH_3)_2 + HCl.$$

[1] *Journ. Chem. Soc.* 1884, i. 106

[2] *Monatsh. Chem.* iii. 705; *Ber. Deutsch. Chem. Ges.* xiii. 2163; xvi. 1415.

It is also formed by the action of methyl iodide on paramidobenzene-azodimethylaniline.[1]

Dimethylaniline-azyline, $N_2(C_6H_4.N(CH_3)_2)_2$, separates from benzene in red crystals, fusing at 266° to a green liquid, and forming a deep-green solution in glacial acetic acid.

Diethylaniline-azyline, $N_2(C_6H_4.N(C_2H_5)_2)_2$, is slightly soluble in cold, more readily in hot alcohol and crystallizes in reddish-brown, monoclinic needles which have a blue surface lustre and melt at 170°. On adding potassium nitrite to its solution in acetic acid, paranitrosodiethylaniline is formed, and it is split up by reducing agents into two molecules of diethylparadiamido-benzene.

The azylines are dyes, but they have received no application on account of their costly preparation. They are derived, like amidobenzene-azodimethylaniline, from parazo-aniline; this may therefore be called azyline, the other compounds being most conveniently designated as follows:

Dimethylparazo-aniline or dimethylazyline.
Tetramethylparazo-aniline or tetramethylazyline.
Tetra-ethylparazo-aniline or tetra-ethylazyline.

Triamido-azobenzene, $NH_2.C_6H_4.N_2.C_6H_3(NH_2)_2$. The hydrochloride of this base, $C_{12}H_{13}N_5(ClH)_2$, is a splendid brown dye, which was first manufactured by Roberts, Dale, and Co., and brought into the market under the name of *Manchester brown*; it has also been called *Phenylene brown*, *Vesuvin*, &c. It is obtained as a brown crystalline mass by treating a cold dilute hydrochloric acid solution of metadiamidobenzene, generally called phenylene diamine, with sodium nitrite, and is much used in wool dyeing. On account of the ready formation and intense colour of this dye, metadiamidobenzene is, as already mentioned (p. 240), employed as a delicate reagent for nitrous acid.

The commercial product also contains other bases in small quantities. When it is decomposed with ammonia and the mixture extracted with boiling water, triamido-azobenzene goes into solution, and on cooling crystallizes in small yellowish-red plates, melting at 137°.[2]

Its constitution follows from that of chrysoïdin, and is expressed by the following formula:

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[1] Nölting, *ibid.* xviii. 1143.

[2] Caro and Griess, *Zeitschr. Chem.* [2], iii. 278.

Azodibenzenephenylenediamine, $C_6H_5.N_2.C_6H_4.N_2.C_6H_3(NH_2)_2$. Griess obtained this compound by the action of diazobenzene chloride on metadiamidobenzene. It crystallizes from chloroform in fine, brownish-red needles, melting at 185°. It differs from the isomeric diamidodisazobenzene (p. 310) in being a tolerably strong diacid base.[1]

THE INDULINES.

1087 This name has been given by H. Caro to a peculiar group of blue, violet, and black dyes, which occur in commerce under the names *Indigo sustitute*, *Bengaline*, *Nigrosine*, *Bleu-Noir*, *Bleu-Coupier*, *Gris-Coupier*, &c. These are employed in dyeing and calico-printing, and are chiefly used for the production of the so-called fancy shades; they give fast colours, but no brilliant shades. They are also used in the preparation of inks and varnishes.[2]

The *water-soluble indulines* are the alkali salts of induline-sulphonic acids, while the *spirit-soluble* consist of the hydrochlorides or sulphates of the bases, and are readily soluble in alcohol, and also, to a slight extent, in water.

Azodiphenyl Blue. The first colouring-matter of this group, the induline, *par excellence*, was prepared by John Dale and H. Caro in 1863 by heating a solution of sodium nitrite with aniline hydrochloride.[3] According to Hofmann and Geyger, the amido-azobenzene first formed acts upon the excess of aniline in the following manner:

$$C_{12}H_{11}N_3 + C_6H_7N = C_{18}H_{15}N_3 + NH_3.$$

The hydrochloride is a crystalline powder which is insoluble in water, and forms a violet-blue solution in hot alcohol.[3]

Azodiphenyl blue is also formed when phenylamido-azobenzene-sulphonic acid (p. 309) is heated with aniline:[4]

$$C_6H_4(SO_3H)N{=}NC_6H_4.NH(C_6H_5) + C_6H_7N = \\ C_6H_4(SO_3H)NH_2 + C_{18}H_{15}N_3.$$

It is further obtained by heating aniline with nitrobenzene; at a higher temperature, and in presence of hydrochloric acid it is

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[1] *Ber. Deutsch. Chem. Ges.* xvi. 2033.

[2] Caro, *Die Induline*, *Neues Handwörterb. d. Chem.* iii. 789.

[3] *Ber. Deutsch. Chem. Ges.* v. 472.

[4] Witt, *ibid.* xvii. 74.

converted into triphenylenediamine, $C_{18}H_{12}N_2$, a substance which is similar to azodiphenyl blue, and may be prepared by heating diphenylamine hydrochloride with nitrobenzene :[1]

$$C_{12}H_{11}N + C_6H_5NO_2 = C_{18}H_{12}N_2 + 2H_2O.$$

Violaniline. This substance, obtained by heating aniline with arsenic acid,[2] and formed as a by-product in the manufacture of rosaniline, is isomeric, or perhaps identical, with azodiphenyl blue; it is prepared from the residue left in the purification of rosaniline.

According to the researches of Thomas and Witt it appears that the reaction which takes place when aniline hydrochloride is heated with amido-azobenzene is not so simple as has hitherto been assumed; but that, as well as azodiphenyl blue, the typical induline, a whole series of other indulines is obtained.[3]

In order to prepare these a mixture of 4 parts of aniline, 1 part of aniline hydrochloride, and 2 parts of diazo-amidobenzene is allowed to stand for twenty-four hours, the latter being thus converted into amido-azobenzene. If the mixture be now heated to 100° the first product of the reaction is *azophenine*, $C_{36}H_{29}N_5$, a monacid base which was first obtained by Kimich by heating nitrosophenol with aniline acetate. It crystallizes from hot aniline in small, garnet-red plates, melting at 236°—237°, and forms a violet solution in sulphuric acid, which becomes azure blue at 300°, and shows a carmine-red fluorescence when diluted with water. By the action of tin and hydrochloric acid on azophenine, various substances, among which aniline and paradiamidobenzene have been recognised, are formed.

When the mixture is heated up to 125°—130°, after the formation of the azophenine, this disappears, the liquid becomes blue, and in twelve hours the formation of a new colouring-matter is complete. On cooling, the hydrochloride of *induline* 3*B*, $C_{30}H_{23}N_5.HCl$, crystallizes out in small, lustrous, brown plates. The base forms warty crystals, dissolving in aniline and alcohol with a purple colour: its salts dye wool and silk a light blue, while the sulphonic acid gives a deep blue, and they are employed for producing a fine, fast grey on cotton.

The mother liquid from the 3*B* contains the hydrochloride of an induline, $C_{18}H\ _5N_3HCl$, which is identical with azodiphenyl

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[1] Wichelhaus and Dechoud, *ibid.* viii. 1609.
[2] Girard Delaire and Chapoteaut, *Ann. Chem. Pharm.* cxlii. 309.
[3] *Journ. Chem. Soc.* 1883, i. 112; Witt, *loc. cit.*

blue; it yields an insoluble sulphonic acid, while its salts form reddish blue solutions and readily dye silk.

Induline 6B, $C_{30}H_{27}NS.HCl$, is formed when the temperature is allowed to rise to 165°—170°; it is, however, best obtained by heating a mixture of 100 parts of amido-azobenzene, 130 parts of aniline hydrochloride, and 300 parts of aniline for four to five hours to 110°, then adding 65 parts of aniline hydrochloride, and maintaining the whole for twenty-four hours at a temperature of 165°—170°.

The salt forms green lustrous crystals which readily lose hydrochloric acid. The base crystallizes from aniline in needles with a green metallic lustre. On heating with sulphuric acid, sulphonic acids are formed, the salts of which are valuable blue dyes.

Blue induline colours are also obtained when amido-azonaphthalene, $C_{20}H_{15}N_3$, is employed instead of amido-azobenzene, &c.; if, however, the aniline be replaced by orthotoluidine, $C_6H_4(NH_2)CH_3$, or amidonaphthalene, $C_{10}H_7(NH_2)$, red dyes are formed.

When a mixture of aniline, nitro-benzene, and hydrochloric acid is heated with iron filings, indulines of a deep blue-black colour are obtained. The *nigrosines*, which also give blue-black shades, are formed when, instead of iron filings, oxidizing agents such as arsenic acid, stannic chloride, &c., are added.

They are employed for producing grey, and greyish blue, to black-blue shades on silk, wool, leather, &c.

Various indulines may be prepared by heating violaniline with aniline and acetic acid.[1]

The water-soluble indulines are used in the preparation of coloured inks; according to R. Böttger, an ink which does not attack steel pens and is not altered by acids or alkalis, may be prepared by triturating 4 grms. of nigrosine[2] with a mixture of 24 grms. of alcohol and 60 drops of hydrochloric acid, and diluting the deep blue liquid with a hot solution of 6 grams. of gum arabic in 100 grms. of water. If, instead of the gum, a solution of 6 grms. of shellac in 100 grms. of alcohol be added, a varnish is obtained which gives a fine black surface to specially prepared wood, leather, or brass.

1088 *Aniline-black* is an oxidation product of aniline, and is much employed in calico-printing, since it gives a deep, fast

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[1] Wolff, *Jahresb. Chem.* 1879, 1159.

[2] Erroneously called aniline-black by him; Schultz, *Chem. Steinkohlentheer*, 1046.

black, and can be produced on the fibre itself in conjunction with any other colours which can be fixed by steaming.

As early as 1834, Runge observed that when a solution of cupric chloride is spread on a porcelain plate heated to 100°, and a drop of a solution of aniline nitrate added to the dry residue, a greenish black stain is obtained (p. 195).

Fritsche, in 1843, found that a dark-blue precipitate is obtained by the action of potassium chlorate on a solution of aniline hydrochloride,[1] and Hofmann obtained the same result with chlorous acid.[2] In 1860 Wilm used this reaction for dyeing cotton, and in the same year Calvert, Cliff and Lowe, of Manchester, found that when a piece of cotton-cloth is saturated with a dilute solution of potassium chlorate, dried and treated with a solution of aniline hydrochloride, a green colour is gradually developed, which is fixed in the fibre and cannot be removed by washing. If the material be then passed through a solution of potassium dichromate the *Emeraldine* is converted into the black-blue *Azurine*.

In 1863, John Lightfoot, of Accrington, found that when the cloth is printed with a mixture of potassium chlorate, aniline hydrochloride, and cupric chloride, and hung up in the ageing-room, a deep green is produced, which is converted into a fine deep black by soaping.

On account of its fastness, aniline-black soon came into general use. It was then found that the above mixture attacked the metallic portions of the printing machines, and also the fibre of the material, and must therefore be improved. Of the various methods proposed for this purpose, that of Lauth has proved the most convenient; copper sulphide, obtained by decomposing copper sulphate with sodium sulphide, is used instead of a soluble copper salt; it is only gradually oxidized, and prevents the presence of free hydrochloric acid or oxides of chlorine.

Lightfoot also observed that salts of many other metals, *e.g.* iron, cerium, vanadium, &c. could be employed instead of those of copper. The compounds of cerium and vanadium were, however, so scarce that no one thought of applying them to calico-printing. Ammonium vanadate has since that time become an article of commerce, and is largely used, in accordance with Guyard's proposal, instead of copper sulphide, since an exceedingly small quantity is required, a very fine black obtained,

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[1] *Journ. Prakt. Chem.* xxviii. 202.

[2] *Ann. Chem. Pharm.* xlvii. 67.

and the rollers and doctors of the printing machines are not attacked by it. Chlorate of sodium or barium is now generally employed instead of the less soluble potassium salt.

In the formation of aniline-black, the metallic compounds act as oxygen carriers, and therefore only those metals can be employed, the compounds of which are readily brought from a higher to a lower state of oxidation, and can then be reoxidized by the chlorate.[1]

The colour obtained in the manner described above was, however, found not to be a permanent black; on exposure for some time it takes a dirty green shade. This alteration is caused by the action of sulphur dioxide, formed in the combustion of imperfectly purified illuminating gas; other dilute mineral acids produce the same shade, which may be removed by washing and soaping. This discolouration may be prevented by passing the cloth, after the black has been developed, through a dilute solution of potassium dichromate to which sulphuric acid has been added (Jeanmaire).

According to Köchlin, aniline black only turns green when it has been prepared in the cold; while when it has been developed at a temperature of 70° no change takes place.

Aniline-black is also formed by the action of potassium permanganate on aniline sulphate,[2] and separates out at the positive pole when salts of aniline are electrolysed.[3]

The homologues of aniline take no share in the formation of the black, and the finest, deepest colour is, therefore, obtained in calico printing when pure aniline is employed.

Aniline-black is an amorphous powder, insoluble in all ordinary reagents; it is a weak base, which has received the name *nigraniline*, $C_{30}H_{25}N_5$, and combines with two equivalents of an acid to form dark-green unstable salts, which are partially decomposed by water. On treating these, or the base itself, with a solution of potassium dichromate to which sulphuric acid has been added, the unalterable black is obtained as a violet-black powder, which takes a yellowish metallic lustre when rubbed. According to Nietzki, this is the chromate and contains about 8·2 per cent. of chromic acid, CrO_3. Aqueous sulphurous acid decomposes it, forming the alterable black, while chromium sesquioxide goes into solution (Nietzki).

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[1] Guyard, *Bull. Soc. Chim.* [2], xv. 58.

[2] R. Meyer, *Ber. Deutsch. Chem. Ges.* ix. 144.

[3] Coquillon, *ibid.* viii. 1345; ix. 352; Goppelsröder, *ibid.* ix. 59, 357, 1033.

Liechti and Suida differ entirely from Nietzki as to the composition of aniline-black and its derivatives. By the action of barium chlorate on aniline sulphate, they obtained aniline chlorate, crystallizing in absence of air in colourless prisms; in presence of air these take a steel lustre, become blue-black, and are completely converted into pseudomorphs of aniline-black or emeraldine, $C_{18}H_{14}ClN_3$. All the salts of this compound contain chlorine, which cannot be removed even by the action of silver oxide. The unalterable black is not a chromate but contains chromium sesquioxide, Cr_2O_3, and is also formed by the action of bleaching powder solution and other oxidizing agents on emeraldine; it is an oxidation product of this, and therefore contains oxygen, while a portion of the carbon is evolved as carbon dioxide during its formation.[1]

Aniline-black dissolves in concentrated sulphuric acid with formation of sulphonic acids, the alkali salts of which dissolve in water with a blue-black colour. The solution is decolourized by reducing agents, but regains its original tint on exposure to the air.

On heating aniline-black with aniline acetate, an induline is formed, the hydrochloride of which crystallizes in needles having a cupreous lustre.

When aniline-black is oxidized with chromic acid solution, a considerable quantity of quinone is formed, while on treatment with tin and hydrochloric acid, or hydriodic acid and phosphorus, it yields paradiamidobenzene and paradiamidodiphenylamine, together with resinous products containing hydrocarbons.[2]

On heating with zinc dust, diphenylamine, diphenylenediamine, and diamidodiphenylamine, together with smaller quantities of aniline, paradiamidobenzene and ammonia are formed (Liechti and Suida).

MAUVEÏNE AND THE SAFRANINES.

1089 The first aniline dye which received practical application was discovered by W. H. Perkin in the Easter vacation, 1856.[3] He writes:

"It has been known for many years that the hypochlorites react on aniline or its salts, producing a purple solution. In

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[1] *Dingl. Polyt. Journ.* ccliv. 265.

[2] Nietzki, *Ber. Deutsch. Chem. Ges.* xi. 1093.

[3] Private communication.

fact, hypochlorites are the distinguishing test for aniline; but nothing definite was known of the nature of this purple solution it being simply stated that aniline produced with hypochlorites a purple liquid, but that its colour was very fugitive.

"As many absurd statements have been made respecting the discovery of aniline purple, I will briefly mention how it was that I first became acquainted with it.

"In the early part of 1856 I commenced an investigation on the artificial formation of quinine. To obtain this base, I proposed to act on toluidine with iodide of allyl, so as to form allyl-toluidine, which has the formula:

$$\left.\begin{matrix}C_7H_7\\C_3H_5\\H\end{matrix}\right\}N = C_{10}H_{13}N,$$

thinking it not improbable that by oxidizing this I might obtain the desired results, thus:

$$\underbrace{2(C_{10}H_{13}N)}_{\text{Allyl-toluidine.}} + O_3 = \underbrace{C_{20}H_{24}N_2O_2}_{\text{Quinine.}} + H_2O.$$

"For this purpose I mixed the neutral sulphate of allyl-toluidine with bichromate of potassium; but, instead of quinine, I obtained a dirty reddish brown precipitate. Nevertheless, being anxious to know more about this curious reaction, I proceeded to examine a more simple base under the same circumstances. For this purpose I selected aniline, and treated its sulphate with bichromate of potassium. The mixture produced nothing but a very unpromising precipitate; but, on investigating this precipitate, I found it to contain that substance which is now, I may say, a commercial necessity, namely, *aniline purple*."[1]

The first aniline colour made a great sensation; Perkin patented it on August 26th, 1856, and prepared it on the large scale. Other patents were soon taken out for the preparation of this colour, and it came into the market under different names, such as Tyrian purple, Aniline violet, Perkin's violet, Mallow dye or Mauve, &c.; the last of which is most generally used.

After Perkin had discovered the dye, he naturally investigated the action of bleaching powder on salts of aniline, to determine whether aniline purple was formed or not, but he obtained no definite results. Some years after, however, mauve was prepared

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[1] *Quart. Journ. Chem. Soc.* xiv. 232.

on the large scale in France by Runge's reaction, and Perkin found that it can readily be obtained in this manner, but that it is not the first product of the reaction. Runge, as we have seen (p. 195), stated that a blue colouration is produced, and gave the name kyanol to aniline on account of this reaction. This colouration is obtained when a dilute solution of bleaching powder is added in small quantities at a time to a solution of aniline hydrochloride. If, however, too much bleaching powder be added, brown products are formed and the solution takes a dirty violet tint. Common salt added to the pure blue solution precipitates a dark tarry mass, from which cold benzene extracts a brown, resinous substance. The residue, which Perkin names Runge's blue, forms a fine blue solution in alcohol, and dyes silk blue. On heating the solution, however, mauve is formed, so that this substance is obtained by heating to boiling the product of the action of bleaching powder on an aniline salt.[1]

To prepare mauve according to Perkin's method a solution of aniline sulphate, containing toluidine, is treated with sufficient potassium dichromate to allow of the formation of normal potassium sulphate. After about twelve hours a black precipitate settles out and is washed, dried at 100°, and extracted with light coal-tar oils to remove resinous products. The colouring matter is obtained from the residue by treatment with boiling wood-spirit or ordinary alcohol, the yield amounting to 4 to 5 per cent. on the aniline employed.

According to the method patented by Dale and Caro, which was employed for a long time by Roberts, Dale and Co., of Manchester, for the manufacture of mauve, a salt of aniline is heated with cupric chloride, the solution being kept neutral. A black precipitate is formed, which is purified by the method just described.

The residue left after the extraction of the colouring matter is aniline-black, or some very similar substance, and is used as a black pigment.

Mauve is the oldest of the so-called aniline dyes, but it was soon superseded by others, such as Hofmann's violet, Paris blue, &c., which are much more fugitive, but at the same time much finer colours. At the present time mauve is only manufactured by Poirrier, of Paris, in small quantities, and occurs in commerce as a paste; it is used for English stamps, and for giving a white appearance to skeins of silk.[2]

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[1] *Quart. Journ. Chem. Soc.* [2], vii. 25.

[2] Schultz, *Steinkohlentheer*, 1049.

According to Perkin's researches, mauve is the sulphate of a powerful base, which he names *Mauveïne*, $C_{27}H_{24}N_4$, and which will be subsequently described.

Mauveïne is not, as was assumed, a derivative of pure benzene, and Perkin found that paratoluidine is necessary for its formation, which proceeds according to the following equation:

$$C_6H_7N + 3C_7H_9N + 5O = C_{27}H_{24}N_4 + 5H_2O.$$

The aniline which was used for the manufacture of the mauve only contained a few per cent. of paratoluidine, and hence only a small yield could be obtained. Mauveïne should therefore be described among the derivatives of toluene, but as its constitution is still completely unknown, it may find its place here as the first aniline dye.

In the preparation of mauve a similar, but much more soluble, colouring matter is formed; Perkin has named the base of this substance *Pseudomauveïne*, $C_{24}H_{20}N_4$, and, as seen from the formula, it is not a lower homologue of mauveïne. Perkin considers it to be a derivative of pure aniline, as by the oxidation of the latter he obtained a colouring matter which resembles pseudomauveïne in every respect. It seems not improbable that the mauve obtained from aniline by the action of bleaching powder is a salt of pseudomauveïne.

1090 Previous to his discovery of pseudomauveïne, Perkin had observed a fine red colouring matter which is obtained from mauveïne by oxidation. This was brought into trade for a long time under the name of *Aniline-pink*, or *Safranine*, but its preparation was given up on account of its costly nature.

At a somewhat later period a safranine with very similar properties was introduced and is still manufactured. It is a derivative of orthotoluidine, has the formula $C_{22}H_{21}N_4Cl$, and is decomposed by silver oxide, but not by alkalis (Hofmann and Geyger).[1] It is now called tolusafranine, to distinguish it from the compound obtained from mauveïne, which is the next lower homologue,[2] and has been named parasafranine by Perkin.

An entire series of safranines is now known. A general method for their formation is the oxidation of a mixture of one molecule of a paradiamido-base with two molecules of a monoamido-base in a hot, neutral, aqueous solution. Potassium dichromate is generally used as the oxidizing agent. The

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[1] *Ber. Deutsch. Chem. Ges.* v. 526.

[2] Dale and Schorlemmer, *Journ. Chem. Soc.* 1879, i. 682; Perkin, *ibid.* 728.

simplest compound, phenosafranine, is obtained from paradiamidobenzene and aniline:

$$C_6H_8N_2 + 2C_6H_7N + 4O = C_{18}H_{14}N_4 + 4H_2O.$$

As it is necessary to work with the salts of the amido-bases, a salt of the safranine, and not the free base, is formed. When the hydrochlorides are used, the chloride, $C_{18}H_{15}N_4Cl$, is obtained; this is generally considered as phenosafranine hydrochloride, $C_{18}H_{14}N_4.HCl$, although, like all saframine salts, it behaves as a salt of a compound ammonium, the base being probably a hydroxide, $C_{18}H_{15}N_4.OH$. The formulæ which have hitherto been given to these bodies will be used in the sequel.

Safranines are also formed when one molecule of aniline and one molecule of orthotoluidine or metatoluidine, or two molecules of the latter are substituted for the two molecules of aniline. One molecule of the monamido-base may also be replaced by paratoluidine, but if two molecules of this be used, the formation of the colouring matter does not take place. A molecule of monomethylaniline, dimethylaniline, &c., may be substituted for one of the molecules of aniline, but if two molecules of a secondary or tertiary monamine are employed, no safranines are obtained. They are also formed when asymmetric diethyldiamidobenzene, $NH_2.C_6H_4N(C_2H_5)_2$, is used, but this cannot be replaced by the symmetric compound $C_6H_4(NHC_2H_5)_2$. The paradiamines may be replaced by substances such as the dichloroquinone-imides, or the tertiary nitrosamines, which yield a paradiamido-compound on reduction, and have a direct oxidizing action on the monamines.

On oxidizing a mixture of a paradiamine and a monamine at the ordinary temperature, blue, green, or violet substances are obtained, some of which remain unchanged, while others decompose, forming safranines and other compounds. If, however, the oxidation be carried on in a warm solution in presence of a monamine, the formation of the safranines proceeds smoothly.[1]

These have the general formula $C_nH_{2n-22}N_4$, *or more probably* $C_nH_{2n-21}N_4OH$; the free bases are almost unknown, but they form salts which, in most cases, crystallize well, are not decomposed by alkalis, and are red to violet dyes. On treatment with reducing agents, they take up four atoms of hydrogen, and are converted into colourless substances, or *leucosafranines*,[2]

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[1] Witt, *Journ. Soc. Chem. Ind.* 1882, 255; Nietzki, *Ber. Deutsch. Chem. Ges.* xvi. 464.

[2] Bindschedler, *ibid.* 869.

which are readily re-oxidized, even by exposure to the air. According to Nietzki, they behave like other colouring matters, and only take up two atoms of hydrogen on reduction.[1]

All safranines form splendid green solutions in sulphuric acid; on the gradual addition of water, the colour changes first into a bluish green, and then into a pure blue. If more water be then added, the solution becomes coloured purple-blue, and passes through all intermediate shades back to the original colour of the safranine.

This, as well as some other facts, which will be subsequently mentioned, points to the conclusion that the safranines not only form a normal salt containing one equivalent of an acid but also a monacid blue, and a diacid green compound, both of which are decomposed by water. This is confirmed by the observations of Landauer, who has found that each of the coloured solutions possesses a characteristic absorption spectrum: "The green solution absorbs the violet, blue, and red rays, the bluish green behaves similarly, but absorbs less in the red; the blue solution only absorbs yellow light, and as the colour changes to violet and red, the region of absorption approaches the green."

Landauer has also observed that the change of colours takes place in the inverse order when the solution is evaporated, and is reproduced on re-dilution as described above. By soaking a piece of filter-paper in a concentrated solution of the sulphate, warming it until it had become green, and then allowing a drop of water to fall upon it, he obtained immediately a red spot surrounded by a deep blue ring. He argues from this that the change of colour is due to the formation of different hydrates,[2] but it seems more probable that the other explanation is correct, and that Landauer's substance contained free acid.

1091 *Mauveine*, $C_{17}H_{24}N_4$. Perkin obtained the free base by adding caustic potash to a boiling solution of commercial crystallized aniline-purple or mauve, which he found to be the sulphate, $(C_{27}H_{24}N_4)_2SO_4H_2$. The base separates out on cooling as an almost black, glistening, crystalline powder. It is almost insoluble in ether and benzene, but forms a violet solution in alcohol, which becomes purple on the addition of an acid; strong acids change the colour to blue, and, on further addition, to

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[1] *Ber. Deutsch. Chem. Ges.* xvii. 223.

[2] *Ibid.* xi. 1772.

dirty green. Mauveïne is a strong base, and readily decomposes ammonium salts.[1]

Mauveïne hydrochloride, $C_{27}H_{24}N_4.HCl$, separates from a boiling alcoholic solution in small prisms having a strong green metallic lustre. It is moderately soluble in alcohol, less so in water, and almost insoluble in ether. If a solution of platinum chloride be added to the warm alcoholic solution, mauveïne platinichloride, $(C_{27}H_{24}N_4)_2H_2PtCl_6$, separates out in crystals with a splendid green surface lustre, which become golden-coloured on drying.

When strong hydrochloric acid is added to a concentrated solution of mauveïne acetate, the blue liquid soon deposits crystals which have a cupreous lustre and appear blue by transmitted light. This compound is the acid salt $C_{27}H_{24}N_4(HCl)_2$, for it gives a platinichloride, $C_{27}H_{24}N_4.H_2PtCl_6$, which also possesses a blue colour and a cupreous lustre. Both compounds are decomposed by water.[2]

Mauveïne hydrobromide, $C_{27}H_{24}N_4.HBr$, is similar to the hydrochloride but less soluble.

Mauveïne hydriodide, $C_{27}H_{24}N_4.HI$, crystallizes in prisms with a green metallic lustre and is still less soluble than the hydrobromide.

Acid mauveïne carbonate, $C_{27}H_{24}N_4.H_2CO_3$. When a solution of the base is allowed to stand over mercury in contact with carbon dioxide, the latter is rapidly absorbed, and the violet solution becomes purple. In order to prepare the carbonate, carbon dioxide is passed through boiling alcohol containing mauveïne in suspension. The salt separates out on cooling in prisms having a green metallic lustre, which are apparently mixed with a little of the normal carbonate. It rapidly loses carbon dioxide in the air, and is completely decomposed at 100°.

Mauveïne acetate, $C_{27}H_{24}N_4.C_2H_4O_2$, also forms fine crystals with a green metallic lustre.

Ethylmauveïne was formerly prepared on the large scale; it is formed when the acetate is heated with ethyl iodide and alcohol. The cooled solution is filtered from the crystals of mauveïne hydriodide which are deposited, the excess of ethyl iodide removed by distillation, and the residue diluted with alcohol and brought into the market under the name of *dahlia*. It dyes a shade which lies between those of mauveïne and

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[1] *Ann. Chem. Pharm.* cxxxi. 201.

[2] Perkin, *Journ. Chem. Soc.* 1879, i. 717.

rosaniline, and is as fast as mauve. In its preparation, splendid crystals with a golden green metallic lustre and of the composition $C_{27}H_{23}(C_2H_5)N_5.HI.I_2$ are frequently formed.

Ethylmauveïne hydrochloride, $C_{27}H_{23}(C_2H_5)N_4.HCl$, is prepared from the hydriodide by double decomposition with common salt. It is a brownish red, crystalline powder, which forms a purple-red solution in alcohol and is not decomposed by alkalis. The nitrate forms crystals having a green metallic lustre.

Pseudomauveïne, $C_{24}H_{20}N_4$, is very readily soluble in alcohol; on allowing the solution to evaporate and grinding the residue with water, the liquid takes a satin lustre, showing that the base is probably crystalline. It dyes the same shade as mauveïne, gives the same reactions with sulphuric acid, and readily absorbs carbon dioxide.

Pseudomauveïne hydrochloride, $C_{24}H_{20}N_4.HCl$, is precipitated by strong hydrochloric acid from a solution of the base in dilute hydrochloric acid. It is tolerably soluble in water, and so readily in alcohol that the solution can be evaporated to a syrup without the salt separating out; on evaporating to dryness, a residue having a golden green metallic lustre is left behind.

1092 *Parasafranine*, $C_{20}H_{18}N_4$, is obtained by the gradual addition of lead peroxide to a boiling solution of mauve acidified with acetic acid;[1] manganese dioxide and sulphuric acid may also be employed as oxidizing agents.[2] In this reaction there is also formed a much less soluble purple colouring matter, which yields colourless products on further oxidation. This persistently adheres to the parasafranine and can only be removed by adding caustic soda to the concentrated solution, filtering, precipitating the parasafranine by common salt, and repeating the operation until the purification is complete. The product consists of the hydrochloride and is obtained pure by recrystallization from water and dilute hydrochloric acid.

Parasafranine hydrochloride, $C_{29}H_{18}N_4.HCl$, forms crystals similar to those of magenta, which have a green metallic lustre, are readily dissolved by water, and dye silk a splendid scarlet-red.

Parasafranine nitrate, $C_{20}H_{18}N_4.HNO_3$, is slightly soluble in cold, more readily in hot water, and crystallizes from hot alcohol in long needles with a dark green metallic lustre, which appears dark garnet-red by transmitted light.

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[1] Perkin, *Journ. Chem. Soc.* 1879. i. 728.

[2] Dale and Schorlemmer, *ibid.* 682.

Phenosafranine, $C_{18}H_{14}N_4$, is formed by oxidizing a hot solution of two molecules of aniline and one molecule of paradiamidobenzene,[1] or of equal molecules of aniline and paradiamidodiphenylamine with potassium dichromate,[2] or by treating aniline with nitrous acid, reducing the product, which contains amido-azobenzene, with tin and hydrochloric acid, and then oxidizing with a boiling solution of potassium dichromate.[3] When pseudomauveïne is oxidized, a colouring matter resembling parasafranine and which is perhaps phenosafranine, is obtained (Perkin).

Phenosafranine hydrochloride, $C_{18}H_{14}N_4.HCl$, crystallizes in flat needles having a beetle-green lustre, which are slightly soluble in cold, readily in hot water. Hydrochloric acid precipitates it almost completely from its aqueous solution. The nitrate is a similar substance, and the sulphate forms long, steel-blue needles. On heating the hydrochloride with acetic anhydride, *diacetylphenosafranine hydrochloride*, $C_{18}H_{11}N_4(C_2H_3O)_2.HCl$, is formed in small, brownish red plates having a metallic lustre, which are insoluble in the ordinary solvents, but form a violet-red solution in weak alcoholic caustic soda, while on heating with a strong alkaline solution they are decomposed into acetic acid and phenosafranine.

When sodium nitrite is added to a solution of phenosafranine acidified with hydrochloric acid, a blue colouration is produced, and on the addition of gold chloride, fine, greenish grey needles of diazophenosafranine aurichloride, $C_{18}H_{13}N_5Cl_2(AuCl_3)_2$. separate out. The corresponding chloride has, therefore, the composition $C_{18}H_{13}N_3ClN{=}NCl$. Since the salts of the diacid diazophenosafranine are coloured blue, like the unstable monacid salts of phenosafranine, it seemed probable that green diacid salts of a diazo-compound, the chloride of which would have the formula $C_{18}H_{12}N_2Cl(N_2Cl)_2$, might be obtained. Nietzki, therefore, added water to the green solution of phenosafranine in sulphuric acid until the colour began to change to bluish green, cooled the liquid with ice, and then added sodium nitrite. The solution thus obtained was coloured green and was not altered by the addition of water; clearly, therefore, a diazo-compound had been formed, but could not be further investigated on account of its instability.

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[1] Witt, *Journ. Chem. Indust.* 1882.
[2] Nietzki, *Ber. Deutsch. Chem. Ges.* xvi. 466.
[3] Bindschedler, *ibid.* xvi. 870.

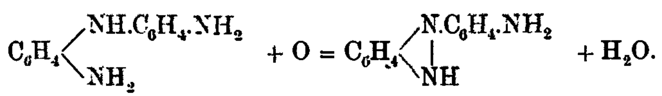
On heating phenosafranine to 170° with strong hydrochloric acid, ammonia is eliminated and a substance is formed which resembles aniline black very closely (Nietzki).

1093 *Dimethylphenylene-green*, $C_{16}H_{19}N_3$. When an aqueous solution of equal molecules of dimethylaniline and dimethylparadiamidobenzene, containing zinc chloride, is heated to about 30° and treated with sufficient potassium dichromate to liberate two atoms of oxygen, splendid crystals of $(C_{16}H_{20}N_3Cl)_2ZnCl_2$ separate out after a few minutes; these have a cupreous lustre, and are insoluble in alcohol but readily form a green solution in water. The solution dyes silk a yellowish green but the colour is not very fast.[1] Alkalis change the colour into blue, and acids into dirty violet; the acid solution is decolourized on heating, quinone being formed.

The iodide, $C_{16}H_{20}N_4I$, crystallizing in splendid green needles, is obtained by the action of potassium iodide on the zinc double salt.[2]

If mercuric chloride be used instead of zinc chloride in the preparation of the green, the compound $(C_{16}H_{20}N_3Cl)_2HgCl_2$, which also crystallizes well, is formed. On decomposing this with sulphuretted hydrogen and making the solution alkaline, *leucodimethylphenylene-green*, $C_{16}H_{21}N_3$, is obtained and may be extracted with ether; it crystallizes from petroleum spirit in large, yellow, quadratic plates, melting at 119° (Bindschedler). This is undoubtedly tetramethyldiamidodiphenylamine, for on oxidizing an ice-cold mixture of paradiamidobenzene and aniline, a blue solution is obtained which contains a compound $C_{12}H_{11}N_3$, corresponding to the green; this is so extremely unstable that it cannot be isolated. On treating its solution with zinc-dust and hydrochloric acid, paradiamidodiphenylamine (p. 244), $C_{12}H_{13}N_3$, is formed and is reconverted into the blue compound on oxidation, just as the leuco-compound of the green is changed into dimethylene-green.

The formation of the blue compound may be simply explained by the following equation:



$$C_6H_4\begin{cases}NH.C_6H_4.NH_2\\NH_2\end{cases} + O = C_6H_4\begin{cases}N.C_6H_4.NH_2\\|\\NH\end{cases} + H_2O.$$

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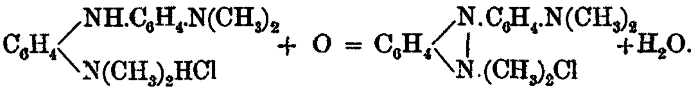
[1] Bindschedler, *Ber. Deutsch. Chem. Ges.* xvi. 864.

[2] Nietzki, *ibid.* xvi. 472.

Methylene-green is an ammonium compound, and is probably formed from the hydrochloride of the leucobase as follows:



$$C_6H_4\left\langle\begin{matrix}NH.C_6H_4.N(CH_3)_2\\N(CH_3)_2HCl\end{matrix}\right. + O = C_6H_4\left\langle\begin{matrix}N.C_6H_4.N(CH_3)_2\\|\\N.(CH_3)_2Cl\end{matrix}\right. + H_2O.$$

Its formation from dimethylaniline and dimethylparadiamidobenzene can also be readily understood.

Tetramethylphenosafranine, $C_{18}H_{10}N_4(CH_3)_4$, is obtained when a boiling solution of equal molecules of the zinc double salt of the green and of aniline acetate is oxidized with potassium dichromate. Its hydrochloride is remarkably soluble in water and alcohol. The nitrate, $C_{22}H_{22}N_4.HNO_3 + H_2O$, separates from solution in brownish violet, prismatic masses which are aggregations of smaller crystals of varying length, and therefore have rough surfaces. The salt loses its water at 130° (Bindschedler).

α-Diethylphenosafranine, $C_{18}H_{12}N_4(C_2H_5)_2$, is prepared from the asymmetric diethylparadiamidobenzene and aniline; its hydrochloride crystallizes in fine needles with a green reflection. Its solution, acidified with hydrochloric acid, is coloured blue by the addition of sodium nitrite. The diazo-compound which is formed gives a platinichloride, $C_{18}H_{11}N_5(C_2H_5)_2PtCl_6$, crystallizing in almost black needles.

β-Diethylphenosafranine is obtained by oxidizing equal molecules of paradiamidobenzene, aniline, and diethylaniline; its hydrochloride is much more soluble than that of the *α*-compound. Its diazo-platinichloride forms crystals having a cupreous lustre.

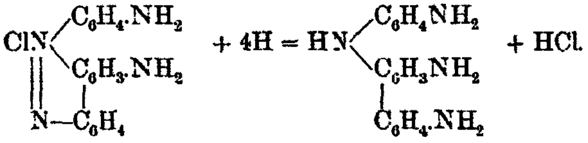
When either of these isomeric compounds is heated with acetic anhydride, only one atom of hydrogen is replaced by acetyl. The compounds thus obtained crystallize in needles having a brown reflection, and have only a slight dyeing power, while the two diethylphenosafranines dye silk a magenta-red (Nietzki).

Tetra-ethylphenosafranine, $C_{18}H_{10}N_4(C_2H_5)_4$, is formed when a mixture of diethylparadiamidobenzene, diethylaniline, and aniline is oxidized. A purer product may be obtained by converting the two diethyl bases into the compounds corresponding to Bindschedler's green, and heating these in aqueous solution with aniline hydrochloride and potassium dichromate. The hydrochloride is very readily soluble in water, and forms a zinc double salt crystallizing in small lustrous, golden plates. The colouring matter dyes silk and wool violet, producing a beautiful fluorescence in the former; it is, however, very fugitive.

Tetra-ethylphenosafranine is not attacked either by nitrous acid or acetic anhydride (Nietzki).

Constitution of the Safranines. These compounds are formed from one molecule of a paradiamine and two molecules of a monamine by the elimination of eight atoms of hydrogen. Two of these are derived from one amido-group of the diamine, and an equal number from that of the aniline or other monamine. This follows from the facts that phenosafranine undoubtedly contains two amido-groups, and that di- and tetra-ethylphenosafranine can be prepared. The four remaining atoms of hydrogen must therefore be removed from the aromatic nuclei. The stability of the safranines and their derivatives renders it probable that two of the aromatic nuclei are directly united, while the third is connected with one of the others by a nitrogen atom, as is shown by the formation of phenosafranine from paradiamidodiphenylamine, and of tetramethylphenosafranine from Bindschedler's green. It must also be borne in mind that the safranines behave as ammonium compounds and, therefore, contain pentavalent nitrogen.

The following formula for phenosafranine is consistent with all these facts, and at the same time explains why four atoms of hydrogen are required for its reduction to a leuco-compound:



$$\begin{array}{lcl}
\mathrm{ClN}{<}^{\mathrm{C_6H_4.NH_2}}_{\mathrm{C_6H_3.NH_2}} & + 4\mathrm{H} = \mathrm{HN}{<}^{\mathrm{C_6H_4NH_2}}_{\mathrm{C_6H_3NH_2}} & + \mathrm{HCl} \\
\| \qquad | & \qquad\qquad | & \\
\mathrm{N{-}C_6H_4} & \qquad \mathrm{C_6H_4.NH_2} &
\end{array}$$

This formula also explains the existence of two isomeric diethylsafranines, each containing an amido-group.

The composition of pseudomauveïne corresponds to that of a phenylphenosafranine. Since, however, its salts are decomposed by alkalis, it cannot belong to this class, and is therefore, an amido- or imido-base.

1094 *The Indophenols.* These blue colouring matters were discovered by Köchlin and Witt. They are formed when equal molecules of a paradiamine and a phenol are oxidized in a neutral or slightly alkaline solution, or when the alkaline solution of a phenol is heated with a tertiary nitrosamine.[1] They are converted by reduction into colourless compounds which unite with acids to form salts. In the presence of alkalis, however, they are rapidly reoxidized, the original colouring matters being formed.

Phenol-blue, $C_{14}H_{14}N_2O$, occurs in commerce as a paste, and is prepared by oxidizing a mixture of phenol and dimethylparadiamidobenzene:

$$C_6H_5.OH + NH_2.C_6H_4.N(CH_3)_2 + 2O = C_6H_4O{:}N.C_6H_4N(CH_3)_2 + 2H_2O.$$

It is also obtained from phenol and nitrosodimethylaniline:

$$C_6H_5.OH + NO.C_6H_4.N(CH_3)_2 = C_6H_4O{:}N.C_6H_4.N(CH_3)_2 + H_2O.$$

On heating dimethylphenylene-green with caustic soda, dimethylamine is formed together with a colouring matter, which is probably phenol-blue.[2]

Trichlorophenol-blue, $C_{14}H_{11}Cl_3N_2O$. Smith and Andresen obtained this compound, which they term trichloroquinonedimethylanilenimide, by the action of trichloroquinonoxime chloride on dimethylaniline. It crystallizes in needles, which are very elastic and tough, give an azure-blue streak, and appear golden-green by reflected light when the beam of light falls in one plane with the longer axis, but deep-red when it is perpendicular to this axis. It is almost insoluble in water, slightly soluble in cold, more readily in hot alcohol, and readily in ether and benzene, forming deep greenish-blue solutions, which produce fast colours on animal fibres.

Reducing agents convert it into *trichlorodimethylanilenamidophenol*, $C_{14}H_{12}Cl_3N_2OH$, crystallizing in colourless needles, which become deep blue and fuse at 138°—139°. It forms stable salts with acids, and, as a phenol, also combines with bases; the compounds thus formed, however, cannot be isolated, as they are reoxidized with great rapidity on exposure to air.[3]

The constitution of these compounds may be deduced both from their formation and their decomposition. Phenol-blue is decomposed by heating with hydrochloric acid into quinone and

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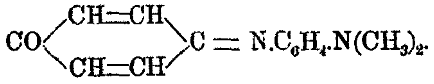
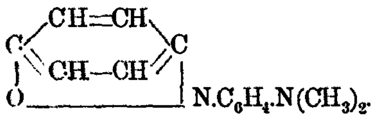
[1] *Journ. Chem. Indust.* 1882, 255.
[2] Möhlau, *Ber. Deutsch. Chem. Ges.* xvi. 2855.
[3] *Journ. Prakt. Chem.* [2], xxiv. 434.

dimethylparadiamidobenzene; its constitution is therefore expressed by one of the following formulæ (p. 169):





By combination with hydrogen, the leuco-compound, $HO.C_6H_4.NH.C_6H_4.N(CH_3)_2$, is formed.

Gallocyanine and naphthol-blue, which is usually called "indophenol," are more important compounds of this class and will be subsequently described.

Dibromoquinonephenolimide, $C_6H_2Br_2O:N.C_6H_4.OH$, is formed by the action of dibromoquinonoxime chloride on a solution of phenol in caustic soda, or when dibromoparamidophenol and phenol are oxidized in alkaline solution. The sodium salt is first obtained in golden-green crystals, which form a blue solution in water. On treating this with acetic acid, the phenolimide is obtained, crystallizing in dark-red prisms with a metallic lustre, which dissolve in water with a magenta-red colour. Hydrochloric acid decomposes it into quinone and paramidodibromophenol, while sulphurous acid reduces it to the leuco-compound, $HO.C_6H_2Br_2.NH.C_6H_4.OH$.

Möhlau considers dibromoquinonephenolimide as an indophenol, and proposes to name the colouring-matters previously mentioned *indoanils*.[1]

SULPHURETTED COLOURING MATTERS DERIVED FROM AMIDO-BASES.

1095 These compounds were discovered by Lauth, who found that when the aromatic diamines are heated with sulphur, combination takes place and bases are formed which yield splendid violet colouring matters on oxidation; he also obtained them in a more simple manner by dissolving the hydrochloride of the

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[1] *Ber. Deutsch. Chem. Ges.* xvi. 2843.

diamine in a large amount of sulphuretted hydrogen water and then adding ferric chloride.[1]

The colouring matter obtained from paradiamidobenzene has been carefully investigated by Koch,[2] and subsequently by Bernthsen.[3] The latter found that it is also obtained when paradiamidodiphenylamine is heated with sulphur and the product treated with ferric chloride, as well as by first reducing the product obtained from paranitraniline and then oxidizing with ferric chloride. Finally, he prepared it from thiodiphenylamine.

Lauth's Violet or Thionine[4] *hydrochloride*, $C_{12}H_9N_3S.HCl$, is only slightly soluble in cold, somewhat more readily in hot water, with an intense violet colour, which appears violet-red by transmitted, and violet-blue by reflected light. It crystallizes from a very slightly acid solution in thin prisms or small needles with a beetle-green lustre. It is almost completely precipitated from its aqueous solution by concentrated hydrochloric acid, but on the addition of an excess of the acid it redissolves with a fine dark-blue colour. Both the free base and its salts dissolve in concentrated sulphuric acid with a fine green colour, which is first turned blue and then violet by the addition of water, just as in the case of the saframines. Like most of the other colouring matters of this group, Lauth's violet forms a compound with filter-paper; on allowing a drop of the solution to fall on a piece of paper, a tolerably well-defined violet stain is produced, round which the paper becomes moist, but is not coloured.

Thionine, $C_{12}H_9N_3S$, is obtained by the precipitation of its salts with ammonia or caustic soda, as a black crystalline powder, or, from a hot solution, in small needles with a feeble green surface lustre. It is only slightly soluble even in hot water, and somewhat more readily in alcohol; its solution is a redder shade of violet than the solutions of its salts, and shows a fine brownish red fluorescence.

Leucothionine, or *Lauth's White*, $C_{12}H_{11}N_3S$, is obtained by treating a boiling alcoholic solution of the violet with a mixture of ammonia and ammonium sulphide until it has become light yellow, and then diluting with an equal volume of water. The base separates out on cooling in small, colourless or slightly yellow plates, which are re-oxidized in the air with great rapidity,

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[1] *Ber. Deutsch. Chem. Ges.* ix. 1035.

[2] *Ann. Chem. Pharm.* ccxxx. 73 and 108.

[3] *Ibid.* xii. 2069.

[4] From θεῖον, sulphur, and τὸ ἴον, the violet, since it is a violet dye containing sulphur.

and on drying in an atmosphere of carbon dioxide become superficially coloured dark-green or black-blue.

The compound is much more stable in the dry state or in acid solution than in a moist condition; its solution is coloured a splendid violet by ferric chloride.

The two other isomeric diamidobenzenes do not yield analogous colouring matters (Koch), while, on the other hand, similar compounds may be obtained from methylparadiamidobenzene and dichloroparadiamidobenzene.[1]

Similarly, the diamidobenzene obtained from nitracet-toluide yields a reddish violet, while paradiamidotoluene yields a violet-red (Lauth).

Lauth's colouring matters have received no practical application, since equally fine violets can be more cheaply prepared. *Methylene-blue*, on the other hand, which was discovered by Caro,[2] and belongs to this group, soon came into general use.

In order to prepare it, a solution of dimethylaniline in hydrochloric acid is treated with nitrous acid or sodium nitrite, and then with sulphuretted hydrogen, the nitrosodimethylaniline first formed being thus converted into dimethylparadiamidobenzene. The treatment with sulphuretted hydrogen is continued until the solution has lost its yellow colour and is covered with a blue scum, at which stage ferric chloride or potassium dichromate is added until the smell of sulphuretted hydrogen has disappeared. The liquid is then saturated with common salt and treated with zinc chloride to precipitate the colouring matter, which is filtered off, redissolved in water, and reprecipitated by common salt and zinc chloride; the residue is then filtered off, pressed, and dried.

Methylene-blue may also be prepared by heating helianthine, $C_6H_4(SO_3NH_4)N_2C_6H_4.NH_2$, with ammonium sulphide to 105°—110° and oxidizing the product with ferric chloride. It is also formed when tetramethyldiamidodiphenylamine, obtained by the reduction of Bindschedler's-green, is treated with sulphuretted hydrogen and ferric chloride.[3]

Methylene-blue produces a fine, fast blue on cotton mordanted with tannate of antimony; it dyes wool and silk directly, but does not give a fast shade. It is also employed for dyeing leather and jute, the latter of which readily takes up the colour.

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[1] Bernthsen and Fränkel, *Ann. Chem. Pharm.* ccxxx. 116.

[2] *Ber. Deutsch. Chem. Ges* xi. 1705.

[3] Bernthsen, *Ibid.* xvi. 2903; *Ann. Chem. Pharm.* ccxxx. 157.

Koch was the first to investigate this compound, but he obtained an incorrect formula for it;[1] this has been accurately determined by Bernthsen, who has also pointed out the constitution of these sulphur-containing colouring matters (p. 336).[2]

1096 *Methylene-blue* or *Tetramethylthionine chloride*, $C_{16}H_{18}N_3SCl + 3H_2O$. When the precipitate obtained by common salt and zinc chloride is dissolved in water and the solution evaporated, a mixture of the chloride and its zinc double-salt is obtained in crystals having a cupreous lustre. After repeated crystallizations from hot, dilute hydrochloric acid, these consist of the pure chloride, crystallizing in small tablets, the surface planes of which have a copper- or bronze-lustre, while that of the planes of fracture is beetle-green. It yields a lustrous, bronze-coloured powder, which loses all its water and becomes coloured dark indigo-blue at 150°. It dissolves in cold water, forming a splendid blue solution, which appears greenish-blue in thin, and bluish violet in thick layers. When a drop of the solution is placed on filter-paper it behaves in a similar manner to Lauth's violet; the colour is not altered by dilute acids or alkalis.

Methylene-blue dissolves in concentrated sulphuric acid with a dark-green colour, which is changed to blue by the addition of water.

Potassium iodide precipitates the iodide, $C_{16}H_{18}N_3SI$ quantitatively from an aqueous solution of the chloride or the commercial product; it crystallizes from hot water containing a little hydriodic acid in needles having a dark bronze lustre. Potassium dichromate precipitates the colouring matter completely as the *purple-violet chromate.*

Tetramethylthionine hydroxide, $C_{16}H_{18}N_3S.OH$, is most readily obtained by treating a solution of the chloride or iodide with freshly-precipitated silver oxide. On evaporating in vacuo, the base is left as a dark, amorphous mass, which takes a green metallic lustre when rubbed, dissolves in water forming a syrup, and is readily soluble in alcohol. It precipitates metallic salts, *e.g.* ferric chloride, the hydroxide of the metal being formed, and is very unstable, especially in solution. Its decomposition products will be subsequently described.

Methylene-white, or *Tetramethyl-leucothionine*, $C_{16}H_{19}N_3S$, is best obtained by reduction of the blue with an alkaline solution of sodium hyposulphite. It crystallizes from ether in flat needles having a satin lustre and a penetrating smell resembling that of

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[1] *Ann. Chem. Pharm.* xii. 592.

[2] *Ibid.* ccxxx. 137.

the lobster, and from alcohol in long, yellow, lustrous needles, readily soluble in water. It rapidly reoxidizes even when quite dry, the change being effected in solution as rapidly as in the case of indigo-white, methylene-blue and decomposition products of this being formed. It is more stablo in acid solution. Its zinc double-salt, $2C_{16}H_{20}N_3SCl + ZnCl_2$, forms prisms readily soluble in water.

In the preparation of methlyene-blue, a red colouring matter, which is not precipitated by zinc chloride, is also formed, and will be described later on.

The formation of methylene-blue is employed as the most certain and delicate reaction for the detection of sulphuretted hydrogen in neutral or acid solution.[1]

In testing for a trace of the gas in an aqueous solution, 2 per cent. by volume of fuming hydrochloric is added; a few grains of dimethylparadiamidobenzene sulphate are then dissolved in the liquid, and one or two drops of ferric chloride added. The addition of a large quantity of acid is necessary to prevent the formation of the red colouring matter.

In a litre of water containing 0·00009 grms. of sulphuretted hydrogen, the colouration became visible after a few minutes, and after half an hour the liquid was coloured a pure blue. This solution, before the addition of the acid, only gave a faint brown colouration with lead acetate, and in the presence of acid remained perfectly colourless.

A litre of water containing only 0·0000182 grms. of sulphuretted hydrogen after standing for half an hour showed a distinct colouration when the vessel containing it was placed on white paper and the solution examined from above. The pure blue colour remained, as in the preceding case, for several days, while the presence of sulphuretted hydrogen in the solution could not be detected by means of lead acetate or sodium nitroprusside.

Methylene-blue has also been applied in physiological researches.[2] "It is an important bacterioscopic reagent. According to Ehrlich, Koch, and others, it surpasses the greater number of colouring matters which have been employed, especially for dry preparations. The baccilli of tuberculosis, of glanders, and of cholera, were first discovered by the aid of methylene-blue."

"It is especially adapted to serve as a measure of the reducing power of the organism. Dreser and Ehrlich simultaneously

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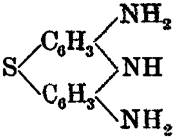
[1] E. Fischer, *Ber. Deutsch. Chem. Ges.* xvi. 2234.

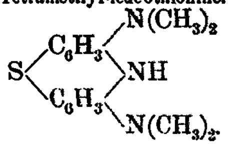
[2] *Ann. Chem. Pharm.* ccxxx. 164.

found that methylene-blue is reduced to methylene-white in the parenchyma of the body, thus affording a new proof of the powerful reducing action of the parenchyma of certain portions of the body, *e.g.* the kidneys."

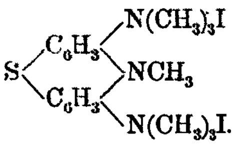
"Ehrlich has found that in the higher animals the peripheral extremities of the sensitive nerve fibres are deeply coloured by injections of methylene-blue, and that it is thus possible to investigate the finest ramifications of the nervous system even in the living animal."

1097 *Constitution of the Sulphuretted Colouring Matters.* Bernthsen has found that thiodiphenylamine is the mother-substance of these compounds. Fuming nitric acid converts it into two isomeric dinitrodiphenylaminesulphoxides, which yield the corresponding diamidothiodiphenylamines, $S(C_6H_3.NH_2)_2NH$, on reduction; one of these, the *a*-compound, is identical with leucothionine, and is, therefore, oxidized by ferric chloride to thionine or Lauth's violet. Methylene-white is tetramethyl-thionine:

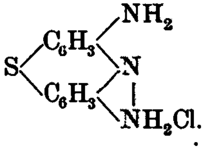

Leucothionine.

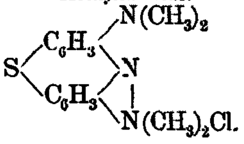

Tetramethyl-leucothionine.

On heating with methyl iodide and methyl alcohol, both compounds are converted into heptamethylthiodiphenylammonium iodide:



This crystallizes from hot water in white or yellow tablets having a pearly lustre, or in needles, and yields the corresponding strongly alkaline hydroxide on treatment with moist silver oxide, the solution of which dries to an amorphous mass. These results, taken in connection with the formation of methylene-blue from Bindschedler's green, lead to the following formulæ for the colouring matters:


Lauth's Violet.


Methylene-blue.

Lauth's violet is therefore the hydrochloride of *a*-amimidothiodiphenylimide, while methylene-blue is an ammonium chloride, a view which is supported by the properties of the compounds in question.

The conversion of methylene-white into methylene-blue is effected by the addition of hydrochloric acid to the former, *accompanied by the elimination of two atoms of hydrogen.* The idea that in the formation of the colouring matter a hydrogen atom of one of the methyl groups is removed, together with that of the imido-group, might be suggested by the choice of the name methylene-blue, but this name is not intended to represent the constitution of the compound any more than in the case of Bindschedler's green and other colouring matters.

It may be remarked, as already mentioned, that methyldiamidothiodiphenylamine also yields a colouring matter on oxidation (p. 263), which is precipitated by zinc chloride and common salt in needles which have a bronze-lustre, and, immediately after their preparation, dissolve in water with a bluish green colour. This compound is, however, very unstable, and decomposes very rapidly, thus showing that it does not correspond to Lauth's violet, and that the formation of the coloured compound proceeds very differently when the hydrogen of the imido-group is replaced by methyl.

1098 *Methylene-red*, $C_{16}H_{18}N_4S_4(HCl)_2$, is formed, as already mentioned, in the preparation of the blue, and remains in the mother-liquor after the precipitation of the latter by salt. Its presence in the original solution can be shown by allowing a drop to fall on filter-paper, a well-defined blue spot being formed, surrounded by a rose-red zone. It crystallizes from alcohol in small, green, glittering prisms; its solution has a splendid fiery purple colour. Potassium iodide produces a precipitate of the hydriodide, crystallizing from a large quantity of water in thick needles or prisms.

Boiling hydrochloric acid has no action upon methylene-red; the alkalis, however, their *carbonates* and *even sodium acetate* or phosphate, decolourize the red solution, the colour not being restored by acids; oxidizing agents, on the other hand, produce a blue colouration, especially after previous reduction.

Reducing agents also decolourize the solution, sulphuretted hydrogen being evolved; commercially the acid solution is first treated with zinc-dust and then with ferric chloride, an additional quantity of the blue being thus formed; this, however, probably differs from methylene-blue (Bernthsen).[1]

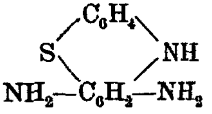
In addition to these colouring matters, Bernthsen has prepared the following closely-related compounds:

Isothionine, or *β-amimidothiodiphenylimide*, $C_{12}H_9N_3S$, is obtained from the β-dinitrosulphoxide, and differs from thionine in being a diacid base.

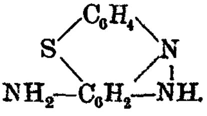
Its hydrochloride is readily soluble, and crystallizes in small dark needles; the violet-red solution dyes silk a fine amethyst with a shade of grey. The colour of the solution is not changed by concentrated hydrochloric acid, and the salt forms a violet solution in strong sulphuric acid, which is scarcely changed by the addition of water. It behaves towards filter-paper like thionine and methylene-blue.

The free base forms a dark greyish brown, glistening, crystalline powder, which is only slightly soluble in water, but dissolves readily in alcohol with a violet-red colour. On reduction it is converted into the leuco-base, or β-diamidothiodiphenylamine, which has not been investigated. The constitution of these compounds is probably expressed by the following formulæ:[2]

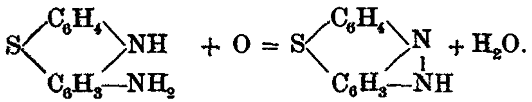
Leuco-isothionine.



Isothionine.



Imidothiodiphenylimide, $C_{12}H_8N_2S$, is formed, as already mentioned, by the oxidation of amidothiodiphenylamine (p. 262):



It crystallizes from hot alcohol on cooling, or on the addition of water, in small, reddish brown needles, or separates out as a crystalline, brick-red powder, which assumes a greenish metallic lustre when rubbed. Its hydrochloride readily dissolves in water with a violet-red colour, and combines with zinc chloride to form the double salt, $(C_{12}H_8N_2S.HCl)_2ZnCl_2$, crystallizing in long, dark violet needles. Its solution, like that of the hydro-

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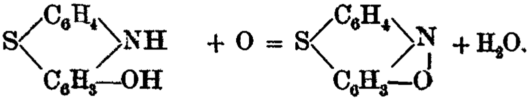
[1] *Ann. Chem. Pharm.* ccxxx. 165.

[2] *Ibid.* ccxxx. 135.

chloride, dyes silk an almost neutral shade of greyish violet. The hydrochloride dissolves in concentrated sulphuric or hydrochloric acid, forming a dark grey solution, which becomes violet-red on the addition of water. Its solution does not give a well-defined spot on filter-paper, like that produced by Lauth's violet or methylene-blue, but diffuses uniformly.[1]

Oxythiodiphenylimide, $C_{12}H_7NSO$. When parahydroxydiphenylamine is melted with sulphur at the lowest possible temperature, hydroxythiodiphenylamine, $C_{12}H_8NSOH$, is formed; this is precipitated by water from an alcoholic solution containing stannous chloride in greenish white flocks, and oxidizes very readily, oxythiodiphenylimide being formed:



This substance is best prepared by decomposing the alcoholic solution with water until it has become turbid, adding a few drops of hydrochloric acid, and then treating with ferric chloride; an amorphous, chocolate-brown precipitate of the compound is thus obtained, which is insoluble in water, slightly soluble in glacial acetic acid, and somewhat more readily in alcohol, benzene, and toluene, crystallizing from the latter in indistinct needles. It readily dissolves in aniline and is precipitated on the addition of ether; it forms a blue-black solution in concentrated sulphuric acid, from which it is precipitated by water.

Reducing agents reconvert it into hydroxythiodiphenylamine, which as a phenol dissolves in alkalis. The colourless solution may be used for dyeing, materials dipped in it becoming coloured reddish brown on exposure to air. Oxythiodiphenylimide dyes silk rose with a shade of violet.[2]

1099 *Dioxythiodiphenylimide*, or *Thionol*, $C_{12}H_7NSO_2$, is formed, together with other products, when thiodiphenylamine is heated for a long time to 150°—160° with concentrated sulphuric acid, to which one-fifth of its weight of water has been added:

$$C_{12}H_9NS + 3H_2SO_4 = C_{12}H_7NSO_2 + 3SO_2 + 4H_2O.$$

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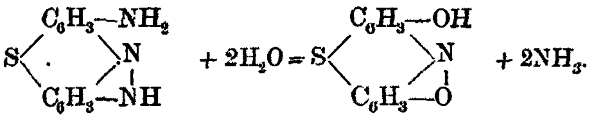
[1] *Ann. Chem. Pharm.* ccxxx. 100.
[2] *Ibid.* ccxxx. 182; Simon, *Dissertation.*

It is also readily formed when thionine is heated with sulphuric acid containing 70—75 per cent. of sulphur trioxide:



Thionol is a brown powder which takes a green metallic lustre when rubbed; it is only slightly soluble even in boiling water, but dissolves in alcohol with a purple colour and in glacial acetic acid with a yellow to blood-red colour; from the last of these it crystallizes in forms resembling oak leaves. It dissolves in concentrated sulphuric acid forming a splendid blue solution, which becomes violet and then reddish brown on the addition of water.

Under certain conditions, which are not accurately known, the sulphate, $(C_{12}H_7NSO_2)_2SO_4H_2$, crystallizes from 40 per cent. sulphuric acid in fine, green needles.

Thionol forms a violet solution in concentrated hydrochloric acid, and the hydrochloride crystallizes from the dilute solution in splendid green needles which readily lose acid.

Thionol also dissolves in the alkalis, or their carbonates and in hot sodium acetate solution, forming splendid violet solutions. The potassium salt is partially precipitated by an excess of caustic potash as a tenacious mass. When thionol is boiled with baryta and a large quantity of water, and the solution evaporated, the barium salt, $C_{12}H_7NSO_3Ba$, is obtained in crusts consisting of small, green, lustrous plates. From a solution of this, silver nitrate precipitates the brown amorphous silver salt, $C_{12}H_7NSO_3Ag_2$. *In the formation of salts, therefore, thionol takes up a molecule of water and the metal replaces two atoms of hydrogen.*

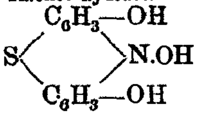
A solution of thionol in an alkaline carbonate dyes silk and mordanted cotton violet; the colour acquires a reddish shade in the air.

Dihydroxythiodiphenylamine, $C_{12}H_6S(NH).(OH_2)$, is the leuco-compound of thionol and is best obtained by reducing an ammoniacal solution of thionol with zinc-dust in absence of air. It forms small needles, slightly soluble in water, more readily in alcohol and ether. It is tolerably stable in acid solution, but rapidly reoxidizes in the presence of alkalis.

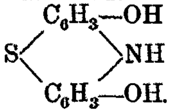
Triacetyl-leucothionol, $C_{12}H_6S(NC_2H_3O)(OC_2H_3O)_2$, is formed on heating the above with acetic anhydride, and separates from hot alcohol in small, tough, yellowish crystals, which are stable in the air and melt at 155°—156°.

The constitution of thionol has already been given; that of the hypothetical hydrate corresponding to its salts, and of leucothionol, are expressed by the following formulæ:[1]

Thionol hydrate.



Leucothionol.



2000 *Thionoline*, $C_{12}H_8N_2SO$. This compound, which lies between thionine and thionol both in its composition and properties, was discovered by Bernthsen, who saturated a solution of paramidophenol in hydrochloric acid with sulphuretted hydrogen and then added ferric chloride. It crystallizes from hot alcohol in small, narrow plates or flat needles, which transmit yellowish brown light, have an intense green metallic lustre and are only slightly soluble in cold alcohol. The solution is purple-red and has a splendid brownish red fluorescence. It dissolves in hot dilute hydrochloric acid forming a purple-violet solution, from which the hydrochloride separates out on cooling in fine black needles; thionoline hydriodide and chromate also crystallize in fine needles, almost insoluble in water.

Thionoline is also formed when thionine is boiled with water for a long time:

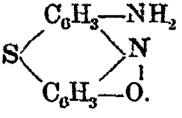
$$NC_{12}H_6S(NH_2)NH + H_2O = NC_{12}H_6S(NH_2)O + NH_3.$$

It dissolves in concentrated sulphuric acid, forming a splendid blue solution, which is decomposed on heating, thionol being formed:

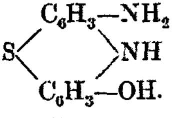
$$NC_{12}H_6OS.NH_2 + H_2O = NC_{12}H_6OS.OH + NH_3.$$

Leucothionoline, $C_{12}H_{10}N_2SO$, is obtained by the reduction of thionoline and is a very unstable compound. As it is both a base and a phenol, it dissolves in acids as well as in alkalis; materials dipped in the alkaline solution become coloured on exposure to the air.

Thionoline.



Leucothionoline.



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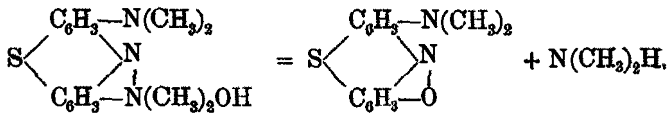
[1] *Ann. Chem. Pharm.* ccxxx. 187.

Dimethylthionoline, or *Methylene-violet*, $C_{14}H_{12}N_2SO$. A solution of methylene-blue to which an excess of an alkali has been added, changes slowly in the cold, more rapidly on boiling, dimethylamine, methylene-white, methylene-azure, and methylene-violet being formed. The last of these is most readily obtained by boiling a solution of methylene-blue, or its iodide, with silver oxide;



It crystallizes in small plates which dissolve slightly in hot water with a blue colour, more readily in alcohol with a colour approaching violet, and in chloroform and ether with a red colour. All its solutions, with the exception of that in aniline, which is violet-red, show a splendid brownish red fluorescence. It crystallizes from cumene in tough needles, and forms a violet-blue solution in concentrated sulphuric acid. Its hydrochloride, $C_{14}H_{12}N_2SO.HCl$, crystallizes in very thin, black needles having a feeble green lustre; its aqueous solution dyes silk and cotton a grey shade of violet.

Leucodimethylthionoline, $SC_{12}H_6(NH)N(CH_3)_2OH$, is readily obtained by warming the colouring matter with dilute alcohol and ammonium sulphide. It crystallizes in needles; materials dipped in an alkaline solution become coloured on exposure to the air, while it is so stable in acid solution that its hydrochloride can be obtained in crystals.[1]

Methylene-azure, remains, together with some methylene-violet, in the mother-liquor obtained in the preparation of the latter. In order to separate them, they are converted by stannous chloride in alkaline solution into the leuco-compounds, that of the violet being soluble, while that of the azure is insoluble in alkalis. The latter is then dissolved in hydrochloric acid, oxidized with ferric chloride, precipitated with common salt, and the chloride thus obtained, which resembles the zinc double salt in being very difficult to purify, converted into the iodide by precipitation with potassium iodide.

Methylene-azure iodide, $C_{16}H_{18}N_3SO_2I$, crystallizes from hot water in fine needles having a green lustre, which take a brassy

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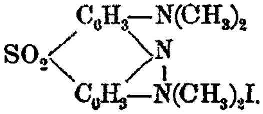
[1] *Ann. Chem. Pharm.* ccxxx. 169.

lustre on being rubbed. It forms a blue solution in water which is more violet than that of methylene-blue; alkalis precipitate the free base which has not yet been obtained pure. The chloride is very soluble and crystallizes with difficulty in small needles; its solution dyes silk a splendid blue, which can scarcely be distinguished from methylene-blue. It dissolves in concentrated sulphuric acid forming a green solution which is changed to blue by the addition of water.

Methylene-azure is clearly an oxidation product of methylene-blue, since it is formed by the action of silver oxide; it is probably the corresponding sulphone:



PHOSPHORUS DERIVATIVES OF BENZENE.

2001 *Phosphenyl chloride*, $C_6H_5PCl_2$, is formed when the vapours of phosphorus trichloride and benzene are repeatedly passed through a red-hot porcelain tube:[1]

$$C_6H_6 + PCl_3 = C_6H_5.PCl_2 + HCl.$$

It is also obtained by boiling 5 parts of aluminium chloride, 30 parts of phosphorus trichloride, and 50 parts of benzene for 36 hours in an apparatus connected with an inverted condenser. According to this method, which is more especially adapted for the preparation of small quantities, 35 grammes of the pure compound may be obtained from 500 grammes of benzene, while according to the first method, with the necessary apparatus at least 500 grammes can be obtained in the same time.[2]

It is also formed when mercury phenyl, $(C_6H_5)_2Hg$, is heated with phosphorus trichloride to 180° (Michaelis):

$$Hg(C_6H_5)_2 + PCl_3 = Hg(C_6H_5)Cl + C_6H_5PCl_2.$$

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[1] Michaelis, *Liebig's Ann.* clxxxi. 280; where the apparatus for the preparation of large quantities is described in detail.

[2] *Ber. Deutsch. Chem. Ges.* xii. 1009.

It is a strongly refractive liquid, which fumes in the air, has a very penetrating smell, and boils at 224°·6 (Thorpe). It is decomposed by water with formation of phosphenylous acid.

Phosphenyl tetrachloride, $C_6H_5PCl_4$, is readily formed by the combination of dry chlorine with the preceding compound, and crystallizes in white prisms, probably belonging to the monoclinic system. They melt at 73° and partially sublime when more strongly heated, another portion being decomposed into chlorine and phosphenyl chloride. On heating to 180° in a sealed tube, it decomposes into chlorobenzene and phosphorus trichloride. With water it first forms phosphenyl oxychloride, which is converted by the further addition of water into phosphenylic acid.

Phosphenyl oxychloride, $C_6H_5POCl_2$, is also obtained by passing air or oxygen into heated phosphenyl chloride; this must be perfectly pure, or, especially when pure oxygen is employed, very violent explosions may occur. It is also formed, together with acetyl chloride, by the action of phosphenyl tetrachloride on acetic acid; it is however best prepared by passing sulphur dioxide into the tetrachloride:

$$C_6H_5PCl_4 + SO_2 = C_6H_5POCl_2 + SOCl_2.$$

The thionyl chloride, boiling at 80°, can readily be separated from the oxychloride, which is a thick liquid having a fruity smell, and boiling at 258°.

It follows from the foregoing decompositions that phosphenyl tetrachloride behaves similarly to phosphorus pentachloride, and Michaelis considers that it might be advantageously employed in organic chemistry in place of the latter for the preparation of chlorides, since, on account of its high boiling point, it can be more readily separated from these than can phosphorus oxychloride, boiling at 110°.

Michaelis has also prepared several bromine derivatives of phosphenyl.

Phosphenyl bromide, $C_6H_5PBr_2$, may be obtained by heating mercury phenyl with phosphorus tribromide, or by passing dry hydrobromic acid gas into boiling phosphenyl chloride. It is a liquid boiling at 257°.[1]

2002 *Phosphenylous acid*, $C_6H_5PO_2H_2$, is obtained by allowing phosphenyl chloride to drop gradually into water; the solution is then heated to boiling and rapidly evaporated in an atmosphere

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[1] Kohler and Michaelis, *Ber. Deutsch. Chem. Ges.* ix. 519.

of carbon dioxide. The acid is slightly soluble in cold, very readily in hot water, and crystallizes in tablets melting at about 70°. When more strongly heated, it decomposes into phenylphosphine, $P(C_6H_5)_3$, phosphenylic acid, $C_6H_5PO_3H_2$, and water.

It is a monobasic acid; its alkaline salts form deliquescent crystals; the barium salt, $(C_6H_5PO_2H)_2Ba + 4H_2O$, crystallizes in fine, oblique, rhombic prisms, and the lead salt, $(C_6H_5PO_2H)_2Pb$, separates out in scales having a mother-of-pearl lustre, when the solution of the sodium salt is treated with lead acetate and acetic acid. The salts of the other heavy metals are insoluble in water; the ferric salt, $(C_6H_5PO_2H)_3Fe$, is a characteristic, granular, white precipitate, insoluble in cold concentrated sulphuric acid but soluble in the hot acid. On cooling it separates out as a tough, white mass, which after some time becomes brittle and crystalline; when again heated, the salt fuses to an oily liquid which gradually dissolves. When the dry salt is heated to 180°, it ignites and burns with a yellowish flame.

Diethyl phosphenylite, $C_6H_5PO_2(C_2H_5)_2$, is obtained by the action of phosphenyl chloride on sodium ethylate free from alcohol; in order to diminish the violence of the reaction a quantity of anhydrous ether is added as a diluent. It is a mobile liquid, which boils at 235° and has an overpowering smell. It dissolves gradually in water with formation of ethyl phosphenylous acid, $C_6H_5O_2(C_2H_5)H$, which is left on the evaporation of the solution as a thick liquid possessing an aromatic odour. It is monobasic and is gradually decomposed by water into phosphenylous acid and alcohol.[1]

The action of phosphorus pentachloride on the latter acid shows that it only contains one hydroxyl (Michaelis):

$$C_6H_5.PHO(OH) + 2PCl_5 = C_6H_5POCl_2 + POCl_3 + PCl_3 + 2HCl.$$

Phosphenyl oxychloride is thus formed, while if the acid contained two hydroxyls, as might be expected from its preparation from phosphenyl chloride, the following reaction would take place:

$$C_6H_5P(OH)_2 + 2PCl_5 = C_6H_5PCl_4 + 2POCl_3 + 2HCl.$$

Michaelis has further shown by the action of phosphenyl

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[1] Köhler and Michaelis, *Ber. Deutsch. Chem. Ges.* x. 816.

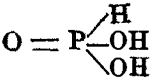
tetrachloride on phosphorous acid that this only contains two hydroxyls:

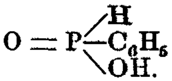
$$PHO(OH)_2 + 3C_6H_5PCl_4 = POCl_3 + 2C_6H_5POCl_2 + C_6H_5PCl_2 + 3HCl.$$

If it had the formula $P(OH)_3$, as was generally supposed, the following reaction would occur:

$$P(OH)_3 + 3C_6H_5PCl_4 = PCl_3 + 3C_6H_5POCl_2 + 3HCl.$$

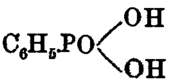
These two acids, therefore, contain pentavalent phosphorus, and have the following constitutions:



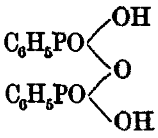


2003 *Phosphenylic acid*, $C_6H_5PO(OH)_2$, is best obtained by gradually adding phosphenyl tetrachloride to water, and finally warming the solution in order to decompose all oxychloride. It crystallizes in small, oblique, rhombic plates, having a vitreous lustre, which melt at 158° and solidify in a radiating crystalline mass. On heating to 200° it is converted into diphosphenylic acid, $(C_6H_5PO)_2O(OH)_2$, which is changed at 210° into triphosphenylic acid, $(C_6H_5PO)_3O_2(OH)_2$. Both these compounds are tough, transparent masses, and recombine with water to form phosphenylic acid. The following formulæ explain the constitution of these substances:

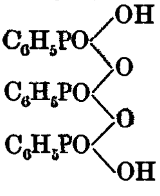
Phosphenylic acid.



Diphosphenylic acid.



Triphosphenylic acid.



When phosphenylic acid is rapidly heated to 100°, it decomposes into benzene and metaphosphoric acid:

$$C_6H_5PO_3H_2 = C_6H_6 + PO_3H.$$

If it be fused with caustic potash, benzene is also formed, together with orthophosphoric acid.

Phosphenylic acid is a strong dibasic acid and is not precipitated by barium chloride or silver nitrate; ammonia produces a white precipitate, while ammonium molybdate does not give any precipitate.

Normal sodium phosphenylate, $C_6H_5PO(ONa)_2 + 12H_2O$, forms long pointed crystals which readily lose water when allowed to stand over sulphuric acid.

Acid sodium phosphenylate, $C_6H_5PO_3NaH$, crystallizes in prisms which contain water of crystallization, but effloresce exceedingly rapidly. The normal potassium salt only crystallizes with great difficulty and in indistinct forms, while the anhydrous acid salt forms microscopic rhombic plates.

Normal calcium phosphenylate, $C_6H_5PO_3Ca + 2H_2O$, is a precipitate consisting of small plates having a silky lustre.

Acid calcium phosphenylate, $(C_6H_5PO_3)_2CaH_2$, separates from solution in acetic acid in small lustrous plates or in lustrous, moss-like aggregates.

All the other metallic salts of phosphenylic acid are insoluble in water.

Acid ethyl phosphenylate, $C_6H_5PO_3(C_2H_5)H$, is obtained by the action of phosphenyl tetrachloride on absolute alcohol, and is a syrupy liquid which has an acid reaction and is monobasic.

Normal ethyl phosphenylate, $C_6H_5PO(OC_2H_5)_2$, is obtained by heating the silver salt with ethyl iodide. It is a thick liquid boiling at 267°, and having a peculiar smell resembling that of mustard oil. The dimethyl ether, which is very similar in its properties and boils at 247°, has a perfectly different smell.

Normal phenyl phosphenylate, $C_6H_5PO(OC_6H_5)_2$, is formed by the action of phosphenyl tetrachloride on phenol:

$$C_6H_5PCl_4 + 3C_6H_5OH = C_6H_5PO(OC_6H_5)_2 + C_6H_5Cl + 3HCl.$$

It is very readily soluble in alcohol and ether, and crystallizes from hot, dilute alcohol in very thin, long needles, melting at 63°·5, which are not attacked by hot aqueous caustic soda, but are decomposed by alcoholic soda. Its boiling point lies above 360°; it is also formed, together with the chloride of phosphenylic acid, $C_6H_5PO(OC_6H_5)Cl$, by the action of phosphenyl oxychloride on phenol. The acid obtained by the decomposition of the chloride with water, *i.e. acid phenyl phosphenylate*, $C_6H_5PO(OC_6H_5)OH$, is only slightly soluble in water, and crystallizes from aqueous alcohol in hair-like needles melting at 57°. It forms salts which crystallize well.

Nitrophosphenylic acid, $C_6N_4(NO_2)PO_3H_2$, is obtained by heating phosphenylic acid with seven parts of fuming nitric acid in a sealed tube for five or six hours to 100°—110°. It crystallizes from ether in white, concentrically arranged needles, which deliquesce in the air and form an intense yellow solution in water. On evaporation of the solution it separates out in white, cauliflower-like masses. It melts at 132° and deflagrates explosively at 200°; on heating with soda-lime it decomposes into phosphoric acid and nitrobenzene, which is converted by the action of the alkali into aniline. It is a strong dibasic acid, the alkali salts of which do not crystallize; the normal barium salt, $C_6H_4(NO_2)PO_3Ba + 2H_2O$, crystallizes from water in lustrous yellow tablets, and the more soluble acid salt, $(C_6H_4(NO_2)PO_3H)_2Ba$, forms small white plates.

Amidophosphenylic acid, $C_6H_4(NH_2)PO_3H_2$, is obtained by the action of tin and hydrochloric acid on the preceding compound. It crystallizes in fine, white, lustrous needles, slightly soluble in water, more readily in hydrochloric acid, no compound being, however, formed. At 280° it decomposes without melting, and becomes coloured bluish-green. On heating with soda-lime it decomposes into phosphoric acid and aniline. Bleaching powder added to its solution in hydrochloric acid produces a dark-red colouration, which is neither destroyed by boiling nor by standing. The solutions of its salts with the metals of the alkalis and alkaline earths are coloured red on evaporation, even when exposed in vacuo over sulphuric acid. The silver salt, $C_6H_4(NH_2)PO_3Ag_2$, is a yellowish white precipitate.

The action of sodium amalgam on a solution of nitrophosphenylic acid does not produce azophosphenylic acid, but sodium amidophosphenylate, $C_6H_4(NH_2)PO_3Na_2 + 3H_2O$, crystallizing in white prisms.

Diazophosphenylic acid nitrate, $C_6H_4(N_2.NO_3)PO_3H_2 + 3H_2O$, is obtained by passing nitrogen trioxide into a boiling solution of amidophosphenylic acid in nitric acid. It crystallizes in colourless prisms, which are readily soluble in water and alcohol with a yellow colour, melt at 188°, and explode violently at a slightly higher temperature. It is a very stable compound, and is not decomposed by long-continued boiling with water. Its salts, which are coloured yellow to red, are explosive; those of the metals of the alkalis and alkaline earths are soluble in water and crystallize; those of most of the other metals are insoluble.[1]

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[1] Michaelis and Benzinger, *Liebig's Ann.* clxxxviii, 275.

2004 *Phenylphosphine*, or *Phosphaniline*, $C_6H_5.PH_2$. Michaelis first prepared this compound by passing hydriodic acid into phosphenyl chloride, the hydriodide of phosphenyl iodide, $C_6H_5PI_2.HI$, being obtained as a dark mass; on treatment with absolute alcohol and subsequent distillation, this yields phenylphosphine, the formation of which is explained by the following equation:

$$3C_6H_5.PI_2.HI + 9C_2H_5.OH = C_6H_5.PH_2 + 2C_6H_5PO_3H_2 + 9C_2H_5I + 3H_2O.$$

Later researches, however, have shown that the reaction is not completely represented by this equation, but that the following also takes place:

$$C_6H_5PI_2.HI + 3C_2H_5.OH = C_6H_5.PO_2H_2 + 3C_2H_5I + H_2O.$$

The phosphenylous acid is then resolved, as already described, into phenylphosphine and phosphenylic acid, a decomposition which is quite analogous to that of hypophosphorus acid into phosphine and phosphoric acid. Phenylphosphine is therefore best prepared by gradually adding crude phosphenyl chloride, which has only been submitted to a few distillations, to an excess of alcohol with continual agitation, distilling off the greater portion of the alcohol in a stream of carbon dioxide, and then further heating the residue over the naked flame.

The distillation of the phenylphosphine, accompanied by violent frothing, commences at 250°; the flame can now be removed as the distillation proceeds spontaneously, frequently with almost explosive outbursts. If it ceases, the flask must again be warmed until the formation of two non-miscible liquids is rendered evident by the turbidity in the condenser. These are water and benzene, formed by the decomposition of the phosphenylic acid. Pure phenylphosphine is readily obtained from the product by distillation in an atmosphere of carbon dioxide.[1]

It is a colourless liquid, boiling at 160°—161°, and possessing a most repulsive, penetrating smell, which is so intense that the mere opening of a flask containing the compound is sufficient to contaminate the air of a tolerably large room. It rapidly absorbs oxygen with evolution of heat and formation of phosphenylous acid.

[1] Köhler and Michaelis, *Ber. Deutsch. Chem. Ges.* x. 807.

When oxygen is passed into uncooled phenylphosphine, the rise of temperature is so great that ignition takes place. It also combines with sulphur on gentle warming, to form phenylphosphine sulphide, $C_6H_5PH_2S$, a thick liquid having an exceedingly unpleasant smell.

Phenylphosphonium iodide, $C_6H_5PH_3I$, is formed by the combination of dry hydriodic acid with phenylphosphine. It is decomposed by heating or by the addition of water; it may, however, be sublimed in needles in a current of hydriodic acid gas.

Phenylphosphonium platinichloride, $(C_6H_5PH_3)_2PtCl_6$. Phenylphosphine is only slightly soluble in concentrated hydrochloric acid; on the addition of platinum chloride, the platinichloride is obtained in yellow crystals almost insoluble in water.

2005 *Diethylphenylphosphine*, $PC_6H_5(C_2H_5)_2$, is obtained by allowing zinc ethyl, diluted with benzene, to drop into a mixture of phosphenyl chloride and benzene contained in a flask which has been filled with carbon dioxide and is surrounded by a freezing mixture; a violent hissing takes place, and so much heat is evolved that the liquid soon begins to boil. When the reaction is complete, a compound of the base with zinc chloride separates out as a viscous liquid, which is then decomposed by caustic soda.

Diethylphenylphosphine is a light, strongly refractive liquid, boiling at 220°, and possessing a characteristic, disagreeable, penetrating odour, which clings to all objects and is difficult to remove.

Diethylphenylphosphine hydrochloride, $PC_6H_5(C_2H_5)_2HCl$, is formed by combination of the base with hydrochloric acid, and is a white crystalline mass which deliquesces in the air, forming a liquid smelling like the base. It readily combines with another molecule of hydrochloric acid, forming the liquid dihydrochloride, $PC_6H_5(C_2H_5)_2(HCl)_2$, which is decomposed on distillation into the base and free hydrochloric acid, a portion of which recombines in the condenser to form the monohydrochloride.

Diethylphenylphosphonium chloride, $P(C_6H_5)(C_2H_5)_2Cl_2$. When chlorine is passed into diethylphenylphosphine, a separation of carbon takes place accompanied by deflagration. If, however, the chlorine be diluted with air and cooled by a freezing mixture, the chloride is formed as a pale yellow liquid possessing a somewhat penetrating but not unpleasant odour. It solidifies in a crystalline mass when cooled by a freezing mixture; when heated it decomposes with carbonization.

Diethylphenylphosphine oxide, $PC_6H_5(C_2H_5)_2O$, is only slowly formed when the base is kept in contact with air or oxygen, while on heating, a more complete oxidation, accompanied by deflagration, takes place. The oxide is, however, readily obtained by decomposing the chloride with water, removing the greater portion of the hydrochloric acid by evaporation, and treating the residue with silver oxide. It forms colourless, transparent needles, which are very hygroscopic, exceptionally soluble in water and have an aromatic, fruity odour. It melts at 55°—56°, and boils above 360°.

Triethylphenylphosphonium iodide, $PC_6H_5(C_2H_5)_3I$, is formed by the combination of diethylphenylphosphine with ethyl iodide. It is soluble in water, and crystallizes from alcohol in radiating needles, melting at 115°.

Triethylphenylphosphonium hydroxide, $PC_6H_5(C_2H_5)_3OH$, is obtained by boiling the aqueous solution of the iodide with silver oxide. It is a crystalline mass which is exceptionally soluble in water, and attracts both moisture and carbon dioxide from the air. The platinichloride, $(PC_6H_5(C_2H_5)_3)_2PtCl_6$, crystallizes in fine, orange-yellow tablets, slightly soluble in alcohol and readily in water.

2006 *Diphenyl phosphorus chloride*, $(C_6H_5)_2PCl$, is formed when mercury phenyl is heated with an excess of phosphenyl chloride for one hour to 220°—230° in an apparatus connected with an inverted condenser:[1]

$$C_6H_5PCl_2 + Hg(C_6H_5)_2 = (C_6H_5)_2PCl + Hg(C_6H_5)Cl.$$

It is also formed when phosphenyl chloride is kept for some time at a temperature of 280°:[2]

$$2(C_6H_5)PCl_2 = P(C_6H_5)_2Cl + PCl_3.$$

It is a colourless, oily liquid, boiling at 320°.

Diphenyl phosphorus trichloride, $(C_6H_5)_2PCl_3$, is readily formed by the combination of the preceding compound with chlorine, and is a crystalline mass.

Diphenylphosphinic acid, $(C_6H_5)_2PO(OH)$, is obtained by the oxidation of diphenyl phosphorus chloride with nitric acid (Michaelis), or by the decomposition of the trichloride with

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[1] Michaelis, *Ber. Deutsch. Chem. Ges.* x. 627; Michaelis and Link, *Ann. Chem. Pharm.* ccvii. 208; Michaelis and La Coste, *Ber. Deutsch. Chem. Ges.* xviii. 2109.

[2] Broglie, *ibid.* x. 628.

water. It is, however, best prepared by warming one molecule of phosphenyl chloride to 100°, and then allowing one molecule of water to flow in gradually, heating first to 200° and then to 260°. On cooling, a very hard, bright yellow mass is obtained, from which water extracts phosphenylic acid, together with a little phosphenylous acid. The diphenylphosphinic acid is obtained from the residue by treatment with alcohol, a yield of about 30 per cent. on the phosphenyl chloride employed being obtained, a tough, yellow mass, which will be subsequently mentioned, is left behind, being insoluble in alcohol.

Diphenylphosphinic acid forms large, apparently triclinic crystals, which melt at 190° and are insoluble in water, slightly soluble in cold, readily in hot alcohol. It dissolves in hot nitric acid, and crystallizes from this solution in needles, which lose a molecule of water at 230°, and are converted into the anhydride $((C_6H_5)_2PO)_2O$.

Its soluble salts also crystallize very well, the most characteristic being the calcium salt, $((C_6H_5)_2PO_2)_2Ca + 3H_2O$, which forms triclinic crystals, and is much more soluble in cold water than in hot.

Ethyl diphenylphosphinate, $(C_6H_5)_2PO(OC_2H_5)$, crystallizes in colourless needles melting at 165°.

The yellow mass mentioned above contains the compound $C_6H_5P_4H$, which is, therefore, phenylated solid phosphuretted hydrogen, and is formed in larger quantities when phosphenylchloride is allowed to decompose gradually in damp air. It is a dark yellow, amorphous powder, having a feeble odour resembling that of phenylphosphine; it is insoluble in water, alcohol, ether and cold carbon disulphide, kindles when warmed in the air, and is oxidized by nitric acid to phosphenylic acid and phosphoric acid.

Together with this body, occurs a compound, $(C_6H_5)_2P_5O_2H$ or $C_6H_5P_4.O.PO(C_6H_5)H$, which is very soluble in carbon disulphide, crystallizes in yellow needles, and yields the same oxidation products as the insoluble compound.

The compounds described above are also formed by the action of phosphenyl chloride on phosphenylous acid:[1]

$$
\begin{aligned}
&C_6H_5PCl_2 + C_6H_5PO_2H_2 = 2C_6H_5PO + 2HCl\\
&5C_6H_5PO = (C_6H_5)_4P_2O_3 + P_2 + C_6H_5PO_2.\\
&5C_6H_5PO + H_2O + 3P_2 = 2C_6H_5P_4H + 3C_6H_5PO_2.\\
&\qquad\qquad = 2(C_6H_5)_2P_5O_2H + C_6H_5PO_2.
\end{aligned}
$$

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[1] Michaelis and Gotter, *Ber. Deutsch. Chem. Ges.* xi. 885.

The anhydrides, $P_2(C_6H_5)_4O_3$, and, $P(C_6H_5)O_2$, then combine with water forming diphenylphosphinic and phosphenylic acids.

2007 *Diphenylphosphine*, $(C_6H_5)_2PH$, is formed, together with diphenylphosphinic acid, by allowing diphenyl phosphoruschloride to drop into a dilute solution of caustic soda, the operation being carried on in an atmosphere of hydrogen. Diphenylphosphinous acid is first formed in this reaction but is immediately decomposed by water:

$$2(C_6H_5)_2POH = (C_6H_5)_2PH + (C_6H_5)_2PO.OH.$$

This behaviour corresponds to the decomposition of phosphenylous acid into phenylphosphine and phosphenylic acid, which, however, only takes place on heating.

Diphenylphosphine is a liquid boiling at 280°, and possessing a very unpleasant smell, which, however, is not so penetrating as that of the primary base. It dissolves in concentrated hydrochloric and hydriodic acids, but is reprecipitated by water. It is oxidized by nitric acid or chlorine water to diphenylphosphoric acid.[1]

Methyldiphenylphosphine, $(C_6H_5)_2PCH_3$, is obtained by the action of zinc methyl on diphenyl phosphorus chloride. It is a colourless, strongly refractive liquid, boiling at 284° (Michaelis and Link), and having a penetrating odour.

Methyldiphenylphosphine oxide, $(C_6H_5)_2CH_3PO$, is formed by the oxidation of the preceding compound in the air, as well as by treating an aqueous solution of triphenylmethylphosphonium iodide with silver oxide, the hydroxide, which is first formed, decomposing even in the cold, more rapidly on warming, with separation of benzene, thus showing that the methyl group is more firmly connected with the phosphorus than is the phenyl:

$$P(C_6H_5)_3(CH_3)OH = P(C_6H_5)_2(CH_3)O + C_6H_6.$$

Methyldiphenylphosphine oxide crystallizes from boiling ether in prisms which melt at 110°—111°, and are odourless in the pure state. In the preparation of this compound, as well as of its homologues, from the phosphonium iodides, resinous by-products are formed, smelling like peppermint or chloral.[2]

Ethyldiphenylphosphine, $(C_6H_5)_2PC_2H_5$, is a liquid boiling at 293°; its oxide, $P(C_6H_5)_2(C_2H_5)O$, forms lustrous prisms melting at 121°.

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[1] Michaelis and Gleichmann, *Ber. Deutsch. Chem. Ges.* xv. 801.

[2] Michaelis and v. Soden, *Ann. Chem. Pharm.* ccxxix. 315.

Diethyldiphenylphosphonium iodide, $P(C_6H_5)_2(C_2H_5)_2I$, is formed by the combination of ethyldiphenylphosphine with ethyl iodide, and forms fine colourless crystals, having a bitter taste and melting at 204°.

Derivatives of phenylphosphine and diphenylphosphine containing both methyl and ethyl, and others containing ethylene, have also been obtained.[1]

Phenoxydiphenylphosphine, $P(C_6H_5)_2OC_6H_5$, is obtained by warming diphenyl phosphorus chloride with phenol in an atmosphere of hydrogen. The mass is then heated somewhat more strongly in a current of hydrogen to remove the hydrochloric acid formed by the reaction, and the temperature is finally raised to 200° and any unaltered phenol distilled off.

Phenoxydiphenylphosphine is a thick, colourless oil, which is soluble in ether and alcohol, boils at 265°—270° under a pressure of 62 mm., and becomes very viscous, without, however, solidifying when cooled in a freezing mixture. As it does not boil under the ordinary pressure without decomposition, its vapour density was determined under diminished pressure and found to be 9·97—10·07.

On boiling with water it decomposes into phenol, diphenylphosphine and diphenylphosphinic acid. This decomposition, which is analogous to that of diphenyl phosphorus chloride, is more rapidly brought about by caustic soda.

Phenoxydiphenylphosphine oxide or *Phenyl diphenylphosphinate*, $(C_6H_5)_2PO(OC_6H_5)$, is obtained by the direct combination of phenoxydiphenylphosphine and oxygen. This also combines with bromine to form the compound $(C_6H_5)_2PBr_2(OC_6H_5)$, which has not been obtained pure, but is converted by treatment with water or boiling with caustic soda into the oxide. This crystallizes from alcohol in small needles or prisms melting at 135°—136°.

Phenoxydiphenylphosphine sulphide, $(C_6H_5)_2PS(OC_6H_5)$, is readily obtained by mixing solutions of phenoxydiphenylphosphine and sulphur in carbon disulphide. It crystallizes from hot alcohol in fine needles, and from ether in small transparent prisms melting at 124°.

The analogous selenium compound has also been prepared.

Phenoxydiphenylmethylphosphonium iodide, $(C_6H_5)_2P(OC_6H_5)CH_3I$, is obtained by the continued heating of phenoxydiphenylphosphine with methyl iodide; it forms a crystalline mass, which

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[1] Gleichmann, *Ber. Deutsch. Chem. Ges.* xv. 198.

deliquesces in damp air, and is decomposed by boiling water with formation of hydriodic acid, phenol and diphenylmethylphosphine oxide.[1]

2008 *Triphenylphosphine*, $P(C_6H_5)_3$, is obtained by adding sodium to an ethereal solution of phosphenyl chloride and bromobenzene (Michaelis and Gleichmann). It may be obtained in a more simple manner by replacing the phosphenyl chloride by phosphorus trichloride:[2]

$$PCl_3 + 3C_6H_5Br + 6Na = P(C_6H_5)_3 + 3NaCl + 3NaBr.$$

The cheaper chlorobenzene may be employed instead of bromobenzene.[3]

Triphenylphosphine crystallizes in imperfect, short, transparent prisms or tablets, which from their optical properties must belong to the monosymmetric system; they are almost odourless and dissolve readily in alcohol and ether. It melts at 79°, but the melting-point is lowered by small traces of impurities. In an atmosphere of any indifferent gas it boils above 360° with slight decomposition, and hence the determinations of its vapour density give too high a number—9·63—10·61 instead of 9·07.

It is not attacked by dry chlorine even on heating; it readily dissolves in concentrated hydrochloric acid even at the ordinary temperature, but is reprecipitated by water. On adding platinum chloride to the hydrochloric acid solution, an amorphous yellow precipitate of $(P(C_6H_5)_3H)_2PtCl_6$ is obtained.

Triphenylphosphonium iodide, $P(C_6H_5)_3HI$, is obtained by dissolving the phosphine in hot hydriodic acid; on cooling it separates out in fine needles, while it crystallizes from hot glacial acetic acid in long prisms. It is resolved into its components by water; it melts at 215° with decomposition, a portion subliming unaltered.

Triphenylphosphine also combines with the elements of the chlorine group, but the compounds formed cannot be obtained pure.

Triphenylphosphine oxide, $P(C_6H_5)_3O$. Oxygen is not absorbed by the phosphine even when the latter is fused. The hydroxide, $P(C_6H_5)_3(OH)_2$, may, however, be obtained by treating it with an excess of water, adding the necessary amount of bromine,

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[1] Michaelis and La Coste, *Ber. Deutsch. Chem. Ges.* xviii. 2109.

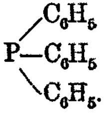
[2] Michaelis and Reese, *ibid.* xv. 1610.

[3] Michaelis and v. Soden, *Ann. Chem. Pharm.* ccxxix. 295.

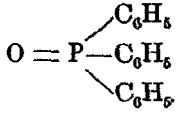
warming, and then boiling with caustic soda until the oily product has become colourless, or by adding potassium chlorate to the warm solution of the phosphine in hydrochloric acid. It is slightly soluble in hot water, readily in alcohol, and crystallizes from a mixture of petroleum ether and benzene in well developed prisms. It readily loses water and is converted at 100° into the oxide, melting at 153°·5 and boiling at 360° without decomposition; the vapour density was found to be 9·79, the theoretical value being 9·68.[1]

Triphenylphosphine oxide is not acted on by bromine, oxygen, sulphur, methyl iodide, &c, while the isomeric phenoxydiphenylphosphine, like triphenylphosphine, readily combines with these. This is due to the fact that the phosphorus is trivalent in the two latter, and pentavalent in their oxides:[2]

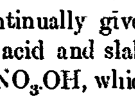
Triphenylphosphine.



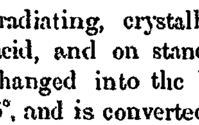
Triphenylphosphine Oxide.



Phenoxydiphenylphosphine.



Phenoxydiphenylphosphine Oxide.



Triphenylphosphine nitrate, $P(C_6H_5)_3(NO_3)_2$, is obtained by dissolving the phosphine in fuming nitric acid and evaporating the solution. It forms a yellow, radiating, crystalline mass which continually gives off nitric acid, and on standing over sulphuric acid and slaked lime is changed into the basic salt $P(C_6H_5)_3NO_3.OH$, which melts at 75°, and is converted into the hydroxide on boiling with water.

Triphenylphosphine sulphide, $P(C_6H_5)_3S$, is obtained by evaporating a solution of the phosphine and sulphur in carbon disulphide; it crystallizes from hot alcohol in long needles having a silky lustre, melting at 157°·5, and boiling with slight decomposition above 360°.

Triphenylphosphine selenide, $P(C_6H_5)_3Se$, is a very similar substance, which melts at 183°—184°, and is obtained by heating the phosphine with selenium.

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[1] Michaelis and La Coste, *Ber. Deutsch. Chem. Ges.* xviii. 2118.

[2] *Ibid.*

Compounds of triphenylphosphine with the alcoholic iodides are very readily obtained; they are only slightly soluble in water, and readily in alcohol, but almost insoluble in ether, have a bitter taste and become coloured yellow in the air.

Triphenylmethylphosphonium iodide, $P(C_6H_5)_3CH_3I$. Methyl iodide combines energetically with the phosphine to form this compound, which crystallizes from water in small plates having a vitreous lustre; the melting point of these crystals lies at first between 165° and 166°, but after repeated recrystallizations rises gradually to 182°—183°, at which point it remains constant.

On boiling its aqueous solution with silver chloride, the chloride, $P(C_6H_5)_3CH_3Cl + H_2O$, is formed and may be obtained by evaporation as a crystalline mass, losing water at 100°—110°, and melting at 212°—213°. The platinichloride, $(P(C_6H_5)_3CH_3)_2PtCl_6$, is a precipitate crystallizing from water or alcohol in yellowish red needles.

	Melting-point.
Triphenylethylphosphonium iodide, $P(C_6H_5)_3C_2H_5I$, broad, colourless tablets . . .	164°—165°
Triphenylpropylphosphonium iodide, $P(C_6H_5)_3C_3H_7I$, strongly lustrous, thick, monosymmetrical plates	201·5°
Triphenylisopropylphosphonium iodide, $P(C_6H_5)_3CH(C_3H_3)_2I + 2H_2O$, thick, opaque plates	—
Triphenylisobutylphosphonium iodide, $P(C_6H_5)_3C_4H_9I$, small lustrous plates or needles .	176°—177°
Triphenylamylphosphonium iodide, $P(C_6H_5)_3C_5H_{11}I$, colourless prisms	174°

By the action of freshly precipitated silver oxide on these compounds the corresponding hydroxides are obtained; these, as already mentioned, are rapidly resolved into benzene and diphenylphosphine oxides, containing an alcohol radical.

Methylenehexphenylphosphonium iodide, $P_2(C_6H_5)_6CH_2I_2$, is formed when the phosphine is dissolved in methylene iodide, and crystallizes in small lustrous needles.

Ethylenehexphenylphosphonium bromide, $P_2(C_6H_5)_6C_2H_4Br_2$, is a crystalline powder, slightly soluble in water.[1]

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[1] Michaelis and Gleichmann, *Ber. Deutsch. Chem. Ges.* xv. 803; *Ann. Chem. Pharm.* ccxxix. 318.

2009 *Trinitrotriphenylphosphine oxide*, $P(C_6H_4.NO_2)_3O$. One part of triphenylphosphine oxide is carefully added to a mixture of two parts of fuming nitric acid and five parts of concentrated sulphuric acid, so that the temperature does not become higher than 15° or 20°, and the mixture then poured into cold water. A mixture of two isomeric nitro-compounds then separates out, one of which can be easily removed by boiling alcohol. This is a bright yellow resinous body, and has not been obtained perfectly pure. The chief product, amounting to from 85 to 90 per cent. of the theoretical yield, remains behind as a yellowish white crystalline powder. It is then dissolved in boiling glacial acetic acid, and precipitated from solution in the form of long, yellowish, oblong plates by the addition of four volumes of alcohol. These can be obtained nearly colourless by recrystallization from glacial acetic acid, with or without subsequent addition of alcohol. The crystals melt at 224° and deflagrate at a higher temperature.

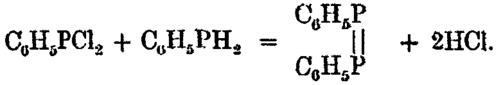
Triamidotriphenylphosphine oxide, $P(C_6H_4.NH_2)_3O$, is obtained by reducing the nitro-compound with tin and hydrochloric acid. It crystallizes from alcohol in colourless prisms containing a molecule of alcohol, which is driven off at from 100° to 110°. It separates from a large quantity of hot water in anhydrous, glittering, reddish-coloured plates melting at 258°. Its salts are very soluble and remain on evaporating their solutions as gum-like or vitreous masses.

When the base is boiled with acetic anhydride a triacetyl compound, $P(C_6H_4.NH.C_2H_3O)_3O + H_2O$, is formed. This separates from solution in dilute acetic acid or alcohol in warty crystals, which do not become perfectly anhydrous until 130°—150°, and then fuse at 186°—187° with evolution of gas.

Hexmethyltriamidotriphenylphosphine oxide, $P[C_6H_4.N(CH_3)_2]_3O$, is formed when the amido-compound is heated with methyl iodide and wood-spirit. It crystallizes from alcohol either in needles containing one molecule of alcohol, or in crystals free from alcohol, melting between 149° and 152°. If an excess of bromine-water be added to the hot aqueous solution of the amido-compound containing hydrochloric acid, a light reddish grey precipitate of $P(C_6H_3Br_2NH_2)_3O$ is formed, whilst chlorine water gives a brown precipitate (Michaelis and von Soden).

Diphosphobenzene hydroxide, $C_6H_5P{=}POH$, is prepared by the action of spontaneously inflammable hydrogen phosphide on phosphophenyl chloride, the product being rubbed up and washed with alcohol. It is a yellow powder, readily soluble in carbon disulphide, which takes fire when warmed in the air, and is oxidized to phosphenylic and phosphoric acids when heated with nitric acid.[1]

Diphosphenyl, $C_6H_5P{=}PC_6H_5$, corresponds to azobenzene, as the foregoing compound does to diazobenzenehydroxide; hence it has been termed *phosphobenzene*. To prepare it, phenylphosphine is brought into a flask through which a current of dry hydrogen is passing, and phosphophenyl chloride allowed to drop in:



$$C_6H_5PCl_2 + C_6H_5PH_2 = \begin{array}{c} C_6H_5P \\ \| \\ C_6H_5P \end{array} + 2HCl.$$

The mass is gently warmed, and the product washed first with water and then with pure ether. It is a yellowish powder readily soluble in hot benzene, melting at 149° to 150° and solidifying to a crystalline mass. It gradually oxidizes in the air forming oxyphosphobenzene, $(C_6H_5P)_2O$. On heating with concentrated hydrochloric acid it splits up into phenylphosphine and phosphophenyl chloride, which latter is, however, at once converted by the water present into phosphophenylous acid. This acid is also formed by oxidation with dilute nitric acid, whilst the concentrated acid converts it into phosphophenylic acid (Köhler and Michaelis).

ARSENIC DERIVATIVES OF BENZENE.

2010 *Arsenphenyl chloride*, $C_6H_5AsCl_2$. This is formed together with diphenyl, $C_{12}H_{10}$, when the vapours of benzene and arsenic trichloride are passed together through a red-hot tube. The two compounds cannot be separated either by crystallization or distillation, and hence the chloride is best prepared by the action of arsenic trichloride on mercury phenyl.[2] It is a colourless, powerfully refracting, not very mobile liquid, boiling at from 252° to 255° and not fuming in the air. When cold it possesses a faint unpleasant smell, but when warm its odour is penetrating; it acts on the skin as a powerful caustic. It is not attacked by

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[1] Michaelis, *Ber. Deutsch. Chem. Ges.* viii. 499.

[2] La Coste and Michaelis, *Liebig's Ann.* cci. 191.

water even when boiling. With chlorine it combines to form a tetrachloride, but bromine decomposes it with formation of paradibromobenzene.

Arsenphenyl oxide, C_6H_5AsO, is prepared by the action of a solution of carbonate of soda on the chloride; it separates from alcoholic solution in crystalline crusts, which melt at from 119° to 120°, and possess when cold a peculiar odour resembling that of aniseed, but when hot have a very penetrating smell, the vapour attacking the mucous membrane of the nose violently. It does not dissolve in water but is soluble in alkalis. When strongly heated it decomposes into arsenic trioxide and triphenylarsine.

Arsenphenyl bromide, $C_6H_5AsBr_2$, is obtained by warming the oxide with an excess of concentrated hydrobromic acid. It is a liquid possessing a faint smell and boiling at 285° with decomposition. It is readily converted by bromine into bromobenzene and arsenic tribromide.

Arsenphenyl iodide, $C_6H_5AsI_2$, is a heavy, oily, red-coloured liquid. When its alcoholic solution is treated with phosphorous acid, iodarsenobenzene, $C_6H_5AsI.AsIC_6H_5$, is formed. This separates out in bright yellow needles, which on addition of iodine are converted into the original compound. It is a very unstable body, and deliquesces in the air.[1]

Arsenphenyl tetrachloride, $C_6H_5AsCl_4$, crystallizes in broad yellow needles melting at 45°, which fume in the air and are readily decomposed by water. It behaves in quite a different manner with acids from the corresponding phosphorus compound; it dissolves readily in cold glacial acetic acid; on warming no acetyl chloride is formed, but chloracetic acid is obtained, whilst sulphur dioxide does not act upon it. When heated in an open vessel, or when carbon dioxide is led through the warm liquid, it is decomposed into chlorine and arsenphenyl chloride. When heated to 150° in a closed vessel, it is converted into arsenic trichloride and monochlorobenzene.

Arsenphenyl oxychloride, $C_6H_5AsOCl_2$, is formed when the tetrachloride is allowed to drop into the necessary quantity of water; it may, however, be obtained more easily and in a purer condition by the combination of chlorine and arsenphenyl oxide. It is a white crystalline mass which fuses about 100° and fumes slightly in the air.

Phenylarsinic acid, $C_6H_5AsO(OH)_2$, is prepared by acting on the oxychloride or tetrachloride with water. It is slightly

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[1] Michaelis and Schulte, *Ber. Deutsch. Chem. Ges.* xiv. 913.

soluble in cold, readily in hot water, and crystallizes from alcohol in long prisms and compact masses. When heated to 140° it is converted into the anhydride, $C_6H_5AsO_2$, an amorphous powder which readily re-combines with water. It is a very stable compound which resists the action of powerful oxidizing agents, and is scarcely acted on by reducing agents; on boiling with iodine and amorphous phosphorus it yields arsenphenyl iodide. When it is heated with soda-lime, benzene is formed, and this together with phenol is obtained on fusing it with alkalis.[1]

Phenylarsinic acid is poisonous; the symptoms begin and death follows rather more slowly than is the case with animals poisoned by arsenious acid, but hardly less rapidly than with arsenic acid. The phenylarsinates of the alkali metals are acid salts, but possess a neutral reaction, and, with the exception of the ammonium salt, they do not crystallize. The metals of the alkaline earths also readily form acid salts, which however crystallize well. The heavy metals replace two atoms of hydrogen, and their salts are either slightly soluble or insoluble in water.

Dimethylphenylarsine, $AsC_6H_5(CH_3)_2$, is formed when zinc methyl acts on the dichloride. It is a thin liquid which boils at 200° and possesses a pungent disagreeable smell.[2]

Diethylphenylarsine, $AsC_6H_5(C_2H_5)_2$, is a colourless, powerfully refracting liquid which possesses a disagreeable smell and boils at 240°. It combines with chlorine forming diethylphenylarsine chloride, $AsC_6H_5(C_2H_5)_2Cl_2$, which forms fine crystals.

Triethylphenylarsonium iodide, $AsC_6H_5(C_2H_5)_3I$, is obtained by heating diethylphenylarsine with ethyl iodide to 100°. It crystallizes from aqueous solution in prisms which have a very bitter taste, fuse at 112°—113°, and are resolved into their constituents when heated in a current of carbon dioxide. The strongly alkaline hydroxide and the chloride obtained from the above compound are syrupy masses (La Coste and Michaelis).

2011 *Arsendiphenyl chloride*, $(C_6H_5)_2AsCl$, is prepared by boiling an excess of arsenphenyl chloride with mercury phenyl. It is a light yellow, oily, non-fuming liquid which when heated has a powerfully pungent smell, and attacks the skin, though less violently than arsenphenyl chloride. It boils at 280° and is converted by alcoholic potash into arsendiphenyl oxide,

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[1] La Coste, *Liebig's Ann.* ccviii. 9.

[2] Link and Michaelis, *ibid.* ccvii. 208.

$[(C_6H_5)_2As]_2O$, which forms a warty crystalline mass melting at 91°—92°.

Arsendiphenyl trichloride, $(C_6H_5)_2AsCl_3$. This compound is formed by the combination of the monochloride with chlorine; it crystallizes from benzene in tablets which melt at 174°. On heating to 200° it decomposes into chlorobenzene and arsenphenyl chloride.

Arsendiphenyl oxychloride, $[(C_6H_5)_2AsCl_2]_2O$, is a white powder melting at 117°, and formed by the direct union of chlorine with diphenylarsine oxide. Water decomposes it with formation of diphenylarsinic acid.

Diphenylarsinic acid, $(C_6H_5)_2AsO(OH)$, is prepared by the action of water on the trichloride. It crystallizes in long needles melting at 174°, and is a weak acid which, together with its soluble salts, acts as a strong poison, being more rapid in its action than phenylarsinic acid. Boiling concentrated nitric acid does not attack it.

Diphenylmethylarsine, $As(C_6H_5)_2CH_3$, is obtained by the action of zinc methyl on the chloride. It is an oily, powerfully refractive liquid, boiling at 206° and possessing a very penetrating smell.

Diphenylethylarsine, $As(C_6H_5)_2C_2H_5$, boils at 220°, and has a not unpleasant fruity smell. It combines with chlorine to form diphenylethylarsine chloride, crystallizing from benzene in long needles fusing at 137°.

2012 *Triphenylarsine*, $As(C_6H_5)_3$, is formed when arsenphenyl oxide is heated to 180°—200°:

$$3C_6H_5AsO = (C_6H_5)_3As + As_2O_3.$$

It can however be prepared more readily by acting on a mixture of arsenic trichloride, bromobenzene and ether with sodium.[1] It crystallizes from arsendiphenyl chloride in thin, brittle plates having a vitreous lustre, and melting at 58°—59°. In a current of carbon dioxide it boils above 360° and does not combine with ethyl iodide even on heating.

Triphenylarsine chloride, $(C_6H_5)_3AsCl_2$, crystallizes from hot benzene in plates which fume slightly in the air and melt at 171°. When heated in a closed tube it decomposes into arsendiphenyl chloride and chlorobenzene.

Triphenylarsine hydroxide, $(C_6H_5)_3As(OH)_2$, is formed by

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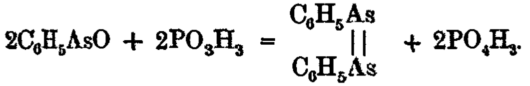
[1] Michaelis and Reese, *Ber. Deutsch. Chem. Ges.* xv. 2876.

boiling the chloride with water, or better with dilute ammonia. It crystallizes on evaporation in plates or white needles which melt at 108°. Over sulphuric acid it effloresces at 105°—110°, forming *triphenylarsine oxide*, $(C_6H_5)_3AsO$, melting at 189°.

Triphenylarsine sulphide, $(C_6H_5)_3AsS$, is obtained by fusing triphenylarsine with sulphur, or more easily by boiling triphenylarsine chloride with yellow ammonium sulphide. It is insoluble in water and the alkali-sulphides, but crystallizes from hot alcohol in silky needles melting at 162° (La Coste and Michaelis).

Arsenobenzene, $C_4H_5As{=}AsC_6H_5$. This body is formed by the action of most reducing agents on an alcoholic solution of arsenphenyl oxide, C_6H_3AsO; the best method is to boil it with crystallized phosphorous acid:



$$2C_6H_5AsO + 2PO_3H_3 = \begin{matrix} C_6H_5As \\ || \\ C_6H_5As \end{matrix} + 2PO_4H_3.$$

It crystallizes in yellowish needles, melting at 196°, slightly soluble in alcohol, but readily in benzene; the solution soon becomes resinous. On heating strongly it decomposes into triphenylarsine and metallic arsenic; chlorine converts it into arsenphenyl chloride.[1]

ANTIMONY DERIVATIVES OF BENZENE.

Triphenylstibine, $Sb(C_6H_5)_3$. is formed when a mixture of bromobenzene and antimony chloride dissolved in benzene is heated with sodium. It is slightly soluble in alcohol, and crystallizes in small plates which have a faint unpleasant smell, and fuse at 48°.[2]

BORON DERIVATIVES OF BENZENE,

2013 *Phenylboron chloride*, $C_6H_5BCl_2$. When boron trichloride is heated to 180°—200° with mercury phenyl, this body is formed. It is a colourless liquid which fumes in the air, and is violently decomposed by water. It boils at 175°, solidifying at the ordinary temperature to a crystalline mass which melts

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[1] Michaelis and Schulte, *Ber. Deutsch. Chem. Ges.* xiv. 912.

[2] Michaelis and Reese, *ibid.* xv. 2876.

about 0°. At the ordinary temperature it does not absorb chlorine, but when placed in a freezing mixture it takes up about two atoms, becoming liquid. If the freezing mixture be removed, a portion of the compound produced is resolved into chlorine and phenylboron chloride, another part yielding chlorobenzene and boron trichloride:

$$C_6H_5BCl_4 = C_6H_5Cl + BCl_3.$$

This decomposition corresponds exactly to that of arsenmethyltetrachloride into methyl chloride and arsenic trichloride.

Phenylboric acid, $C_6H_5B(OH)_2$, is obtained by slowly dropping the chloride into water. It crystallizes from warm water in aggregations of needles melting at 204° and volatilizing slightly in a current of steam. The acid reddens litmus feebly and yields crystallizable salts.

Sodium phenylborate, $C_6H_5B(ONa)_2$, is soluble in water and crystallizes in large quadratic tablets.

Acid calcium phenylborate, $(C_6H_5BO_2)CaH_2$, forms warty druses.

Acid silver phenylborate, $C_6H_5.BOAg(OH)$, is a yellow precipitate which rapidly undergoes change on exposure to light. It is formed by adding silver nitrate and some ammonia to a solution of the acid. Heated with water it decomposes into benzene, boric acid, and silver oxide:

$$2C_6H_5BO_2.AgH + 3H_2O = 2C_6H_6 + 2B(OH)_3 + Ag_2O.$$

Ethylphenylborate, $C_6H_5B(OC_2H_5)_2$, is formed by acting on the chloride with absolute alcohol. It is a colourless, pleasantly smelling liquid, boiling at 176° and readily passing into the acid on standing in moist air.

A characteristic reaction for phenylboric acid is that, even in very dilute solutions, it gives a precipitate of phenylmercuric chloride with corrosive sublimate solution:

$$C_6H_5B(OH)_2 + HgCl_2 + H_2O = C_6H_5HgCl + B(OH)_3 + HCl.$$

By this test one part of the acid in 25,000 parts of water can be detected.

Phenylboron oxide, C_6H_5BO. This anhydride of phenylboric acid is obtained when the latter compound is heated above its melting-point. It forms a colourless crystalline mass which melts at 190° and boils without decomposition above 360°. It is soluble in alcohol and ether, but not in water, although it combines with water on long continued boiling, yielding phenylboric acid.[1]

Boric acid possesses well-known antiseptic properties, and it was natural to expect that its phenyl compound would exhibit similar properties in even a more marked degree. The experiments of Filehne and Rothaas seem to promise a future for phenylboric acid in therapeutic practice, as it possesses a mild aromatic taste, and even when taken in large doses does not produce any corrosive action, only giving rise in the human subject to singing in the ears, giddiness, and headache, which soon disappear, though it acts as a powerful poison on the lower animals. Thus, 2 mgm. acts fatally on a frog, whilst 0·5 grm. can be given to a rabbit without producing any serious effects. Its antiseptic action is from five to ten times as powerful as that of its sodium salt; a solution of the acid of the strength of 1 to 100,000 diminishes the rate of putrefactive decomposition, and meat can be preserved fresh in a solution of 1 to 5,000 provided the quantity of preservative solution employed is large enough to prevent the acid from being neutralized by the alkaline salts contained in the flesh. The formation of bacteria is prevented by a solution containing 1 to 1,000, and greatly retarded by one of from 1 to 10,000.[2]

SILICON DERIVATIVES OF BENZENE.

2014 *Phenylsilicon chloride*, $C_6H_5SiCl_3$, is obtained by heating silicon tetrachloride with mercury phenyl to 300°. It is a powerfully refractive liquid which fumes in the air and possesses a smell similar to that of silicon chloride. It boils at 197°, and on ignition burns with a strong, smoky, green-mantled flame, leaving a residue of silica.

Phenylsilicic acid, or *Silico-benzoic acid*, $C_6H_5.SiO.OH$, is formed when the chloride is added drop by drop to an excess of dilute ammonia. The acid which separates out is dissolved in ether, and on evaporation remains as a transparent mass resembling solidified beads of molten glass. From alcoholic solution it separates out as a syrup which dries to a solid mass and is then insoluble in alcohol though dissolving in ether. It melts at 92°,

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[1] Michaelis and Becker, *Ber. Deutsch. Chem. Ges.* xiii. 58; xv. 180.
[2] Michaelis and Becker, *ibid.* xv. 182.

and dissolves in caustic potash, from which it is not reprecipitated by hydrochloric acid, but if this solution be allowed to stand in the air, or if ammonia be added to the acid solution, the acid separates out. On evaporating the alkaline solution and heating the residue, benzene distils over:

$$C_6H_5SiO_2K + K.OH = C_6H_6 + SiO_3K_2.$$

This decomposition corresponds to that of benzoic acid into benzene and carbon dioxide.

The salts of this acid have not been prepared. If the acid be dried at 100° it is converted into silicobenzoic anhydride, $(C_6H_5SiO)_2O$, an amorphous powder which, like the acid, burns with a smoky flame, silica coloured black by carbon remaining behind.

Phenylsilicon ether, or *Ethyl orthosilicobenzoate*, $C_6H_5Si(OC_2H_5)_3$, is formed by the action of the chloride on absolute alcohol, and is a pungent smelling ethereal liquid boiling at 235°. When heated with concentrated hydriodic acid, silicobenzoic acid is formed:

$$C_6H_5Si(OC_2H_5)_3 + 3HI = C_6H_5.SiO_2H + 3C_2H_5I + H_2O.$$

Silicontriethylphenyl, $C_6H_5Si(C_2H_5)_3$, is obtained when the chloride is heated with zinc ethyl from 150°—165°. It is a colourless liquid boiling at 230°, its vapour possessing a faint smell of oil of cloves. The chloride, $SiC_{12}H_{19}Cl$, is formed by passing chlorine into the above compound, kept well cooled; it is a thick liquid boiling between 260° and 265°, and possessing a faint aromatic odour. It is not converted into an acetate when treated with an alcoholic solution of potassium acetate even at 250°, and it is therefore probably silicon chlorophenyltriethyl, $C_6H_4ClSi(C_2H_5)_3$.[1]

Silicontetraphenyl, or *Silicontetraphenylmethane*, $Si(C_6H_5)_4$, is formed by the violent reaction of sodium on a mixture of silicon tetrachloride and chlorobenzene, diluted with ether, to which some acetic ether has been added. It is sparingly soluble in alcohol and ether but readily in hot benzene, separating from this solution as a crystalline powder, or in larger ill-defined crystals; it melts at 228° and boils above 360°. On heating in the air it burns with separation of light flocks of silica which are carried off by the products of combustion, leaving no residue.[2]

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[1] Ladenburg, *Ann. Chem. Pharm.* clxxiii. 151.

[2] Polis, *Ber. Deutsch. Chem. Ges.* xviii. 1540.

TIN DERIVATIVES OF BENZENE.

2015 *Tin triethylphenyl*, $C_6H_5Sn(C_2H_5)_3$, is formed when a mixtue of triethyl tin iodide and bromobenzene diluted with ether is heated with sodium:

$$C_6H_5Br + (C_2H_5)_3SnI + 2Na = (C_2H_5)_3SnC_6H_5 + NaBr + NaI.$$

It is a colourless, powerfully refractive liquid possessing rather a pleasant smell, and boiling at 254°. Its vapour undergoes partial oxidation on exposure to air, and on ignition it burns with a luminous smoky flame leaving a residue of tin. If its alcoholic solution be warmed with silver nitrate, a fine silver mirror is deposited and diphenyl, $C_{12}H_{10}$, and triethyl tin nitrate are formed. When acted on by iodine it decomposes into iodobenzene and triethyl tin iodide, while fuming hydrochloric acid converts it into benzene and triethyl tin chloride.

Ethylphenyl tin chloride, $C_6H_5(C_2H_5)SnCl_2$, is formed by the action of tin tetrachloride on the last named compound:

$$C_6H_5(C_2H_5)_3Sn + SnCl_4 = C_6H_5(C_2H_5)SnCl_2 + (C_2H_5)_2SnCl_2.$$

It crystallizes from ether in scales which melt at 45° and are only slightly soluble in water and hydrochloric acid, but dissolve readily in absolute alcohol.[1]

Diphenyl tin chloride, $(C_6H_5)_2SnCl_2$. In order to prepare this compound, a mixture of equal parts of tin tetrachloride and mercury phenyl with petroleum spirit is boiled in a flask connected with a reversed condenser for twelve hours, and the liquid then distilled at a temperature below 160°. The product obtained from 300 grms. of mercury phenyl is next poured into 500 to 750 cbc. of cold water and the mixture well shaken. The aqueous solution contains hydrochloric acid, stannic chloride, and diphenyl tin chloride; it is warmed on the water-bath from 85° to 90°, when, after standing for a short time, a part of the diphenyl tin chloride separates out as a heavy oil. The aqueous solution is then poured off and again warmed for two hours, a gummy powder being deposited. This consists of a mixture of the chloride and hydroxychloride; this is then removed, and after heating for two hours almost pure hydroxychloride separates out, and at last a mixture of this compound with diphenyl-

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[1] Ladenburg, *Ann. Chem. Pharm.* clix. 251.

tin oxide and stannic oxide. The pure chloride is obtained from this last named mixture and from that of diphenyl tin chloride and hydroxychloride by passing hydrochloric acid gas over the substance and finally warming to 45°.[1] The product is then extracted with petroleum spirit.

Diphenyl tin chloride is readily soluble in alcohol and petroleum spirit, crystallizing from the latter solvent in compact, transparent prisms often an inch in length, which have a diamond lustre and belong to the triclinic system. It possesses a penetrating sweetish taste, melts at 42° and boils with partial decomposition at from 333° to 337°. When heated with concentrated hydrochloric acid to 100° it decomposes into benzene and stannic chloride.

Diphenyl tin hydroxychloride, $(C_6H_5)_2Sn(OH)Cl$, is formed when the chloride is gently warmed with water, or when it is exposed to most air. As stated above, it is also obtained in the preparation of the chloride, and it is prepared in the pure state from the product, containing some chloride, by washing it with alcohol and then allowing the residue to stand for some time in contact with water.

It is an amorphous powder, fusing at 187° and insoluble in the ordinary solvents. Concentrated hydrochloric acid converts it into the chloride.

Diphenyl tin oxide, $(C_6H_5)_2SnO$, is obtained by the decomposition of the chloride or hydroxychloride by alkalis. It is a white powder which after drying does not fuse, and possesses analogous properties to the hydroxychloride.

Diphenyl tin chlorobromide, $(C_6H_5)_2SnClBr$. When hydrobromic acid gas acts upon the chloride or oxychloride, this compound is formed. It closely resembles the chloride but possesses a more powerful odour, and separates from its solutions as an oily liquid which is converted into a mass of crystals on bringing into it a fragment of the crystallized compound. These crystals fuse at 37°.

Diphenyl tin chloriodide, $(C_6H_5)_2SnClI$, is formed in a similar way to the above-mentioned compound. It crystallizes in transparent, glistening monoclinic prisms melting at 69°.

A fact worthy of note is that by the action of hydrobromic or hydriodic acids on the chloride, the weaker halogen displaces the stronger, just as phosphenyl chloride is converted by hydrobromic acid into phosphenyl bromide. This shows that diphenyl

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[1] Aronheim, *Ann. Chem. Pharm.* cxciv. 145.

tin chloride does not act like the chloride of an organo-metallic radical but like that of a non-metal.

Diphenyl tin bromide, $(C_6H_5)_2SnBr_2$, is formed by the action of hydrobromic acid on the oxide. It is a thick oily liquid, which on standing for some days does not solidify, but does so at once when a crystal of the chlorobromide is placed in the liquid, showing that this latter compound is isomorphous with the bromide, which it otherwise closely resembles. It melts at 38°. Hydriodic acid acts in a similar way on the oxide, but the iodide has not yet been isolated as it at once undergoes the further change into benzene and stannic iodide:

$$(C_6H_5)_2SnI_2 + 2HI = 2C_6H_6 + SnI_4.$$

Diphenyl tin di-ethyl ether, $(C_6H_5)_2Sn(OC_2H_5)_2$. This compound is prepared by adding sodium to a solution of the chloride in absolute alcohol. It separates from this solution in very bright cube-shaped crystals or in long prisms which melt with decomposition at 124° and are readily decomposed by water into the oxide and alcohol.

Triphenyl tin chloride, $(C_6H_5)_3SnCl$, is prepared by the action of sodium amalgam on an ethereal solution of diphenyl tin chloride, or by heating the latter in a current of ammonia from 100° to 200°. Alcohol extracts from this triphenyl tin chloride and stannic chloride, whilst diphenyl tin hydroxychloride remains behind. This latter compound is probably derived from $(C_6H_5)_3SnCl(NH_2)$ which is previously formed. The reaction, doubtless, takes place in two separate stages:

$$(1)\ 3(C_6H_5)_2SnCl_2 = 2(C_6H_5)_3SnCl + SnCl_4.$$
$$(2)\ (C_6H_5)_2SnCl_2 + 2NH_3 = (C_6H_5)_2SnCl(NH_2) + NH_4Cl.$$

The best mode of preparing triphenyl tin chloride is to dissolve one part of diphenyl tin chloride in from four to five parts of glacial acetic acid, and to add one molecule of sodium nitrite for every molecule of the former compound. Triphenyl tin chloride is here formed in the same way as above but, in this case, it is the chief product. At the same time nitrosobenzene[1] is produced:

$$(C_6H_5)_2SnCl_2 + N_2O_3 = 2C_6H_5NO + SnOCl_2.$$

Triphenyl tin chloride separates from solution in large crystals melting at 106°. Its alcoholic solution yields a gelatinous

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[1] Aronheim, *Ber Deutsch Chem. Ges.* xii. 509.

precipitate with ammonia, and this on drying forms a white, strongly electric powder which melts at 117° to 118°, and has the formula $2(C_6H_5)_3SnOH + 3H_2O$, or $[(C_6H_5)_3Sn]_2O + 4H_2O$. It is soluble in hot water and yields stable, crystallizable salts.

MERCURY DERIVATIVES OF BENZENE.

2016 *Mercury phenyl*, $Hg(C_6H_5)_2$, was prepared by Dreher and Otto by acting on bromobenzene with sodium amalgam.[1]

The best yield is obtained by boiling a mixture of bromobenzene with its own volume of anhydrous coal-tar naphtha boiling between 120° and 140°, one-tenth of its weight of acetic ether and an excess of 2·7 per cent. sodium amalgam,[2] for some hours in connection with a reversed condenser. The product is filtered whilst hot, and the crystals which deposit purified by recrystallization from benzene and absolute alcohol.

This compound crystallizes from its saturated benzene solution in small, brilliant needles, which have a strong lustre and resemble asbestos. It separates from dilute solutions in long white prisms, which melt at 120°, and with care can be sublimed. It is somewhat volatile in a current of steam, but boils far above 300°, being then partially converted into mercury, benzene, diphenyl, and charcoal, and completely converted into these products at a red-heat.

It is odourless, perfectly insoluble in water, slightly soluble in cold, more readily in hot alcohol and ether, but very soluble in benzene, carbon disulphide, and chloroform.

Ladenburg, when working with this compound, suffered severely from the irritant power of its vapour, especially on the eyes, and became so sensitive to its action that he found himself unable to remain in the room where it was being prepared.

When hydrochloric acid gas is passed over it, this compound splits up into benzene and mercuric chloride; the concentrated aqueous acid acts in a similar way, as does strong hydriodic or moderately concentrated sulphuric acid, &c. The halogens decompose it, according as an excess is employed or not, either into monochloro-substitution-products of benzene and salts of mercury, or into those of mercury phenyl. On heating it with

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[1] *Ann. Chem. Pharm.* cliv. 93.

[2] *Ibid.* cxciv. 148.

sodium, benzene and sodium amalgam are obtained. It combines with sulphur trioxide forming mercuric benzenesulphonate $(C_6H_5SO_3)_2Hg$.

Phenyl mercury hydroxide, C_6H_5HgOH, is readily formed by the decomposition of the haloid salts by alkalis, but is best prepared by acting on the alcoholic solution of the chloride with moist oxide of silver.[1] It forms small rhombic crystals slightly soluble in cold but readily in hot water, benzene and alcohol. It acts as a powerful base; its aqueous solution has a strong alkaline reaction, precipitating alumina from its salts, decomposing ammonium salts and absorbing carbon dioxide from the air.

Phenyl mercury chloride, C_6H_5HgCl, is best obtained by heating equal molecules of mercury phenyl and mercuric chloride together with alcohol in a sealed tube at 100°—110°. It crystallizes in rhombic scales melting at 250° and subliming when gently heated; these are insoluble in water and slightly soluble in cold alcohol.

Phenyl mercury bromide, C_6H_5HgBr., is formed, together with bromobenzene, when equal molecules of mercury phenyl and bromine dissolved in carbon disulphide are brought together. It crystallizes from a hot mixture of alcohol and benzene in glistening rhombic scales melting at 275°—276°.[2]

Phenyl mercury iodide, C_6H_5HgI, is prepared in a similar way to the bromide, and also forms rhombic scales melting at 265°—266°. Sodium amalgam decomposes it into mercury, mercury phenyl, and sodium iodide.

Phenyl mercury nitrate, $C_6H_5HgNO_3$. This body is prepared by boiling the chloride with alcohol and silver nitrate. It is insoluble in water, but dissolves slightly in cold and readily in boiling alcohol and benzene, crystallizing in fine rhombic tablets possessing a silky or pearly lustre.

Phenyl mercury carbonate, $(C_6H_5Hg)_2CO_3$, is obtained by the action of silver carbonate on the chloride. It crystallizes in small white needles slightly soluble in boiling water, readily so in alcohol.

Phenyl mercury cyanide, C_6H_5HgCN. This is formed when mercury phenyl is heated with mercuric cyanide and alcohol to 120°. It crystallizes in long, glistening, rhombic prisms, fusing at 203°—204°. When heated to 120° with strong hydro-

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[1] Otto. *Journ. Prakt. Chem.* [2], i. 179.
[2] *Ibid.* i. 186.

chloric acid, it decomposes into benzene, formic acid, sal-ammoniac, and mercuric chloride, whilst when heated with alcoholic potash it yields mercury, benzene, and potassium cyanate:

$$C_6H_5HgCN + KOH = Hg + C_6H_6 + CNOK.$$

Phenyl mercury formate, $C_6H_5HgCHO_2$. When mercury phenyl is heated with concentrated formic acid this compound is produced together with benzene. It crystallizes on cooling in small plates having a vitreous lustre, and fusing at 171°.

Phenyl mercury acetate, $C_6H_5HgC_2H_3O_2$, is obtained in a similar way, and crystallizes from boiling water in small, oblique, rhombic prisms having a vitreous lustre, which are usually grouped in star-shaped masses and fuse at 148°—149°.[1] It is also easily prepared by boiling phenyl mercury iodide with silver acetate or by heating mercuric acetate with mercury phenyl and alcohol to 120° (Otto).

Phenyl mercury myristate, $C_6H_5HgC_{14}H_{27}O_2$, is formed when equal molecules of mercury phenyl and myristic acid are heated with alcohol to 120°. It is deposited in rhombic scales possessing an unctuous touch.

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[1] Otto, *Journ. Prakt. Chem.* [2], i. 180.

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THE END.

RICHARD CLAY AND SONS, LONDON AND BUNGAY.