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Organic chemistry

William Henry Perkin, Frederic Stanley Kipping

ORGANIC CHEMISTRY

NEW AND REVISED EDITION

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PART II.

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PREFACE.

The present volume (Part II.) consists principally of a description of the aromatic compounds, and, together with Part I., forms an introduction to Organic Chemistry.

The opening chapters of Part II. contain an account of coal-tar and its treatment. This leads naturally to a description of the preparation and properties of benzene, and to a discussion of its constitution in the light of facts previously dealt with; the student is thus made acquainted with the principal characteristics of aromatic, as distinct from fatty, compounds, and is then in a position to understand the classification of organic substances into these two main divisions.

The more important classes of aromatic compounds are then described, but in a somewhat different manner from that adopted in Part I., inasmuch as a general account of the properties of each class of substances is given before, instead of after, the more detailed description of typical compounds; this course is to a great extent free from the disadvantages which are found to attend its adoption at earlier stages, as the student has by this time acquired some experience of the more systematic method from a study of the summaries given in Part I.

Special attention has been given, as before, to questions of constitution, one of the objects being to train the student to think out such matters, and to try and deduce a constitutional formula for a given substance, by comparing its properties with those of others of known constitution; with this end in view, it has often been thought desirable to withhold the most important evidence in favour of the accepted constitutional formula until the subject had been discussed at some length.

The concluding chapters on dyes, alkaloids, and stereoisomerism will doubtless offer the greatest difficulties, but, considering the importance of the matters with which they deal, their omission or curtailment was deemed unadvisable. The account of the alkaloids should be useful, more particularly to medical students, whilst the chapter on dyes deals with a variety of substances of even greater practical value, and indicates the methods employed in one of the most important applications of organic chemistry. The chapter on stereo-isomerism was included because, owing to the importance to which this theory has now attained, a text-book on organic chemistry would be incomplete without a brief discussion of the subject. The full directions which are given for the use of models will, it is hoped, lead to a clear conception of the views set forth.

The practical aspect of the science has again been kept well to the front, a detailed description of the preparation of all the more typical compounds being given (usually in smaller type), in order to facilitate the laboratory work, which must be regarded as a necessary accompaniment to the theoretical knowledge.

Our thanks are again due to Dr A. Harden for many valuable suggestions, as well as for help in revising the proof-sheets and in preparing the index.

PREFACE TO REVISED EDITION.

THE favourable reception accorded to our Text-book on Organic Chemistry, and the constantly increasing support which it has received during recent years, have led us to undertake already a complete revision of Parts I. and II. in order to bring the whole of the subject-matter thoroughly up to date. Although, in doing so, we have not introduced any noteworthy change in the general plan of the work, we have found it necessary to make throughout many alterations of considerable importance in order to take account of the new facts and views which have come into prominence in the course of the rapid and continued progress of Organic Chemistry. Certain chapters, indeed, have been almost entirely rewritten and numerous additions have been made, but as it has also been possible to omit or condense portions of the old text dealing with matters of diminishing importance, the size of the book has not been very materially increased; we trust, therefore, that the revised edition will prove useful to the same classes of students as those for whom the original one was intended.

ARITHMETIC, Theoretical and Practical. By J. S. Mackay, M.A., LL.D., Author of 'Mackay's Euclid.' 4/6.

ALGEBRA FOR SCHOOLS. By William Thomson, M.A., B.Sc., Registrar, University of the Cape of Good Hope, formerly Assistant-Professor of Mathematics and Mathematical Examiner, University of Edinburgh. 576 pages. Cloth, 4/6.

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CONTENTS.

ORGANIC CHEMISTRY.

PART II.

CHAPTER XVIII.

MANUFACTURE, PURIFICATION, AND PROPERTIES OF BENZENE.

Distillation of Coal-tar.—When coal is strongly heated out of contact with air, it undergoes very complex changes, and yields a great variety of gaseous, liquid, and solid volatile products, together with a non-volatile residue of coke. This process of dry or destructive distillation is carried out on the large scale in the manufacture of **coal-gas,** for which purpose the coal is heated in clay or iron retorts, provided with air-tight doors; the gas and other volatile products escape from the retort through a pipe, and when distillation is at an end, the **coke,** a porous mass of impure carbon, containing the ash or mineral matter of the coal, is withdrawn.

The hot coal-gas passes first through a series of pipes or *condensers,* kept cool by immersion in water or simply by exposure to the air, and, as its temperature falls, it deposits a considerable quantity of **tar** and **gas-liquor,** which are run together into a large tank; the gas is then forced through, or sprayed with, water, in *washers* and *scrubbers,* and, after having been further freed from tar, ammonia, carbon dioxide, and hydrogen sulphide by suitable processes of purification, it is led into the gas-holder and used for illuminating and heating purposes. The average volume percentage composition of purified coal-gas is $H_2 = 47, CH_4 = 36, CO = 8, CO_2 = 1, N_2 = 4$, and hydrocarbons, other than marsh-gas (acetylene, ethylene, benzene, &c.) = 4, but its composition is very variable.

The coal-tar and the gas-liquor in the tank separate into two layers ; the upper one consists of gas-liquor or ammoniacal-liquor (a yellow, unpleasant-smelling, aqueous solution of ammonium carbonate, ammonium sulphide, and numerous other compounds), from which practically the whole of the ammonia and ammonium salts of commerce are obtained. The lower layer in the tank is a dark, thick, oily liquid of sp. gr. 1·1 to 1·2, known as coal-tar. It is a mixture of a great number of organic compounds, and, although not long ago it was considered to be an obnoxious by-product, it is now the sole source of very many substances of great industrial importance.

In order to partially separate the several constituents, the tar is submitted to fractional distillation ; it is heated in large wrought-iron stills or retorts, and the vapours which pass off are condensed in long iron or lead worms immersed in water, the liquid distillate being collected in *fractions.* The point at which the receiver is changed is ascertained by means of a thermometer which dips into the tar, as well as by the character of the distillate.

In this way the tar is roughly separated into the following fractions :

I.	Light oil or crude naphtha	Collected	up to 170°.	
II.	Middle oil or carbolic oil	"	between 170° and 230°.	
III.	Heavy oil or creosote oil	"	" 230° " 270°.	
IV.	Anthracene oil	"	above 270°.	
V.	Pitch	Residue in the still.		

I. The first crude fraction separates into two layers—namely, gas-liquor (which the tar always retains mechanically to some extent) and an oil which is lighter than water, its sp. gr. being about 0·975, hence the name, *light oil.* This oil is first redistilled from a smaller iron retort and the distillate collected in three principal portions, passing over between 82–110°, 110–140°, and 140–170° respectively. All these fractions consist principally of **hydrocarbons,** but contain basic substances, such as **pyridine,** acid substances, such as **phenol** or **carbolic acid,** and various other impurities; they are, therefore, separately agitated, first with concentrated sulphuric acid, which dissolves out the basic substances, and then with caustic soda, which removes the phenols (p. 398), being washed with water after each treatment; afterwards they are again distilled. The oil obtained in this way from the fraction collected between 82° and 110° consists principally of the hydrocarbons **benzene** and **toluene,** and is sold as '90 per cent. benzol;' that obtained from the fraction 110–140° consists essentially of the same two hydrocarbons (but in different proportions) together with **xylene,** and is sold as '50 per cent. benzol.'* These two products are not usually further treated by the tar-distiller, but are worked up in the manner described later. The oil from the fraction collected between 140–170° consists of xylene, pseudocumene, mesitylene, &c., and is principally employed as **'solvent naphtha,'** also as 'burning naphtha.'

II. The second crude fraction, or middle oil, collected between 170° and 230°, has a sp. gr. of about 1·002, and consists principally of **naphthalene** and **carbolic acid.** On cooling, the naphthalene separates in crystals, which are drained and pressed to squeeze out adhering carbolic acid and other substances; the crude crystalline product is further purified by treatment with caustic soda and sulphuric acid successively, and finally sublimed or distilled. The oil from which the crystals have been separated is agitated with warm caustic

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* Commercial '90 per cent. benzol' contains about 70 per cent., and '50 per cent. benzol' about 46 per cent., of pure benzene; the terms refer to the proportion of the mixture which passes over below 100° when the commercial product is distilled. Benzene, toluene, and xylene are known commercially as benzol, toluol, and xylol respectively.

soda to dissolve the carbolic acid; the alkaline solution is then drawn off from the insoluble portions of the oil and treated with sulphuric acid, whereupon crude carbolic acid separates as an oil, which is washed with water and again distilled; it is thus separated into crystalline (pure) carbolic acid and liquid (impure) carbolic acid.

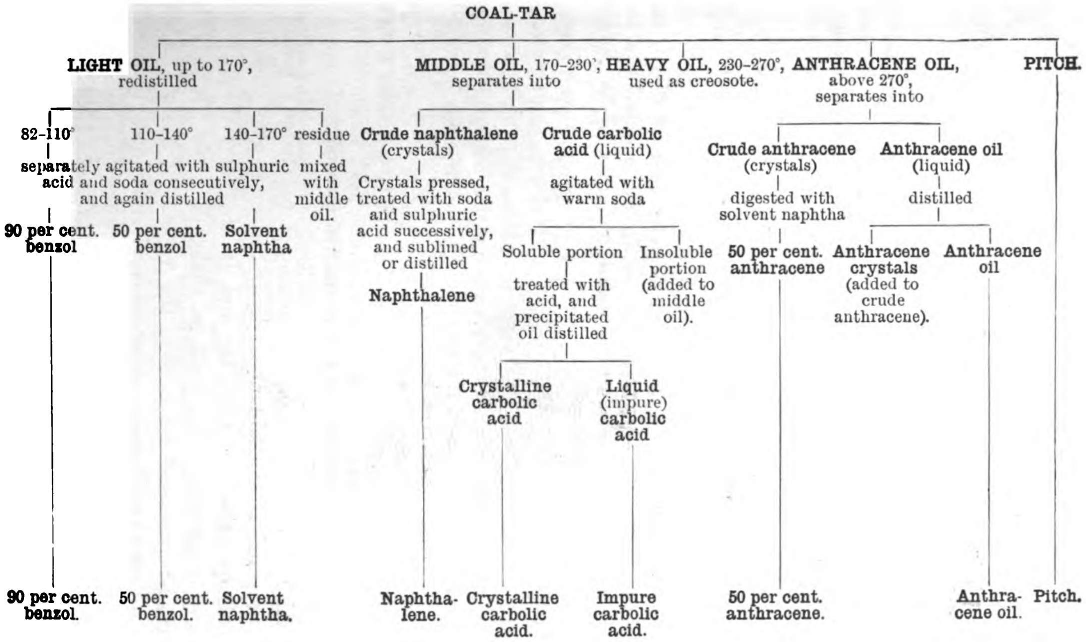
III. The third crude fraction, collected between 230° and 270°, is a greenish-yellow, fluorescent oil, specifically heavier than water; it contains **carbolic acid, cresol, naphthalene, anthracene,** and other substances, and is chiefly employed under the name of '**creosote oil**' for the preservation of timber.

IV. The fourth crude fraction, collected at 270° and upwards, consists of **anthracene, phenanthrene,** and other hydrocarbons which are solid at ordinary temperatures; the crystals which are deposited on cooling, after having been freed from oil by pressure, contain about 30 per cent. of anthracene, and are further purified by digestion with solvent naphtha, which dissolves the other hydrocarbons more readily than the anthracene; the product is then sold as '50 per cent. anthracene,' and is employed in the manufacture of alizarin dyes. The oil drained from the anthracene is redistilled, to obtain a further quantity of the crystalline product, the non-crystallisable portions being known as '**anthracene oil.**'

V. The **pitch** in the still is run out while still hot, and is employed in the preparation of varnishes, for protecting wood and metal work, and in making asphalt.

The table (p. 309), taken partly from Ost's *Lehrbuch der technischen Chemie*, shows in a condensed form the process of tar distillation and the more important commercial products obtained.

Benzene, C_6H_6.—The crude '90 per cent. benzol' of the tar-distiller consists essentially of a mixture of benzene and toluene, but contains small quantities of xylene and other substances; on further fractional distillation in specially


COAL-TAR
LIGHT OIL, up to 170°, redistilled
MIDDLE OIL, 170–230°, separates into
HEAVY OIL, 230–270°, used as creosote.
ANTHRACENE OIL, above 270°, separates into
PITCH.
82–110°
110–140°
140–170°
residue
separately agitated with sulphuric acid and soda consecutively, and again distilled
mixed with middle oil.
90 per cent. benzol
50 per cent. benzol
Solvent naphtha
Crude naphthalene (crystals)
Crystals pressed, treated with soda and sulphuric acid successively, and sublimed or distilled
Naphthalene
Crude carbolic acid (liquid)
agitated with warm soda
Soluble portion
treated with acid, and precipitated oil distilled
Insoluble portion (added to middle oil).
Crystalline carbolic acid
Liquid (impure) carbolic acid
Crude anthracene (crystals)
digested with solvent naphtha
50 per cent. anthracene
Anthracene oil (liquid)
distilled
Anthracene crystals (added to crude anthracene).
Anthracene oil
90 per cent. benzol.
50 per cent. benzol.
Solvent naphtha.
Naphthalene.
Crystalline carbolic acid.
Impure carbolic acid.
50 per cent. anthracene.
Anthracene oil.
Pitch.

constructed apparatus, it is separated more or less completely into its constituents. The benzene prepared in this way still contains small quantities of toluene, paraffins, carbon disulphide, and other impurities, and may be further treated in the following manner: It is first cooled in a freezing mixture and the crystals of benzene quickly separated by filtration from the mother-liquor, which contains most of the impurities; after repeating this process, the benzene is carefully distilled, and the portion boiling at 80–81° collected separately.

For ordinary purposes this purification is sufficient, but even now the benzene is not quite pure, and, when it is shaken with cold concentrated sulphuric acid, the latter darkens in colour owing to its having charred and dissolved the impurities; pure benzene, on the other hand, does not char with sulphuric acid, so that if the impure liquid be repeatedly shaken with small quantities of the acid, until the latter ceases to be discoloured, most of the foreign substances will be removed.

All coal-tar benzene which has not been purified in this way contains an interesting sulphur compound, C_4H_4S, named *thiophene*, which was discovered by V. Meyer; the presence of this substance is readily detected by shaking the sample with a little concentrated sulphuric acid and a trace of isatin (an oxidation product of indigo), when the acid assumes a beautiful blue colour (indophenin reaction); thiophene resembles benzene very closely in chemical and physical properties, and for this reason cannot be separated from it except by repeated treatment with sulphuric acid, which dissolves thiophene more readily than it does the hydrocarbon.

Although the whole of the benzene of commerce ('benzol') is prepared from coal-tar, the hydrocarbon is also present in small quantities in wood-tar and in the tarry distillate of many other substances, such as shale, peat, &c.; it may, in fact, be produced by passing the vapour of alcohol, ether, petroleum, or of many other organic substances through a red-hot tube, because under these conditions such compounds lose hydrogen (and oxygen), and are converted into benzene and its derivatives.

Benzene may be produced *synthetically* by simply heating acetylene at a dull-red heat, when 3 mols. (or 6 vols.) of the latter are converted into 1 mol. (or 2 vols.) of benzene,

$$3C_2H_2 = C_6H_6.$$

Acetylene (Part I. p. 81) is collected over mercury in a piece of hard glass-tubing, closed at one end and bent at an angle of about 120°; when the tube is about half-full of gas, the lower end is closed with a cork, and a piece of copper gauze wrapped round a portion of the horizontal limb, as shown (fig. 23). This portion of the tube is then carefully heated with a Bunsen burner, the other end remaining immersed in the mercury; after a short time vapours appear in the tube, and minute drops of benzene condense on the sides, and if, after heating for about fifteen minutes, the tube be allowed to cool and the cork then removed, the mercury will rise, showing that a diminution in volume has taken place.

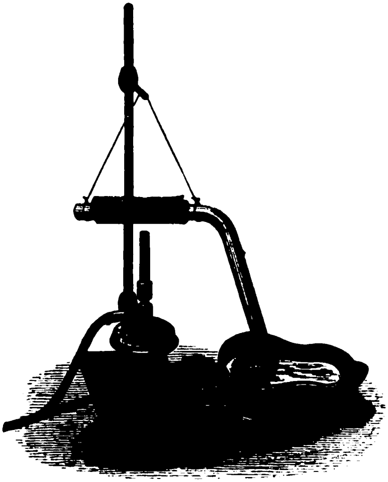


Fig. 23.

This conversion of acetylene into benzene is a process of polymerisation, and was first accomplished by Berthelot. It is, at the same time, an exceedingly important synthesis of benzene from its elements, because acetylene may be obtained by the direct combination of carbon and hydrogen (Part I. p. 81).

Pure benzene may be conveniently prepared in small quantities by heating pure benzoic acid or calcium benzoate with soda-lime, a reaction which recalls the formation of marsh-gas from calcium acetate,

$$(C_6H_5{\cdot}COO)_2Ca + 2NaOH = 2C_6H_6 + CaCO_3 + Na_2CO_3,$$
$$\text{or } C_6H_5{\cdot}COOH = C_6H_6 + CO_2.$$

The analysis of pure benzene shows that it consists of 92·31 per cent. of carbon and 6·69 per cent. of hydrogen, a result which gives the empirical formula CH; the vapour density of benzene, however, is 39, so that its molecular weight is 78, which corresponds with the *molecular formula* C_6H_6.

At ordinary temperatures benzene is a colourless, highly refractive, mobile liquid of sp. gr. 0·8799 at 20°, but when cooled in a freezing mixture it solidifies to a crystalline mass, melting again at 5·4°, and boiling at 80·5°. It has a burning taste, a peculiar, not unpleasant smell, and is highly inflammable, burning with a luminous, very smoky flame, which is indicative of its richness in carbon; the luminosity of an ordinary coal-gas flame is, in fact, largely due to the presence of benzene. Although practically insoluble in water, benzene mixes with liquids such as ether and petroleum in all proportions; like the latter, it readily dissolves fats, resins, iodine, and other substances which are insoluble in water, and is for this reason extensively used as a solvent and for cleaning purposes; its principal use, however, is for the manufacture of nitrobenzene (p. 365) and other benzene derivatives.

Benzene is a very stable substance, and is resolved into simpler substances only with great difficulty; when boiled with concentrated alkalies, for example, it undergoes no change, and even when heated with solutions of such powerful oxidising agents as chromic acid or potassium permanganate, it is only very slowly attacked and decomposed, carbon dioxide, water, and traces of other substances being formed. Under certain conditions, however, benzene readily yields *substitution* products; concentrated nitric acid, even at ordinary temperatures, converts the hydrocarbon into *nitrobenzene* by the substitution of the monovalent nitro-group $-NO_2$ for an atom of hydrogen,

$$C_6H_6 + HNO_3 = C_6H_5 \cdot NO_2 + H_2O,$$

and concentrated sulphuric acid, slowly at ordinary temperatures, but more rapidly on heating, transforms it into *benzene-sulphonic acid*,

$$C_6H_6 + H_2SO_4 = C_6H_5{\cdot}SO_3H + H_2O.$$

The action of chlorine and bromine on benzene is very remarkable: at moderately high temperatures, or in presence of direct sunlight, the hydrocarbon is rapidly converted into *additive* products, such as benzene hexachloride, $C_6H_6Cl_6$, and benzene hexabromide, $C_6H_6Br_6$, by direct combination with six (but never more than six) atoms of the halogen; in absence of sunlight and at ordinary temperatures, however, the hydrocarbon is only slowly attacked, yielding *substitution* products, such as chlorobenzene, C_6H_5Cl, bromobenzene, C_6H_5Br, dichlorobenzene, $C_6H_4Cl_2$, &c.; when, again, some halogen carrier (p. 352), such as iron or iodine, is present, action takes place readily at ordinary temperatures even in the dark, and substitution products are formed.

CHAPTER XIX.

CONSTITUTION OF BENZENE, AND ISOMERISM OF BENZENE DERIVATIVES.

It will be seen from the facts just stated that although benzene, like the paraffins, is an extremely stable substance, it differs from them very considerably in chemical behaviour, more especially in being comparatively readily acted on by nitric acid, sulphuric acid, and halogens, and in forming additive products with the last-named under certain conditions; if, again, its properties be compared with those of the unsaturated hydrocarbons of the ethylene or acetylene series, the contrast is even more striking, particularly when it is borne in mind that the proportion of carbon to hydrogen in the molecular formula of benzene,

C_6H_6, would seem to indicate a relation to these unsaturated hydrocarbons.

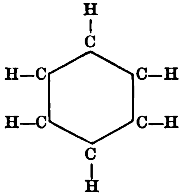
In order, then, to obtain some clue to the constitution of benzene, it is clearly of importance to carefully consider the properties of other unsaturated hydrocarbons of known constitution, and to ascertain in what respects they differ from benzene; for this purpose the compound *dipropargyl*, $CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$ (Part I. p. 87), may be chosen, as it has the same molecular formula as benzene.

Now, although dipropargyl and benzene are isomeric, they are absolutely different in chemical behaviour; the former is very unstable, readily undergoes polymerisation, combines energetically with bromine, giving *additive* compounds, and is immediately oxidised even by weak agents; it shows, in fact, all the properties of an unsaturated hydrocarbon of the acetylene series. Benzene, on the other hand, is extremely stable, is comparatively slowly acted on by bromine, giving (usually) *substitution* products, and is oxidised only very slowly even by the most powerful agents. Since, therefore, dipropargyl must be represented by the above formula in order to account for its method of formation and chemical properties, the constitution of benzene could not possibly be expressed by any similar formula, such as

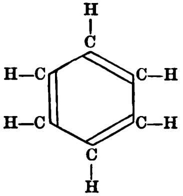
$$CH_3{\cdot}C{:}C{\cdot}C{:}C{\cdot}CH_3 \qquad \text{or} \qquad CH_2{:}C{:}CH{\cdot}CH{:}C{:}CH_2,$$

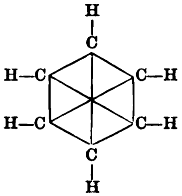
because compounds similar in constitution are always more or less similar in properties, and any such formula would not afford the slightest indication of the enormous differences between benzene and ordinary unsaturated hydrocarbons of the ethylene or acetylene series.

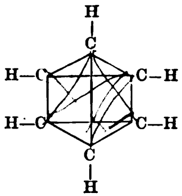
These, and many other facts which were established during the investigation of benzene and its derivatives, led Kekulé in 1865 to the conclusion that *the six carbon atoms in benzene form a closed-chain or nucleus*, that *the molecule of benzene is symmetrical*, and that *each carbon atom is directly united with* *one* (and only one) *atom of hydrogen*, as may be represented by the formula,



These views are now universally accepted, as the evidence which can be brought forward in support of them is most conclusive; there is, however, at least one important point which has still to be settled before it can be said that the constitution of benzene is established as far as present theories permit. The point referred to is, the manner in which the carbon atoms are united with one another. The whole theory of the constitution of organic compounds is based on the assumption that carbon is always tetravalent, and this assumption, as already explained (Part I. p. 51), is expressed in graphic formulæ by drawing four lines from each carbon atom, in such a way as to show what other atoms or groups the particular carbon atom in question is directly united with. Now, if this be done in the case of benzene, it is clear that two of the four lines or bonds, which represent the valencies of each carbon atom, must be drawn to meet two other carbon atoms, because unless each carbon atom is directly united with two others, the six could not together form a closed-chain; a third line or bond is easily accounted for, because each carbon atom is directly united with hydrogen. In this way, however, only three of the four affinities of each carbon atom are disposed of, and the next question, then, to be considered is, how may the fourth affinity or combining power of each carbon atom be represented so as to give the clearest indication of the behaviour of benzene? Many chemists have attempted to answer this question, and several constitutional formulæ for benzene have been put forward; that suggested by Kekulé in 1865, and given below, was for a long time considered to be the most satisfactory, but others, such as those of Claus and Ladenburg, have also received support.

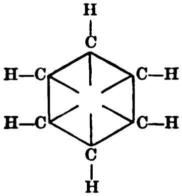

Kekulé.

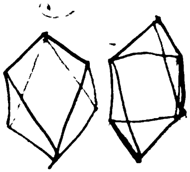

Claus.
(Diagonal formula.)


Ladenburg.
(Prism formula.)

It will be seen that these three formulæ all represent the molecule of benzene as a symmetrical closed-chain of six carbon atoms, and that they differ, in fact, only as regards the way in which the carbon atoms are represented as being united with one another; a little consideration will make it clear, moreover, that the only difference between them lies in the manner of indicating the state or condition of the fourth affinity of each carbon atom. In Kekulé's formula, for example, two lines (or a double bond) are drawn between alternate carbon atoms, a method of representation which is analogous to that adopted in the case of ethylene and other olefines; in the formulæ of Claus and Ladenburg, on the other hand, each carbon atom is represented as directly united with three others (but with a different three in the two cases).

As it would be impossible to enter here into a discussion of the relative merits of the above three formulæ, it may at once be stated that they are all to some extent unsatisfactory, as they do not account for certain facts which have been established by Baeyer and others during an extended study of benzene derivatives. In order to meet these objections, it was suggested by Armstrong, and shortly afterwards by Baeyer, that the constitution of benzene should be represented by the formula,





Armstrong, Baeyer (Centric formula).

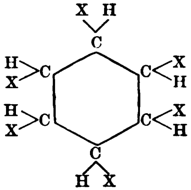
which, although in the main similar to those given above, especially to that of Claus, differs from them all in this: The fourth affinity of each of the six carbon atoms is represented as merely *directed* towards a centre (as shown by the short lines) in order to indicate that, by the mutual action of the six affinities, the power of each is rendered latent, without bringing about *actual union* with another carbon atom. This formula, named by Baeyer the *centric formula*, summarises all facts relating to benzene and its derivatives, at least as well as, and in some respects better than, any which has yet been advanced; unlike Kekulé's formula, it does not represent benzene as containing 'double bindings' similar to those in the olefines, and thus it affords some indication of the great difference between benzene and the olefines in chemical behaviour; the very indefiniteness of the centric formula may, in fact, be regarded as a point in its favour until more is known of the nature of chemical affinity, and it is, therefore, generally adopted at the present time.

It now becomes necessary to give at greater length a few of the more important arguments which, in addition to those already considered, have led to the conclusion that the molecule of benzene consists of a symmetrical closed-chain of six carbon atoms, each of which is united with one atom of hydrogen; also to point out how simply and accurately this view of its constitution accounts for a number of facts, relating to benzene and its derivatives, which would otherwise be incapable of explanation.

In the first place, then, it may be repeated that benzene is a very stable substance; although it is readily acted on by powerful chemical agents, such as nitric acid, sulphuric acid, and bromine, and thereby converted into new compounds, all these products or derivatives of benzene contain *six* carbon atoms; the hydrogen atoms may be displaced by certain atoms or groups, which, in their turn, may be displaced by others, but in spite of all these changes, the six atoms of carbon remain, forming, as it were, a stable and permanent *nucleus.* This is expressed in the formula by the closed-chain of six carbon atoms, all of which are represented in the same state of combination, which implies that there is no reason why one should be attacked and taken away more readily than another.

Again, a great many compounds, which are known to be derivatives of benzene, contain more than six atoms of carbon; when, however, such compounds are treated in a suitable manner, they are easily converted into substances containing six, but not less than six, atoms of carbon. This fact shows that in these benzene derivatives there are six atoms of carbon which are in some way different from the others, and this is also accounted for by assuming the existence of the stable nucleus; the additional carbon atoms, not forming part of, but being simply united with, this nucleus, are more easily attacked and removed.

Further, it must be remembered that although benzene usually gives substitution products, it is capable, under certain conditions, of forming additive products of the type $C_6H_6X_6$; this behaviour is also accounted for, since, in the formula, only three of the four affinities of each carbon atom are represented as actively engaged, and each carbon atom is therefore capable of combining directly with one monovalent atom or group, so as to form finally a fully saturated compound of the type,



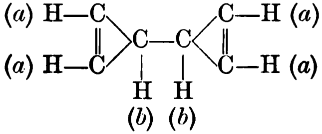
Isomerism of Benzene Derivatives.

The most convincing evidence that the molecule of benzene is symmetrical is derived from a study of the isomerism of benzene derivatives. It has been proved, in the first place, that it is possible to substitute 1, 2, 3, 4, 5, or 6 monovalent atoms or groups for a corresponding number of the hydrogen atoms in benzene, compounds such as bromobenzene, C_6H_5Br, dinitrobenzene, $C_6H_4(NO_2)_2$, trimethylbenzene, $C_6H_3(CH_3)_3$, tetrachlorobenzene, $C_6H_2Cl_4$, pentamethylbenzene, $C_6H(CH_3)_5$, and hexacarboxybenzene, $C_6(COOH)_6$, being produced; the substituting atoms or groups may, moreover, be identical or dissimilar.

An examination of such substitution products of benzene has shown that when only *one* atom of hydrogen is displaced by any given atom or group, the same compound is always produced—that is to say, *the mono-substitution products of benzene exist only in one form;* when, for example, one atom of hydrogen is displaced by a nitro-group, no matter in what way this change may be brought about, the same substance, nitrobenzene, $C_6H_5{\cdot}NO_2$, is always produced.

This might be explained, of course, by assuming that one particular hydrogen atom was always displaced first; when, for example, acetic acid is treated with soda, only one of the four hydrogen atoms is displaceable, and consequently the same salt is invariably produced. In the case of benzene, however, it has been shown that the same substance is formed no matter which of the six hydrogen atoms is displaced.

The only possible conclusion to be drawn from this fact is, that *all* the hydrogen atoms are in exactly similar positions relatively to the rest of the molecule; if this were not so, and the constitution of benzene were represented by a formula, such as the following,

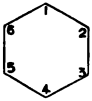


in which the hydrogen atoms are not all identically situated, it would be possible, by displacing one of them, to obtain (at least) two isomeric products; one by displacing one of the (*a*), another by displacing one of the (*b*), hydrogen atoms.

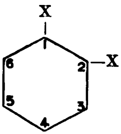
As an example of the way in which it has been proved that the six hydrogen atoms in benzene are all similarly situated, the following may serve (Ladenburg): Phenol, $C_6H_5{\cdot}OH$, or hydroxybenzene, obtained indirectly by displacing one atom of hydrogen (A) by the hydroxyl-group, may, with the aid of phosphorus pentabromide, be directly converted into bromobenzene, C_6H_5Br, and the latter may be transformed into benzoic acid (or carboxybenzene), $C_6H_5{\cdot}COOH$ (A), by submitting it to the action of sodium and carbon dioxide; as these three substances are produced from one another by simple interactions, there is every reason to suppose that the carboxyl-group in benzoic acid is united with the same carbon atom as the bromine atom in bromobenzene and the hydroxyl-group in phenol; that is to say, that the same hydrogen atom (A) has been displaced in all three cases. Now three different hydroxybenzoic acids of the composition $C_6H_4(OH){\cdot}COOH$ are known, and these three compounds may be either converted into or obtained from benzoic acid, $C_6H_5{\cdot}COOH$ (A), the difference between them being due to the fact that the hydroxyl-group has displaced a different hydrogen atom (B.C.D.) in each case; each of these hydroxybenzoic acids forms a calcium salt which yields phenol on distillation (the carboxyl-group being displaced by hydrogen), and the three specimens of phenol thus produced are identical with the original phenol; it is evident, therefore, that at least four (A.B.C.D.) hydrogen atoms in benzene are in the same state of combination, and occupy the same relative position in the molecule; in a somewhat similar manner it can be shown that this is true of all six.

By substituting *two* monovalent atoms or groups for two of the atoms of hydrogen in benzene, *three*, but not more than three, substances having different properties are obtained; there are, for example, three dinitrobenzenes, $C_6H_4(NO_2)_2$, three dibromobenzenes, $C_6H_4Br_2$, three dihydroxybenzenes, $C_6H_4(OH)_2$, three nitrohydroxybenzenes, $C_6H_4(NO_2)\cdot OH$; and so on.

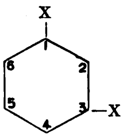
Now the existence of these three isomerides can be accounted for in a very simple manner with the aid of the formula already given, which, for this purpose, may conveniently be represented by a simple hexagon, numbered as shown, the symbols C and H being omitted for the sake of simplicity.



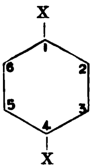
Suppose that any mono-substitution product, C_6H_5X, which, as already stated, exists only in one form, be converted into a di-substitution product, $C_6H_4X_2$; then if it be assumed that the atom or group (X) first introduced occupied any given position, say that numbered 1, the second atom or group may have substituted any one of the hydrogen atoms at 2, 3, 4, 5, or 6, giving a substance the constitution of which might be represented by one of the following five formulæ:



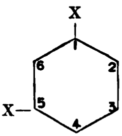
I.



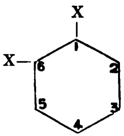
II.



III.



IV.



V.

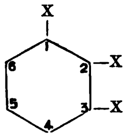
These five formulæ, however, represent *three* isomeric substances, and three only. The formula IV. represents a compound in which the several atoms occupy the same relative positions as in the substance represented by the formula II., and for the same reason the formula V. is identical with I. Although there is at first sight an apparent difference, a little consideration will show that this is simply due to the fact that the formulæ are viewed from one point only; if the formulæ IV. and V. be written on thin paper and then viewed *through* the paper, it will be seen at once that they are identical with II. and I. respectively. Each of the formulæ I., II., and III., on the other hand, represents a different substance, because in no two cases are all the atoms in the same relative positions; in other words, the di-substitution products of benzene exist theoretically in three isomeric forms.

In the foregoing examples the two substituting atoms or groups have been considered to be identical, but even when they are different, experience has shown that only three di-substitution products can be obtained, and this fact, again, is in accordance with the theory. If in the above five formulæ a Y be written in the place of one X to express a difference in the substituting groups, it will be seen that, as before, the formula I. is identical with V., and II. with IV., but that I., II., and III. all represent different arrangements of the atoms—that is to say, three different substances.

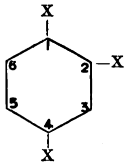
Since *the di-substitution products of benzene exist in three isomeric forms*, it is convenient to have some way of distinguishing them by name; for this reason all di-substitution products which are found to have the constitution represented by formula I. are called **ortho**-compounds, and the substituting atoms or groups are said to be in the ortho- or 1:2-position to one another; those substances which may be represented by the formula II. are termed **meta**-compounds, and the substituting atoms or groups are spoken of as occupying the meta- or 1:3-position; the term **para** is applied to compounds represented by the formula III., in which the atoms or groups are situated in the para- or 1:4-position.

Ortho-compounds, then, are those in which it is assumed, for reasons given below, that the two substituting atoms or groups are combined with carbon atoms which are themselves *directly united;* instead of expressing the constitution of any ortho-compound by the formula I., and representing the substituting atoms or groups as combined with the carbon atoms 1 and 2, it would therefore be just the same if they were represented as united with the carbon atoms 2 and 3, 3 and 4, 4 and 5, 5 and 6, or 6 and 1; the arrangement of all the atoms would be the same, because the benzene molecule is symmetrical, and the numbering of the carbon atoms simply a matter of convenience. In a similar manner the substituting atoms or groups in meta-compounds may be represented as combined with any two carbon atoms which are themselves not directly united, but linked together by one carbon atom; it is quite immaterial which two carbon atoms are chosen, since atoms or groups occupying the 1:3, 2:4, 3:5, 4:6, or 5:1-position are identically situated with regard to all the other atoms of the molecule. For the same reason para-compounds may be represented by placing the substituting atoms or groups in the 1:4, 2:5, or 3:6-position.

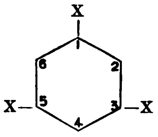
When more than two atoms of hydrogen in benzene are substituted, it has been found that the number of isomerides differs according as the substituting atoms or groups are identical or not. By displacing *three* atoms of hydrogen by three identical atoms or groups, three isomerides can be obtained, three trimethylbenzenes, $C_6H_3(CH_3)_3$, for example, being known. Again, the existence of these isomerides can be easily accounted for, since their constitutions may be represented as follows,



1:2:3- or Adjacent.



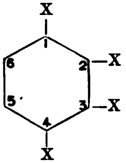
1:2:4- or Asymmetrical.



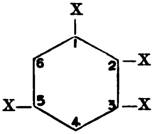
1:3:5- or Symmetrical.

No matter in what other positions the substituting atoms or groups be placed, it will be found that the arrangement is the same as that represented by one of the formulæ (p. 323); the position 1:2:3, for example, is identical with 2:3:4, 3:4:5, &c.; 1:3:4 with 2:4:5, 3:5:6, &c.; and 1:3:5 with 2:4:6. For the purpose of referring to such tri-substitution products, the terms already given are often employed.

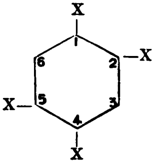
The tetra-substitution products of benzene, in which all the substituting atoms or groups are identical, also exist in three isomeric forms represented by the following formulæ,



1:2:3:4.



1:2:3:5.



1:2:4:5.

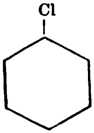
When, however, five or six atoms of hydrogen are displaced by identical atoms or groups, only one substance is produced.

When more than two atoms of hydrogen are displaced by atoms or groups which are not all identical, the number of isomerides which can be obtained is very considerable; in the case of any tri-substitution product, $C_6H_3X_2Y$, for example, six isomerides might be formed, as may be easily seen by assigning a definite position, say 1, to Y; the isomerides would then be represented by formulæ in which the groups occupied the position 1:2:3, 1:2:4, 1:2:5, 1:2:6, 1:3:4, or 1:3:5, all of which would be different. In a similar manner the number of isomerides theoretically obtainable in the case of all benzene derivatives, however complex, may be deduced with the aid of the hexagon formula.

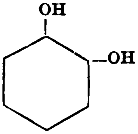
All the cases of isomerism considered up to the present have been those due to the substituting atoms or groups occupying different relative positions in the benzene nucleus; as, however, many benzene derivatives contain groups of atoms which themselves exist in isomeric forms, such compounds also exhibit isomerism exactly similar to that already met with in the case of the paraffins, alcohols, &c. There are, for example, two isomeric hydrocarbons of the composition

$C_6H_5{\cdot}C_3H_7$, namely, *propylbenzene*, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, and *isopropylbenzene*, $C_6H_5{\cdot}CH(CH_3)_2$, just as there are two isomeric ethereal salts of the composition C_3H_7I. As, moreover, propyl- and isopropyl-benzene, $C_6H_5{\cdot}C_3H_7$, are isomeric with the three (ortho-, meta-, and para-) ethylmethylbenzenes, $C_6H_4(C_2H_5){\cdot}CH_3$, and also with the three (adjacent, symmetrical, and asymmetrical) trimethylbenzenes, $C_6H_3(CH_3)_3$, there are in all eight hydrocarbons of the molecular formula, C_9H_{12}, derived from benzene.

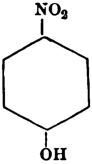
In studying the isomerism of benzene derivatives, the clearest impressions will be gained by invariably making use of a simple, unnumbered hexagon to represent C_6H_6, and by expressing the constitutions of simple substitution products by formulæ such as,



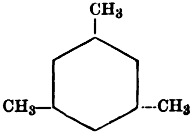
Chlorobenzene.



Pyrocatechol.



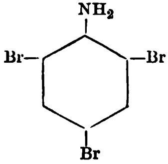
Nitrophenol.



Trimethylbenzene.

The omission of the symbols C and H is attended by no disadvantage whatsoever, because, in order to convert the above into the ordinary molecular formulæ, it is only necessary to write C_6 instead of the hexagon, and then to count the unoccupied corners of the hexagon to find the number of hydrogen atoms in the nucleus, the substituting atoms or groups being added afterwards. In the case of chlorobenzene, for example, there are five unoccupied corners, so that the molecular formula is C_6H_5Cl; whereas in the case of trimethylbenzene there are three, and the formula, therefore, is $C_6H_3(CH_3)_3$.

As, however, such graphic formulæ occupy a great deal of space, their constant use in a text-book is inconvenient, and other methods are adopted. The most usual course in the case of the di-derivatives is to employ the terms ortho-, meta-, and para-, or simply the letters *o*, *m*, and *p*, as, for example, ortho-dinitrobenzene or *o*-dinitrobenzene, meta-nitraniline or *m*-nitraniline, para-nitrophenol or *p*-nitrophenol; the relative positions of the atoms or groups may also be expressed by numbers; *o*-chloronitrobenzene, for example, may be described as 1:2-chloronitrobenzene, as $C_6H_4{<}\begin{matrix}Cl\ {\scriptstyle(1)}\\ NO_{2(2)}\end{matrix}$, or as $C_6H_4\overset{1}{Cl}\cdot N\overset{2}{O}_2$, the corresponding para-compound as 1:4-chloronitrobenzene, as $C_6H_4{<}\begin{matrix}Cl\ {\scriptstyle(1)}\\ NO_{2(4)}\end{matrix}$, or as $C_6H_4\overset{1}{Cl}\cdot N\overset{4}{O}_2$. In the case of the tri-derivatives the terms symmetrical, asymmetrical, and adjacent (compare p. 323) may be employed when all the atoms or groups are the same, but when they are different the constitution of the compound is usually expressed with the aid of numbers; the tribromaniline of the constitution,



for example, is described as $C_6H_2Br_3\cdot NH_2[\overset{1}{NH_2}:\overset{2}{Br}:\overset{4}{Br}:\overset{6}{Br}]$, or as $C_6H_2Br_3\cdot NH_2[NH_2:3Br = 1:2:4:6]$, but it is of course quite immaterial from which corner of the imaginary hexagon the numbering is commenced.

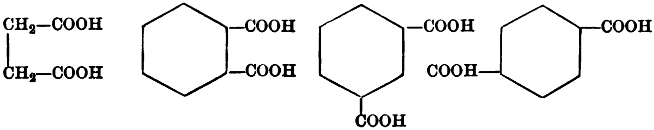
Determination of the Constitution of Benzene Derivatives.

It has been pointed out that the di-substitution products of benzene, such as dibromobenzene, $C_6H_4Br_2$; dihydroxybenzene, $C_6H_4(OH)_2$; and nitraniline, $C_6H_4(NO_2)\cdot NH_2$, exist in three isomeric forms, and that their isomerism is due to the different relative positions of the substituting atoms or groups in the benzene nucleus; it is evident, however, that in order to arrive at the constitution of any one of these substances, and to be able to say whether it is an ortho-, meta-, or para-compound, a great deal of additional information is required.

Now the methods which are adopted in deciding questions of this kind at the present time are comparatively simple, but they are based on the results of work which has extended over many years. One of the most important results of such work has been to prove that a given di-substitution product of benzene may be converted by more or less direct methods into many of the other di-substitution products of the *same series; ortho*-dinitrobenzene, $C_6H_4(NO_2)_2$, for example, may be transformed into *o*-diamidobenzene, $C_6H_4(NH_2)_2$; *o*-dihydroxybenzene, $C_6H_4(OH)_2$; *o*-dibromobenzene, $C_6H_4Br_2$; *o*-dimethylbenzene, $C_6H_4(CH_3)_2$, and so on, corresponding changes being also possible in the case of meta- and para-compounds. If, therefore, it can be ascertained to which series a given di-substitution product belongs, the constitution of other di-substitution products which may be derived from, or converted into it, is thereby determined. There are, for example, three dinitrobenzenes melting at 90°, 116°, and 173° respectively; now if it could be proved that the compound melting at 90° is a meta-derivative, then it would necessarily follow that the diamido-, dihydroxy-, dibromo-, and other di-derivatives of benzene obtained from this particular dinitro-compound by substituting other atoms or groups for the two nitro-groups, must also be meta-compounds; it would also be known that the di-derivatives of benzene obtained from the other two dinitrobenzenes, melting at 116° and 173° respectively, in a similar manner must be either ortho- or para-compounds respectively.

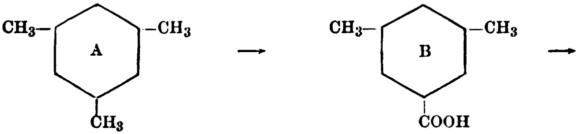
Obviously, then, it is necessary, in the first place, to determine the constitution of those di-derivatives which are afterwards to be used as standards.

As an illustration of the methods and arguments originally employed in the solution of problems of this nature, the case of the dicarboxy- and dimethyl-derivatives of benzene may be quoted. Of the three dicarboxybenzenes, $C_6H_4(COOH)_2$, one—namely, phthalic acid (p. 438)—is very readily converted into its anhydride, but all attempts to prepare the anhydrides of the other two acids (isophthalic acid and terephthalic acid, pp. 439, 440) result in failure; it is assumed, therefore, that the acid which gives the anhydride is the *o*-compound, because, from a study of the behaviour of many other dicarboxylic acids, it has been found that anhydride formation takes place most readily when the two carboxyl-groups are severally combined with two carbon atoms which are themselves directly united, as, for example, in the case of succinic acid. In other words, if the graphic formulæ of succinic acid and of the three dicarboxy-derivatives of benzene be compared, it will be evident that in the *o*-compound the relative position or state of combination of the two carboxyl-groups is practically the same as in succinic acid, but quite otherwise in the case of the *m*- and *p*-compounds.

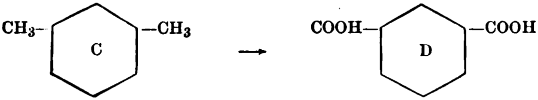


For this, and other reasons not stated here, phthalic acid may be provisionally regarded as an *ortho*-dicarboxybenzene.

Again, the hydrocarbon mesitylene or trimethylbenzene, $C_6H_3(CH_3)_3$, may be produced synthetically from acetone (p. 348), and its formation in this way can be explained in a simple manner only by assuming that mesitylene is a symmetrical trimethylbenzene of the constitution (A),



Mesitylene. Mesitylenic Acid.



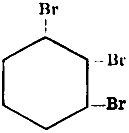
Dimethylbenzene. (*m*-Xylene.) Isophthalic Acid

When this hydrocarbon is carefully oxidised, it yields an acid (B) of the composition $C_6H_3(CH_3)_2 \cdot COOH$ (by the conversion of one of the methyl-groups into carboxyl), from which a dimethylbenzene, $C_6H_4(CH_3)_2$ (C), is easily obtained by the substitution of hydrogen for the carboxyl-group. This dimethylbenzene, therefore, is a *meta*-compound, because no matter which of the original three methyl-groups in mesitylene has been finally displaced by hydrogen, the remaining two must occupy the *m*-position. Now when this dimethylbenzene is oxidised with chromic acid, it is converted into a dicarboxylicacid (D)—namely, isophthalic acid, $C_6H_4(COOH)_2$, which, therefore, must also be regarded as a meta-compound; the constitution of two of the three isomeric dicarboxy-derivatives of benzene having been thus determined, the third—namely, terephthalic acid, can only be the *para*-compound.

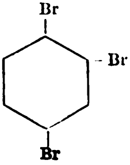
It is now a comparatively simple matter to ascertain to which series any of the three dimethylbenzenes belongs; one of them having been found to be the meta-compound, all that is necessary is to submit each of the other two to oxidation, and that which gives phthalic acid will be the ortho-compound, whilst that which yields terephthalic acid will be the para-derivative. Moreover, the constitution of any other di-substitution product of benzene may now be determined without difficulty, provided that it is possible to convert it into one of these standards by simple reactions.

As the methods which have just been indicated are based entirely on arguments drawn from analogy, or from deductions as to the probable course of certain reactions, the conclusions to which they lead cannot be accepted without reserve; there are, however, several other ways in which it is possible to distinguish with much greater certainty between ortho-, meta-, and para-compounds, and of these that employed by Körner may be given as an example.

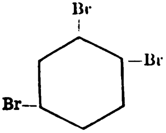
Körner's method is based on the fact that, if any di-substitution product of benzene be converted into a tri-derivative by further displacement of hydrogen of the nucleus, the number of isomerides which may be obtained from an ortho-, meta-, or para-compound is different in the three cases, so that by ascertaining the number of these products the constitution of the original di-derivative may be established. In the investigation of the dibromobenzenes, $C_6H_4Br_2$, for example, three isomerides melting at −1°, +1°, and 89° respectively were discovered, and the question arose, which of these is the ortho-, which the meta-, and which the para-compound? Suppose now that each of these isomerides is separately converted into a tribromobenzene of the composition $C_6H_3Br_2\cdot\mathbf{Br}$; then, if it be the *ortho*-dibromo-compound, it is possible to obtain from it *two*, but only two, tribromobenzenes, because, although there are four hydrogen atoms, any one of which may be displaced, the compound of the constitution III. is identical with II., and IV. with I., the relative positions of all the atoms being the same in the two cases respectively.



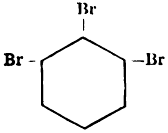
I.



II.

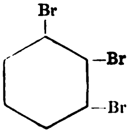


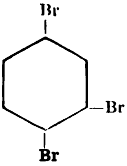
III.

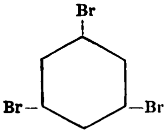


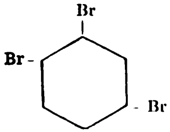
IV.

If, on the other hand, the dibromobenzene be the *meta*-compound, it might yield *three*, but only three, isomeric tri-derivatives, which would be represented by the first three of the following formulæ, the fourth being identical with the second,

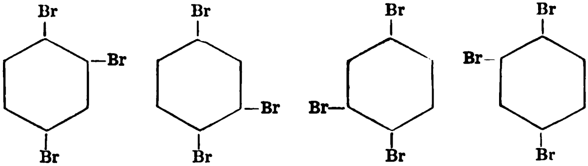








Finally, if the substance in question be *para*-dibromobenzene, it could give only *one* tri-derivative, the following four formulæ being identical,



Experiments showed that the compound melting at −1° gave *two* tribromobenzenes; it is therefore the *ortho*-compound. The dibromobenzene melting at +1° gave *three* such derivatives, and is thus proved to be the *meta*-compound; the isomeride melting at 89° gave only *one*, and is therefore the *para*-compound. It is obvious, then, that this method may be applied in ascertaining to which series *any* di-substitution product belongs; it may also be employed in determining the constitution of the tri-derivatives in a similar manner.

At the present time the constitution of any new benzene derivative is, as a rule, very easily ascertained, because it is simply converted into one of the many compounds of known constitution.

CHAPTER XX.

GENERAL PROPERTIES OF AROMATIC COMPOUNDS.

Classification of Organic Compounds. — The examples given in the foregoing pages will have afforded some indication of the large number of compounds which it is possible to prepare from benzene, by the substitution of various elements or groups for atoms of hydrogen; as the substances formed in this way, and many other benzene derivatives which occur in nature, or may be prepared synthetically, still retain much of the characteristic chemical behaviour of benzene, and differ in many respects from the paraffins, alcohols, acids, and all other compounds previously considered (Part I.), it is convenient to class benzene and its derivatives as a separate group.

Organic compounds are therefore classed in two principal divisions, the **fatty** or **aliphatic** (from ἄλειφαρ, fat) and the **aromatic.** The word 'fatty,' originally applied to some of the acids of the $C_nH_{2n}O_2$ series (Part I. p. 145), is now used to denote all compounds which may be considered as derivatives of marsh-gas, and which cannot be regarded as directly derived from benzene; all the compounds described in Part I. belong to the fatty group or division. Benzene and its derivatives, on the other hand, are classed in the 'aromatic' group, this term having been first applied to certain naturally occurring compounds (which have since been proved to be benzene derivatives) on account of their peculiar aromatic odour.

The fundamental distinction between fatty and aromatic compounds is one of constitution. All derivatives of benzene, and all other compounds which contain a closed-chain or nucleus *similar to* that of benzene, are classed as aromatic. Fatty compounds, on the other hand, such as $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, $CH_2(OH){\cdot}CH(OH){\cdot}CH_2(OH)$, and $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, do not, as a rule, contain a closed-, but an open-chain* of carbon atoms; such compounds, moreover, may be regarded as derived from marsh-gas by a series of simple steps.

It must not be supposed, however, that all aromatic compounds are sharply distinguished from all aliphatic or fatty substances, or that either class can be defined in very exact terms. The mere fact that the constitution of a substance must be represented by a closed-chain formula does not make it an aromatic compound; succinimide (Part I. p. 243),

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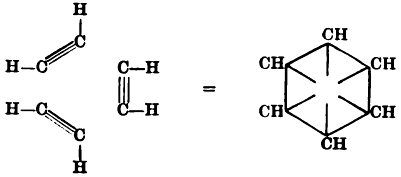
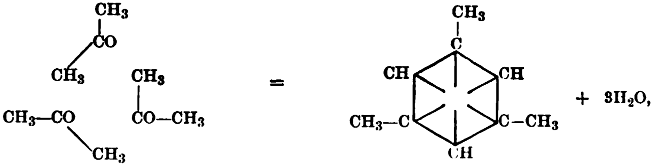
* The terms 'open-chain' and 'closed-chain' originated in the chain-like appearance of the graphic formulæ as usually written, and are not intended to convey the idea that the atoms are joined together by any form of matter, or that they are all arranged in straight lines.

for example, although it is a closed-chain compound, is clearly a member of the fatty series, because of its relationship to succinic acid. Although, again, the members of the aromatic group may all be regarded as derivatives of benzene, they may also be considered as derived from marsh-gas, since not only benzene itself, but many other aromatic compounds, may be directly obtained from members of the fatty series by simple reactions, and, conversely, many aromatic compounds may be converted into those of the fatty series.

Some examples of the production of aromatic from fatty compounds have already been given—namely, the formation of benzene by the polymerisation of acetylene, and that of mesitylene by the condensation of acetone; these two changes may be expressed graphically in the following manner,





and may be regarded as typical reactions, because many other substances, similar in constitution to acetylene and acetone respectively, may be caused to undergo analogous transformations. Bromacetylene, CBr⋮CH, for example, may be converted into (symmetrical) tribromobenzene, simply by leaving it exposed to direct sunlight,

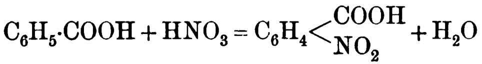
$$3C_2HBr = C_6H_3Br_3\,;$$

and methylethyl ketone (a homologue of acetone) is transformed into symmetrical triethylbenzene (a homologue of mesitylene or trimethylbenzene) by distilling it with sulphuric acid,

$$3CH_3{\cdot}CO{\cdot}C_2H_5 = C_6H_3(C_2H_5)_3 + 3H_2O.$$

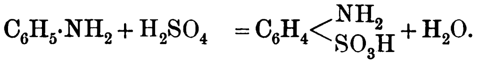
General Character of Aromatic Compounds.—Although, then, it is impossible to draw any sharp line between fatty and aromatic compounds, and many substances are known which form a connecting link between the two classes, the great majority of aromatic substances differ materially from those of the fatty division in constitution, and consequently also in properties.

Speaking generally, aromatic compounds contain a larger percentage of carbon and have a higher molecular weight than those of the fatty division, and for these reasons they are more frequently crystalline at ordinary temperatures. They are, as a rule, less readily resolved into simple substances than are the members of the fatty series (except the very stable paraffins), although in most cases they are more easily converted into substitution products. Their behaviour with nitric acid and with sulphuric acid is very characteristic, and distinguishes them from nearly all fatty compounds, inasmuch as they are, as a rule, readily converted into nitro- and sulphonic-derivatives respectively by the displacement of hydrogen atoms of the nucleus,



$$C_6H_5{\cdot}COOH + HNO_3 = C_6H_4{<}\begin{matrix}COOH\\NO_2\end{matrix} + H_2O$$

$$C_6H_5{\cdot}OH + 3HNO_3 = C_6H_2(OH)(NO_2)_3 + 3H_2O$$



$$C_6H_5{\cdot}NH_2 + H_2SO_4 = C_6H_4{<}\begin{matrix}NH_2\\SO_3H\end{matrix} + H_2O.$$

Fatty compounds rarely give sulphonic- or nitro-derivatives under the same conditions, but are oxidised and resolved into two or more simpler substances.

When aromatic nitro-compounds are reduced, they are converted into amido-compounds,

$$C_6H_5{\cdot}NO_2 + 6H = C_6H_5{\cdot}NH_2 + 2H_2O$$
$$C_6H_4(NO_2)_2 + 12H = C_6H_4(NH_2)_2 + 4H_2O.$$

These amido-compounds differ from the fatty amines in at least one very important respect, inasmuch as they are converted into diazo-compounds (p. 381) on treatment with nitrous acid in the cold; this behaviour is highly characteristic, and the diazo-compounds form one of the most interesting and important classes of aromatic substances.

It has already been pointed out that benzene does not show the ordinary behaviour of unsaturated fatty compounds, although under certain conditions both the hydrocarbon and its derivatives are capable of forming additive compounds by direct combination with two, four, or six (but not with one, three, or five) monovalent atoms. This fact proves that benzene is not really a saturated compound like methane or ethane, for example, both of which are quite incapable of yielding derivatives except by substitution. Nevertheless, the conversion of benzene and its derivatives into additive products is, as a rule, much less readily accomplished than in the case of fatty, unsaturated compounds; the halogen acids, for example, which unite directly with so many unsaturated fatty compounds, have no such action on benzene and its derivatives, and even in the case of the halogens and nascent hydrogen, direct combination occurs only under particular conditions. The additive compounds obtained from benzene and its derivatives form a connecting link between the members of the aromatic and fatty divisions.

Benzene itself is reduced only with great difficulty, and when strongly heated with hydriodic acid it yields *normal hexane*, C_6H_{14}, as principal product, the closed-chain suffering disruption.

Hexahydrobenzene (*hexamethylene* *), C_6H_{12}, is formed, but only in small quantities, when benzene is reduced with hydriodic acid; it occurs in Russian petroleum, from which it can be isolated by repeated fractional distillation. It melts at 4·7°, boils at 81°, and when treated with bromine it gives *bromohexahydrobenzene* or *bromohexamethylene* (b.p. 162°),

$$C_6H_{12} + Br_2 = C_6H_{11}Br + HBr;$$

---

* The name *hexamethylene* serves to recall the fact that the compound is composed of six methylene ($-CH_2-$) groups.

when this bromo-derivative is digested with alcoholic potash, it is converted into tetrahydrobenzene, just as ethyl bromide is converted into ethylene under similar conditions.

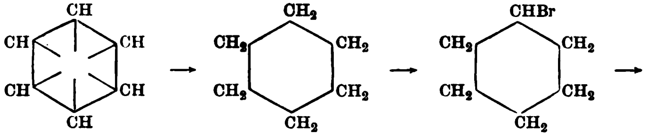
Tetrahydrobenzene, C_6H_{10}, boils at 83-84°, and combines directly with bromine at ordinary temperatures, yielding *dibromohexahydrobenzene* or *dibromohexamethylene*, $C_6H_{10}Br_2$.

Dihydrobenzene, C_6H_8, is obtained by heating dibromohexahydrobenzene with alcoholic potash or with quinoline (which acts like alcoholic potash and removes hydrogen bromide),

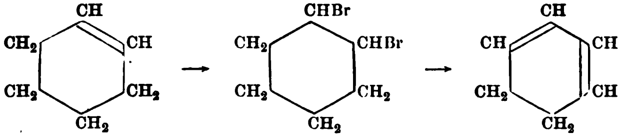
$$C_6H_{10}Br_2 = C_6H_8 + 2HBr ;$$

it boils at 84–86°, combines directly with bromine, giving a crystalline *tetrabromide*, $C_6H_8Br_4$, and rapidly oxidises on exposure to the air, being converted into a resin.

The following formulæ may serve to represent the above series of changes:



Benzene. Hexahydrobenzene. (Hexamethylene.) Bromohexahydrobenzene. (Bromohexamethylene.)



Tetrahydrobenzene. Dibromohexahydrobenzene. (Dibromohexamethylene.) Dihydrobenzene.

It is very important to note that *dihydro-* and *tetrahydro-*benzene, which must be regarded as incompletely or partially reduced benzene, differ very much from the original hydrocarbon, the difference being, in fact, much the same as that which exists between unsaturated and saturated compounds; in other words, when benzene combines with two or four atoms of hydrogen, the product is no longer characterised by great stability, but shows the ordinary behaviour of *unsaturated* compounds, inasmuch as it is readily oxidised and readily combines with bromine; this is also true in the case of all *partially reduced* benzene derivatives.

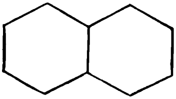
As expressed by the above formulæ, the conversion of benzene or of a benzene derivative into a *di-* or *tetra-*additive product is accompanied by a change in the mode of combination of all the carbon atoms; two or four of the six carbon affinities (represented in the centric formula by the short lines directed towards the centre) being required to take up the additive atoms, the remainder are released from their original state of combination, and become united in the same way as in ethylene.

When the hydrogen atoms in benzene are displaced by groups or radicles which are composed of several atoms, these groups are spoken of as *side-chains;* ethylbenzene, $C_6H_5 \cdot CH_2 \cdot CH_3$, benzyl alcohol, $C_6H_5 \cdot CH_2 \cdot OH$, and methylaniline, $C_6H_5 \cdot NH \cdot CH_3$, for example, would each be said to contain a side-chain, whereas the term would not, as a rule, be applied in the case of phenol, $C_6H_5 \cdot OH$, nitrobenzene, $C_6H_5 \cdot NO_2$, &c., where the substituting groups are comparatively simple, and do not contain carbon atoms.

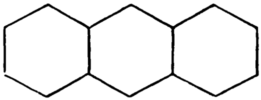
Now the character of any particular atom or group in the side-chain, although influenced to some extent by the fact that the group is united with the benzene nucleus, is on the whole very similar to that which it possesses in fatty compounds. The consequence is that aromatic compounds containing side-chains of this kind have not only the properties already referred to, as characteristic of the derivatives of benzene, but show also, to a certain extent, the behaviour of fatty compounds. Benzyl chloride, $C_6H_5 \cdot CH_2Cl$, for example, may be directly converted into the nitro-derivative, $C_6H_4(NO_2) \cdot CH_2Cl$, and the sulphonic acid, $C_6H_4(SO_3H) \cdot CH_2Cl$, reactions characteristic of aromatic compounds; on the other hand, the $-CH_2Cl$ group may be transformed into $-CH_2 \cdot OH$, $-CHO$, $-COOH$, and so on, just as may the same group in ethyl chloride, $CH_3 \cdot CH_2Cl$, and similar fatty compounds, and in all cases the products retain, to some extent, the properties of fatty substances as long as the side-chain remains. The carbon atoms contained in the side-chains, however, are generally more easily attacked and separated from the rest of the molecule than are those of the closed-chain or nucleus; when ethylbenzene, $C_6H_5 \cdot CH_2 \cdot CH_3$, or propylbenzene,

$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, for example, is boiled with chromic acid, the side-chain undergoes oxidation, carbon dioxide is evolved, and benzoic acid, $C_6H_5{\cdot}COOH$, is produced in both cases, the six atoms of carbon in the nucleus being unchanged (p. 429).

Although the compounds derived from benzene by direct substitution are very numerous, the aromatic group also contains a great many other substances which are more distantly related to benzene, and which can only be regarded as derived from it indirectly. The hydrocarbon *diphenyl*, $C_6H_5{-}C_6H_5$, for example, which, theoretically, is formed by the union of two *phenyl* or $C_6H_5{-}$ groups, just as dimethyl or ethane, $CH_3{-}CH_3$, is produced by the combination of two methyl-groups, is an important member of the aromatic division, and, like benzene, is capable of yielding a very large number of substitution products. Other hydrocarbons are known in which the presence of two or more closed carbon chains, combined in different ways, must be assumed, as, for example, in the cases of naphthalene (p. 454) and anthracene (p. 470),

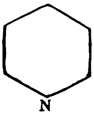


Naphthalene.

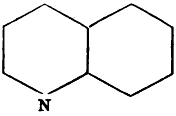


Anthracene.

and there are also substances, such as pyridine (p. 485) and quinoline (p. 493), in which a nitrogen atom occupies the position of one of the $CH\equiv$ groups in the closed-chain.



Pyridine.



Quinoline.

All these, and many other compounds and their derivatives, are classed as aromatic, because they show the general behaviour already referred to, and resemble benzene more or less closely in constitution.

CHAPTER XXI.

HOMOLOGUES OF BENZENE AND OTHER HYDROCARBONS.

Benzene, the simplest hydrocarbon of the aromatic group, is also the first member of a homologous series of the general formula C_nH_{2n-6}; the hydrocarbons of this series are derived from benzene by the substitution of alkyl-groups for hydrogen atoms, just as the homologous series of paraffins is derived from marsh-gas. The second member, toluene or methylbenzene, $C_6H_5{\cdot}CH_3$, like benzene itself, exists in only one form, but the next higher homologue, which has the molecular composition C_8H_{10}, occurs in four isomeric forms —namely, as ethylbenzene, $C_6H_5{\cdot}C_2H_5$, and as ortho-, meta-, and para-dimethylbenzene, $C_6H_4(CH_3)_2$; on passing up the series, the number of theoretically possible isomerides rapidly increases.

By substituting a methyl-group for one atom of hydrogen in the hydrocarbon C_8H_{10}, for example, eight isomerides of the composition C_9H_{12} may theoretically be obtained, and are, in fact, known; of these isomerides, five—namely, propylbenzene and isopropylbenzene, $C_6H_5{\cdot}C_3H_7$, and *o*-, *m*-, and *p*-methylethylbenzene, $C_6H_4(CH_3){\cdot}C_2H_5$, are derived from ethylbenzene, the other three —namely, symmetrical, adjacent, and asymmetrical trimethylbenzene, $C_6H_3(CH_3)_3$, being derived from the dimethylbenzenes.

Most of the hydrocarbons of this series, and others which will be mentioned later, occur in coal-tar, from which they are extracted in much the same way as benzene; it is, however, exceedingly difficult to obtain any of them in a pure state directly from this source by fractional distillation, as the boiling-points of some of the compounds lie very close together; nevertheless, the process is now carried out on the large scale with such care and with such perfect apparatus that the purified compounds contain, in some cases, only traces of foreign substances.

The homologues of benzene may be obtained by the following general methods:

(1) By treating benzene (or its homologues) with alkyl halogen compounds in presence of anhydrous aluminium chloride (Friedel and Crafts' reaction); under these conditions the hydrogen atoms of the nucleus are displaced by alkyl-groups, benzene and methyl chloride, for example, giving toluene, $C_6H_5{\cdot}CH_3$, xylene, $C_6H_4(CH_3)_2$, trimethylbenzene, $C_6H_3(CH_3)_3$, &c.; whereas ethylbenzene, with the same alkyl compound, yields methylethylbenzene, $C_6H_4(CH_3){\cdot}C_2H_5$; dimethylethylbenzene, $C_6H_3(CH_3)_2{\cdot}C_2H_5$, and so on,

$$C_6H_6 + CH_3Cl = C_6H_5{\cdot}CH_3 + HCl$$
$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl$$
$$C_6H_5{\cdot}C_2H_5 + CH_3Cl = C_6H_4(CH_3){\cdot}C_2H_5 + HCl.$$

Anhydrous benzene, or one of its homologues, is placed in a flask connected with a reflux condenser, and about one-third of its weight of anhydrous aluminium chloride added; the alkyl chloride or bromide is then passed into the liquid if a gas, or poured in if a liquid, and the mixture heated on a water-bath until the evolution of hydrogen chloride or bromide is at an end; the apparatus and materials must be dry. In some cases ether, carbon disulphide, or petroleum is previously mixed with the hydrocarbon in order to dilute it, experience having shown this to be advantageous. When quite cold, water is gradually added to dissolve the aluminium compounds, and after having been separated and dried with calcium chloride, the mixture of hydrocarbons is submitted to fractional distillation; in some cases a preliminary distillation in steam is advisable.

It is probable that an aluminium compound, such as $C_6H_5{\cdot}Al_2Cl_5$, is first formed with evolution of hydrogen chloride, this substance then interacting with the alkyl halogen compound to form the new hydrocarbon, aluminium chloride being regenerated,

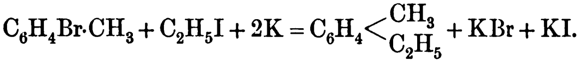
$$C_6H_5{\cdot}Al_2Cl_5 + CH_3Cl = C_6H_5{\cdot}CH_3 + Al_2Cl_6.$$

Anhydrous ferric or zinc chloride may be employed in the place of aluminium chloride, but, as a rule, not so successfully.

(2) By treating a mixture, consisting of a halogen derivative of benzene or of one of its homologues, and an alkyl

halogen compound, with sodium or potassium (Fittig's reaction); this method of formation is similar to that by which the higher paraffins may be synthetically produced from methane (Part I. p. 68), and has the advantage over Friedel and Crafts' method that the constitution of the product is known. Bromobenzene and methyl iodide, for example, give toluene, whereas *o*-, *m*-, or *p*-bromotoluene and ethyl iodide yield *o*-, *m*-, or *p*-ethylmethylbenzene,

$$C_6H_5Br + CH_3I + 2Na = C_6H_5{\cdot}CH_3 + NaI + NaBr$$



$$C_6H_4Br{\cdot}CH_3 + C_2H_5I + 2K = C_6H_4{<}^{CH_3}_{C_2H_5} + KBr + KI.$$

The bromo-derivatives of the aromatic hydrocarbons are usually employed in such cases because the chloro-derivatives are not so readily acted on, and the iodo-compounds are not so easily prepared; the alkyl iodides are also used in preference to the chlorides or bromides because they interact more readily. Dry ether is usually employed as a diluent.

(3) By heating carboxy-derivatives of benzene and its homologues with soda-lime, a method analogous to that employed in converting the fatty acids into paraffins (Part I. p. 68),

$$C_6H_4(CH_3){\cdot}COOH = C_6H_5{\cdot}CH_3 + CO_2$$
$$C_6H_4(COOH)_2 = C_6H_6 + 2CO_2.$$

(4) By passing the vapour of hydroxy-derivatives of benzene and its homologues over heated zinc-dust, which combines with the oxygen in the compound,

$$C_6H_5{\cdot}OH + Zn = C_6H_6 + ZnO$$
$$C_6H_4(CH_3){\cdot}OH + Zn = C_6H_5{\cdot}CH_3 + ZnO.$$

(5) By the destructive distillation of coal, wood, peat, &c., and by passing the vapour of many fatty compounds through red-hot tubes (compare p. 310).

General Properties.—Most of the homologues of benzene are colourless, mobile liquids; one or two, however, are crystalline at ordinary temperatures. They all distil without decomposing, are volatile in steam, and burn with a smoky flame; they are insoluble in water, but miscible with (absolute) alcohol, ether, petroleum, &c., in all proportions; they dissolve fats and many other substances which are insoluble in water.

Just as in other homologous series, the homologues of benzene show a gradual variation in physical properties with increasing molecular weight, but owing to the large number of isomerides, this is only obvious when *corresponding* compounds are compared; as an example of this, the following *mono*-substitution products of benzene may be considered:

Benzene, C_6H_6	Sp. gr. at 0°, 0·899	B.p., 80·5°
Toluene, C_7H_8	" 0·882	" 110·3°
Ethylbenzene, C_8H_{10}	" 0·883	" 134°
Propylbenzene, C_9H_{12}	" 0·881	" 158°

There are, however, three hydrocarbons isomeric with ethylbenzene (p. 347), whilst propylbenzene has seven isomerides (p. 339), so that the original homologous series given above branches into a number of series, in which the homology becomes rather confused. In the case of isomeric *di*-substitution products there is usually some difference in physical properties, but the extent to which they differ is rather variable; the three xylenes, $C_6H_4(CH_3)_2$, for example, show the following differences:

	Orthoxylene.	Metaxylene.	Paraxylene.
Sp. gr. at 0°	0·893	0·881	0·880
B.p.	142°	139°	138° (M.p. 15°)

As a general rule, to which, however, there are some exceptions, para-compounds melt at a higher temperature than the corresponding meta-compounds, and the latter usually at a higher temperature than the corresponding ortho-compounds; the boiling-points also vary, but with less regularity. This applies to all benzene derivatives, not to hydrocarbons only.

The homologues of benzene show the characteristic chemical behaviour of the simplest hydrocarbon, inasmuch as they readily yield nitro- and sulphonic-derivatives; toluene, for example, gives nitrotoluene, $C_6H_4(CH_3)\cdot NO_2$, and toluenesulphonic acid, $C_6H_4(CH_3)\cdot SO_3H$, xylene yielding nitroxylene, $C_6H_3(CH_3)_2\cdot NO_2$, and xylenesulphonic acid,

$$C_6H_3(CH_3)_2\cdot SO_3H.$$

In these, and in all similar reactions, the product invariably consists of a mixture of isomerides, the course of the reaction depending both on the nature of the interacting compounds and on the conditions of the experiment (compare p. 364); as a rule, the greater the number of alkyl-groups in the hydrocarbon, the more readily does it yield nitro- and sulphonic-derivatives.

The fact that benzene and its homologues gradually dissolve in concentrated sulphuric acid, especially on warming, is sometimes made use of in separating these aromatic hydrocarbons from the paraffins, as, for example, in the analysis of coal-gas; their separation from unsaturated fatty hydrocarbons could not of course be accomplished in this way, as the latter are also dissolved by concentrated sulphuric acid.

All the homologues of benzene are very stable, and are with difficulty resolved into compounds containing a smaller number of carbon atoms; powerful oxidising agents, however, such as chromic acid, potassium permanganate, and *dilute* nitric acid, act on them slowly, the alkyl-groups or side-chains being attacked, and as a rule converted into carboxyl-groups; toluene and ethylbenzene, for example, give benzoic acid, whereas the xylenes yield dicarboxylic acids (p. 436),

$$C_6H_5\cdot CH_3 + 3O = C_6H_5\cdot COOH + H_2O$$
$$C_6H_5\cdot CH_2\cdot CH_3 + 6O = C_6H_5\cdot COOH + CO_2 + 2H_2O$$
$$C_6H_4(CH_3)_2 + 6O = C_6H_4(COOH)_2 + 2H_2O.$$

Although in most cases oxidation leads to the formation of a carboxy-derivative of benzene, the stable nucleus of six carbon atoms remaining unchanged, some of the homologues are completely oxidised to carbon dioxide and water (compare p. 347), and benzene itself undergoes a similar change on prolonged and vigorous treatment.

Aromatic hydrocarbons, like those of the fatty series, may be regarded as hydrides of hypothetical *radicles;* in other words, radicles may theoretically be derived from aromatic hydrocarbons by taking away atoms of hydrogen. These radicles have no actual existence, but the assumption is useful in naming aromatic compounds; the mono- and di-substitution products of benzene, for example, may be regarded as compounds of the monovalent radicle *phenyl*, C_6H_5-, or of the divalent radicle *phenylene*, $C_6H_4<$, respectively, as in phenylamine (aniline), $C_6H_5 \cdot NH_2$, and in *o*-, *m*- and *p*-phenylenediamine, $C_6H_4(NH_2)_2$. Toluene derivatives, again, may be named as if they were derived from the radicle *toluyl*, $CH_3 \cdot C_6H_4-$, or from the radicle *benzyl*, $C_6H_5 \cdot CH_2-$, according as hydrogen of the nucleus, or of the side-chain, has been displaced. The compound $C_6H_5 \cdot CH_2 \cdot OH$, for example, is called benzyl alcohol. The isomeric hydroxy-compounds, $C_6H_4(CH_3) \cdot OH$, however, are usually known as the (*o.m.p.*) cresols (p. 408). Other hypothetical radicles, such as *xylyl*, $C_6H_3(CH_3)_2-$, and *xylylene*, $C_6H_4{<}\begin{smallmatrix}CH_2- \\ CH_2-\end{smallmatrix}$, are also made use of.

Toluene, methylbenzene, or phenylmethane, $C_6H_5 \cdot CH_3$, although always prepared from the '90 per cent. benzol' separated from coal-tar (p. 307), can be obtained by any of the general reactions given above, and also by the dry distillation of balsam of Tolu (hence the name toluene) and other resins.

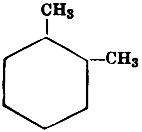
Commercial toluene is invariably impure, and when shaken with concentrated sulphuric acid it colours the acid brown or black. It may be purified by repeated fractional distillation, but even then it will contain *thiotolene*, C_5H_6S, a homologue of thiophene (p. 310), and will show the indophenin reaction (with isatin and concentrated sulphuric acid).

Pure toluene is most conveniently prepared from balsam of Tolu, or by distilling pure toluic acid with lime,

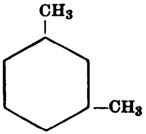
$$C_6H_4(CH_3) \cdot COOH = C_6H_5 \cdot CH_3 + CO_2.$$

It is a mobile liquid of sp. gr. 0·882 at 0°, and boils at 110°; it does not solidify even at − 28°, and cannot, therefore, like benzene, be purified by freezing. It resembles benzene very closely in most respects, differing from it principally in those properties which are due to the presence of the methyl-group. Its behaviour with nitric acid and with sulphuric acid, for example, is similar to that of benzene, inasmuch as it yields nitro- and sulphonic-derivatives; these compounds, moreover, exist in three isomeric (*o.m.p.*) forms, since they are di-substitution products of benzene. The presence of the methyl-group, on the other hand, causes toluene to show in some respects the properties of a paraffin. The hydrogen of this methyl-group may be displaced by chlorine, for example, and the latter by a hydroxyl- or amido-group, by methods exactly similar to those employed in bringing about similar changes in fatty compounds, substances such as $C_6H_5{\cdot}CH_2Cl$, $C_6H_5{\cdot}CH_2{\cdot}OH$, and $C_6H_5{\cdot}CH_2{\cdot}NH_2$ being obtained. This behaviour was of course to be expected, since toluene or phenylmethane is a mono-substitution product of marsh-gas just as much as a derivative of benzene.

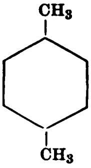
The next homologue of toluene—namely, the hydrocarbon of the molecular formula C_8H_{10}—exists in the following four isomeric forms, of which the three *xylenes* or dimethylbenzenes are the most important,



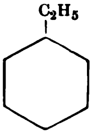
Ortho-xylene.



Meta-xylene.



Para-xylene.



Ethylbenzene.

The three **xylenes** occur in coal-tar, and may be partially separated from the other constituents of '50 per cent. benzol' (p. 307) by fractional distillation. The portion boiling at 136–141°, after repeated distillation contains a large quantity (up to 85 per cent.) of *m*-xylene and smaller quantities of the *o*- and *p*-compounds; the three isomerides cannot be separated from one another or from all impurities by further distillation, or by any simple means, although it is possible to obtain a complete separation by taking advantage of differences in chemical behaviour.

m-Xylene is readily separated from the other isomerides by digesting with dilute nitric acid, which oxidises *o*- and *p*-xylene to the corresponding toluic acids, $C_6H_4(CH_3)\cdot COOH$, but does not readily attack *m*-xylene; the product is rendered alkaline by the addition of potash, and the unchanged hydrocarbon purified by distillation in steam and fractionation. The isolation of *o*- and *p*-xylene depends on the following facts: (1) When crude xylene is agitated with concentrated sulphuric acid, *o*- and *m*-xylene are converted into sulphonic acids, $C_6H_3(CH_3)_2\cdot SO_3H$; *p*-xylene remains unchanged, as it is only acted on by fuming sulphuric acid. (2) The sodium salt of *o*-xylenesulphonic acid is less soluble in water than the sodium salt of *m*-xylenesulphonic acid; it is purified by recrystallisation, and converted into *o*-xylene by heating with hydrochloric acid under pressure (p. 394).

The three xylenes may all be prepared by one or other of the general methods; when, for example, methyl chloride is passed into benzene in presence of aluminium chloride, *o*-xylene and a small quantity of the *p*-compound are obtained,

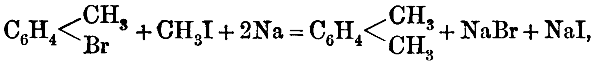
$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl\,;$$

toluene, under the same conditions, yields the same two compounds,

$$C_6H_5\cdot CH_3 + CH_3Cl = C_6H_4(CH_3)_2 + HCl.$$

The non-formation of *m*-xylene in these two cases shows that the methyl-group first introduced into the benzene molecule exerts some *directing influence* on the position taken up by the second one (p. 364).

Orthoxylene is obtained in a state of purity by treating *o*-bromotoluene with methyl iodide and sodium,

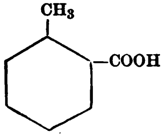


$$C_6H_4<\begin{matrix}CH_3\\Br\end{matrix} + CH_3I + 2Na = C_6H_4<\begin{matrix}CH_3\\CH_3\end{matrix} + NaBr + NaI,$$

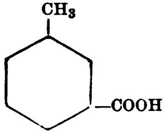
pure *paraxylene* being produced in a similar manner from *p*-bromotoluene; *metaxylene* cannot be prepared by treating *m*-bromotoluene with methyl iodide and sodium, but is easily obtained in a pure condition by distilling mesitylenic acid (p. 328) with lime,

$$C_6H_3(CH_3)_2 \cdot COOH = C_6H_4(CH_3)_2 + CO_2.$$

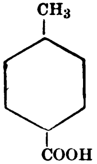
The three xylenes are very similar in physical properties (compare p. 342), being all mobile, rather pleasant-smelling, inflammable liquids (*p*-xylene melts at 15°), which distil without decomposing, and are readily volatile in steam. They also resemble one another in chemical properties, although in some respects they show important differences, which must be ascribed to their difference in constitution. On oxidation, under suitable conditions, they are all converted in the first place into monocarboxylic acids which are represented by the formulæ,



Ortho-toluic Acid.



Meta-toluic Acid.



Para-toluic Acid.

On further oxidation the second methyl-group undergoes a like change, and the three corresponding dicarboxylic acids, $C_6H_4(COOH)_2$, are formed (p. 436).

The three hydrocarbons show slight differences in behaviour on oxidation, one being more easily acted on than another by a particular oxidising agent. With chromic acid, for example, *o*-xylene is completely oxidised to carbon dioxide and water, whereas *m*-xylene and *p*-xylene yield the dicarboxylic acids (see above); with dilute nitric acid *o*-xylene gives *o*-toluic acid, and *p*-xylene, *p*-toluic acid, but *m*-xylene is not readily acted on. Their behaviour with sulphuric acid is also different (p. 346).

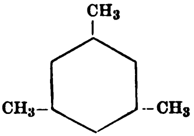
Ethylbenzene, or *phenylethane*, $C_6H_5 \cdot C_2H_5$, an isomeride of the xylenes, is not of much importance; it occurs in coal-tar, and may be obtained by the general methods.

It is a colourless liquid, boiling at 134°, and on oxidation with dilute nitric acid or chromic acid it is converted into benzoic acid,

$$C_6H_5{\cdot}CH_2{\cdot}CH_3 + 6O = C_6H_5{\cdot}COOH + CO_2 + 2H_2O.$$

The next member of the series has the molecular formula C_9H_{12}, and exists, as already pointed out (p. 339), in eight isomeric forms, of which the three trimethylbenzenes and isopropylbenzene are the most important.

Mesitylene, 1:3:5- or symmetrical trimethylbenzene,



occurs in small quantities in coal-tar, but is most conveniently prepared by distilling a mixture of acetone (2 vols.), concentrated sulphuric acid (2 vols.), and water (1 vol.), sand being added to prevent frothing,

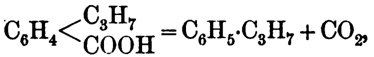
$$3(CH_3)_2CO = C_6H_3(CH_3)_3 + 3H_2O.$$

The formation of mesitylene in this way is of interest not only because it affords a means of synthesising the hydrocarbon from its elements, but also because it throws light on the constitution of the compound. Although the change is a process of condensation, and is most simply expressed by the graphic equation already given (p. 333), it might be assumed that the acetone is first converted into $CH_3{\cdot}C{:}CH$, or into $CH_3{\cdot}C(OH){:}CH_2$ (by intramolecular change), and that mesitylene is then produced by a secondary reaction; whatever view, however, is adopted as to the actual course of the reaction (unless, indeed, highly improbable assumptions be made), the final result is always the same, and the constitution of the product is best expressed by a symmetrical formula; for this and other reasons, mesitylene is regarded as *symmetrical* or 1:3:5-trimethylbenzene.

Mesitylene is a colourless, mobile, pleasant-smelling liquid, boiling at 164·5°, and volatile in steam; when treated with concentrated nitric acid it yields mono- and di-nitromesitylene, whereas with a mixture of nitric and sulphuric acids it is converted into *trinitromesitylene*, $C_6(NO_2)_3(CH_3)_3$. On oxidation with dilute nitric acid it yields *mesitylenic acid*, $C_6H_3(CH_3)_2{\cdot}COOH$; *uvitic acid*, $C_6H_3(CH_3)(COOH)_2$; and *trimesic acid*, $C_6H_3(COOH)_3$, by the transformation of successive methyl- into carboxyl-groups.

Pseudocumene, or 1:2:4-trimethylbenzene, $C_6H_3(CH_3)_3$, and *hemimellitene*, or 1:2:3-trimethylbenzene, also occur in small quantities in coal-tar, and are very similar to mesitylene in properties; on oxidation, they yield various acids by the conversion of one or more methyl- into carboxyl-groups.

Cumene, or isopropylbenzene, $C_6H_5{\cdot}CH(CH_3)_2$, is usually obtained from coal-tar; it may be prepared in a pure condition by distilling *cumic acid* (*isopropylbenzoic acid*) with lime,



$$C_6H_4{<}\begin{matrix}C_3H_7\\COOH\end{matrix} = C_6H_5{\cdot}C_3H_7 + CO_2,$$

by treating a mixture of isopropyl bromide and benzene with aluminium chloride,

$$C_6H_6 + C_3H_7Br = C_6H_5{\cdot}C_3H_7 + HBr,$$

and by the action of sodium on a mixture of bromobenzene and isopropyl bromide,

$$C_6H_5Br + C_3H_7Br + 2Na = C_6H_5{\cdot}C_3H_7 + 2NaBr.$$

It is a colourless liquid, boiling at 153°, and on oxidation with dilute nitric acid it is converted into benzoic acid.

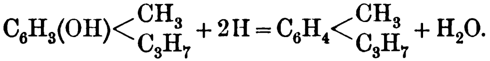
Cymene, or *para*-methylisopropylbenzene, $C_6H_4(CH_3){\cdot}C_3H_7$, is a hydrocarbon of considerable importance, as it occurs in the ethereal oils or essences of many plants; it is easily prepared in many ways, as, for example, by heating camphor with phosphorus pentoxide or phosphorus pentasulphide,

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O,$$

by heating turpentine with concentrated sulphuric acid or with iodine (both of which, in this case, act as oxidising agents),

$$C_{10}H_{16} + O = C_{10}H_{14} + H_2O,$$

and by heating thymol (p. 409), or carvacrol (p. 410), with phosphorus pentasulphide (which acts as a reducing agent),



$$C_6H_3(OH)<^{CH_3}_{C_3H_7} + 2H = C_6H_4<^{CH_3}_{C_3H_7} + H_2O.$$

Cymene is a pleasant-smelling liquid of sp. gr. 0·8722 at 0°, and boils at 175–176°; on oxidation with dilute nitric acid it yields *p-toluic acid*, $C_6H_4(CH_3)\cdot COOH$, and *terephthalic acid*, $C_6H_4(COOH)_2$.

Diphenyl, Diphenylmethane, and Triphenylmethane.

All the hydrocarbons hitherto described contain only *one* benzene nucleus, and may be regarded as derived from benzene by the substitution of fatty alkyl-groups for atoms of hydrogen; there are, however, several other series of aromatic hydrocarbons, which include compounds of very considerable importance.

Diphenyl, $C_6H_5–C_6H_5$, contains *two* benzene nuclei, and is the hydrocarbon in the aromatic series which corresponds with ethane in the fatty series, although it is not a homologue of benzene. It is formed on treating bromobenzene in ethereal solution with sodium,

$$2C_6H_5Br + 2Na = C_6H_5\cdot C_6H_5 + 2NaBr,$$

the reaction being analogous to the formation of ethane (dimethyl) from methyl iodide by the action of sodium (Part I. p. 58).

Diphenyl is prepared by passing benzene vapour through a red-hot tube filled with pieces of pumice (Berthelot),

$$2C_6H_6 = C_6H_5\cdot C_6H_5 + H_2.$$

The dark-coloured distillate is fractionated, and the diphenyl purified by recrystallisation from alcohol.

Diphenyl is a colourless, crystalline substance, melts at 71°, and boils at 254°; when oxidised with chromic acid it yields benzoic acid, one of the benzene nuclei being destroyed. Its behaviour with halogens, nitric acid, and sulphuric acid is similar to that of benzene, substitution products being formed.

Diphenylmethane, $C_6H_5 \cdot CH_2 \cdot C_6H_5$, also contains *two* benzene nuclei; it may be regarded as derived from marsh-gas by the substitution of two phenyl-groups for two atoms of hydrogen, just as toluene or phenylmethane may be considered as a mono-substitution product of methane.

Diphenylmethane may be prepared by treating benzene with benzyl chloride (p. 361) in presence of aluminium chloride,

$$C_6H_6 + C_6H_5 \cdot CH_2Cl = C_6H_5 \cdot CH_2 \cdot C_6H_5 + HCl.$$

It is a crystalline substance, and melts at 26·5°; when treated with nitric acid it yields nitro-derivatives in the usual way, and on oxidation with chromic acid it is converted into diphenyl ketone or benzophenone, $C_6H_5 \cdot CO \cdot C_6H_5$ (p. 424).

Triphenylmethane, $(C_6H_5)_3CH$, is the parent substance of an important group of compounds all of which contain *three* benzene nuclei. It is formed when benzal chloride (p. 362) is treated with benzene in presence of aluminium chloride,

$$C_6H_5 \cdot CHCl_2 + 2C_6H_6 = (C_6H_5)_3CH + 2HCl,$$

but it is usually prepared by heating a mixture of chloroform and benzene with aluminium chloride,

$$CHCl_3 + 3C_6H_6 = (C_6H_5)_3CH + 3HCl.$$

Aluminium chloride (5 parts) is gradually added to a mixture of chloroform (1 part) and benzene (5 parts), which is then heated at about 60° until the evolution of hydrogen chloride ceases, an operation occupying about thirty hours; after cooling and adding water, the oily product is separated and submitted to fractional distillation; those portions of the distillate which solidify on cooling consist of crude triphenylmethane, which is further purified by recrystallisation from benzene and then from ether.

Triphenylmethane is a colourless, crystalline compound, which melts at 92°, and boils at 358°; it is readily soluble in ether and benzene, but only sparingly so in cold alcohol.

When treated with fuming nitric acid it is converted into a yellow, crystalline *trinitro*-derivative, $CH(C_6H_4 \cdot NO_2)_3$, which, like other nitro-compounds, is readily reduced to the corresponding *triamido*-compound, $CH(C_6H_4 \cdot NH_2)_3$; the last-named substance is of considerable importance, as many of its derivatives are largely employed as dyes (p. 519).

On oxidation with chromic acid, triphenylmethane is converted into triphenyl carbinol, $(C_6H_5)_3C \cdot OH$.

CHAPTER XXII.

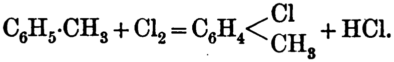
HALOGEN DERIVATIVES OF BENZENE AND ITS HOMOLOGUES.

The action of halogens on benzene has already been referred to (p. 313), and it has been pointed out that the hydrocarbon yields either additive or substitution products according to the conditions of the experiment; at ordinary temperatures, in absence of direct sunlight, substitution products are formed, the action being greatly hastened by the presence of a halogen carrier, such as iodine, iron, or antimony;* at its boiling-point, however, or in presence of direct sunlight, the hydrocarbon yields additive compounds by direct combination with six atoms of the halogen.

The homologues of benzene also show a curious behaviour; when treated with chlorine or bromine at ordinary temperatures in absence of direct sunlight, they are converted into substitution products by the displacement of hydrogen of the *nucleus*, and, as in the case of benzene itself, interaction is greatly promoted by the presence of a halogen carrier;

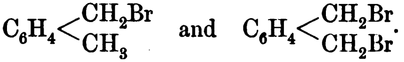
*** The action of iodine has been explained (Part I. p. 165); iron, antimony, molybdenum, and certain other metals act as halogen carriers, probably because they are converted into compounds ($FeCl_3$, $SbCl_5$, $MoCl_5$) which readily dissociate, yielding *nascent* halogen and lower halogen derivatives ($FeCl_2$, $SbCl_3$, $MoCl_3$); the latter then combine again with a fresh quantity of the halogen, and thus the processes are repeated.**

under these conditions toluene, for example, gives a mixture of *o*- and *p*-chlorotoluenes or bromotoluenes,



$$C_6H_5{\cdot}CH_3 + Cl_2 = C_6H_4{<}\begin{matrix}Cl\\CH_3\end{matrix} + HCl.$$

When, on the other hand, no halogen carrier is present, and the hydrocarbons are treated at their boiling-points, or in direct sunlight, with chlorine or bromine, they yield derivatives by the substitution of hydrogen of the *side-chain;* when, for example, chlorine is passed into *boiling* toluene, the three hydrogen atoms of the methyl-group are successively displaced, benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, benzal chloride, $C_6H_5{\cdot}CHCl_2$, and benzotrichloride, $C_6H_5{\cdot}CCl_3$, being formed; xylene, again, when heated at its boiling-point and treated with bromine, gives the compounds,



$$C_6H_4{<}\begin{matrix}CH_2Br\\CH_3\end{matrix} \quad \text{and} \quad C_6H_4{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix}.$$

Although these statements are true in the main, it must not be supposed that substitution takes place only in the nucleus or side-chain, as the case may be, because this is not so; in presence of a halogen carrier traces of a halogen derivative are formed by substitution of hydrogen of the side-chain, and at the boiling-point of the hydrocarbon, or in direct sunlight, traces of substitution products, formed by displacement of hydrogen of the nucleus, are obtained.

Iodine seldom acts on benzene and its homologues under any of the above-mentioned conditions, partly because of the slight affinity of iodine for hydrogen, partly because the hydrogen iodide which is produced interacts with the iododerivative, and reconverts it into the hydrocarbon,

$$C_6H_6 + I_2 = C_6H_5I + HI$$
$$C_6H_5I + HI = C_6H_6 + I_2;$$

if, however, iodic acid, or some other substance which decomposes hydrogen iodide, be present, iodo-derivatives may sometimes be prepared by direct treatment with the halogen at high temperatures.*

Preparation.—Chloro- and bromo-derivatives of benzene and its homologues may be prepared by direct '*chlorination*' or '*bromination*,' the conditions employed depending on whether hydrogen of the nucleus or of the side-chain is to be displaced; if, for example, it were desired to convert toluene into *p-chlorobenzyl chloride*, $C_6H_4Cl{\cdot}CH_2Cl$, the hydrocarbon might be first treated with chlorine at ordinary temperatures in presence of iodine, and the *p-chlorotoluene*, $C_6H_4Cl{\cdot}CH_3$, after having been separated from the accompanying ortho-compound, would then be heated to boiling in a flask connected with a reflux condenser, and a stream of dry chlorine led into it.

In all operations of this kind the theoretical quantity, or a slight excess of halogen, is employed; the bromine is weighed directly, but the weight of the chlorine is usually ascertained indirectly by continuing the process until the theoretical gain in weight has taken place; the halogen should be dry, as in presence of water oxidation products of the hydrocarbon may be formed. The fumes of hydrogen chloride or bromide evolved during such operations are conveniently absorbed by passing them to the bottom of a deep vessel containing damp coke.

A very important general method for the preparation of aromatic halogen derivatives, *containing the halogen in the nucleus*, consists in the decomposition of the diazo-compounds. As the properties and decompositions of the last-named substances are described later (p. 381), it is only necessary to state here that this method is used in the preparation of nearly all iodo-compounds, and that it affords a means of indirectly substituting any of the halogens, not only for hydrogen, but also for nitro- or amido-groups.

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* $HIO_3 + 5HI = 3I_2 + 3H_2O$. Iodo-substitution products are also frequently formed on employing $FeCl_3$, or $AlCl_3$, as a carrier, because the ICl which is formed has a much more energetic substituting action than the iodine itself, owing to the simultaneous formation of HCl,

$$C_6H_6 + ICl = C_6H_5I + HCl.$$

The conversion of benzene or toluene, for example, into a mono-halogen derivative by this method involves the following steps,

$$C_6H_6 \longrightarrow C_6H_5{\cdot}NO_2 \longrightarrow C_6H_5{\cdot}NH_2 \longrightarrow C_6H_5{\cdot}N_2Cl \longrightarrow C_6H_5Cl$$

Benzene. Nitrobenzene. Amidobenzene. Diazobenzene Chloride. Chlorobenzene.

$$C_6H_5{\cdot}CH_3 \longrightarrow C_6H_4{<}\substack{CH_3\\NO_2} \longrightarrow C_6H_4{<}\substack{CH_3\\NH_2} \longrightarrow C_6H_4{<}\substack{CH_3\\N_2Br} \longrightarrow C_6H_4{<}\substack{CH_3\\Br}.$$

Toluene. Nitrotoluene. Amidotoluene. Diazotoluene Bromide. Bromotoluene.

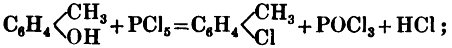
The preparation of a *di*-halogen derivative may sometimes be carried out in a similar manner, the hydrocarbon being first converted into the *di*-nitro-derivative; in most cases, however, it is necessary to prepare the *mono*-halogen derivative by the reactions given above, and after converting it into the nitro-compound, the nitro-group is displaced by a second atom of halogen by repeating the series of operations,

$$C_6H_5Br \longrightarrow C_6H_4{<}\substack{Br\\NO_2} \longrightarrow C_6H_4{<}\substack{Br\\NH_2} \longrightarrow C_6H_4{<}\substack{Br\\N_2Cl} \longrightarrow C_6H_4{<}\substack{Br\\Cl}.$$

Bromobenzene. Nitrobromobenzene. Amidobromobenzene. Diazobromobenzene Chloride. Bromochlorobenzene.

Halogen derivatives of benzene and its homologues are sometimes prepared by treating hydroxy-compounds with pentachloride or pentabromide of phosphorus, the changes being similar to those which occur in the case of fatty hydroxy-compounds; if the hydroxyl-group be present in the nucleus, the halogen naturally takes up the same position, phenol, for example, giving chlorobenzene, and cresol, chlorotoluene,

$$C_6H_5{\cdot}OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$$



$$C_6H_4{<}\substack{CH_3\\OH} + PCl_5 = C_6H_4{<}\substack{CH_3\\Cl} + POCl_3 + HCl;$$

an aromatic alcohol (p. 414), such as benzyl alcohol, also yields the corresponding halogen derivative (benzyl chloride), containing the halogen in the side-chain,

$$C_6H_5{\cdot}CH_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}CH_2Cl + POCl_3 + HCl.$$

Halogen derivatives may also be obtained by distilling halogen acids with lime,

$$C_6H_4Br{\cdot}COOH = C_6H_5Br + CO_2,$$

by heating sulphonic chlorides (p. 394) with phosphorus pentachloride,

$$C_6H_5{\cdot}SO_2Cl + PCl_5 = C_6H_5Cl + POCl_3 + SOCl_2,$$

and by several other methods of less importance.

Properties.—At ordinary temperatures, some of the halogen derivatives of benzene and its homologues are colourless liquids; the majority, however, are crystalline solids. They are all insoluble, or nearly so, in water, but readily soluble in alcohol, ether, &c. Many are readily volatile in steam, and distil without decomposing, the boiling-point being higher and the specific gravity greater than that of the parent hydrocarbon, and rising also on substituting bromine for chlorine, or iodine for bromine.

	Benzene.	Chlorobenzene.	Bromobenzene.	Iodobenzene.
B.p............	80·5°	132°	155°	188°
Sp. gr. at 0°	0·899	1·128	1·521	1·857.

They are not so inflammable as the hydrocarbons, and the vapours of many of them have a very irritating action on the eyes and respiratory organs.

When the halogen is united with carbon of the benzene nucleus, it is, as a rule, very firmly combined, and *cannot be displaced by the hydroxyl- or amido-group with the aid of aqueous potash, ammonia, or silver hydroxide;* such halogen derivatives, moreover, are *not acted on by alcoholic potash,* and cannot be converted into less saturated compounds in the same way as ethyl bromide, for example, may be converted into ethylene; in fact, no derivative of benzene containing less than six monovalent atoms, or their valency equivalent, is known. If, however, hydrogen of the nucleus has been displaced by one or more nitro-groups, as well as by a halogen, the latter often becomes much more open to attack; *o*- and *p*-chloronitrobenzene, $C_6H_4Cl{\cdot}NO_2$, for example, are moderately easily acted on by alcoholic potash and by alcoholic ammonia at high temperatures, yielding the corresponding nitrophenols, $C_6H_4(OH){\cdot}NO_2$, and nitranilines, $C_6H_4(NH_2){\cdot}NO_2$; *m*-chloronitrobenzene, however, is not acted on under these conditions, a fact which shows that such isomerides sometimes differ very considerably in chemical properties.

Halogen atoms in the side-chains are very much less firmly combined than those in the nucleus, and may be displaced by hydroxyl- or amido-groups just as in fatty compounds; benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, for example, is converted into benzyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}OH$, by boiling sodium carbonate solution, and when heated with alcoholic ammonia it yields benzylamine, $C_6H_5{\cdot}CH_2{\cdot}NH_2$ (p. 380).

Halogen atoms in the nucleus, as well as those in the side-chain, are displaced by hydrogen on treatment with hydriodic acid and amorphous phosphorus at high temperatures, or with sodium amalgam in alcoholic solution; the former, however, are much less readily displaced than the latter.

Chlorobenzene, or phenyl chloride, C_6H_5Cl, may be described as a typical example of those halogen derivatives in which the halogen is combined with carbon of the nucleus. It may be obtained (together with dichlorobenzenes, $C_6H_4Cl_2$, trichlorobenzenes, $C_6H_3Cl_3$, &c.) by chlorinating benzene; also by treating phenol (p. 404) with phosphorus pentachloride, just as ethyl chloride may be produced from alcohol,

$$C_6H_5{\cdot}OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl.$$

It is usually prepared by Sandmeyer's reaction—that is to say, by warming an aqueous solution of diazobenzene chloride with cuprous chloride (p. 383); this method, therefore, affords a means of preparing chlorobenzene, not only from the diazo-compound, but also indirectly from amidobenzene (aniline), nitrobenzene, and benzene, in the manner already indicated (p. 355). Chlorobenzene is a colourless, mobile, pleasant-smelling liquid, specifically heavier than water; it boils at 132°, and is readily volatile in steam. Like benzene, it is capable of yielding nitro-, amido-, and other derivatives by the displacement of one or more hydrogen atoms; it differs from ethyl chloride and from other fatty alkyl halogen compounds in being unacted on by water and alkalies, or by metallic salts; it is impossible, for example, to prepare phenyl acetate, $CH_3\cdot COOC_6H_5$, by treating silver acetate with chlorobenzene, although ethyl acetate is easily obtained from ethyl chloride in this way.

Bromobenzene, or phenyl bromide, C_6H_5Br, may be prepared from diazobenzene sulphate by Sandmeyer's reaction, using cuprous bromide (p. 384); also by brominating benzene in presence of iron.

Benzene (1 part) is placed in a flask, provided with a reflux condenser, together with a little iron wire, and the bromine (2 parts) is added gradually from a stoppered funnel, the bent stem of which passes through the cork of the flask; the hydrogen bromide which is evolved is absorbed by leading it into a tower containing moist coke. The product is washed well with dilute caustic soda and water successively, dried, and separated from any unchanged benzene by fractional distillation. The *p-dibromobenzene* (m.p. 89°; b.p. 219°), which is also formed in the above reaction, remains as a residue if the distillation be stopped when the thermometer rises to about 170°; it solidifies on cooling, and may be recrystallised from aqueous alcohol.

Bromobenzene is a colourless liquid, boiling at 155°, and closely resembles chlorobenzene in all respects. As a rule, however, the bromo-derivatives crystallise more readily, and have a higher melting-point than the corresponding chloro-compounds.

Iodobenzene, C_6H_5I, cannot be obtained by the action of iodine alone on benzene, but it is formed when the hydrocarbon is heated with iodine in presence of iodic acid at about 220° (p. 353); it is most conveniently prepared by decomposing diazobenzene sulphate with potassium iodide in aqueous solution,

$$C_6H_5\cdot N_2HSO_4 + KI = C_6H_5I + KHSO_4 + N_2.$$

Aniline (1 part) is *diazotised* with sodium nitrite and sulphuric acid (compare p. 384), the cold solution of the diazo-sulphate poured into a concentrated solution of potassium iodide (2½ parts), and the mixture gradually heated until nitrogen is no longer evolved; the iodobenzene is then separated by steam distillation, washed with dilute caustic soda, dried, and distilled.

It is a heavy, colourless, mobile liquid, boiling at 188°; when it is dissolved in chloroform and dry chlorine, passed into the *well-cooled* solution, the *dichloride* $C_6H_5I<{Cl \atop Cl}$ separates in crystals (Willgerodt), the iodine becoming trivalent, as it probably is in iodine trichloride, ICl_3.

Iodobenzene dichloride is slowly decomposed by dilute caustic soda (4–5 per cent.), and if ground up with excess of such a solution, and left in contact with it for 6–8 hours, it is converted into *iodosobenzene*,

$$C_6H_5ICl_2 + 2NaOH = C_6H_5IO + 2NaCl + H_2O,$$

which can be separated by filtration, washed with water, and dried on porous earthenware.

Iodosobenzene, C_6H_5IO, is a colourless, amorphous substance, moderately easily soluble in warm water and alcohol; it explodes at about 210°. It has *basic* properties, and unites with acids forming a salt and water,

$$C_6H_5IO + 2C_2H_4O_2 = C_6H_5I(C_2H_3O_2)_2 + H_2O;$$

it is also an oxidising agent, and liberates iodine from potassium iodide in acid solution,

$$C_6H_5IO + 2HI = C_6H_5I + I_2 + H_2O.$$

When iodosobenzene is submitted to distillation in steam it undergoes a most interesting decomposition giving iodobenzene, which distils over with the water, and *iodoxybenzene*, which is non-volatile,

$$2C_6H_5IO = C_6H_5I + C_6H_5IO_2.$$

Iodoxybenzene, $C_6H_5IO_2$, separates in colourless needles when the aqueous solution is evaporated to a small volume and then allowed to cool; it explodes when heated at about 230°. Unlike iodosobenzene, it does not show basic properties, but it is an oxidising agent and liberates iodine (4 atoms) from hydriodic acid.

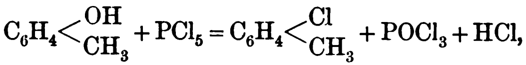
When a mixture of iodosobenzene and iodoxybenzene is shaken with water and freshly precipitated silver hydroxide, interaction takes place and *diphenyliodonium iodate* is formed,

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2I{\cdot}IO_3 + AgOH.$$

This product is the salt of a strongly basic hydroxide, $(C_6H_5)_2I{\cdot}OH$, *diphenyliodonium hydroxide*, which has only been isolated in the form of its salts; it is an interesting fact that such derivatives of trivalent iodine should show basic properties.

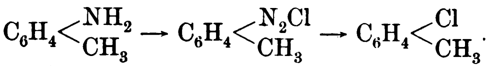
These remarkable compounds were discovered and investigated by Willgerodt and by V. Meyer; analogous compounds have been obtained from other iodo-derivatives containing the iodine atom directly united with the benzene (or naphthalene) nucleus.

Chlorotoluene, or toluyl chloride, $C_6H_4Cl{\cdot}CH_3$, being a di-substitution product of benzene, exists in three isomeric modifications, only two of which—namely, the *o-* and *p*-compounds, are formed on treating *cold* toluene with chlorine in presence of iodine or iron; the three isomerides may be separately prepared by treating the corresponding cresols (p. 408) with phosphorus pentachloride,



$$C_6H_4{<}\begin{matrix}OH\\CH_3\end{matrix} + PCl_5 = C_6H_4{<}\begin{matrix}Cl\\CH_3\end{matrix} + POCl_3 + HCl,$$

but they are best prepared from the corresponding toluidines by Sandmeyer's method,



$$C_6H_4{<}\begin{matrix}NH_2\\CH_3\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}N_2Cl\\CH_3\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}Cl\\CH_3\end{matrix}.$$

Toluidine. Diazotoluene Chloride. Chlorotoluene.

Orthochlorotoluene boils at 156°, *metachlorotoluene* at 150°, and *parachlorotoluene* at 160°; they resemble chlorobenzene in most respects, but, since they contain a methyl-group, they have also some of the properties of fatty compounds; on oxidation, they are converted into the corresponding *chlorobenzoic acids*, $C_6H_4Cl{\cdot}COOH$, just as toluene is transformed into benzoic acid.

Benzyl chloride, $C_6H_5{\cdot}CH_2Cl$, although isomeric with the three chlorotoluenes, differs from them very widely, and may be taken as an example of the class of halogen-compounds in which the halogen is present in the side-chain. It can be obtained by treating benzyl alcohol (p. 415) with phosphorus pentachloride,

$$C_6H_5{\cdot}CH_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}CH_2Cl + POCl_3 + HCl,$$

but is always prepared by passing chlorine into boiling toluene,

$$C_6H_5{\cdot}CH_3 + Cl_2 = C_6H_5{\cdot}CH_2Cl + HCl.$$

The toluene is contained in a flask which is heated on a sand-bath and connected with a reflux condenser; a stream of dry chlorine is then passed into the boiling liquid until the theoretical gain in weight has taken place and the product is purified by fractional distillation; the action takes place most rapidly in strong sunlight.

Benzyl chloride is a colourless, unpleasant-smelling liquid, boiling at 176°; it is insoluble in water, but miscible with alcohol, ether, benzene, &c. It behaves like other aromatic compounds towards nitric acid, by which it is converted into a mixture of isomeric nitro-compounds, $C_6H_4(NO_2){\cdot}CH_2Cl$. At the same time, however, it has many properties in common with the alkyl halogen compounds; like ethyl chloride, it is slowly decomposed by boiling water, yielding the corresponding hydroxy-compound, benzyl alcohol (p. 415),

$$C_6H_5{\cdot}CH_2Cl + H_2O = C_6H_5{\cdot}CH_2{\cdot}OH + HCl,$$

and just as ethyl chloride interacts with silver acetate, giving ethyl acetate, so benzyl chloride, under the same conditions, yields the ester, *benzyl acetate*,

$$C_6H_5{\cdot}CH_2Cl + CH_3{\cdot}COOAg = CH_3{\cdot}COOCH_2{\cdot}C_6H_5 + AgCl.$$

Benzyl chloride is a substance of considerable commercial importance, inasmuch as it is used for the preparation of benzaldehyde (p. 418).

Benzal chloride, $C_6H_5{\cdot}CHCl_2$, may be obtained by treating benzaldehyde with phosphorus pentachloride,

$$C_6H_5{\cdot}CHO + PCl_5 = C_6H_5{\cdot}CHCl_2 + POCl_3,$$

but it is prepared by chlorinating toluene just as described in the case of benzyl chloride, except that the process is continued until twice as much chlorine has been absorbed. It is a colourless liquid, boiling at 206°, and is extensively used for the preparation of benzaldehyde.

Benzotrichloride, or phenylchloroform, $C_6H_5{\cdot}CCl_3$, is also prepared by chlorinating boiling toluene; it boils at 213°, and when heated with water it is converted into benzoic acid,

$$C_6H_5{\cdot}CCl_3 + 2H_2O = C_6H_5{\cdot}COOH + 3HCl.$$

CHAPTER XXIII.

NITRO-COMPOUNDS.

It has already been stated that one of the most characteristic properties of aromatic compounds is the readiness with which they may be converted into nitro-derivatives by the substitution of nitro-groups for hydrogen of the *nucleus;* the compounds formed in this way are of the greatest importance, more especially because it is from them that the amido- and diazo-compounds are prepared.

Preparation.—Many aromatic compounds may be '*nitrated*'—that is to say, converted into their nitro-derivatives, by dissolving them in concentrated nitric acid (sp. gr. 1·3 to 1·5), in the cold or at ordinary temperatures, and under such conditions a mononitro-compound is usually produced; benzene, for example, yields nitrobenzene, and toluene, a mixture of *o*- and *p*-nitrotoluenes,

$$C_6H_6 + HNO_3 = C_6H_5{\cdot}NO_2 + H_2O$$
$$C_6H_5{\cdot}CH_3 + HNO_3 = C_6H_4(CH_3){\cdot}NO_2 + H_2O.$$

Some aromatic compounds, however, are insoluble in nitric acid, and are then only very slowly acted on; in such cases a mixture of concentrated nitric and sulphuric acids is used. This mixture is also employed in many cases, even when the substance is soluble in nitric acid, because the sulphuric acid combines with the water which is produced during the interaction. When a large excess of such a mixture is used, and especially when heat is applied, the aromatic compound is usually converted into (a mixture of isomeric) dinitro- or trinitro-derivatives; benzene, for instance, yields a mixture of three dinitro-benzenes, the principal product, however, being the meta-compound,

$$C_6H_6 + 2HNO_3 = C_6H_4(NO_2)_2 + 2H_2O.$$

As soon as nitration is complete (portions of the product may be tested from time to time), the solution or mixture, having been cooled if necessary, is poured on to ice or into a large volume of water, and the product, which is usually precipitated in crystals, separated by filtration, or if an oil, by extraction with ether, or in some other manner.

Generally speaking, the number of hydrogen atoms displaced by nitro-groups is greater the higher the temperature and the more concentrated the acid, or mixture of acids, employed, but depends to an even greater extent on the nature of the substance undergoing nitration, because the introduction of nitro-groups is facilitated when other atoms or groups, especially alkyl radicles, have already been substituted for hydrogen of the nucleus. The nature of these atoms or groups determines, moreover, the position taken up by the entering nitro-group; if the former be strongly negative or acid in character, as, for example, $-NO_2$, $-COOH$, and $-SO_3H$, a *m*-nitro-derivative is formed, whereas, when the atom or group in question is a halogen, an alkyl, or an amido- or hydroxyl-group, a mixture of the *o*- and *p*-nitro-derivatives is produced.

This *directing* influence of an atom or group already combined with the nucleus, on the position which is taken up by a second atom or group, is by no means restricted to the case of nitro-compounds, but is observed in the formation of all benzene substitution derivatives, except, of course, in that of the mono-substitution products; so regularly, in fact, is this influence exercised that it is possible to summarise the course of those reactions which take place in the formation of the best-known di-derivatives in the following statements:

The relative position taken up by the following atoms or groups, Cl, Br, NO_2, SO_3H, which are capable of directly displacing hydrogen of the nucleus, depends on the nature of the atom or group, A, already united with the nucleus.

When A = Cl, Br, I, NH_2, OH, CH_3 (or other fatty alkyl), a *para*-compound is the principal product, but it is usually accompanied by smaller and varying quantities of the ortho-compound.

When, on the other hand,

$$A = NO_2, COOH, SO_3H, CHO, CO{\cdot}CH_3, CN,$$

a *meta*-derivative is the principal product, and only very small quantities of the ortho- and para-compounds are formed.

These statements also hold good when two identical atoms or groups are introduced in one operation, since the change really takes place in two stages; when benzene, for example, is treated with nitric acid, meta-dinitrobenzene is the principal product, whereas with bromine it yields para-dibromobenzene.

Properties.—As a rule, aromatic nitro-compounds are yellowish, well-defined, crystalline substances, and are, therefore, of great service in identifying hydrocarbons and other liquids; many of them are volatile in steam, but, with the exception of certain mono-nitro-derivatives, cannot be distilled under ordinary pressure, as when heated strongly they undergo decomposition, sometimes with explosive violence; they are generally insoluble in water, but soluble in benzene, ether, alcohol, &c. As in the case of the nitro-paraffins (Part I. p. 184), the nitro-group is very firmly combined, and is not, as a rule, displaced by the hydroxyl-group on treatment with aqueous or alcoholic potash even at high temperatures.

The most important reaction of the nitro-compounds—namely, their behaviour on reduction, is described later (p. 368).

Nitrobenzene, $C_6H_5 \cdot NO_2$, is usually prepared in the laboratory by slowly adding to benzene (10 parts) a mixture of nitric acid of sp. gr. 1·45 (12 parts) and concentrated sulphuric acid (16 parts), the temperature being kept below about 40° by cooling in water.

The nitrobenzene separates at the surface as a yellow oil, which takes up the benzene, so that it is necessary to bring the latter into contact with the acid mixture by giving the vessel a rotatory motion. As soon as all the benzene has been added, the mixture is heated at about 80° for half-an-hour, then cooled, and poured into a large volume of water; the nitrobenzene, which collects at the bottom of the vessel, is separated with the aid of a funnel, washed with a little water or dilute soda until free from acid, dried with anhydrous calcium chloride, and fractionated, in order to separate it from unchanged benzene and from small quantities of dinitrobenzene which may have been produced; this is very easily accomplished, as the boiling-points of the three compounds are widely different.

On the large scale, nitrobenzene is prepared in a similar manner, the operation being carried out in iron vessels provided with an arrangement for stirring, and the product is distilled from iron retorts, or, better, in a current of steam.

Nitrobenzene is a pale-yellow oil of sp. gr. 1·2 at 20°, and has a strong smell, which is very like that of benzaldehyde (p. 418); it boils at 205°, is volatile in steam, and is miscible with organic liquids, but practically insoluble in water; in spite of the fact that it is poisonous, it is often employed instead of oil of bitter almonds for flavouring and perfuming purposes, under the name of 'essence of mirbane;' its principal use, however, is for the manufacture of aniline (p. 373).

Meta-dinitrobenzene, $C_6H_4(NO_2)_2$, is obtained, together with small quantities of the *o*- and *p*-dinitro-compounds, when nitrobenzene (1 part) is gradually added to a mixture of nitric acid (sp. gr. 1·5; 1½ parts) and concentrated sulphuric acid (1½ parts), and the whole then heated on a sand-bath, until a drop of the oil, which floats on the surface, solidifies completely when stirred with cold water.

After cooling, the mixture is poured into a large volume of water, the solid product separated by filtration, washed with water, and recrystallised from hot alcohol until its melting-point is constant; the *o*- and *p*-compounds, formed only in very small quantities, remain dissolved in the mother-liquors.

Meta-dinitrobenzene crystallises in pale-yellow needles, melts at 90°, and is volatile in steam; it is only sparingly soluble in boiling water, but dissolves freely in most organic liquids. On reduction with alcoholic ammonium sulphide (p. 369) it is first converted into *m*-nitraniline (p. 375), and then into *m*-phenylenediamine or meta-diamidobenzene, $C_6H_4(NH_2)_2$ (p. 376).

o-Dinitrobenzene and *p-dinitrobenzene* are colourless, crystalline compounds, melting at 118° and 173° respectively; they resemble the corresponding *m*-compound in their behaviour on reduction, and in most other respects. *o*-Dinitrobenzene, however, differs notably from the other two isomerides, inasmuch as it interacts with boiling soda, yielding *o*-nitrophenol (p. 405), and, with alcoholic ammonia at moderately high temperatures, giving *o*-nitraniline (p. 375). A similar behaviour is observed in the case of other *o*-dinitro-compounds, the presence of the one nitro-group rendering the other more easily displaceable.

Symmetrical *trinitrobenzene*, $C_6H_3(NO_2)_3$, is formed when the *m*-dinitro-compound is heated with a mixture of nitric and anhydrosulphuric acids; it crystallises in colourless plates and needles, melting at 121–122°.

The halogen derivatives of benzene are readily nitrated, yielding, however, the *o*- and *p*-mononitro-derivatives only, according to the general rule; the *m*-nitro-halogen compounds are therefore prepared by chlorinating or brominating nitrobenzene. All these nitro-halogen derivatives are crystalline, and, as will be seen from the following table, their melting-points exhibit the regularity already mentioned (p. 342), except in the case of *m*-iodonitrobenzene.

		Ortho.	Meta.	Para.
Chloronitrobenzene,	$C_6H_4Cl{\cdot}NO_2$,	32·5°	44·4°	83°
Bromonitrobenzene,	$C_6H_4Br{\cdot}NO_2$,	41·5	56	126
Iodonitrobenzene,	$C_6H_4I{\cdot}NO_2$,	49	33	171

They are, on the whole, very similar in chemical properties, except that, as already pointed out (p. 356), the *o*- and *p*-compounds differ from the *m*-compounds in their behaviour with alcoholic potash and ammonia, a difference which recalls that shown by the three dinitrobenzenes.

The **nitrotoluenes**, $C_6H_4(CH_3){\cdot}NO_2$, are important, because they serve for the preparation of the toluidines (p. 376). The *o*- and *p*-compounds are prepared by nitrating toluene, and may be partially separated by fractional distillation; *o-nitrotoluene* melts at 10·5° and boils at 218°, whereas *p-nitrotoluene* melts at 54° and boils at 230°. *m-Nitrotoluene* is not easily prepared; it melts at 16°, and boils at 230°.

Many other nitro-compounds are mentioned later.

CHAPTER XXIV.

AMIDO-COMPOUNDS AND AMINES.

The hydrogen atoms in ammonia may be displaced by aromatic radicles, bases, such as aniline, $C_6H_5{\cdot}NH_2$, benzylamine, $C_6H_5{\cdot}CH_2{\cdot}NH_2$, and diamidobenzene, $C_6H_4(NH_2)_2$, which are analogous to, and have many properties in common with, the fatty amines, being produced; as, however, those compounds which contain the amido-group directly united with carbon of the nucleus differ in many important respects from those in which this group is present in the side-chain, the former are usually called *amido-compounds*, whereas the latter are classed as *aromatic amines*, because they are the true analogues of the fatty amines.

Amido-compounds.

The amido-compounds may, therefore, be regarded as derived from benzene and its homologues by the substitution of one or more amido-groups for hydrogen atoms of the *nucleus;* they may be classed as mono-, di-, tri-, &c., amido-compounds, according to the number of such groups which they contain.

$C_6H_5{\cdot}NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$.
Amidobenzene (Aniline).	Diamidobenzene.	Triamidobenzene.

With the exception of aniline, all amido-compounds exist in three or more isomeric modifications; there are, for example, three isomeric (*o.m.p.*) diamidobenzenes, and three isomeric (*o.m.p.*) amidotoluenes, or toluidines, $C_6H_4(CH_3){\cdot}NH_2$, a fourth isomeride of the toluidines—namely, benzylamine, $C_6H_5{\cdot}CH_2{\cdot}NH_2$ (p. 380)—being also known.

Preparation.—The amido-compounds are almost always prepared by the reduction of the nitro-compounds; various reducing agents, such as tin, zinc, or iron, and hydrochloric or acetic acid, are employed, but perhaps the most common one is a solution of stannous chloride in hydrochloric acid,

$$C_6H_5{\cdot}NO_2 + 6H = C_6H_5{\cdot}NH_2 + 2H_2O$$
$$C_6H_4(CH_3){\cdot}NO_2 + 6H = C_6H_4(CH_3){\cdot}NH_2 + 2H_2O$$
$$C_6H_5{\cdot}NO_2 + 3SnCl_2 + 6HCl = C_6H_5{\cdot}NH_2 + 3SnCl_4 + 2H_2O.$$

Reduction is usually effected by simply treating the nitro-compound with the reducing mixture without a special solvent, when a vigorous reaction often ensues, heating being seldom necessary except towards the end of the operation. The solution contains the amido-compound, combined as a salt with the acid which has been employed; when, however, tin or stannous chloride and hydrochloric acid have been used, a double salt of the hydrochloride of the base and stannic chloride is produced; in the reduction of nitrobenzene, for example, the double salt, *aniline stannichloride*, has the composition $(C_6H_5{\cdot}NH_2, HCl)_2, SnCl_4$. The amido-compound is liberated by adding excess of caustic soda or lime, and distilled with steam, extracted with ether, or isolated in some other manner suitable to the special case.

The reduction of nitro-compounds takes place in two stages: in the first there is produced an unstable derivative of hydroxylamine,

$$R{\cdot}NO_2 + 4H = R{\cdot}NH{\cdot}OH + H_2O,$$

which, by the further action of the reducing agent, is converted into the amido-compound.

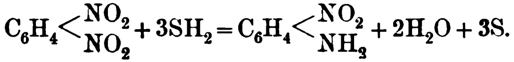
β-Phenylhydroxylamine is a crystalline substance, melting at 81°, and, like hydroxylamine, it is a base and forms salts such as the hydrochloride $C_6H_5{\cdot}NH{\cdot}OH, HCl$. When oxidised with potassium dichromate and dilute sulphuric acid, it yields *nitrosobenzene*, $C_6H_5{\cdot}NO$, a crystalline, very volatile substance, melting at 68°, which on oxidation is converted into nitrobenzene, and on reduction, into aniline.

Nitro-compounds may also be reduced to amido-compounds by employing hydrogen sulphide in alkaline solution, or, more conveniently, an alcoholic solution of ammonium sulphide,

$$C_6H_5{\cdot}NO_2 + 3SH_2 = C_6H_5{\cdot}NH_2 + 2H_2O + 3S.$$

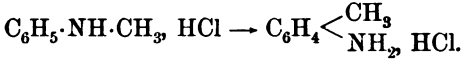
The nitro-compound is dissolved in alcohol, concentrated ammonia added, and a stream of hydrogen sulphide passed into the solution, until reduction is complete, heat being applied if necessary. The solution is then filtered from precipitated sulphur, the alcohol distilled off, and the residue acidified with hydrochloric acid; the filtered solution of the hydrochloride of the base is now evaporated to a small bulk and treated with soda, when the base separates as an oil or solid, and may then be purified by distillation, recrystallisation, &c.

When there are two or more nitro-groups in a compound, partial reduction may be accomplished either by treating its alcoholic solution with the calculated quantity of stannous chloride and hydrochloric acid, or by adding strong ammonia and passing hydrogen sulphide; in the latter, as in the former case, one nitro-group is reduced before a second is attacked, so that by stopping the current of gas at the right time (sometimes ascertained by finding the increase in weight), only partial reduction takes place. Dinitrobenzene, for example, can be converted into nitraniline by either of these methods, the latter being the more convenient,



$$C_6H_4<\begin{matrix}NO_2\\NO_2\end{matrix} + 3SH_2 = C_6H_4<\begin{matrix}NO_2\\NH_2\end{matrix} + 2H_2O + 3S.$$

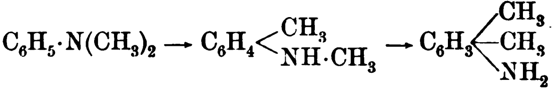
The amido-derivatives of toluene, xylene, &c. are prepared commercially by heating the hydrochlorides of the isomeric alkylanilines, such as methylaniline and dimethylaniline (p. 378), at 280–300°, when the alkyl-group leaves the nitrogen atom and enters the nucleus,



$$C_6H_5{\cdot}NH{\cdot}CH_3,\ HCl \longrightarrow C_6H_4<\begin{matrix}CH_3\\NH_2\end{matrix},\ HCl.$$

Methylaniline Hydrochloride. **p-Toluidine Hydrochloride.**

In the case of dimethylaniline the change takes place in two stages, which may be represented as follows,



$$C_6H_5{\cdot}N(CH_3)_2 \longrightarrow C_6H_4<\begin{matrix}CH_3\\NH{\cdot}CH_3\end{matrix} \longrightarrow C_6H_3\begin{matrix}CH_3\\CH_3\\NH_2\end{matrix}$$

Dimethylaniline. **Methyl-p-toluidine.** **Xylidine.**

In this remarkable *isomeric change* the alkyl-group displaces hydrogen from the ortho- and from the para-position to the amido-group, but principally the latter; meta-derivatives cannot be prepared in this way.

The diamido-compounds, such as the *o*-, *m*-, and *p*-diamidobenzenes or phenylenediamines, $C_6H_4(NH_2)_2$, are prepared by reducing either the corresponding dinitrobenzenes, $C_6H_4(NO_2)_2$, or the nitranilines, $C_6H_4(NO_2){\cdot}NH_2$, generally with tin and hydrochloric acid.

Properties.—The *monamido*-compounds are mostly colourless liquids, which distil without decomposing, and are specifically heavier than water; they have a faint but characteristic odour, and dissolve freely in alcohol, ether, and other organic solvents, but they are only sparingly soluble or insoluble in water; on exposure to air and light they darken, and ultimately become brown or black.

They are comparatively weak bases, and are neutral to litmus, in which respect they differ from the strongly basic fatty amines and from the true aromatic amines, such as benzylamine (p. 380); nevertheless they combine with acids to form salts, such as aniline hydrochloride, $C_6H_5 \cdot NH_2$, HCl, which, however, are readily decomposed by weak alkalies or alkali carbonates, with liberation of the bases.

It will be seen, therefore, that the substitution of the phenyl radicle, C_6H_5-, for one of the hydrogen atoms in ammonia has the effect of diminishing or partially neutralising the basic character of the latter, a result which is directly the opposite of that arrived at by displacing the hydrogen atoms of ammonia by an alkyl (or positive) group, since the amines are stronger bases than ammonia; for this and other reasons (p. 403) the hypothetical phenyl-group is regarded as a negative or acid radicle.

When two hydrogen atoms in ammonia are displaced by phenyl-groups, as in diphenylamine, $(C_6H_5)_2NH$ (p. 379), the product is so feebly basic that its salts are decomposed by water. Triphenylamine, $(C_6H_5)_3N$ (p. 380), moreover, does not form salts at all.

For the same reason the hydroxy-, nitro-, and halogen-derivatives of the amido-compounds, such as amido-phenol, $C_6H_4(OH) \cdot NH_2$, nitraniline, $C_6H_4(NO_2) \cdot NH_2$, chloraniline, $C_6H_4Cl \cdot NH_2$, &c., are even weaker bases than the amido-compounds themselves, because the presence of the negative group or atom, $HO-$, NO_2-, $Cl-$, &c., enhances the acid character of the phenyl radicle.

The amido-compounds differ from the fatty primary amines and from the true aromatic primary amines in their remarkable behaviour with nitrous acid. Although when *warmed* with nitrous acid in aqueous solution they yield phenols by the substitution of hydroxyl for the amido-group, just as the fatty amines under similar treatment are converted into alcohols (Part I. p. 207),

$$C_6H_5 \cdot NH_2 + NO_2H = C_6H_5 \cdot OH + N_2 + H_2O$$
$$C_2H_5 \cdot NH_2 + NO_2H = C_2H_5 \cdot OH + N_2 + H_2O,$$

yet when treated with nitrous acid in *cold* aqueous solution, they are converted into diazo-compounds (p. 381), substances which are not produced from the primary amines, It will be evident from the above statements that there are several important differences between the amido-compounds and the true primary amines, the character of an amido-group in the nucleus being influenced by its state of combination; nevertheless, except as regards those points already mentioned, amido-compounds have, on the whole, properties very similar to those of the true primary amines.

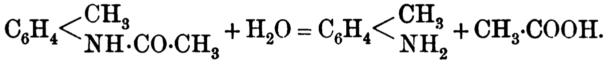
The amido-compounds, like the primary amines, interact readily with alkyl halogen compounds, yielding alkyl-derivatives, such as methylaniline, $C_6H_5{\cdot}NH{\cdot}CH_3$, dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$, &c., and also compounds such as phenyltrimethylammonium iodide, $C_6H_5{\cdot}N(CH_3)_3I$, which correspond with the quaternary ammonium salts (Part I. p. 210).

They are also readily acted on by acid chlorides and anhydrides, and even by acids on prolonged heating, yielding substances such as acetanilide and acetotoluidide, which are closely allied to the fatty amides (Part I. p. 164), and from which they may be regarded as derived,

$$C_6H_5{\cdot}NH_2 + CH_3{\cdot}COCl = C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3 + HCl$$

$$\underset{p\text{-Toluidine.}}{C_6H_4(CH_3){\cdot}NH_2} + (CH_3{\cdot}CO)_2O = \underset{\text{Aceto-}p\text{-toluidide.}}{C_6H_4(CH_3){\cdot}NH{\cdot}CO{\cdot}CH_3} + CH_3{\cdot}COOH;$$

these compounds are crystalline, and serve for the identification of the (liquid) amido-compounds; like the amides, they are generally resolved into their constituents when boiled with acids or alkalies,



$$C_6H_4{<}\begin{matrix}CH_3\\NH{\cdot}CO{\cdot}CH_3\end{matrix} + H_2O = C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix} + CH_3{\cdot}COOH.$$

The amido-compounds, like the fatty primary amines, give the carbylamine reaction; when a trace of aniline, for example, is heated with alcoholic potash and chloroform, an intensely nauseous smell is observed, due to the formation of phenylcarbylamine (Part I. pp. 207, 294),

$$C_6H_5{\cdot}NH_2 + CHCl_3 + 3KOH = C_6H_5{\cdot}N\vdots C + 3KCl + 3H_2O.$$

Diamido- and *triamido-compounds*, such as the three (*o. m. p.*) phenylenediamines or diamidobenzenes, $C_6H_4(NH_2)_2$, and the triamidobenzenes, $C_6H_3(NH_2)_3$, are very similar to the mon-amido-compounds in chemical properties, but differ from them usually in being solid, more readily soluble in water, and less volatile; the triamido-compounds generally form salts, such as $C_6H_3(NH_2)_3, 2HCl$, with only *two* equivalents of an acid.

Aniline and its Derivatives.

Aniline, amidobenzene, or phenylamine, $C_6H_5{\cdot}NH_2$, was first prepared by Unverdorben in 1826 by distilling indigo, the name aniline being derived from *anil*, the Spanish for indigo. Runge in 1834 showed that aniline is contained in small quantities in coal-tar, but its preparation from nitrobenzene was first accomplished by Zinin in 1841.

Aniline is manufactured on a very large scale by the reduction of nitrobenzene with scrap iron and crude hydrochloric acid; but in preparing small quantities in the laboratory, the most convenient reducing agent is tin and hydrochloric acid,

$$C_6H_5{\cdot}NO_2 + 6H = C_6H_5{\cdot}NH_2 + 2H_2O,$$
$$2C_6H_5{\cdot}NO_2 + 3Sn + 12HCl = 2C_6H_5{\cdot}NH_2 + 3SnCl_4 + 4H_2O.$$

Nitrobenzene (50 grams) and granulated tin (80 grams) are placed in a flask, and concentrated hydrochloric acid (290 grams) added in small quantities at a time; at first the mixture must be cooled if the reaction be too violent, but when all the acid has been added, the product is gently heated on a water-bath until drops of nitrobenzene are no longer visible. The solution of aniline stannichloride is now treated with soda until strongly alkaline, the liberated aniline distilled in steam, and, after saturating the distillate with salt, the base is separated with the aid of a funnel, dried over solid potash, and purified by distillation.

Aniline is a poisonous oil, boiling at 184°; it has a faint, characteristic odour, and is sparingly soluble in water, but readily in alcohol and ether; it gradually turns yellow when exposed to light and air, becoming ultimately almost black. Although neutral to litmus, aniline has very decided basic properties, and neutralises acids, forming soluble salts, such as aniline *hydrochloride*, $C_6H_5{\cdot}NH_2$, HCl, and the rather sparingly soluble *sulphate*, $(C_6H_5{\cdot}NH_2)_2$, H_2SO_4. The former, like the hydrochlorides of ethylamine, &c., forms double salts with platinic and auric chlorides; on treating a moderately concentrated solution of the hydrochloride with platinic chloride, for example, the *platinichloride*,

$$(C_6H_5{\cdot}NH_2)_2,\ H_2PtCl_6,$$

is precipitated in yellow plates, which are moderately soluble in water.

When aniline (*one drop* *) is heated with chloroform and alcoholic potash it yields phenylcarbylamine, $C_6H_5{\cdot}N{\vdots}C$, a substance readily recognised by its extremely disagreeable odour; the presence of aniline may also be detected by treating its aqueous solution with bleaching-powder solution or sodium hypochlorite, when an intense purple colouration is produced.

When solutions of the salts of aniline are treated with nitrous acid, at ordinary temperatures, salts of diazo-compounds (p. 381) are formed; but on warming, the latter are decomposed with formation of phenol (p. 404).

Aniline is very largely employed in the manufacture of dyes, and in the preparation of a great number of benzene derivatives.

Acetanilide, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$, is readily prepared by boiling aniline with excess of glacial acetic acid on a reflux apparatus for several hours, when the aniline acetate first formed is slowly converted into acetanilide, with elimination of water. The product is purified by distillation or simply by recrystallisation from boiling water,

$$C_6H_5{\cdot}NH_2,\ CH_3{\cdot}COOH = C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3 + H_2O.$$

It crystallises in glistening plates, melts at 112°, and is sparingly soluble in cold, but readily in hot water; when heated with acids or alkalies it is rapidly hydrolysed, giving

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* Compare Part I. p. 176.

aniline and acetic acid. It is used in medicine, under the name of *antifebrin*, for reducing the temperature of the body in cases of fever, &c.

Formanilide, $C_6H_5\cdot NH\cdot CHO$, the anilide of formic acid, and *oxanilide*, $C_6H_5\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_5$, the anilide of oxalic acid, may be similarly prepared.

Substitution Products of Aniline.—Aniline and, in fact, all amido-compounds are much more readily attacked by halogens than are the hydrocarbons. When aniline, for example, is treated with chlorine or bromine in aqueous solution, it is at once converted into *trichloraniline*, $C_6H_2Cl_3\cdot NH_2$, or *tribromaniline*, $C_6H_2Br_3\cdot NH_2$, so that in order to obtain mono- and di-substitution products indirect methods must be employed.

The *o*- and *p-chloranilines*, $C_6H_4Cl\cdot NH_2$, may be prepared by passing chlorine into acetanilide, the *p*-derivative being obtained in the larger quantity. The two isomerides are first separated by crystallisation, and then decomposed by boiling with an alkali or acid,

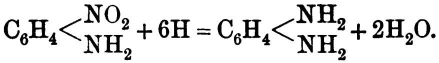
$$\underset{\text{Chloracetanilide.}}{C_6H_4Cl\cdot NH\cdot CO\cdot CH_3} + KOH = \underset{\text{Chloraniline.}}{C_6H_4Cl\cdot NH_2} + CH_3\cdot COOK.$$

The effect of introducing an acetyl-group into the amido-group is therefore to render aniline less readily attacked; acetanilide, in fact, behaves towards chlorine and bromine more like benzene than aniline. *m*-Chloraniline is most conveniently prepared by the reduction of *m*-chloronitrobenzene, $C_6H_4Cl\cdot NO_2$ (a substance formed by chlorinating nitrobenzene in the presence of antimony). *o*-Chloraniline and *m*-chloraniline are oils boiling at 207° and 230° respectively, but *p*-chloraniline is a solid, which melts at 70° and boils at 230°.

Nitranilines, $C_6H_4(NO_2)\cdot NH_2$, cannot be obtained by nitrating aniline, as the nitrous acid, produced by the reduction of the nitric acid, converts the amido- into the hydroxyl-group, and nitro-derivatives of phenol are formed.

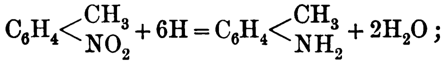
The *o*- and *p*-compounds are prepared by nitrating acetanilide, the *o*- and *p*-nitracetanilides thus obtained being separated by fractional crystallisation, and then converted into the corresponding nitranilines by heating with alkalies. *m*-Nitraniline is very readily prepared by the partial reduction of *m*-dinitrobenzene, $C_6H_4(NO_2)_2$, with ammonium sulphide (p. 369).

o-Nitraniline melts at 71°, *m*- at 114°, and *p*- at 147°; they are all sparingly soluble in cold water, readily in alcohol, and on reduction they yield the corresponding *o*-, *m*-, and *p*-phenylenediamines,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{NO_2}{NH_2} + 6H = C_6H_4{<}\genfrac{}{}{0pt}{}{NH_2}{NH_2} + 2H_2O.$$

Homologues of Aniline.—The *toluidines*, or amido-toluenes, $C_6H_4(CH_3){\cdot}NH_2$, are prepared by reducing the corresponding *o*-, *m*-, and *p*-nitrotoluenes (p. 367), by means of tin and hydrochloric acid, the details of the process being exactly similar to those already given in the case of the preparation of aniline from nitrobenzene,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{NO_2} + 6H = C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{NH_2} + 2H_2O;$$

the *o*- and *p*-compounds may also be prepared from methylaniline (p. 370). Both *o*- and *m*-toluidine are oils boiling at 197° and 199° respectively, but *p*-toluidine is crystalline, and melts at 45°, boiling at 198°. When treated with nitrous acid the toluidines yield diazo-salts, from which the corresponding cresols, $C_6H_4(CH_3){\cdot}OH$, are obtained, and in all other reactions they show the greatest similarity to aniline; *o*- and *p*-toluidine are largely employed in the manufacture of dyes.

Diamidobenzenes.—The *phenylenediamines*, $C_6H_4(NH_2)_2$, are obtained by the reduction of the corresponding dinitrobenzenes, or the nitranilines, and a general description of their properties has already been given (p. 373); *o*-phenylenediamine melts at 102°, the *m*- and *p*-compounds at 63° and 147° respectively. *m*-Phenylenediamine gives an intense yellow colouration with a trace of nitrous acid, and is employed in water-analysis for the detection and estimation of nitrites; both the *m*- and *p*-compounds are largely employed in the manufacture of dyes.

Alkylanilines.

Those derivatives of the amido-compounds obtained by displacing one or both of the hydrogen atoms of the amido-group by alkyl radicles are substances of considerable importance, and are usually known as **alkylanilines.** They are prepared by heating the amido-compounds, for some hours, with the alkyl halogen compounds, the reaction being analogous to that which occurs in the formation of secondary and tertiary from primary amines (p. 381),

$$C_6H_5{\cdot}NH_2 + RCl = C_6H_5{\cdot}NHR,\ HCl$$
$$C_6H_5{\cdot}NH_2 + 2RCl = C_6H_5{\cdot}NR_2,\ HCl + HCl.$$

Instead of employing the alkyl halogen compounds, a mixture of the corresponding alcohol and halogen acid may be used; methyl- and dimethyl-aniline, for example, are prepared, on the large scale, by heating aniline with methyl alcohol and hydrochloric acid at 200–250°,

$$C_6H_5{\cdot}NH_2,\ HCl + CH_3{\cdot}OH = C_6H_5{\cdot}NH(CH_3),\ HCl + H_2O$$
$$C_6H_5{\cdot}NH_2,\ HCl + 2CH_3{\cdot}OH = C_6H_5{\cdot}N(CH_3)_2,\ HCl + 2H_2O.$$

These mono- and di-alkyl derivatives are stronger bases than the amido-compounds from which they are derived, the presence of the positive alkyl-group counteracting to some extent the action of the negative phenyl-group (compare p. 371); they are, in fact, very similar in properties to the fatty secondary and tertiary amines respectively, and may be regarded as derived from the fatty primary amines by the substitution of a phenyl-group for a hydrogen atom, just as the secondary and tertiary amines are obtained by displacing hydrogen atoms by alkyl-groups. Methylaniline, for example, is also phenylmethylamine, and its properties are those of a substitution product of methylamine.

The mono-alkylanilines, like the secondary amines, are converted into yellowish nitroso-compounds on treatment with nitrous acid,

$$C_6H_5{\cdot}NH{\cdot}CH_3 + HO{\cdot}NO = C_6H_5{\cdot}N(NO){\cdot}CH_3 + H_2O.$$

Methylaniline. Nitrosomethylaniline.

$$(CH_3)_2NH + HO{\cdot}NO = (CH_3)_2{\cdot}N{\cdot}NO + H_2O.$$

Dimethylamine. Nitrosodimethylamine.

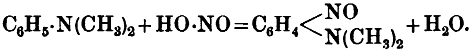
These nitroso-compounds give Liebermann's nitroso-reaction (Part I. p. 209), and on reduction they yield ammonia and the original alkylaniline,

$$C_6H_5{\cdot}N(NO){\cdot}CH_3 + 6H = C_6H_5{\cdot}NH{\cdot}CH_3 + NH_3 + H_2O.$$

Methylaniline, $C_6H_5{\cdot}NH{\cdot}CH_3$, prepared as just described, is a colourless liquid which boils at 192°, and, compared with aniline, has strongly basic properties. On adding sodium nitrite to its solution in hydrochloric acid, *nitrosomethylaniline*, $C_6H_5{\cdot}N(NO){\cdot}CH_3$, separates as a light-yellow oil.

Dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$, the preparation of which has just been given, is a colourless, strongly basic oil, which boils at 192°; it is largely used in the manufacture of dyes.

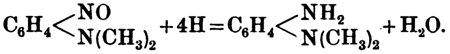
The di-alkylanilines, such as dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$, also interact readily with nitrous acid (a behaviour which is *not* shown by tertiary fatty amines), intensely green (iso)nitroso-compounds being formed, the NO– group displacing hydrogen of the *nucleus* from the *p*-position to the nitrogen atom,



$$C_6H_5{\cdot}N(CH_3)_2 + HO{\cdot}NO = C_6H_4{<}\begin{array}{l}NO\\N(CH_3)_2\end{array} + H_2O.$$

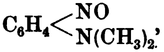
Nitrosodimethylaniline.

These substances do not give Liebermann's nitroso-reaction, and when reduced they yield derivatives of *p*-phenylenediamine,

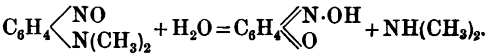


$$C_6H_4{<}\begin{array}{l}NO\\N(CH_3)_2\end{array} + 4H = C_6H_4{<}\begin{array}{l}NH_2\\N(CH_3)_2\end{array} + H_2O.$$

Dimethyl-*p*-phenylenediamine.



p-Nitrosodimethylaniline, $C_6H_4{<}\begin{array}{l}NO\\N(CH_3)_2\end{array}$, is prepared by dissolving dimethylaniline (1 part) in water (5 parts), and concentrated hydrochloric acid (2·5 parts), and gradually adding to the well-cooled solution the calculated quantity of sodium nitrite, dissolved in a little water. The yellow crystalline precipitate of nitrosodimethylaniline hydrochloride is separated by filtration, dissolved in water, decomposed by potassium carbonate, and the free base extracted with ether. Nitrosodimethylaniline crystallises from ether in dark-green plates, and melts at 85°; it is not a nitrosamine, because the NO– group is not united to nitrogen, and does not give Liebermann's nitroso-reaction. When reduced with zinc and hydrochloric acid it is converted into *dimethyl-p-phenylenediamine* (see above), and when boiled with dilute soda it is decomposed into dimethylamine and *p-nitrosophenol* or *quinone monoxime* (compare p. 426),



$$C_6H_4\left\langle\begin{matrix}NO\\N(CH_3)_2\end{matrix}\right. + H_2O = C_6H_4\left\langle\!\!\left\langle\begin{matrix}N\cdot OH\\O\end{matrix}\right.\right. + NH(CH_3)_2.$$

Diphenylamine and Triphenylamine.

The hydrogen atoms of the amido-group in aniline may also be displaced by phenyl radicles, the compounds diphenylamine, $(C_6H_5)_2NH$, and triphenylamine, $(C_6H_5)_3N$, being produced. These substances, however, cannot be obtained by treating aniline with chlorobenzene, C_6H_5Cl, a method which would be analogous to that which is employed in the preparation of diethylamine and triethylamine, because the halogen is so firmly bound to the nucleus that no action takes place even when the substances are heated together.

Diphenylamine is most conveniently prepared by heating aniline hydrochloride with aniline at about 240° in closed vessels,

$$C_6H_5\cdot NH_2,\ HCl + C_6H_5\cdot NH_2 = (C_6H_5)_2\cdot NH + NH_4Cl.$$

It is a crystalline substance, melts at 54°, boils at 310°, and is insoluble in water. It is only a feeble base, and its salts are decomposed by water; its solution in concentrated sulphuric acid gives with a trace of nitric acid an intense blue colouration, and it therefore serves as a very delicate test for nitric acid or nitrates. Diphenylamine is largely used in the manufacture of dyes, also for experiments in which a high constant temperature is required, as, for example, in determining the vapour density of substances of high boiling-point by V. Meyer's method. When treated with potassium, diphenylamine yields a solid potassium derivative, $(C_6H_5)_2NK$, the presence of the two phenyl-groups being sufficient to impart to the >NH group a feeble acid character, similar to that of imides (Part I. p. 243).

Triphenylamine, $(C_6H_5)_3N$, may be prepared by heating potassium diphenylamine with bromobenzene at 300°,

$$(C_6H_5)_2NK + C_6H_5Br = (C_6H_5)_3N + KBr.$$

It is a colourless, crystalline substance, melts at 127°, and does not combine with acids.

Aromatic Amines.

The true aromatic amines—namely, those compounds in which the amido-group is united with carbon of the *side-chain*—are of far less importance than the amido-compounds, and, as will be seen from the following example, they closely resemble the fatty amines in chemical properties.

Benzylamine, $C_6H_5{\cdot}CH_2{\cdot}NH_2$, may be obtained by reducing phenyl cyanide (benzonitrile, p. 433) or benzaldoxime (p. 419),

$$C_6H_5{\cdot}CN + 4H = C_6H_5{\cdot}CH_2{\cdot}NH_2$$
$$C_6H_5{\cdot}CH{:}NOH + 4H = C_6H_5{\cdot}CH_2{\cdot}NH_2 + H_2O,$$

by treating the amide of phenylacetic acid (p. 442) with bromine and potash,

$$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH_2 + Br_2 + 4KOH = C_6H_5{\cdot}CH_2{\cdot}NH_2 + 2KBr + K_2CO_3 + 2H_2O,$$

and by heating benzyl chloride with alcoholic ammonia,

$$C_6H_5{\cdot}CH_2Cl + NH_3 = C_6H_5{\cdot}CH_2{\cdot}NH_2,\ HCl.$$

All these methods are similar to those employed in the preparation of fatty primary amines (Part I. pp. 211–212).

Benzylamine is a colourless, pungent-smelling liquid, boiling at 187°; it closely resembles the fatty amines in nearly all respects, and differs from the monamido-compounds (aniline, toluidine, &c.) in being strongly basic, alkaline to litmus, and readily soluble in water. Like the fatty primary amines, it gives the carbylamine reaction, and when solutions of its salts are treated with nitrous acid it is converted into the corresponding alcohol (benzyl alcohol, p. 415), and *not* into a diazo-compound.

Secondary and tertiary aromatic amines are formed when a primary amine is heated with an aromatic halogen compound, containing the halogen in the side-chain; when, for example, benzylamine is heated with benzyl chloride, both *dibenzylamine* and *tribenzylamine* are produced, just as diethylamine and triethylamine are obtained when ethylamine is heated with ethyl bromide,

$$C_6H_5{\cdot}CH_2{\cdot}NH_2 + C_6H_5{\cdot}CH_2Cl = (C_6H_5{\cdot}CH_2)_2NH,\ HCl$$
$$C_6H_5{\cdot}CH_2{\cdot}NH_2 + 2C_6H_5{\cdot}CH_2Cl = (C_6H_5{\cdot}CH_2)_3N,\ HCl + HCl.$$

When, therefore, benzyl chloride is heated with ammonia, the product consists of a mixture of the salts of all three amines.

CHAPTER XXV.

DIAZO-COMPOUNDS AND THEIR DERIVATIVES.

It has already been stated that when the amido-compounds or their salts are treated with nitrous acid in *warm* aqueous solution, they yield phenols; if, however, a *well-cooled*, dilute solution of aniline hydrochloride (1 mol.) be mixed with sodium nitrite (1 mol.), and hydrochloric acid (1 mol.) added to set free the nitrous acid, phenol is *not* produced, and the solution contains an unstable substance called *diazobenzene chloride*, the formation of which may be expressed by the equation,

$$C_6H_5{\cdot}NH_2,HCl + NO_2H = C_6H_5{\cdot}N_2Cl + 2H_2O.$$

In this respect, then, the amido-compounds differ from the fatty amines; the latter are at once converted into alcohols by nitrous acid in the cold, whereas the former are first transformed into diazo-compounds, which, usually only on warming, decompose more or less readily with formation of phenols (p. 398).

All amido-compounds (that is to say, compounds in which the $-NH_2$ group is directly united with the benzene nucleus) behave in this way, and yield diazo-salts similar to diazobenzene chloride in constitution.

The diazo-salts were discovered in 1860 by P. Griess, and may be regarded as salts of diazobenzene, $C_6H_5{\cdot}N_2{\cdot}OH$, and its derivatives.

The bases or hydroxides from which these salts are derived have not yet been isolated, as when liberated from their compounds they immediately change into highly explosive, very unstable products which seem to be their anhydrides.

The diazo-*salts* (usually spoken of as the diazo-compounds) may be isolated without much difficulty, although, as a matter of fact, they are seldom separated from their aqueous solutions, partly because of their highly *explosive* character, but principally because for most purposes for which they are prepared this operation is quite unnecessary.

Preparation.—Diazo-salts may be obtained *in crystals* by treating a well-cooled solution of an amido-compound in absolute alcohol with amyl nitrite and a mineral acid, as far as possible in absence of water,*

$$C_6H_5{\cdot}NH_2,HCl + C_5H_{11}{\cdot}O{\cdot}NO = C_6H_5{\cdot}N_2Cl + C_5H_{11}{\cdot}OH + H_2O.$$

Diazobenzene sulphate, $C_6H_5{\cdot}N_2{\cdot}SO_4H$, for example, is prepared by dissolving aniline (15 parts) in absolute alcohol (10 parts), adding concentrated sulphuric acid (20 parts), and after cooling in a freezing mixture, slowly running in pure amyl nitrite (20 grams); after 10–15 minutes diazobenzene sulphate separates in crystals, which are washed with alcohol and ether, and dried in the air at ordinary temperatures.

Diazobenzene chloride and *diazobenzene nitrate* may be obtained in a similar manner, employing alcoholic solutions of hydrogen chloride and of nitric acid in the place of sulphuric acid.

Diazobenzene nitrate, $C_6H_5{\cdot}N_2{\cdot}NO_3$, may also be conveniently isolated as follows: Aniline nitrate is suspended in a small quantity of water, and the liquid saturated with nitrous acid (generated from As_4O_6 and HNO_3), when the crystals gradually dissolve with

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* Amyl nitrite is used instead of sodium nitrite because it is soluble in alcohol.

formation of diazobenzene nitrate; on the addition of alcohol and ether, this salt separates in colourless needles. Special precautions are to be observed in preparing this substance, as when dry it is highly explosive, although it may be handled with comparative safety if kept moist.

Solutions of the diazo-salts are prepared by dissolving the amido-compound in an aqueous mineral acid, and adding the proper quantity of a solution of sodium nitrite, the temperature being kept at or below 0° ; examples are given later (pp. 384–385).

Properties.—The diazo-salts are colourless, crystalline compounds, very readily soluble in water; in the dry state they are more or less explosive, and should be handled only with the greatest caution. They are of immense value in synthetical chemistry and in the preparation of dyes, as they undergo a number of remarkable reactions, of which the following are some of the more important.

When heated with (absolute) alcohol they yield hydrocarbons, part of the alcohol being oxidised to aldehyde,

$$C_6H_5{\cdot}N_2Cl + C_2H_5{\cdot}OH = C_6H_6 + N_2 + HCl + CH_3{\cdot}CHO.$$

When warmed in aqueous solution they decompose rapidly, with evolution of nitrogen and formation of phenols (p. 398),

$$C_6H_5{\cdot}N_2{\cdot}SO_4H + H_2O = C_6H_5{\cdot}OH + N_2 + H_2SO_4$$

$$\underset{p\text{-Diazotoluene Chloride.}}{C_6H_4(CH_3){\cdot}N_2Cl} + H_2O = \underset{p\text{-Cresol.}}{C_6H_4(CH_3){\cdot}OH} + N_2 + HCl,$$

but if warmed with concentrated halogen acids they give halogen derivatives,

$$C_6H_5{\cdot}N_2{\cdot}SO_4H + HI = C_6H_5I + N_2 + H_2SO_4\,;$$

this last reaction is made use of principally for the preparation of iodo-derivatives (p. 358), because when the other halogen acids are used, the product contains the corresponding phenol.

The diazo-compounds behave in a very remarkable way when treated with cuprous salts; if, for example, a solution of diazobenzene chloride be warmed with cuprous chloride, nitrogen is evolved, but instead of phenol, chlorobenzene is produced. In this reaction the diazo-salt combines with the cuprous chloride to form a brownish additive compound, which is decomposed at higher temperatures, cuprous chloride being regenerated; theoretically, therefore, the reaction is continuous,

$$C_6H_5{\cdot}N_2Cl,\ 2CuCl = C_6H_5Cl + N_2 + 2CuCl.$$

If, instead of the chloride, cuprous bromide or cuprous iodide be employed, bromobenzene or iodobenzene is produced,

$$\underset{\text{Additive Compound.}}{C_6H_5{\cdot}N_2Cl,\ 2CuBr} = \underset{\text{Bromobenzene.}}{C_6H_5Br} + N_2 + CuCl + CuBr,$$

whereas by using cuprous cyanide, a cyanide or nitrile is formed (compare p. 434),

$$\underset{\text{Additive Compound.}}{C_6H_5{\cdot}N_2Cl,\ 2CuCN} = \underset{\text{Phenyl Cyanide.}}{C_6H_5{\cdot}CN} + N_2 + CuCl + CuCN.$$

By means of these very important reactions, which were discovered by Sandmeyer in 1884, it is possible to displace the NH_2– group in amido-compounds by Cl, Br, I, CN, and indirectly by COOH (by the hydrolysis of the CN– group), and indeed by other atoms or groups; as, moreover, the yield is generally good, Sandmeyer's reaction is of great practical value. The amido-compounds being readily obtainable from the nitro-compounds, and the latter from the hydrocarbons, this method affords a means of preparing halogen, cyanogen, and other derivatives indirectly from the hydrocarbons.

It will be seen from the above statements that the preparation of a halogen, cyanogen, or other derivative from the amido-compound involves two distinct reactions: firstly, the preparation of a *solution* of the diazo-salt; and secondly, the decomposition of this salt in the most suitable manner.

As an example of the method employed in preparing a solution of the diazo-salt, the following may serve: Aniline (1 part) is dissolved in a mixture of ordinary concentrated hydrochloric acid (about 2½ parts) and water (about 2½ parts), and the solution is cooled by the addition of coarsely powdered ice; when the temperature has fallen to about 5° an aqueous solution of the theoretical quantity of sodium nitrite* is slowly run in from a tap-funnel, stirring constantly and keeping the temperature as low as possible. The solution now contains *diazobenzene chloride;* if sulphuric had been used instead of hydrochloric acid, diazobenzene sulphate would have been formed. The aniline is said to be *diazotised.*

If, now, the solution of the diazo-salt be warmed *alone*, nitrogen is evolved and phenol is produced; if, however, it be slowly added to a hot solution of cuprous chloride, *chlorobenzene* is produced, whereas by using cuprous cyanide, *cyanobenzene* is formed (p. 434). In all these cases the final product is usually separated by distillation in steam (compare also p. 358).

Gattermann has shown that in many cases the decomposition of the diazo-compounds is best brought about by adding copper powder (prepared by the action of zinc-dust on a solution of copper sulphate) to the *cold* acid solution of the diazo-salt; when, for example, a solution of diazobenzene chloride is treated in this way, nitrogen is evolved and chlorobenzene produced, the reaction being complete in about half-an-hour.

The diazo-compounds also serve for the preparation of an important class of compounds known as the *hydrazines*, these substances being obtained by reducing the diazo-compounds, usually with stannous chloride and hydrochloric acid (p. 388),

$$\underset{\text{Diazochloride.}}{R{\cdot}N_2Cl} + 4H = \underset{\text{Hydrazine Hydrochloride.}}{R{\cdot}NH{\cdot}NH_2,HCl.}$$

Constitution of Diazo-compounds.—The state of combination of the two nitrogen atoms and of the acid radicle in diazo-salts has formed the subject of much discussion, and until recently the view first expressed by Kekulé (1866), that diazo-salts have the constitution $C_6H_5{\cdot}N{:}NR$ (where $R = Cl$, Br, I, NO_3, HSO_4, &c.), was generally adopted. That only *one* of the two nitrogen atoms is directly united to the nucleus is clearly shown by many facts—as, for example, by the conversion of the diazo-salts into *mono*-halogen derivatives, *mono*hydric phenols, &c., and by their conversion into hydrazines, such as $C_6H_5{\cdot}NH{\cdot}NH_2$, on reduction (p. 388).

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* As commercial sodium nitrite is often highly impure and the quantity to be used cannot be determined by weighing, a considerable excess is dissolved and the solution is run in until the solution of the diazo-salt contains free nitrous acid (as shown by starch-potassium-iodide paper) after stirring well and leaving for a short time.

That the acid radicle is combined with the nitrogen atom which is *not* directly united to the nucleus seems to be proved by many reactions of diazo-salts—as, for example, the following: Diazobenzene chloride interacts readily with dimethylaniline, giving dimethylamidoazobenzene (p. 388),

$$C_6H_5\cdot\underset{a}{N}:\underset{b}{N}Cl + C_6H_5\cdot N(CH_3)_2 = C_6H_5\cdot\underset{a}{N}:\underset{b}{N}\cdot C_6H_4\cdot N(CH_3)_2 + HCl,$$

and this substance, on reduction, yields aniline and dimethyl-*p*-phenylenediamine (p. 388),

$$C_6H_5\cdot\underset{a}{N}:\underset{b}{N}\cdot C_6H_4\cdot N(CH_3)_2 + 4H = C_6H_5\cdot\underset{a}{N}H_2 + \underset{b}{N}H_2\cdot C_6H_4\cdot N(CH_3)_2.$$

These changes are easily explained on the assumption that the acid radicle is attached to the *b*-nitrogen atom, as in the above formula, but apparently they could not very well take place if the acid radicle were united to the *a*-nitrogen atom, as in the formula $C_6H_5\cdot\underset{a}{N}Cl:\underset{b}{N}$, suggested by Bloomstrand.

There is, however, one fact which seems to point to the formula $C_6H_5\cdot NR:N$, namely, that the physical properties of dilute solutions of the diazo-salts are similar to those of solutions of quaternary ammonium salts, such as $C_6H_5\cdot NR{\equiv}(CH_3)_3$, in which the acid radicle is directly united to *pentavalent* nitrogen. Probably, therefore, the two formulæ $C_6H_5\cdot N:NR$ and $C_6H_5\cdot NR:N$ represent *tautomeric* forms (Part I. p. 200), and the diazo-salts interact in one or the other form according to the conditions of the experiment; for these reasons the diazo-group may be conveniently represented by $-N_2-$, as in most of the formulæ used above, without indicating the actual state of combination of the two nitrogen atoms.

Diazoamido- and Amidoazo-compounds.

Although some of the more characteristic reactions of diazo-compounds have already been mentioned, there are numerous other changes of great interest and of great commercial importance which these substances undergo.

When, for example, diazobenzene chloride is treated with aniline, a reaction takes place similar to that which occurs when benzoyl chloride is treated with aniline (p. 432), and diazoamidobenzene is formed,

$$C_6H_5\cdot N_2Cl + NH_2\cdot C_6H_5 = \underset{\text{Diazoamidobenzene.}}{C_6H_5\cdot N_2\cdot NH\cdot C_6H_5} + HCl$$

$$C_6H_5\cdot COCl + NH_2\cdot C_6H_5 = \underset{\text{Benzoylamidobenzene or Benzanilide.}}{C_6H_5\cdot CO\cdot NH\cdot C_6H_5} + HCl.$$

As, moreover, other diazo-compounds and other amido-compounds interact in a similar manner, numerous diazoamido-compounds may be obtained.

Diazoamidobenzene, $C_6H_5\cdot N_2\cdot NH\cdot C_6H_5$, may be described as a typical compound of this class; it is conveniently prepared by passing nitrous fumes into an alcoholic solution of aniline, the diazobenzene hydroxide, which is probably first produced, interacting with excess of aniline,

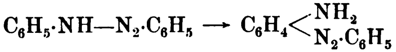
$$C_6H_5\cdot N_2\cdot OH + C_6H_5\cdot NH_2 = C_6H_5\cdot N_2\cdot NH\cdot C_6H_5 + H_2O.$$

Diazoamidobenzene crystallises in brilliant yellow needles, and is sparingly soluble in water, but readily in alcohol and ether; it is very feebly basic, and forms only very unstable salts with acids.

Amidoazobenzene, $C_6H_5\cdot N_2\cdot C_6H_4\cdot NH_2$, is formed when diazoamidobenzene is warmed with a small quantity of aniline hydrochloride at 40°, intramolecular change taking place,

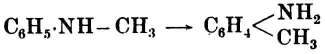
$$C_6H_5\cdot N_2\cdot NH\cdot C_6H_5 = C_6H_5\cdot N_2\cdot C_6H_4\cdot NH_2.$$

This remarkable reaction, which is a general one and shown by all diazoamido-compounds, may be compared with that which occurs in the transformation of methylaniline into paratoluidine (p. 370), the group $-N_2\cdot C_6H_5$ leaving the nitrogen atom and migrating to the *para*-position in the nucleus,



$$C_6H_5\cdot NH{-}N_2\cdot C_6H_5 \longrightarrow C_6H_4{<}\substack{NH_2\\ N_2\cdot C_6H_5}$$

Diazoamidobenzene. *p*-Amidoazobenzene.



$$C_6H_5\cdot NH-CH_3 \longrightarrow C_6H_4{<}\substack{NH_2\\ CH_3}$$

Methylaniline. *p*-Toluidine.

That the group $-N_2\cdot C_6H_5$ displaces hydrogen from the *p*-position to the $-NH_2$ group is proved by the fact that the amidoazobenzene thus produced is converted into *para*-phenylenediamine and aniline on reduction with tin and hydrochloric acid,

$$NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5 + 4H = {}_{(1)}NH_2{\cdot}C_6H_4{\cdot}NH_{2(4)} + NH_2{\cdot}C_6H_5.$$

Amidoazobenzene may also be prepared by nitrating azobenzene (p. 391), and then reducing with ammonium sulphide the *p*-nitroazobenzene, $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$, which is thus produced; these changes are analogous to those which occur in the formation of aniline from benzene—and the formation of amidoazobenzene in this way proves that it is an amido-derivative of azobenzene.

Amidoazobenzene crystallises from alcohol in brilliant orange-red plates, and melts at 123°; its salts are intensely coloured, the hydrochloride, $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2, HCl$, for example, forms beautiful steel-blue needles, and used to come into the market under the name of 'aniline yellow' as a silk dye (p. 535).

Other amidoazo-compounds may be obtained *directly* by treating tertiary alkylanilines (p. 377) with diazo-salts: dimethylaniline, for example, interacts with diazobenzene chloride, yielding dimethylamidoazobenzene,

$$C_6H_5{\cdot}N_2Cl + C_6H_5{\cdot}N(CH_3)_2 = C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N(CH_3)_2, HCl,$$

no intermediate diazoamido-compound being formed, because dimethylaniline does not contain an $NH<$ or NH_2- group.

In this case also the diazo-group, $C_6H_5{\cdot}N_2-$, takes up the *p*-position to the $N(CH_3)_2-$ group, as is shown by the fact that, on reduction, dimethylamidoazobenzene is converted into aniline and dimethyl-*p*-phenylenediamine, the latter being identical with the base which is produced by reducing *p*-nitrosodimethylaniline (p. 378).

Phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH_2$, a compound of great practical importance, is easily prepared by the reduction of diazobenzene chloride,

$$C_6H_5{\cdot}N_2Cl + 4H = C_6H_5{\cdot}NH{\cdot}NH_2, HCl.$$

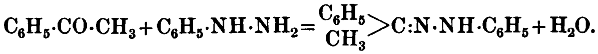
Aniline (1 part) is dissolved in concentrated hydrochloric acid (20 parts), and diazotised in the usual way (p. 384); the solution of diazobenzene chloride is then mixed with stannous chloride (45 grams) dissolved in concentrated hydrochloric acid (45 grams).

The precipitate of phenylhydrazine hydrochloride, which rapidly forms, is separated by filtration, dissolved in water, decomposed with potash, and the free base extracted with ether and purified by distillation, preferably under reduced pressure.

Phenylhydrazine crystallises in colourless prisms, melts at 23°, and boils at 241°, decomposing slightly. It is sparingly soluble in cold water, readily in alcohol and ether; it is a strong base, and forms well-characterised salts, such as the hydrochloride, $C_6H_5{\cdot}NH{\cdot}NH_2, HCl$, which crystallises in colourless needles, and is readily soluble in hot water; solutions of the free base and of its salts reduce Fehling's solution in the cold. The *constitution* of phenylhydrazine is established by the fact that, when heated with zinc-dust and hydrochloric acid, it is converted into aniline and ammonia.

Phenylhydrazine interacts readily with aldehydes, ketones, and most substances containing a carbonyl-group, with elimination of water and formation of *phenylhydrazones* (hydrazones); as these compounds are usually sparingly soluble and often crystallise well, they may frequently be employed with advantage in the identification and isolation of aldehydes and ketones (Part I. p. 136),

$$\underset{\text{Benzaldehyde.}}{C_6H_5{\cdot}CHO} + C_6H_5{\cdot}NH{\cdot}NH_2 = \underset{\text{Benzylidene Hydrazone.}}{C_6H_5{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5} + H_2O$$



$$\underset{\text{Acetophenone.}}{C_6H_5{\cdot}CO{\cdot}CH_3} + C_6H_5{\cdot}NH{\cdot}NH_2 = \underset{\text{Acetophenone Hydrazone.}}{\begin{matrix}C_6H_5\\CH_3\end{matrix}{>}C{:}N{\cdot}NH{\cdot}C_6H_5} + H_2O.$$

Many hydrazones are decomposed by strong mineral acids, with regeneration of the aldehyde or ketone, and formation of a salt of phenylhydrazine,

$$C_6H_5{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5 + H_2O + HCl = C_6H_5{\cdot}CHO + C_6H_5{\cdot}NH{\cdot}NH_2, HCl;$$

on reduction with zinc-dust and acetic acid they yield primary amines,

$$\underset{\text{Benzylidenehydrazone.}}{C_6H_5{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_5} + 4H = \underset{\text{Benzylamine.}}{C_6H_5{\cdot}CH_2{\cdot}NH_2} + C_6H_5{\cdot}NH_2.$$

The value of phenylhydrazine as a means of detecting and isolating the sugars has already been explained (Part I. p. 272).

In preparing hydrazones, the reacting substances may either be heated together without a solvent, or more frequently the substance is dissolved in water (or alcohol), and the solution of the requisite amount of phenylhydrazine in *dilute* acetic acid added. On warming, the hydrazone frequently separates in a crystalline form, and may be readily purified by recrystallisation.

Osazones (Part I. p. 273) are prepared by boiling an aqueous solution of a sugar with excess of phenylhydrazine acetate; after some time the osazone begins to be deposited in a crystalline form, the separation increasing as the liquid cools.

Azo- and Azoxy-compounds.

It has already been stated that when nitro-compounds are treated with tin and hydrochloric acid, and other *acid* reducing agents, they are converted into amido-compounds, a similar change taking place when alcoholic ammonium sulphide is employed; when, however, nitro-compounds are treated with other *alkaline* reducing agents, such as alcoholic potash, sodium amalgam and water, stannous oxide and soda, or zinc-dust and soda, they yield *azo-compounds*, such as azobenzene—*azoxy-compounds*, such as azoxybenzene, being formed as intermediate products; in these reactions two molecules of the nitro-compound afford one molecule of the azoxy- or azo-compound,

$$2C_6H_5{\cdot}NO_2 + 6H = C_6H_5{\cdot}N{<}\overset{O}{\underline{\quad}}{>}N{\cdot}C_6H_5 + 3H_2O$$

Azoxybenzene.

$$2C_6H_5{\cdot}NO_2 + 8H = C_6H_5{\cdot}N{:}N{\cdot}C_6H_5 + 4H_2O.$$

Azobenzene.

Azoxybenzene, $C_6H_5{\cdot}N{<}\overset{O}{\underline{\quad}}{>}N{\cdot}C_6H_5$, is generally prepared by adding nitrobenzene ($1\frac{1}{2}$ parts) to a solution of sodium (1 part) in methyl alcohol and then boiling (reflux condenser) for about four hours; after distilling the alcohol, water is added, and when sufficiently hard the pasty product is pressed on porous earthenware, left to dry, and crystallised from light petroleum. It forms yellow needles melting at 36°, and is insoluble in water, but readily soluble in most organic liquids.

Azobenzene, $C_6H_5\cdot N:N\cdot C_6H_5$, may be prepared by mixing azoxybenzene (1 part) with iron filings (3 parts) and distilling carefully from a small retort; the solid distillate is purified as described in the case of the azoxy-compound. Azobenzene crystallises in brilliant red plates, melts at 68°, and distils at 293°; it is readily soluble in ether and alcohol, but insoluble in water. Alkaline reducing agents, such as ammonium sulphide, zinc-dust and soda, &c., convert azobenzene into *hydrazobenzene*, a colourless, crystalline substance, which melts at 131°,

$$C_6H_5\cdot N:N\cdot C_6H_5 + 2H = C_6H_5\cdot NH\cdot NH\cdot C_6H_5,$$

whereas a mixture of zinc-dust and acetic acid decomposes it, with formation of aniline,

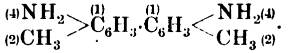
$$C_6H_5\cdot N:N\cdot C_6H_5 + 4H = 2C_6H_5\cdot NH_2.$$

Other azo-compounds behave in a similar manner.

Hydrazobenzene, $C_6H_5\cdot NH\cdot NH\cdot C_6H_5$, is readily converted into azobenzene by mild oxidising agents such as mercuric oxide, and slowly even when air is passed through its alcoholic solution. When treated with strong acids it undergoes a very remarkable intramolecular change, and is converted into *p*-diamidodiphenyl or *benzidine*, a strongly basic substance largely used in the preparation of azo-dyes (p. 537),

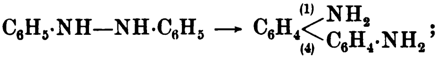
$$\underset{\text{Hydrazobenzene.}}{C_6H_5\cdot NH\cdot NH\cdot C_6H_5} \longrightarrow \underset{\text{Benzidine.}}{NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2.}$$

Benzidine may be produced in one operation by reducing azobenzene with tin and strong hydrochloric acid. Other azo-compounds behave in a similar manner; orthoazo-toluene, $CH_3\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot CH_3$, for example, is first converted into the corresponding hydrazo-compound, which then undergoes isomeric or intramolecular change into *dimethylbenzidine* (tolidine),



$$\begin{matrix}{}^{(4)}NH_2\\ {}^{(2)}CH_3\end{matrix}\!>\overset{(1)}{C}_6H_3\cdot\overset{(1)}{C}_6H_3<\!\begin{matrix}NH_2{}^{(4)}\\ CH_3{}^{(2)}\end{matrix}.$$

These changes, like that of diazoamidobenzene into *p*-amidoazobenzene (p. 387), involve the *migration* of a complex group of atoms from an amido-group to the *para*-position in the nucleus,



$$C_6H_5\cdot NH{-}NH\cdot C_6H_5 \longrightarrow C_6H_4{<}\begin{matrix}^{(1)}NH_2\\ ^{(4)}C_6H_4\cdot NH_2\end{matrix};$$

if the *p*-position be already occupied, isomeric change takes place far *less readily*, and the group migrates to the *ortho*-position.

CHAPTER XXVI.

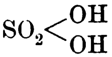
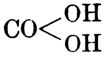
SULPHONIC ACIDS AND THEIR DERIVATIVES.

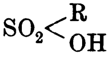
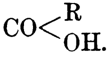
When benzene is heated with concentrated sulphuric acid it gradually dissolves, and *benzenesulphonic acid* is formed by the substitution of the *sulphonic* group $-SO_3H$ or $-SO_2\cdot OH$ for an atom of hydrogen,

$$C_6H_6 + H_2SO_4 = C_6H_5\cdot SO_3H + H_2O.$$

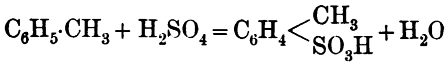
The homologues of benzene and aromatic compounds in general behave in a similar manner, and this property of readily yielding sulphonic derivatives by the displacement of hydrogen of the *nucleus* is one of the important characteristics of aromatic, as distinct from fatty, compounds.

The sulphonic acids are not analogous to the alkylsulphuric acids (Part I. p. 185), which are esters, but rather to the carboxylic acids, since they may be regarded as derived from sulphuric acid, $SO_2(OH)_2$, just as the carboxylic acids are derived from carbonic acid, $CO(OH)_2$, namely, by the substitution of an aromatic radicle for one of the hydroxyl-groups.

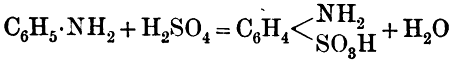
Sulphuric acid,  $SO_2{<}\begin{matrix}OH\\OH\end{matrix}$ Carbonic acid,  $CO{<}\begin{matrix}OH\\OH\end{matrix}$

Sulphonic acid,  $SO_2{<}\begin{matrix}R\\OH\end{matrix}$ Carboxylic acid,  $CO{<}\begin{matrix}R\\OH.\end{matrix}$

Preparation.—Sulphonic acids are prepared by treating an aromatic compound with sulphuric acid, or with anhydrosulphuric acid,



$$C_6H_5{\cdot}CH_3 + H_2SO_4 = C_6H_4{<}\begin{array}{l}CH_3\\SO_3H\end{array} + H_2O$$



$$C_6H_5{\cdot}NH_2 + H_2SO_4 = C_6H_4{<}\begin{array}{l}NH_2\\SO_3H\end{array} + H_2O$$

$$C_6H_6 + 2H_2SO_4 = C_6H_4(SO_3H)_2 + 2H_2O.$$

The number of hydrogen atoms displaced by sulphonic groups depends (as in the case of nitro-groups) on the temperature, on the concentration of the acid, and on the nature of the substance undergoing *sulphonation.*

The substance to be sulphonated is mixed with, or dissolved in, excess of the acid, and, if necessary, the mixture or solution is then heated on a water- or sand-bath until the desired change is complete. After cooling, the product is carefully poured into water, and the acid isolated as described later (p. 395). In the case of a substance which is insoluble in water or dilute sulphuric acid, the point at which the whole is converted into a monosulphonic acid is easily ascertained by taking out a small portion of the mixture and adding water; unless the whole is soluble, unchanged substance is still present.

Sometimes chlorosulphonic acid, $Cl{\cdot}SO_3H$, is employed in sulphonating substances, and in such cases chloroform or carbon disulphide may be used as a solvent to moderate the action,

$$C_6H_6 + Cl{\cdot}SO_3H = C_6H_5{\cdot}SO_3H + HCl.$$

Properties.—Sulphonic acids are, as a rule, crystalline, readily soluble in water, and often very hygroscopic; they have seldom a definite melting-point, and gradually decompose when heated, so that they cannot be distilled. They have a sour taste, a strongly acid reaction, and show, in fact, all the properties of powerful acids, their basicity depending on the number of sulphonic groups in the molecule. They decompose carbonates, and dissolve certain metals with evolution of hydrogen; their metallic salts (including the barium salts), as a rule, are readily soluble in water.

Although, generally speaking, the sulphonic acids are very stable, and are not decomposed by boiling aqueous alkalies or mineral acids, they undergo certain changes of great importance. When fused with potash they yield phenols (p. 398), and when strongly heated with potassium cyanide, or with potassium ferrocyanide, they are converted into cyanides (or nitriles, p. 434), which distil off, leaving a residue of potassium sulphite,

$$C_6H_5 \cdot SO_3K + KCN = C_6H_5 \cdot CN + K_2SO_3.$$

The sulphonic group may also be displaced by hydrogen. This may be done by strongly heating the acids alone, or with hydrochloric acid in sealed tubes, or by passing superheated steam into the acids, or into their solution in concentrated sulphuric acid.

Sulphonic acids yield numerous derivatives, which may generally be prepared by methods similar to those used in the case of the corresponding derivatives of carboxylic acids. When, for example, a sulphonic acid (or its alkali salt) is treated with phosphorus pentachloride, the hydroxyl-group is displaced by chlorine, and a *sulphonic chloride* is obtained,

$$C_6H_5 \cdot SO_2 \cdot OH + PCl_5 = C_6H_5 \cdot SO_2Cl + POCl_3 + HCl.$$

All sulphonic acids behave in this way, and their sulphonic chlorides are of great value, not only because they are often useful in isolating and identifying the ill-characterised acids, but also because, like the chlorides of the carboxylic acids, they interact readily with many other compounds.

The sulphonic chlorides are decomposed by water and by alkalies, giving the sulphonic acids or their salts; they interact with alcohols at high temperatures, yielding ethereal salts, such as *ethyl benzenesulphonate*,

$$C_6H_5 \cdot SO_2Cl + C_2H_5 \cdot OH = C_6H_5 \cdot SO_2 \cdot OC_2H_5 + HCl,$$

and when shaken with concentrated ammonia they are usually converted into well-defined crystalline *sulphonamides*, which also serve for the identification of the acids,

$$\underset{\text{Benzenesulphonic Chloride.}}{C_6H_5 \cdot SO_2Cl} + NH_3 = \underset{\text{Benzenesulphonamide.}}{C_6H_5 \cdot SO_2 \cdot NH_2} + HCl.$$

The isolation of sulphonic acids is very often a matter of some difficulty, because they are readily soluble in water and non-volatile, and cannot be extracted from their aqueous solutions by shaking with ether, &c., or separated from other substances by steam distillation. The first step usually consists in separating them from the excess of sulphuric acid employed in their preparation; this may be done in the following manner:—The aqueous solution of the product of sulphonation (see above) is boiled with excess of barium (or calcium) carbonate, filtered from the precipitated barium (or calcium) sulphate, and the filtrate—which contains the barium (or calcium) salt of the sulphonic acid—treated with sulphuric acid drop by drop as long as a precipitate is produced; after again filtering, an aqueous solution of the sulphonic acid is obtained, and on evaporating to dryness, the acid remains as a syrup or in a crystalline form. If calcium carbonate has been used, the acid will contain a little calcium sulphate, which may be got rid of by adding a little alcohol, filtering, and again evaporating.

Lead carbonate is sometimes employed instead of barium or calcium carbonate; in such cases the filtrate from the lead sulphate is treated with hydrogen sulphide, filtered from lead sulphide, and then evaporated. These methods are, of course, only applicable provided that the barium, calcium, or lead salt of the acid be soluble in water; in other cases the separation is much more troublesome.

When two or more sulphonic acids are present in the product, they are usually separated by fractional crystallisation of their salts; the alkali salts are easily prepared from the barium, calcium, or lead salts by treating the solution of the latter with the alkali carbonate as long as a precipitate is produced, filtering from the insoluble carbonate, and then evaporating.

Sometimes a complete separation cannot be accomplished with the aid of any of the salts, and in such cases the sulphonic chlorides are prepared by treating the alkali salts with phosphorus pentachloride; these compounds are soluble in ether, chloroform, &c., and generally crystallise well, so that they are easily separated and obtained in a state of purity.

Benzenesulphonic acid, $C_6H_5 \cdot SO_3H$, is prepared by gently boiling a mixture of equal volumes of benzene and concentrated sulphuric acid for twenty to thirty hours, using a reflux condenser; it is isolated with the aid of its barium or lead salt, both of which are soluble in water. It crystallises with 1½ mols. H_2O in colourless, hygroscopic plates, and dissolves freely in alcohol; when fused with potash it yields phenol (p. 404). *Benzenesulphonic chloride*, $C_6H_5{\cdot}SO_2Cl$, is an oil, but the *sulphonamide*, $C_6H_5{\cdot}SO_2{\cdot}NH_2$, is crystalline, and melts at 150°.

Benzene-*m*-disulphonic acid, $C_6H_4(SO_3H)_2$, is also prepared by heating the hydrocarbon with concentrated sulphuric acid, but a larger proportion (two volumes) of the acid is employed, and the solution is heated more strongly (or anhydrosulphuric acid is used); when fused with potash, it yields resorcinol (p. 411).

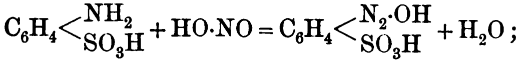
The three (*o.m.p.*) *toluenesulphonic acids*, $C_6H_4(CH_3){\cdot}SO_3H$, are crystalline, and their barium salts are soluble in water; only the *o*- and *p*-acids are formed when toluene is dissolved in anhydrosulphuric acid.

Sulphanilic acid, amidobenzene-*p*-sulphonic acid, or aniline-*p*-sulphonic acid, $C_6H_4(NH_2){\cdot}SO_3H$, is easily prepared by heating aniline sulphate at about 200° for some time.

Aniline is slowly added to a slight excess of the theoretical quantity of sulphuric acid contained in a porcelain dish, the mixture being constantly stirred as it becomes solid; the dish is then gently heated on a sand-bath, the contents being stirred, and care being taken to prevent charring. The process is at an end as soon as a small portion of the product, dissolved in water, gives no oily precipitate of aniline on adding excess of soda. After cooling, a little water is added, and the sparingly soluble sulphonic acid separated by filtration, and purified by recrystallisation from boiling water, with addition of animal charcoal if necessary.

Sulphanilic acid crystallises with 2 mols. H_2O, and is readily soluble in hot, but only sparingly in cold, water. It forms salts with bases, but it does not combine with acids, the basic character of the amido-group being neutralised by the acid character of the sulphonic group; in this respect, therefore, it differs from glycine (Part I. p. 299), which forms salts both with acids and bases.

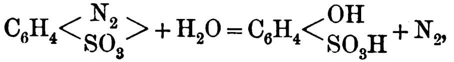
When sulphanilic acid is dissolved in dilute soda, the solution mixed with a slight excess of sodium nitrite, and poured into well-cooled, dilute sulphuric acid, *diazobenzene-p-sulphonic acid* is formed,



$$C_6H_4<\begin{matrix}NH_2\\SO_3H\end{matrix} + HO{\cdot}NO = C_6H_4<\begin{matrix}N_2{\cdot}OH\\SO_3H\end{matrix} + H_2O\,;$$

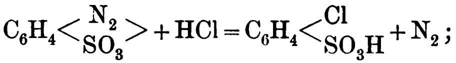
this compound, however, immediately loses water, and is converted into its anhydride,* $C_6H_4<\begin{matrix}N_2\\SO_3\end{matrix}>$, which separates from the solution in colourless crystals.

Diazobenzenesulphonic acid, or rather its anhydride, shows the characteristic properties of diazo-compounds in general; when boiled with water it is converted into phenol-*p*-sulphonic acid (p. 408),



$$C_6H_4<\begin{matrix}N_2\\SO_3\end{matrix}> + H_2O = C_6H_4<\begin{matrix}OH\\SO_3H\end{matrix} + N_2,$$

whereas when heated with concentrated hydrochloric or hydrobromic acid it gives chlorobenzene- or bromobenzene-*p*-sulphonic acid,



$$C_6H_4<\begin{matrix}N_2\\SO_3\end{matrix}> + HCl = C_6H_4<\begin{matrix}Cl\\SO_3H\end{matrix} + N_2\,;$$

it interacts readily with dimethylaniline, giving helianthin (p. 536).

Amidobenzene-o-sulphonic acid and the *m*-acid (*metanilic acid*) may be obtained by reducing the corresponding nitrobenzenesulphonic acids, $C_6H_4(NO_2){\cdot}SO_3H$, both of which are formed, together with the *p*-acid, on nitrating benzenesulphonic acid; they resemble sulphanilic acid in properties, and are readily converted into the anhydrides of the corresponding diazobenzenesulphonic acids.

Many other sulphonic acids are described later.

* The existence of this anhydride (and of that of *amidobenzene-m-sulphonic acid*) is a very interesting fact because, as a rule, anhydride formation takes place only between groups in the *o*-position to one another (compare p. 437).

CHAPTER XXVII.

PHENOLS.

The hydroxy-compounds of the aromatic series, such as phenol or hydroxy-benzene, $C_6H_5 \cdot OH$, the isomeric hydroxy-toluenes, $C_6H_4(CH_3) \cdot OH$, and benzyl alcohol, $C_6H_5 \cdot CH_2 \cdot OH$, are derived from the aromatic hydrocarbons by the substitution of hydroxyl-groups for atoms of hydrogen, just as the fatty alcohols are derived from the paraffins. It will be seen, however, from the examples just given that whereas, in benzene, hydrogen atoms of the nucleus must necessarily be displaced, in the case of toluene and all the higher homologues this is not so, since the hydroxyl-groups may displace hydrogen either of the nucleus or of the side-chain. Now the hydroxy-derivatives of benzene, and all those aromatic hydroxy-compounds formed by the substitution of hydroxyl-groups for hydrogen atoms of the *nucleus*, differ in many respects not only from the fatty alcohols, but also from those aromatic compounds which contain the hydroxyl-group in the side-chain; it is convenient, therefore, to make some distinction between the two kinds of aromatic hydroxy-compounds, and for this reason they are classed in two groups, (*a*) the **phenols,** and (*b*) the **aromatic alcohols** (p. 414).

The **phenols,** then, are hydroxy-compounds in which the hydroxyl-groups are united directly with carbon of the nucleus; they may be subdivided into monohydric, dihydric, trihydric phenols, &c., according to the number of hydroxyl-groups which they contain. Phenol, or carbolic acid, $C_6H_5 \cdot OH$, for example, is a monohydric phenol, as are also the three isomeric cresols or hydroxytoluenes, $C_6H_4(CH_3) \cdot OH$; the three isomeric dihydroxybenzenes, $C_6H_4(OH)_2$, on the other hand, are dihydric phenols, whereas phloroglucinol, $C_6H_3(OH)_3$, is an example of a trihydric compound.

Many of the phenols are easily obtainable, well-known compounds; carbolic acid, for instance, is prepared from coal-tar in large quantities; carvacrol and thymol occur in various plants; and catechol, pyrogallol, &c. may be obtained by the dry distillation of certain vegetable products.

Preparation.—Phenols may be prepared by treating salts of amido-compounds with nitrous acid in aqueous solution, and then heating until nitrogen ceases to be evolved,

$$C_6H_5{\cdot}NH_2,HCl + HO{\cdot}NO = C_6H_5{\cdot}OH + N_2 + H_2O + HCl$$

$$C_6H_4{<}{}^{CH_3}_{NH_2},\ HCl + HO{\cdot}NO = C_6H_4{<}{}^{CH_3}_{OH} + N_2 + H_2O + HCl.$$

It is possible, therefore, to prepare phenols not only from the amido-compounds themselves, but also indirectly from the corresponding nitro-derivatives and from the hydrocarbons, since these substances may be converted into amido-compounds,

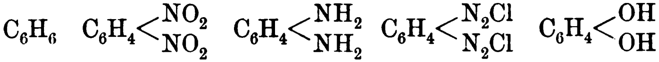
$$\underset{\text{Benzene.}}{C_6H_6} \longrightarrow \underset{\text{Nitrobenzene.}}{C_6H_5{\cdot}NO_2} \longrightarrow \underset{\text{Amidobenzene.}}{C_6H_5{\cdot}NH_2} \longrightarrow \underset{\text{Phenol.}}{C_6H_5{\cdot}OH.}$$

The conversion of an amido-compound into a phenol really takes place in two stages, as already explained (p. 381); at ordinary temperatures the salt of the amido-compound is transformed into a salt of a diazo-compound, but on heating its aqueous solution the latter decomposes, yielding a phenol,

$$C_6H_5{\cdot}NH_2,\ HCl + HCl + KNO_2 = C_6H_5{\cdot}N_2Cl + KCl + 2H_2O$$
$$C_6H_5{\cdot}N_2Cl + H_2O = C_6H_5{\cdot}OH + HCl + N_2.$$

The amido-compound, aniline, for example, is dissolved in dilute hydrochloric acid or sulphuric acid, and *diazotised* in the manner already described (p. 384). The solution of the diazo-salt is then gradually heated to boiling (reflux condenser), until the evolution of nitrogen (which at first causes brisk effervescence) is at an end; the phenol is afterwards separated from the tarry matter, which is almost invariably produced, by distillation in steam, by crystallisation from hot water, or by extraction with ether; in the last case the ethereal solution is usually shaken with dilute caustic soda, which dissolves out the phenol, leaving most of the impurities in the ether.

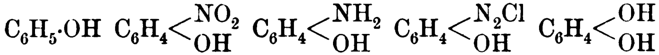
Dihydric phenols may sometimes be prepared from the corresponding di-substitution products of the hydrocarbon, as indicated by the following series of changes,



$$C_6H_6 \quad C_6H_4{<}\begin{matrix}NO_2\\NO_2\end{matrix} \quad C_6H_4{<}\begin{matrix}NH_2\\NH_2\end{matrix} \quad C_6H_4{<}\begin{matrix}N_2Cl\\N_2Cl\end{matrix} \quad C_6H_4{<}\begin{matrix}OH\\OH\end{matrix}$$

Benzene. Dinitrobenzene. Diamidobenzene. Diazo-salt. Dihydric Phenol.

They may also be obtained from the monohydric compounds in the following manner,



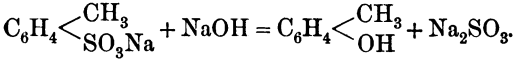
$$C_6H_5{\cdot}OH \quad C_6H_4{<}\begin{matrix}NO_2\\OH\end{matrix} \quad C_6H_4{<}\begin{matrix}NH_2\\OH\end{matrix} \quad C_6H_4{<}\begin{matrix}N_2Cl\\OH\end{matrix} \quad C_6H_4{<}\begin{matrix}OH\\OH\end{matrix}$$

Phenol. Nitrophenol. Amidophenol. Diazo-salt. Dihydric Phenol.

These two methods, however, are limited in their application, because *o*- and *m*-diamido-compounds cannot always be converted into the corresponding diazo-salts, but more often yield products of quite a different nature; *o*- and *p*-amido-hydroxy-compounds also show an abnormal behaviour with nitrous acid, the former not being acted on at all, the latter only with difficulty. For these reasons dihydric phenols are usually most conveniently prepared by the methods given later.

Another important general method of preparing phenols consists in fusing sulphonic acids or their salts with potash or soda; in this case, also, their preparation from the hydrocarbons is often easily accomplished, since the latter are usually converted into sulphonic acids without difficulty,

$$C_6H_5{\cdot}SO_3K + KOH = C_6H_5{\cdot}OH^* + K_2SO_3$$



$$C_6H_4{<}\begin{matrix}CH_3\\SO_3Na\end{matrix} + NaOH = C_6H_4{<}\begin{matrix}CH_3\\OH\end{matrix} + Na_2SO_3.$$

The sulphonic acid or its alkali salt is placed in an iron or, better, nickel or silver dish,[†] together with excess of solid potash (or soda) and a little water, and the dish is heated over a free flame, the mixture being constantly stirred with a nickel or silver spatula, or with a thermometer, the bulb of which is encased in a

[*] In all cases the phenols are present in the product as alkali salts.

[†] Caustic alkalies readily attack platinum and porcelain at high temperatures, but have little action on nickel and none on silver.

glass tube, or covered with a film of silver;* after the potash and the salt have dissolved, the temperature is slowly raised, during which process the mixture sometimes undergoes a variety of changes in colour, by which an experienced operator can tell when the decomposition of the sulphonic acid is complete; as a rule, a temperature considerably above 200° is required, so that simply boiling the sulphonic acid with concentrated potash does not bring about the desired change. When the operation is finished the fused mass is allowed to cool, dissolved in water, the solution acidified with dilute sulphuric acid, and the liberated phenol isolated in some suitable manner (p. 399).

Dihydric phenols may often be obtained in a similar manner from the disulphonic acids,

$$C_6H_4(SO_3K)_2 + 2KOH = C_6H_4(OH)_2 + 2K_2SO_3.$$

Owing to the high temperature at which these reactions must be carried out, secondary changes very often occur. When the sulphonic acid contains halogen atoms, the latter are usually displaced by hydroxyl-groups, especially if other acid radicles, such as $-NO_2$ or $-SO_3H$, be also present; when, for example, chlorobenzenesulphonic acid, $C_6H_4Cl{\cdot}SO_3H$, is fused with potash, a dihydric phenol, $C_6H_4(OH)_2$, is produced, the halogen as well as the sulphonic group being eliminated. For this reason also, compounds such as *o*- and *p*-chloronitrobenzene may be converted into the corresponding nitrophenols (p. 405), even by boiling them with concentrated potash, the presence of the nitro-group facilitating the displacement of the halogen atom; *m*-chloronitrobenzene, on the other hand, is not acted on under these conditions. Sometimes also the process is not one of direct substitution only —that is to say, the hydroxyl-groups in the product are not united with the same carbon atoms as those with which the displaced atoms or groups were united; the three (*o.m.p.*) bromobenzenesulphonic acids, for example, all yield *one and the same* dihydric phenol—namely, the *m*-compound, resorcinol, $C_6H_4(OH)_2$, because the *o*- and *p*-dihydric compounds,

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* As the mixture is very liable to spirt, the eyes of the operator must be protected by spectacles or by a sheet of glass placed suitably before him.

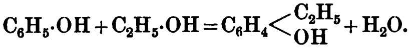
which are first produced from the corresponding bromosulphonic acids, are converted into the more stable *m*-derivative by intramolecular change.

There are several less important methods by which phenols may be obtained, as, for example, by distilling hydroxy-acids, such as salicylic acid, with lime,

$$C_6H_4(OH){\cdot}COOH = C_6H_5{\cdot}OH + CO_2,$$

a reaction which is similar to that which occurs in preparing the hydrocarbons from the acids.

Also by heating other phenols with fatty alcohols in presence of zinc chloride, when the alkyl-group displaces hydrogen of the nucleus, just as in the production of toluidine, &c., from aniline (p. 370),



$$C_6H_5{\cdot}OH + C_2H_5{\cdot}OH = C_6H_4<\begin{matrix}C_2H_5\\OH\end{matrix} + H_2O.$$

Properties.—Most phenols are colourless, crystalline substances, readily soluble in alcohol and ether; their solubility in water usually increases with the number of hydroxyl-groups in the molecule, phenol and cresol, for example, being sparingly soluble, whereas the three dihydric phenols and the trihydric compounds are readily soluble. Conversely, their volatility diminishes; so that although phenol and cresol distil without decomposing, and are readily volatile in steam, the trihydric phenols usually undergo decomposition, and volatilise very slowly in steam. Alcoholic and aqueous solutions of phenols (and of some of their carboxylic acids) give a green, violet, or yellow colouration with ferric salts, the particular colouration depending, in the case of the di- and poly-hydric compounds, on the relative positions of the hydroxyl-groups.

o-Dihydroxy-compounds give an *intense green* colouration, which first becomes deep violet and then bright red on addition of sodium bicarbonate; *m*-dihydroxy-compounds give a deep *violet* colouration; *p*-dihydroxy-compounds give a faint green colouration, which immediately changes to yellow owing to the formation of a quinone (p. 425).

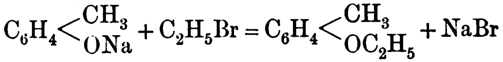
All phenols give Liebermann's reaction; when dissolved in concentrated sulphuric acid and treated with a nitroso-compound or a nitrite, they yield coloured solutions, which, after diluting and adding excess of alkali, assume an intense blue or green colour. This reaction, therefore, affords a convenient test for phenols as well as for nitroso-compounds (Part I. p. 209).

Although phenols resemble the fatty alcohols and the alcohols of the aromatic series in some respects, they have, on the whole, very little in common with these substances. The reason of this is, that the character of the hydroxyl-group (like that of the amido-group, p. 371) is greatly modified by its union with carbon of the benzene nucleus, just as that of the hydroxyl-group in water is altered by combination with acid-forming atoms or radicles such as $Cl-$, NO_2-, &c., as, for example, in $HOCl$ and $HO{\cdot}NO_2$; in other words, the phenolic hydroxyl-group has a much more pronounced acid character than that in alcohols, the radicles *phenyl*, C_6H_5-, *phenylene*, $C_6H_4<$, &c., being therefore regarded as acid-forming.

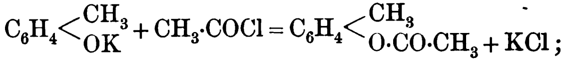
The acid character of the hydroxyl-group in phenols is shown in their behaviour with *caustic* alkalies, in which they dissolve freely, forming metallic derivatives or salts, such as *sodium phenate*, $C_6H_5{\cdot}ONa$, and *potassium cresate*, $C_6H_4(CH_3){\cdot}OK$; these compounds, unlike the alkali derivatives of the alcohols, are stable in presence of water, but are decomposed by carbon dioxide and by all other acids, with regeneration of the phenols. For this reason phenols which are insoluble in water are *insoluble* in alkali carbonates, unless they contain other acid-forming groups or atoms, as, for example, in nitrophenol, $C_6H_4(NO_2){\cdot}OH$, and picric acid, $C_6H_2(NO_2)_3{\cdot}OH$, when their acid character is often enhanced to such an extent that they decompose and dissolve in alkali carbonates.

The metallic derivatives of the phenols, like those of the alcohols, interact with alkyl halogen compounds and with acid chlorides, yielding substances analogous to the ethers and esters respectively,

$$C_6H_5{\cdot}OK + CH_3I = C_6H_5{\cdot}O{\cdot}CH_3 + KI$$

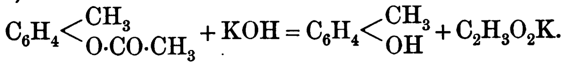


$$C_6H_4{<}\begin{array}{l}CH_3\\ ONa\end{array} + C_2H_5Br = C_6H_4{<}\begin{array}{l}CH_3\\ OC_2H_5\end{array} + NaBr$$



$$C_6H_4{<}\begin{array}{l}CH_3\\ OK\end{array} + CH_3{\cdot}COCl = C_6H_4{<}\begin{array}{l}CH_3\\ O{\cdot}CO{\cdot}CH_3\end{array} + KCl;$$

the former, like the ethers, are *not* decomposed by boiling alkalies, but the latter undergo hydrolysis, just as do the esters,



$$C_6H_4{<}\begin{array}{l}CH_3\\ O{\cdot}CO{\cdot}CH_3\end{array} + KOH = C_6H_4{<}\begin{array}{l}CH_3\\ OH\end{array} + C_2H_3O_2K.$$

Towards pentachloride and pentabromide of phosphorus, and towards acetic anhydride and acetyl chloride, phenols behave in the same way as the alcohols,

$$C_6H_5{\cdot}OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl\,^*$$
$$C_6H_5{\cdot}OH + (CH_3{\cdot}CO)_2O = C_6H_5{\cdot}O{\cdot}CO{\cdot}CH_3 + C_2H_4O_2.$$

When heated with acids, however, the phenols are not changed to any appreciable extent, because, being less basic in character than the alcohols, they do not so readily form salts.

The constitution of a phenol being quite different from that of a primary or secondary alcohol, the fact that they do not yield aldehydes or ketones on oxidation was only to be expected; they are, however, somewhat similar in constitution to the *tertiary* alcohols, and, like the latter, they often undergo complex changes on oxidation.

Monohydric Phenols.

Phenol, *carbolic acid,* or hydroxybenzene, $C_6H_5{\cdot}OH$, occurs in very small quantities in human urine and also in that of cows; it may be obtained from benzene, nitrobenzene, aniline, diazobenzene chloride, benzenesulphonic acid, and salicylic acid (p. 450) by the methods already given, but the whole of the phenol of commerce is prepared from coal-tar

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* Compare foot-note, Part I. p. 92.

(compare p. 307), in which it was discovered by Runge in 1834.

Phenol crystallises in colourless, deliquescent prisms, which melt at 42° and turn pink on exposure to air and light; it boils at 183°, and is volatile in steam. It has a very characteristic smell, is highly poisonous, and has a strong caustic action on the skin, quickly causing blisters. It dissolves freely in most organic liquids, but is only sparingly soluble (1 part in about 15) in cold water; its aqueous solution gives a violet colouration with ferric chloride, and a pale-yellow precipitate of *tribromophenol*, $C_6H_2Br_3{\cdot}OH$ (m.p. 92°), with bromine water; both these reactions may serve for the detection of phenol. Owing to its poisonous and antiseptic properties, phenol is extensively used as a disinfectant; it is also employed in large quantities for the manufacture of picric acid. *Potassium phenate*, $C_6H_5{\cdot}OK$, is obtained when phenol is dissolved in potash and the solution evaporated; it is a crystalline substance, readily soluble in water, and is decomposed by carbon dioxide with separation of phenol.

Phenyl methyl ether, or *anisole*, $C_6H_5{\cdot}O{\cdot}CH_3$, may be prepared by heating potassium phenate with methyl iodide; it is a colourless liquid, boiling at 155°, and is similar to the ethers of the fatty series in chemical properties, although it also shows the usual behaviour of aromatic compounds, and readily yields nitro-derivatives, &c. When warmed with concentrated hydriodic acid it yields phenol and methyl iodide,

$$C_6H_5{\cdot}O{\cdot}CH_3 + HI = C_6H_5{\cdot}OH + CH_3I.$$

Phenyl ethyl ether, or *phenetole*, $C_6H_5{\cdot}O{\cdot}C_2H_5$, can be obtained in a similar manner; it boils at 172°.

Nitrophenols, $C_6H_4(NO_2){\cdot}OH$, are formed very readily on treating phenol even with dilute nitric acid, the presence of the hydroxyl-group not only facilitating the introduction of the nitro-group, but also determining the position taken up by the latter. When phenol is gradually added to nitric acid of sp. gr. 1·11 (6 parts), the mixture being kept cold and frequently shaken, it is converted into *ortho-* and *para-*nitrophenol, which separate as a dark-brown oil or resinous mass.

This product is allowed to settle, washed with water by decantation, and then submitted to distillation in steam, whereupon the *ortho-*nitrophenol passes over as a yellow oil, which crystallises on cooling; the solution in the flask is heated to boiling, and filtered from tarry matter, the *para-*nitrophenol which separates on cooling being purified by recrystallisation from boiling water with addition of animal charcoal.

Meta-nitrophenol is prepared by reducing meta-dinitrobenzene to meta-nitraniline (p. 375), and treating a solution of the latter in excess of dilute sulphuric acid with nitrous acid; the solution of the diazo-salt is then slowly heated to boiling, and the meta-nitrophenol thus produced purified by recrystallisation from water.

The melting-points of the three compounds are:

Ortho-nitrophenol,	Meta-nitrophenol,	Para-nitrophenol,
45°.	96°.	114°.

The *o-* and the *m-*compounds are yellow, but the *p-*derivative is colourless; only the *o-*compound is volatile in steam. The three compounds are all sparingly soluble in cold water, but dissolve freely in alkalies and also in alkali carbonates, forming dark-yellow or red salts which are not decomposed by carbon dioxide; they have, therefore, a more marked acid character than phenol itself, the presence of the nitro-group having an effect comparable to that of the nitro-group in nitric acid, $HO{\cdot}NO_2$.

Picric acid, or trinitrophenol, $C_6H_2(NO_2)_3{\cdot}OH$, is formed when substances such as wool, silk, leather, and resins are heated with concentrated nitric acid, very complex reactions taking place; it may be obtained by heating phenol, or the *o-* and *p-*nitrophenols, with nitric acid, but the product is not very easily purified from resinous substances which are formed at the same time.

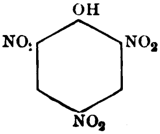
Picric acid is best prepared by dissolving phenol (1 part) in an equal weight of concentrated sulphuric acid, and adding this solution to nitric acid of sp. gr. 1·4 (3 parts) in small quantities at a time; after the first energetic action has subsided, the mixture is carefully heated on a water-bath for about two hours. On cooling, the product solidifies to a mass of crystals, which are collected, washed, and recrystallised from hot water.

When phenol is dissolved in sulphuric acid it is converted into a mixture of *o*- and *p*-phenolsulphonic acids, $C_6H_4(OH)\cdot SO_3H$ (see below); on subsequent treatment with nitric acid, the sulphonic group, as well as two atoms of hydrogen, are displaced by nitro-groups,

$$C_6H_4{<}^{OH}_{SO_3H} + 3HO\cdot NO_2 = C_6H_2(NO_2)_3\cdot OH + H_2SO_4 + 2H_2O.$$

Picric acid is a yellow crystalline compound, melting at 122·5°. It is only very sparingly soluble in cold, but moderately easily in hot, water, and its solutions dye silk and wool (not cotton, p. 514) a beautiful yellow colour; it is, in fact, one of the earliest known artificial organic dyes. It has very marked acid properties, and readily decomposes carbonates. The *potassium* derivative, $C_6H_2(NO_2)_3\cdot OK$, and the *sodium* derivative, $C_6H_2(NO_2)_3\cdot ONa$, are yellow crystalline compounds, the former being sparingly, the latter readily, soluble in cold water. These compounds, and also the ammonium derivative, *explode* violently on percussion or when heated, and are employed in the preparation of explosives; picric acid itself burns quietly when ignited, but can be caused to explode violently with a detonator.

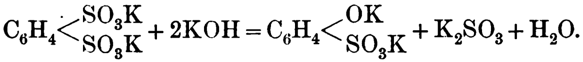
Picric acid may be produced by oxidising 1:3:5-trinitrobenzene, $C_6H_3(NO_2)_3$, with potassium ferricyanide, the presence of the nitro-groups facilitating the substitution of hydroxyl for hydrogen; as, moreover, it is quite immaterial which of the three hydrogen atoms is displaced, since they all occupy a similar position relatively to the rest of the molecule, the constitution of picric acid must be represented by the formula,



Picric acid has the curious property of forming crystalline compounds with benzene, naphthalene, anthracene, and many other hydrocarbons, so that it is sometimes used in detecting and also in purifying small quantities of the substances in question; the compound which it forms with benzene, for example, crystallises in yellow needles, is decomposed by water, and has the composition $C_6H_2(NO_2)_3{\cdot}OH, C_6H_6$.

Phenol-o-sulphonic acid, $C_6H_4(OH){\cdot}SO_3H$, is formed, together with a comparatively small quantity of the *p*-acid, when a solution of phenol in concentrated sulphuric acid is kept for some time at ordinary temperatures; if, however, the solution be heated at 100–110°, the *o*-acid, which is the primary product, is gradually converted into *phenol-p-sulphonic acid.*

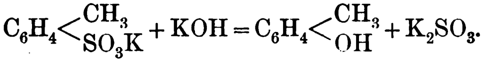
Phenol-m-sulphonic acid is prepared by carefully heating benzene-*m*-disulphonic acid with potash at 170–180°; under these conditions only one of the sulphonic groups is displaced,



$$C_6H_4{<}\begin{matrix}SO_3K\\SO_3K\end{matrix} + 2KOH = C_6H_4{<}\begin{matrix}OK\\SO_3K\end{matrix} + K_2SO_3 + H_2O.$$

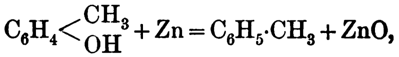
The *o*-acid is interesting on account of the fact that it is converted into the *p*-acid when boiled with water, and also because it is used as an antiseptic under the name *aseptol.*

The three (*o.m.p.*) **cresols** or hydroxytoluenes, $C_6H_4(CH_3){\cdot}OH$, the next homologues of phenol, occur in coal-tar, but cannot be conveniently isolated from this source owing to the difficulty of separating them from one another; they are prepared from the corresponding toluidines or amidotoluenes, $C_6H_4(CH_3){\cdot}NH_2$, by means of the diazo-reaction, or by fusing the corresponding toluenesulphonic acids with potash,



$$C_6H_4{<}\begin{matrix}CH_3\\SO_3K\end{matrix} + KOH = C_6H_4{<}\begin{matrix}CH_3\\OH\end{matrix} + K_2SO_3.$$

They resemble phenol in most ordinary properties, as, for example, in being sparingly soluble in water, and in forming potassium and sodium derivatives, which are decomposed by carbon dioxide; they also yield alkyl-derivatives, &c., by the displacement of the hydrogen of the hydroxyl-group. On distillation with zinc-dust they are all converted into toluene,



$$C_6H_4<\begin{matrix}CH_3\\OH\end{matrix} + Zn = C_6H_5 \cdot CH_3 + ZnO,$$

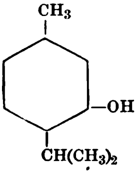
and they all give a bluish colouration with ferric chloride.

One very curious fact regarding the three cresols is that they are not oxidised by chromic acid, although toluene, as already stated, is slowly converted into benzoic acid; the presence of the hydroxyl-group, therefore, protects the methyl-group from the attack of acid oxidising agents, and this is true also in the case of other phenols of similar constitution. If, however, the hydrogen of the hydroxyl-group be displaced by an alkyl, or by an acid group such as acetyl, then the protection is withdrawn, and the methyl-group is converted into the carboxyl-group in the usual manner; the *methylcresols*, $C_6H_4(OCH_3) \cdot CH_3$, for example, are oxidised by chromic acid, yielding the corresponding methoxybenzoic acids, $C_6H_4(OCH_3) \cdot COOH$.

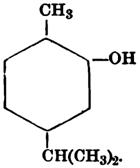
The melting and boiling points of the three cresols are given below.

	Ortho-cresol.	Meta-cresol.	Para-cresol.
M.p.	31°	5°	36°
B.p.	188°	201°	198°

Of the higher monohydric phenols, **thymol** and **carvacrol** may be mentioned; these two compounds are isomeric mono-hydroxy-derivatives of cymene, $C_6H_4(CH_3) \cdot C_3H_7$ (p. 349), and their constitutions are respectively represented by the formulæ,

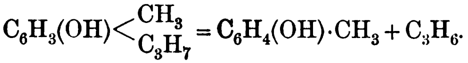


Thymol.



Carvacrol.

Thymol occurs in oil of thyme, together with cymene; it crystallises in large plates, melts at 51·5°, and has a characteristic smell like that of thyme. It is only very sparingly soluble in water, and does not give a colouration with ferric chloride; when heated with phosphoric anhydride it yields propylene and *m*-cresol,



$$C_6H_3(OH){<}\begin{matrix}CH_3\\C_3H_7\end{matrix} = C_6H_4(OH)\cdot CH_3 + C_3H_6.$$

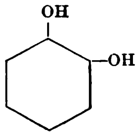
Carvacrol occurs in the oil of *Origanum hirtum*, and is easily prepared by heating camphor with iodine,

$$C_{10}H_{16}O + I_2 = C_{10}H_{14}O + 2HI;$$

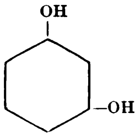
it is an oil boiling at 237°, and its alcoholic solution gives a green colouration with ferric chloride. When heated with phosphoric anhydride, it is decomposed into propylene and *o*-cresol.

Dihydric Phenols.

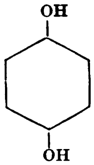
The isomeric dihydric phenols—catechol, resorcinol, and hydroquinone—are well-known compounds of considerable importance, and are respectively represented by the formulæ,



Catechol
(Ortho-dihydroxybenzene).

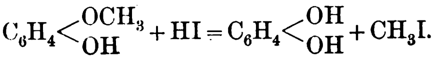


Resorcinol
(Meta-dihydroxybenzene).



Hydroquinone
(Para-dihydroxybenzene).

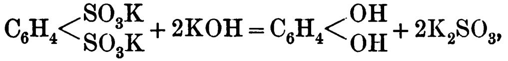
Catechol, or pyrocatechol, $C_6H_4(OH)_2$, occurs in *catechu*, a substance obtained in India from *Acacia catechu* and other trees, and was first obtained by the dry distillation of this vegetable product; it may be obtained by fusing phenol-*o*-sulphonic acid, $C_6H_4(OH)\cdot SO_3H$, with potash, but is most conveniently prepared by heating *guaiacol* or *methylcatechol*, a solid (m.p. 28°) contained in the tar of beechwood, with concentrated hydriodic acid,



$$C_6H_4{<}\begin{matrix}OCH_3\\OH\end{matrix} + HI = C_6H_4{<}\begin{matrix}OH\\OH\end{matrix} + CH_3I.$$

It is a colourless, crystalline substance, melting at 104°, and is readily soluble in water; its aqueous solution gives, with ferric chloride, a *green* colouration, which, on the addition of sodium bicarbonate, changes first to violet and then to red, a reaction which is common to all *ortho*-dihydric phenols (p. 402). Guaiacol shows a similar behaviour with ferric chloride, but when the hydrogen atoms of both the hydroxyl-groups are displaced, as, for example, in *dimethylcatechol* or *veratrol*, $C_6H_4(OCH_3)_2$, there is no colouration.

Resorcinol, $C_6H_4(OH)_2$, is prepared on a large scale by fusing benzene-*m*-disulphonic acid with potash,



$$C_6H_4{<}\begin{matrix}SO_3K\\SO_3K\end{matrix} + 2KOH = C_6H_4{<}\begin{matrix}OH\\OH\end{matrix} + 2K_2SO_3,$$

but it is also obtained when the para-disulphonic acid, and many other ortho- and para-derivatives of benzene are treated in the same way, owing to intramolecular change taking place (compare p. 401). It is a crystalline substance, melting at 110°, and dissolves freely in water, alcohol, and ether; its aqueous solution gives a dark-violet colouration, with ferric chloride and a crystalline precipitate of *tribromoresorcinol*, $C_6HBr_3(OH)_2$, with bromine water. When resorcinol is strongly heated for a few minutes with phthalic anhydride (p. 439), and the brown or red mass is then dissolved in soda, there results a brownish-red solution, which when poured into a large volume of water shows a beautiful green fluorescence; this phenomenon is due to the formation of *fluoresceïn* (p. 532). Other *m*-dihydric phenols give this *fluoresceïn reaction*, which, therefore, affords a convenient and very delicate test for such compounds; the fluoresceïn reaction may also be employed as a test for anhydrides of certain *dicarboxylic acids* (p. 437).

Resorcinol is used in large quantities in preparing fluoresceïn, eosin, and various azo-dyes.

Hydroquinone, or quinol, $C_6H_4(OH)_2$, is formed, together with glucose, when the glucoside, *arbutin*—a substance which occurs in the leaves of the bear-berry—is boiled with water,

$$C_{12}H_{16}O_7 + H_2O = C_6H_4(OH)_2 + C_6H_{12}O_6.$$

It is usually prepared by reducing quinone (p. 425) with sulphurous acid in aqueous solution, and then extracting with ether,

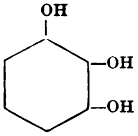
$$C_6H_4O_2 + H_2SO_3 + H_2O = C_6H_4(OH)_2 + H_2SO_4.$$

It melts at 169°, is readily soluble in water, and when treated with ferric chloride or other mild oxidising agents it is converted into quinone,

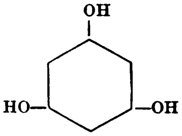
$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$

Trihydric Phenols.

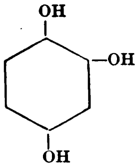
The three trihydric phenols, $C_6H_3(OH)_3$, which should exist in accordance with theory, are all known, and are respectively represented by the following formulæ,



Pyrogallol.
1:2:3-Trihydroxybenzene.



Phloroglucinol.
1:3:5-Trihydroxybenzene.



Hydroxyhydroquinone.
1:2:4-Trihydroxybenzene.

Pyrogallol, $C_6H_3(OH)_3$, sometimes called pyrogallic acid, is prepared by heating gallic acid (p. 452) alone or with glycerol, at about 210°, until the evolution of carbon dioxide ceases,

$$C_6H_2(OH)_3 \cdot COOH = C_6H_3(OH)_3 + CO_2.$$

It is a colourless, crystalline substance, melting at 115°, and is readily soluble in water, but more sparingly in alcohol and ether (the effect of hydroxyl-groups); its aqueous solution gives, with ferric chloride, a red, and with ferrous sulphate containing a trace of ferric chloride, a deep, dark-blue colouration. It dissolves freely in alkalies, giving solutions which rapidly absorb oxygen and turn black on exposure to the air, a fact which is made use of in gas analysis for the estimation of oxygen. Pyrogallol has powerful reducing properties, and precipitates gold, silver, and mercury from solutions of their salts, being itself oxidised to oxalic and acetic acids; many other phenols, such as catechol, resorcinol, and hydroquinone, show a similar behaviour, especially in alkaline solution, but the monohydric-compounds are much less readily oxidised, and consequently do not exhibit reducing properties. Pyrogallol and hydroquinone are used in photography as developers.

Like glycerol and other trihydric-compounds, pyrogallol forms mono-, di-, and tri-alkyl-derivatives, as, for example, $C_6H_3(OH)_2 \cdot OC_2H_5$, $C_6H_3(OH)(OC_2H_5)_2$, and $C_6H_3(OC_2H_5)_3$; the *dimethyl*-derivative, $C_6H_3(OCH_3)_2 \cdot OH$, occurs in beechwood tar.

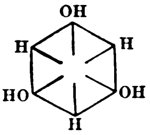
Phloroglucinol, 1:3:5-, or symmetrical trihydroxybenzene, $C_6H_3(OH)_3$, is produced when phenol, resorcinol, and many resinous substances, such as gamboge, dragon's-blood, &c., are fused with potash.

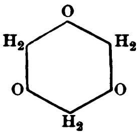
It is best prepared by fusing resorcinol (1 part) with soda (6 parts) for about twenty-five minutes, or until the vigorous evolution of hydrogen has ceased; the chocolate-coloured melt is dissolved in water, acidified with sulphuric acid, extracted with ether, the ethereal extract evaporated, and the residue recrystallised from water.

It crystallises with 2 mols. H_2O in colourless prisms, melts at about 218°, and is very soluble in water; the solution, which has a sweet taste, gives, with ferric chloride, a bluish-violet colouration, and when mixed with potash it rapidly turns brown in contact with air owing to absorption of oxygen. When digested with acetyl chloride, phloroglucinol yields a *triacetate*, $C_6H_3(C_2H_3O_2)_3$, melting at 106°, and in many other reactions its behaviour points to the conclusion that it contains three *hydroxyl*-groups; on the other hand, when treated with hydroxylamine it gives a *trioxime*,

$C_6H_6(N{\cdot}OH)_3$, and in this and certain other respects it behaves as though it were a *triketone.*

For these reasons phloroglucinol may be represented by one of the following formulæ,





and it may be assumed that the *trihydroxy*-compound is readily convertible into the triketone and *vice versâ* by tautomeric change (compare Part I. p. 200).

Hydroxyhydroquinone, or 1:2:4-trihydroxybenzene, is formed when hydroquinone is fused with potash. It melts at 140°, is very soluble in water, and its aqueous solution is coloured greenish-brown by ferric chloride, but on the addition of sodium bicarbonate the colour changes to blue and then to red (p. 402).

CHAPTER XXVIII.

AROMATIC ALCOHOLS, ALDEHYDES, KETONES, AND QUINONES.

Alcohols.

The aromatic alcohols are derived from the hydrocarbons by substituting hydroxyl-groups for hydrogen atoms of the *side-chain:* benzyl alcohol, $C_6H_5{\cdot}CH_2{\cdot}OH$, for example, is derived from toluene; tolyl alcohol, $C_6H_4(CH_3){\cdot}CH_2{\cdot}OH$, from xylene; and so on. The compounds of this kind are very closely related to the alcohols of the fatty series, although, of course, they show at the same time the general behaviour of aromatic substances.

They may be prepared by methods exactly analogous to those employed in the case of the aliphatic alcohols—namely, by heating the corresponding halogen derivatives with water, weak alkalies, or silver hydroxide,

$$C_6H_5{\cdot}CH_2Cl + H_2O = C_6H_5{\cdot}CH_2{\cdot}OH + HCl,$$

and by reducing the corresponding aldehydes and ketones,

$$C_6H_5{\cdot}CHO + 2H = C_6H_5{\cdot}CH_2{\cdot}OH$$
$$C_6H_5{\cdot}CO{\cdot}CH_3 + 2H = C_6H_5{\cdot}CH(OH){\cdot}CH_3.$$

Those compounds which, like benzyl alcohol, contain the carbinol group, $-CH_2{\cdot}OH$, directly united with the benzene nucleus, may also be prepared by treating the corresponding aldehydes with potash (compare p. 420),

$$2C_6H_5{\cdot}CHO + KOH = C_6H_5{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}COOK.$$

The aromatic alcohols are usually colourless liquids or solids, sparingly soluble in water; their behaviour with alkali metals, phosphorus pentachloride, and acids is similar to that of the fatty compounds, as will be seen from a consideration of the properties of benzyl alcohol, one of the few well-known aromatic alcohols.

Benzyl alcohol, or phenylcarbinol, $C_6H_5{\cdot}CH_2{\cdot}OH$, an isomeride of the three cresols (p. 408), occurs in storax (a resin obtained from the tree, *Styrax officinalis*), and also in balsam of Peru and balsam of Tolu, either in the free state or as an ester in combination with cinnamic or benzoic acid.

It may be obtained by reducing benzaldehyde (p. 418) with sodium amalgam,

$$C_6H_5{\cdot}CHO + 2H = C_6H_5{\cdot}CH_2{\cdot}OH,$$

and by boiling benzyl chloride with a solution of sodium carbonate,

$$C_6H_5{\cdot}CH_2Cl + H_2O = C_6H_5{\cdot}CH_2{\cdot}OH + HCl\,;$$

but it is most conveniently prepared by treating benzaldehyde with cold potash,

$$2C_6H_5{\cdot}CHO + KOH = C_6H_5{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}COOK.$$

The aldehyde (10 parts) is shaken with a solution of potash (9 parts) in water (10 parts) until the whole forms an emulsion, which is then allowed to stand for twenty-four hours; after adding water to dissolve the potassium benzoate, the solution is extracted with ether, the dried ethereal extract evaporated, and the benzyl alcohol purified by distillation.

Benzyl alcohol is a colourless liquid, boiling at 206°; it is only sparingly soluble in water, but miscible with alcohol, ether, &c., in all proportions. It dissolves sodium and potassium with evolution of hydrogen, yielding metallic derivatives which are decomposed by water, and when treated with phosphorus pentachloride it is converted into benzyl chloride,

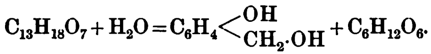
$$C_6H_5{\cdot}CH_2{\cdot}OH + PCl_5 = C_6H_5{\cdot}CH_2Cl + POCl_3 + HCl.$$

When heated with concentrated acids, or treated with anhydrides or acid chlorides, it gives esters; with hydrobromic acid, for example, it yields *benzyl bromide*, $C_6H_5{\cdot}CH_2Br$ (b.p. 199°), and with acetyl chloride or acetic anhydride it gives *benzyl acetate*, $C_6H_5{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$ (b.p. 206°). On oxidation with dilute nitric acid, it is first converted into benzaldehyde and then into benzoic acid,

$$C_6H_5{\cdot}CH_2{\cdot}OH + O = C_6H_5{\cdot}CHO + H_2O$$
$$C_6H_5{\cdot}CH_2{\cdot}OH + 2O = C_6H_5{\cdot}COOH + H_2O.$$

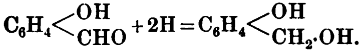
All these changes are strictly analogous to those undergone by the fatty alcohols.

Saligenin, $C_6H_4(OH){\cdot}CH_2{\cdot}OH$, also known as *o*-hydroxybenzyl alcohol, or salicyl alcohol, is an example of a substance which is both a phenol and an alcohol. It is produced, together with glucose, by the action of dilute acids or ferments on ***salicin***, a glucoside existing in the bark of the willow-tree,



$$C_{13}H_{18}O_7 + H_2O = C_6H_4{<}\begin{matrix}OH\\CH_2{\cdot}OH\end{matrix} + C_6H_{12}O_6.$$

It may be prepared synthetically by reducing salicylaldehyde (p. 422) with sodium amalgam and alcohol,

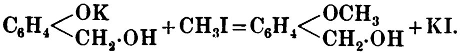


$$C_6H_4{<}\begin{matrix}OH\\CHO\end{matrix} + 2H = C_6H_4{<}\begin{matrix}OH\\CH_2{\cdot}OH.\end{matrix}$$

Saligenin melts at 82°, and is readily soluble in water, the solution acquiring a deep-blue colouration on the addition of ferric chloride. Owing to its phenolic nature, it forms alkali salts, which, when heated with alkyl halogen compounds, give the corresponding ethers (the *methyl ether*, $C_6H_4(OCH_3)\cdot CH_2\cdot OH$, is a colourless oil, boiling at 247°); on the other hand, it shows the properties of an alcohol, and yields salicylaldehyde and salicylic acid on oxidation.

The *m-* and *p-hydroxybenzyl alcohols* may be prepared by the reduction of the *m-* and *p*-hydroxybenzaldehydes (p. 423); they melt at 67° and 110° respectively.

Anisyl alcohol, or *p*-methoxybenzyl alcohol, $C_6H_4(OCH_3)\cdot CH_2\cdot OH$, is obtained by treating anisaldehyde, $C_6H_4(OCH_3)\cdot CHO$ (p. 423), with sodium amalgam and alcohol or with alcoholic potash. It has been prepared synthetically by heating a mixture of *p*-hydroxybenzyl alcohol, potash, and methyl iodide in alcoholic solution at 100°,



$$C_6H_4<\begin{matrix}OK\\CH_2\cdot OH\end{matrix} + CH_3I = C_6H_4<\begin{matrix}OCH_3\\CH_2\cdot OH\end{matrix} + KI.$$

It is crystalline, melts at 25°, and boils at 258°; on oxidation it yields anisaldehyde and anisic acid, $C_6H_4(OCH_3)\cdot COOH$.

Aldehydes.

The relation between the aromatic aldehydes and the aromatic alcohols is the same as that which exists between the corresponding classes of fatty compounds—that is to say, the aldehydes are derived from the primary alcohols by taking away two atoms of hydrogen from the $-CH_2\cdot OH$ group; benzaldehyde, $C_6H_5\cdot CHO$, for example, corresponds with benzyl alcohol, $C_6H_5\cdot CH_2\cdot OH$; salicylaldehyde, $C_6H_4(OH)\cdot CHO$, with salicyl alcohol, $C_6H_4(OH)\cdot CH_2\cdot OH$; phenylacetaldehyde, $C_6H_5\cdot CH_2\cdot CHO$, with phenylethyl alcohol, $C_6H_5\cdot CH_2\cdot CH_2\cdot OH$; and so on.

Now those compounds which contain an aldehyde-group directly united with carbon of the nucleus are of far greater importance than those in which the aldehyde-group is combined with a carbon atom of the side-chain, as in phenylacetaldehyde (see above), cinnamic aldehyde, $C_6H_5\cdot CH{:}CH\cdot CHO$, &c.; whereas, moreover, the latter resemble the fatty aldehydes very closely in general character, and do not therefore require any detailed description, the former differ from the fatty compounds in several important particulars, as will be seen from the following account of benzaldehyde and salicylaldehyde, two of the best-known aromatic compounds which contain the aldehyde group directly united with the benzene nucleus.

Benzaldehyde, $C_6H_5{\cdot}CHO$, sometimes called 'oil of bitter almonds,' was formerly obtained from the glucoside (compare foot-note, Part I. p. 287), amygdalin, which occurs in bitter almonds, and which, in contact with water, gradually undergoes decomposition into benzaldehyde, hydrogen cyanide, and glucose.

Benzaldehyde may be obtained by oxidising benzyl alcohol with nitric acid, and by distilling a mixture of calcium benzoate and calcium formate,

$$(C_6H_5{\cdot}COO)_2Ca + (H{\cdot}COO)_2Ca = 2C_6H_5{\cdot}CHO + 2CaCO_3,$$

reactions analogous to those employed in the fatty series.

It is prepared both in the laboratory and on the large scale either by heating benzal chloride (p. 362) with moderately dilute sulphuric acid, or calcium hydroxide, under pressure, or by boiling benzyl chloride with an aqueous solution of lead nitrate or copper nitrate. In the first method, the benzal chloride is probably first converted into the corresponding dihydroxy-derivative of toluene,

$$C_6H_5{\cdot}CHCl_2 + 2H_2O = C_6H_5{\cdot}CH(OH)_2 + 2HCl\,;$$

but as this compound contains two hydroxyl-groups united with one and the same carbon atom, it is very unstable (Part I. p. 129, foot-note), and subsequently undergoes decomposition into benzaldehyde and water. In the second method, the benzyl chloride is probably transformed into benzyl alcohol, which is then oxidised to the aldehyde by the metallic nitrate, with evolution of oxides of nitrogen and formation of copper or lead chloride, as indicated by the equation,

$$2C_6H_5{\cdot}CH_2{\cdot}OH + Cu(NO_3)_2 + 2HCl = \\ 2C_6H_5{\cdot}CHO + CuCl_2 + N_2O_3 + 3H_2O.$$

Benzyl chloride (5 parts), water (25 parts), and copper nitrate (4 parts) are placed in a flask connected with a reflux condenser, and the mixture is boiled for six to eight hours, a stream of carbon dioxide being passed into the liquid all the time, in order to expel the oxides of nitrogen, which would otherwise oxidise the benzaldehyde to benzoic acid; the process is at an end when the oil contains only traces of chlorine, which is ascertained by washing a small portion with water, and boiling it with silver nitrate and nitric acid. The benzaldehyde is then extracted with ether, the ethereal extract shaken with a concentrated solution of sodium bisulphite, and the crystals of the bisulphite compound, $C_6H_5{\cdot}CHO, NaHSO_3$, separated by filtration and washed with ether; the benzaldehyde is then regenerated by decomposing the crystals with dilute sulphuric acid, extracted with ether, and distilled.

Benzaldehyde is a colourless, highly refractive liquid of sp. gr. 1·05 at 15°; it boils at 179°, and is volatile in steam. It has a pleasant smell like that of bitter almonds, and is only sparingly soluble in water, but miscible with alcohol, ether, &c., in all proportions. It is extensively used for flavouring purposes, and is employed on the large scale in the manufacture of various dyes.

Benzaldehyde, and aromatic aldehydes in general, *resemble* the fatty aldehydes in the following respects: They readily undergo oxidation, sometimes merely on exposure to the air, yielding the corresponding acids,

$$C_6H_5{\cdot}CHO + O = C_6H_5{\cdot}COOH,$$

and consequently they reduce ammoniacal solutions of silver hydroxide. On reduction they are converted into the corresponding alcohols,

$$C_6H_5{\cdot}CHO + 2H = C_6H_5{\cdot}CH_2{\cdot}OH.$$

When treated with phosphorus pentachloride, they give dihalogen derivatives such as benzal chloride, $C_6H_5{\cdot}CHCl_2$, two atoms of chlorine being substituted for one atom of oxygen. They interact with hydroxylamine, yielding aldoximes, and with phenylhydrazine, giving hydrazones,

$$C_6H_5{\cdot}CHO + NH_2{\cdot}OH = H_2O + \underset{\text{Benzaldoxime.}}{C_6H_5{\cdot}CH{:}N{\cdot}OH}$$

$$C_6H_5{\cdot}CHO + NH_2{\cdot}NH{\cdot}C_6H_5 = H_2O + \underset{\text{Benzylidenehydrazone.}}{C_6H_5{\cdot}CH{:}N_2H{\cdot}C_6H_5.}$$

They combine directly with sodium bisulphite, forming crystalline compounds, and with hydrogen cyanide they yield hydroxycyanides such as *benzylidenehydroxycyanide*,* $C_6H_5{\cdot}CH(OH){\cdot}CN$. They readily undergo condensation with many other fatty and aromatic compounds; when, for example, a mixture of benzaldehyde and acetone is treated with a few drops of soda at ordinary temperatures, condensation occurs, and *benzylideneacetone*, $C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$ (m.p. 42°), is formed.

Benzaldehyde, and other aromatic aldehydes which contain the $-CHO$ group directly united with the benzene nucleus, *differ* from the fatty aldehydes in the following respects: They do not reduce Fehling's solution, and they do not undergo polymerisation; they do not form additive compounds with ammonia, but yield complex products such as *hydrobenzamide*, $(C_6H_5{\cdot}CH)_3N_2$, which is obtained by treating benzaldehyde with ammonia. When shaken with concentrated potash (or soda) they yield a mixture of the corresponding alcohol and acid (compare p. 415),

$$2C_6H_5{\cdot}CHO + KOH = C_6H_5{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}COOK.$$

When benzaldehyde (5 parts) is heated with a solution of potassium cyanide (1 part) in aqueous alcohol for about an hour, it is converted into *benzoïn*, which separates on cooling in colourless crystals; benzoïn is a ketonic alcohol, formed in accordance with the equation,

$$2C_6H_5{\cdot}CHO = C_6H_5{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_5;$$

it melts at 137°, and is oxidised by boiling concentrated nitric acid, giving a diketone, *benzil*, $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$, which is yellow and melts at 95°.

Nitrobenzaldehydes, $C_6H_4(NO_2){\cdot}CHO$.—When treated with a mixture of nitric and sulphuric acids, benzaldehyde yields *m*-nitrobenzaldehyde (m.p. 58°) as principal product, small quantities of *o*-nitrobenzaldehyde (m.p. 46°) being formed at the same time.

p-Nitrobenzaldehyde (m.p. 107°), and also the *o*-compound, are most conveniently prepared by the oxidation of the corresponding nitrocinnamic acids (p. 445) with potassium permanganate,

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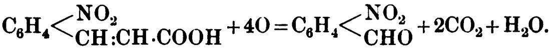
* The name *benzylidene* is given to the group of atoms, $C_6H_5{\cdot}CH=$, which is analogous to ethylidene, $CH_3{\cdot}CH=$ (Part I. p. 142).

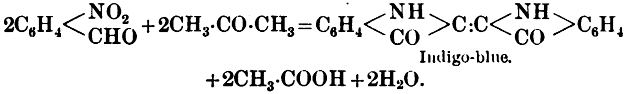


$$C_6H_4 < \begin{matrix} NO_2 \\ CH{:}CH\cdot COOH \end{matrix} + 4O = C_6H_4 < \begin{matrix} NO_2 \\ CHO \end{matrix} + 2CO_2 + H_2O.$$

During the operation the mixture is shaken with benzene in order to extract the aldehyde as fast as it is formed, and thus prevent it from being further oxidised. The benzene solution is then evaporated, and the aldehyde purified by recrystallisation.

The nitrobenzaldehydes are colourless, crystalline substances, which show much the same behaviour as benzaldehyde itself; when reduced with ferrous sulphate and ammonia they are converted into the corresponding *amidobenzaldehydes*, $C_6H_4(NH_2)\cdot CHO$.

o-Nitrobenzaldehyde is a particularly interesting substance, as, when its solution in acetone is mixed with a few drops of dilute soda, a precipitate of *indigo-blue* gradually forms (Baeyer). This important synthesis of this vegetable dye may be represented by the equation,

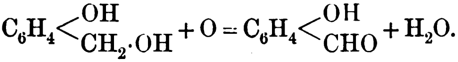


$$2C_6H_4 < \begin{matrix} NO_2 \\ CHO \end{matrix} + 2CH_3\cdot CO\cdot CH_3 = \underbrace{C_6H_4 < \begin{matrix} NH \\ CO \end{matrix} > C{:}C < \begin{matrix} NH \\ CO \end{matrix} > C_6H_4}_{\text{Indigo-blue.}}$$
$$+ 2CH_3\cdot COOH + 2H_2O.$$

Hydroxy-aldehydes.

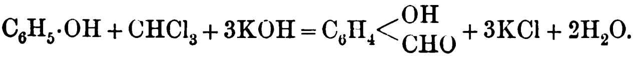
The hydroxy-derivatives of the aldehydes, such as the hydroxybenzaldehydes, $C_6H_4(OH)\cdot CHO$, which contain the hydroxyl-group united with the nucleus, combine the properties of phenols and aldehydes.

They may be obtained by the oxidation of the corresponding hydroxy-alcohols; saligenin (p. 416), or *o*-hydroxybenzyl alcohol, for example, yields salicylaldehyde or *o*-hydroxybenzaldehyde,



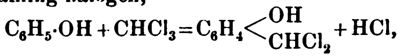
$$C_6H_4 < \begin{matrix} OH \\ CH_2\cdot OH \end{matrix} + O = C_6H_4 < \begin{matrix} OH \\ CHO \end{matrix} + H_2O.$$

As, however, such alcohols are not easily obtained, and indeed in many cases have only been produced by the reduction of the hydroxy-aldehydes, the latter are usually prepared by heating the phenols with chloroform in alkaline solution (Reimer's reaction),



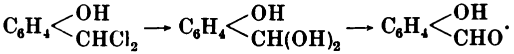
$$C_6H_5\cdot OH + CHCl_3 + 3KOH = C_6H_4 < \begin{matrix} OH \\ CHO \end{matrix} + 3KCl + 2H_2O.$$

The actual changes which occur in carrying out Reimer's reaction are not clearly understood; possibly the phenol interacts with the chloroform, in the presence of the alkali, yielding an intermediate product containing halogen,



$$C_6H_5{\cdot}OH + CHCl_3 = C_6H_4{<}\begin{matrix}OH\\ CHCl_2\end{matrix} + HCl,$$

which by the further action of the alkali is converted into a hydroxybenzaldehyde, just as benzalchloride, $C_6H_5{\cdot}CHCl_2$, is transformed into benzaldehyde (compare p. 418),



$$C_6H_4{<}\begin{matrix}OH\\ CHCl_2\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}OH\\ CH(OH)_2\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}OH\\ CHO\end{matrix}.$$

As a rule, the principal product is the *o*-hydroxyaldehyde, small quantities of the corresponding *p*-compound being produced at the same time.

Salicylaldehyde (*o*-hydroxybenzaldehyde), $C_6H_4(OH){\cdot}CHO$, may be obtained by oxidising saligenin with chromic acid (see above), but it is usually prepared from phenol by Reimer's reaction.

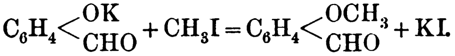
Phenol (20 grams) is dissolved in caustic soda (60 grams) and water (120 grams), the solution heated to 60° in a flask provided with a reflux condenser, and chloroform (30 grams) added in small quantities at a time from a dropping funnel. After slowly heating to boiling, the unchanged chloroform is distilled off, the alkaline liquid acidified and distilled in steam, when a mixture of phenol and salicylaldehyde passes over. (The residue in the flask contains *p*-hydroxybenzaldehyde, which may be extracted from the filtered liquid with ether, and purified by recrystallisation.) The oily mixture is extracted from the distillate with ether, and the extract shaken with a solution of sodium bisulphite, which dissolves the aldehyde in the form of its bisulphite compound. The solution is then separated, decomposed with sodium carbonate, and the regenerated salicylaldehyde extracted with ether and purified by distillation.

Salicylaldehyde is a colourless oil which boils at 196°, and has a penetrating, aromatic odour; it is moderately soluble in water, its solution giving a deep violet colouration with ferric chloride. When reduced with sodium amalgam it yields saligenin, $C_6H_4(OH){\cdot}CH_2{\cdot}OH$ (p. 416), whereas oxidising agents convert it into salicylic acid, $C_6H_4(OH){\cdot}COOH$.

p-Hydroxybenzaldehyde melts at 116°; it dissolves readily in hot water, and gives, with ferric chloride, a violet colouration.

m-Hydroxybenzaldehyde is obtained by converting *m*-nitrobenzaldehyde into *m*-amidobenzaldehyde, and then displacing the amido-group by hydroxyl, by means of the diazo-reaction. It crystallises from water in needles, and melts at 104°.

Anisaldehyde (*p*-methoxybenzaldehyde), $C_6H_4(OCH_3)\cdot CHO$, is prepared from oil of aniseed. This ethereal oil contains *anethole*, $C_6H_4(OCH_3)\cdot CH{:}CH\cdot CH_3$, a crystalline substance (m.p. 21°), which on oxidation with potassium dichromate and sulphuric acid is converted into anisaldehyde, the propenyl group $-CH{:}CH\cdot CH_3$ being oxidised to the aldehyde group. It may be prepared synthetically by digesting *p*-hydroxybenzaldehyde with alcoholic potash and methyl iodide,



$$C_6H_4{<}{\scriptstyle\begin{matrix}OK\\CHO\end{matrix}} + CH_3I = C_6H_4{<}{\scriptstyle\begin{matrix}OCH_3\\CHO\end{matrix}} + KI.$$

Anisaldehyde boils at 248°, and has a penetrating, aromatic odour; on reduction with sodium amalgam it yields anisyl alcohol, $C_6H_4(OCH_3)\cdot CH_2\cdot OH$ (p. 417); oxidising agents convert it into anisic acid, $C_6H_4(OCH_3)\cdot COOH$ (p. 452).

Ketones.

The ketones of the aromatic, like those of the fatty series, have the general formula $R-CO-R'$, where R and R′ represent different or identical radicles, one of which must, of course, be aromatic.

Acetophenone, phenylmethyl ketone, or acetylbenzene, $C_6H_5\cdot CO\cdot CH_3$, may be described as a typical aromatic ketone. It is formed on distilling a mixture of calcium benzoate and calcium acetate, a reaction which is exactly analogous to that which is made use of in obtaining mixed ketones of the fatty series,

$$(C_6H_5\cdot COO)_2Ca + (CH_3\cdot COO)_2Ca = 2C_6H_5\cdot CO\cdot CH_3 + 2CaCO_3.$$

It is most conveniently prepared by dropping acetyl chloride

(1 mol.) into well-cooled benzene (1 mol.) in presence of aluminium chloride,

$$C_6H_6 + CH_3{\cdot}COCl = C_6H_5{\cdot}CO{\cdot}CH_3 + HCl.$$

This method is of general use, as by employing other acid chlorides and other hydrocarbons, many other ketones may be prepared; it is an extension of Friedel and Crafts' method of preparing hydrocarbons (p. 340).

Acetophenone melts at 20·5°, and boils at 202°; it is used as a hypnotic in medicine, under the name of *hypnone.* Its chemical behaviour is so similar to that of the fatty ketones that most of its reactions, or at any rate those which are determined by the carbonyl-group, might be foretold from a consideration of those of acetone; on reduction with sodium amalgam and aqueous alcohol, acetophenone is converted into phenylmethyl carbinol, $C_6H_5{\cdot}CH(OH){\cdot}CH_3$, just as acetone is transformed into isopropyl alcohol; like acetone, and other fatty ketones, it interacts with hydroxylamine and with phenylhydrazine, giving the *oxime*, $C_6H_5{\cdot}C(NOH){\cdot}CH_3$, and the *hydrazone*, $C_6H_5{\cdot}C(N_2HC_6H_5){\cdot}CH_3$, respectively. On oxidation it is resolved into benzoic acid and carbon dioxide, just as acetone is oxidised to acetic acid and carbon dioxide,

$$C_6H_5{\cdot}CO{\cdot}CH_3 + 4O = C_6H_5{\cdot}COOH + CO_2 + H_2O.$$

Acetophenone shows also the general behaviour of aromatic compounds, inasmuch as it may be converted into nitro-, amido-, and halogen-derivatives by displacement of hydrogen of the nucleus.

The homologues of acetophenone, such as *propiophenone*, $C_6H_5{\cdot}CO{\cdot}C_2H_5$, *butyrophenone*, $C_6H_5{\cdot}CO{\cdot}C_3H_7$, &c., are of little importance, but benzophenone, an aromatic ketone of a different series, may be briefly described.

Benzophenone, diphenyl ketone, or benzoylbenzene, $C_6H_5{\cdot}CO{\cdot}C_6H_5$, may be obtained by distilling calcium benzoate, and by treating benzene with benzoyl chloride, or with carbonyl chloride, in presence of aluminium chloride,

$$C_6H_6 + C_6H_5{\cdot}COCl = C_6H_5{\cdot}CO{\cdot}C_6H_5 + HCl$$
$$2C_6H_6 + COCl_2 = C_6H_5{\cdot}CO{\cdot}C_6H_5 + 2HCl.$$

It melts at 48–49°, and is very similar to acetophenone in most respects; when distilled over zinc-dust it is converted into *diphenylmethane*, $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$ (p. 351).

Quinones.

When hydroquinone is oxidised with excess of ferric chloride in aqueous solution a yellowish colouration is produced, and the solution acquires a very penetrating odour; if sufficiently strong, yellow crystals are deposited.

The substance formed in this way is named *quinone* (benzoquinone), and is the simplest member of a very interesting class of compounds; its formation may be expressed by the equation,

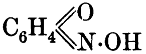
$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$

Quinone, $C_6H_4O_2$, is usually prepared by oxidising aniline with potassium dichromate and sulphuric acid.

Aniline (1 part) is dissolved in water (25 parts) and sulphuric acid (8 parts), and finely-powdered potassium dichromate (3·5 parts) gradually added, the whole being well cooled and constantly stirred during the operation; the product, which is very dark-coloured owing to the presence of aniline black, may be extracted with ether, but is more conveniently isolated by submitting the liquid, in *small* portions at a time, to steam distillation, as rapidly as possible. The quinone is then separated by filtration, the filtrate being extracted with ether if necessary.

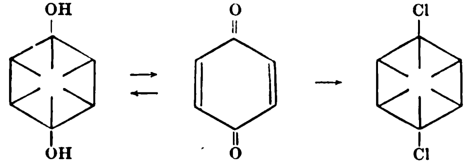
Quinone crystallises in golden-yellow prisms, melts at 116°, sublimes very readily, and is volatile in steam; it has a peculiar, irritating, and very characteristic smell, and is only sparingly soluble in water, but dissolves freely in alcohol and ether. It is readily reduced by sulphurous acid, zinc and hydrochloric acid, &c., being converted into hydroquinone,

$$C_6H_4O_2 + 2H = C_6H_4(OH)_2.$$

In some respects quinone behaves as if it contained two carbonyl-groups, each having properties similar to those of the carbonyl-groups in compounds such as acetone, acetophenone, &c.; when treated with hydroxylamine hydrochloride, for example, quinone yields a *monoxime*,  $C_6H_4\langle^{O}_{N\cdot OH}$ (identical with *p*-nitrosophenol, p. 379), and also a *dioxime*,  $C_6H_4\langle^{N\cdot OH}_{N\cdot OH}$. The two carbonyl-groups, moreover, are in the *para*-position to one another, as is shown by the facts that when quinone is reduced it gives hydroquinone (*para*-dihydroxybenzene), and when quinone-dioxime is reduced with tin and hydrochloric acid it yields *p*-phenylenediamine (p. 376).

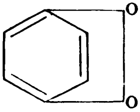
In other respects, however, quinone undergoes changes which are quite different from those observed in the case of ordinary ketones; on reduction, for instance, each >CO group is transformed into $\geqslant$C·OH, and not into >CH·OH, as might have been expected from analogy; again, on treatment with phosphorus pentachloride, each oxygen atom is displaced by *one* atom of chlorine, *p*-dichlorobenzene, $C_6H_4Cl_2$, being formed, and not a tetrachloro-derivative, as might have been expected.

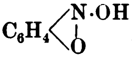
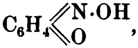
This curious behaviour, and the close relation between hydroquinone and quinone, is explained by assuming that in the conversion of the former into the latter by oxidation intramolecular change also takes place, and in such a way as to bring about a rearrangement of the carbon affinities. On reducing quinone, or on treating it with phosphorus pentachloride, this change is reversed, and the condition represented by the centric formula is again established; the following formulæ indicate the nature of these changes,



Hydroquinone. **Quinone.** **Dichlorobenzene.**

The constitution of quinone may also be represented by the following formula,



which was first suggested by Graebe, and which does not necessitate the view that intramolecular change occurs in the conversion of quinone into hydroquinone. If this formula be adopted, the constitution of quinone monoxime would be,  $C_6H_4\left\langle\begin{array}{l}N\cdot OH\\ |\\ O\end{array}\right.$, and the formation of this compound from *p*-nitrosodimethylaniline (p. 379) would involve no change in the nucleus; if, however, quinone be really a *diketone*,  $C_6H_4\left\langle\!\!\left\langle\begin{array}{l}O\\ O\end{array}\right.\right.$, its monoxime would be  $C_6H_4\left\langle\!\!\left\langle\begin{array}{l}N\cdot OH\\ O\end{array}\right.\right.$, and intramolecular change must be assumed to occur during its formation from *p*-nitrosodimethylaniline. The principal arguments which can be advanced in favour of the diketone formula are, firstly, that quinone gives a *dioxime*, and secondly, that it combines *directly* with bromine, giving a di- and a tetra-bromide, $C_6H_4Br_2O_2$ and $C_6H_4Br_4O_2$. The latter behaviour seems to show that the carbon atoms in quinone are united in the same way as those in unsaturated compounds, such as ethylene, and not as those in benzene and its ordinary substitution products (compare p. 336).

Benzoquinone and many other para-quinones (that is to say, quinones in which the two carbonyl-groups are in the para-position to one another *) may be produced by the oxidation, with chromic acid or ferric chloride, of many hydroxy- and amido-compounds, which contain the substituting groups in the para-position; quinone, for example, is formed on oxidising aniline, *p*-amidophenol, $C_6H_4(OH)\cdot NH_2$, and *p*-phenylenediamine, $C_6H_4(NH_2)_2$, whereas *o*-toluidine and *p*-toluylenediamine, $C_6H_4(NH_2)_2\cdot CH_3$, $[NH_2:NH_2:CH_3 = 1:4:2]$, yield *toluquinone* $[O:O:CH_3 = 1:4:2]$. All *para*-quinones resemble

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* Other quinones, of a somewhat different class from benzoquinone, are described later (pp. 468, 483).

(benzo)quinone in smell, in having a yellow colour, and in being readily volatile.

When bleaching-powder is used in oxidising amido-compounds such as the above, *quinone chlorimides* and *quinone dichlorodiimides* are formed in the place of quinones,

$$NH_2 \cdot C_6H_4 \cdot OH + 4Cl = \underset{\text{Quinone Chlorimide.}}{NCl : C_6H_4 : O} + 3HCl$$

$$NH_2 \cdot C_6H_4 \cdot NH_2 + 6Cl = \underset{\text{Quinone Dichlorodiimide.}}{NCl : C_6H_4 : NCl} + 4HCl.$$

The quinone chlorimides and dichlorodiimides resemble quinone in many respects; they are crystalline, readily volatile in steam, and are respectively converted into *p*-amidophenol and *p*-phenylenediamine or their derivatives on reduction.

Chloranil, or tetrachloroquinone, $O : C_6Cl_4 : O$, is produced when chlorine acts on quinone, but it is usually prepared by treating phenol with hydrochloric acid and potassium chlorate, oxidation and chlorination taking place simultaneously,

$$C_6H_5 \cdot OH + 10Cl + O = O : C_6Cl_4 : O + 6HCl.$$

It crystallises in yellow plates, sublimes without melting, and is sparingly soluble in alcohol, and insoluble in water.

It is readily reduced to tetrachlorohydroquinone, $HO \cdot C_6Cl_4 \cdot OH$, and is therefore a powerful oxidising agent, for which reason it is much employed in colour chemistry, when the use of inorganic oxidising agents is undesirable.

CHAPTER XXIX.

CARBOXYLIC ACIDS.

The carboxylic acids of the aromatic series are derived from the aromatic hydrocarbons, just as those of the fatty series are derived from the paraffins—namely, by the substitution of one or more carboxyl-groups for a corresponding number of hydrogen atoms. In this, as in other cases, however, one of two classes of compounds may be obtained according as substitution takes place in the nucleus or in the side-chain; benzene yields, of course, only acids of the first class, such as benzoic acid, $C_6H_5 \cdot COOH$, the three (*o.m.p.*) phthalic acids,

$C_6H_4(COOH)_2$, the three tricarboxylic acids, $C_6H_3(COOH)_3$, &c., but toluene (and all the higher homologues) may give rise to derivatives of both kinds—as, for example, the three toluic acids, $C_6H_4(CH_3)\cdot COOH$, and phenylacetic acid, $C_6H_5\cdot CH_2\cdot COOH$.

Although there are no very important differences in the properties of these two classes of acids, it is more convenient to describe them separately, taking first those compounds in which the carboxyl-groups are directly united with carbon of the nucleus.

Preparation.—Such acids may be obtained by oxidising the alcohols or aldehydes,

$$C_6H_5\cdot CH_2\cdot OH + 2O = C_6H_5\cdot COOH + H_2O$$
$$C_6H_5\cdot CHO + O = C_6H_5\cdot COOH,$$

and by hydrolysing the nitriles (p. 433) with alkalies or mineral acids,

$$C_6H_5\cdot CN + 2H_2O = C_6H_5\cdot COOH + NH_3$$
$$C_6H_5\cdot CH_2\cdot CN + 2H_2O = C_6H_5\cdot CH_2\cdot COOH + NH_3,$$

reactions which are exactly similar to those employed in the case of the fatty acids (Part I. p. 168).

Perhaps, however, the most important method, and one which has no counterpart in the fatty series, consists in oxidising the homologues of benzene with dilute nitric acid or chromic acid,

$$C_6H_5\cdot CH_3 + 3O = C_6H_5\cdot COOH + H_2O$$
$$C_6H_5\cdot CH_2\cdot CH_3 + 6O = C_6H_5\cdot COOH + CO_2 + 2H_2O.$$

In this way only those acids which contain the *carboxyl-group united with the nucleus* can be obtained, because the side-chain is always oxidised to $-COOH$, no matter how many $-CH_2-$ groups it may contain; in other words, all homologues of benzene which contain only one side-chain yield benzoic acid, whereas those containing two give one of the phthalic acids. In the latter case, however, one of the side-chains may be oxidised before the other is attacked, so that by stopping the process at the right time, an alkyl-derivative of benzoic acid is first obtained,

$$C_6H_4(CH_3)_2 + 3O = C_6H_4(CH_3)\cdot COOH + H_2O$$
$$C_6H_4(CH_3)\cdot COOH + 3O = C_6H_4(COOH)_2 + H_2O.$$

Oxidation is frequently carried out by boiling the hydrocarbon (1 vol.) with nitric acid (1 vol.) diluted with water (2-4 vols.) until brown fumes are no longer formed. The mixture is then made slightly alkaline with soda, and any unchanged hydrocarbon and traces of nitro-hydrocarbon separated by distilling with steam or by extracting with ether; the alkaline solution is then acidified and the acid separated by filtration and purified by recrystallisation.

Most hydrocarbons are only very slowly attacked by oxidising agents generally, and it is often advantageous to first substitute chlorine or some other group for hydrogen of the side-chain, as in this way oxidation is facilitated. Benzyl chloride, $C_6H_5\cdot CH_2Cl$, and benzyl acetate, $C_6H_5\cdot CH_2\cdot OC_2H_3O$ (p. 361), for example, are much more readily oxidised than toluene, because they first undergo hydrolysis, giving alcohols.

Properties.—The aromatic acids are crystalline, and generally distil without decomposing; they are sparingly soluble in cold water, but much more readily in hot water, alcohol, and ether. As regards all those properties which are determined by the carboxyl-group, the aromatic acids are closely analogous to the fatty compounds, and give corresponding derivatives, as the following examples show,

Benzoic acid,	$C_6H_5\cdot COOH$	Benzoyl chloride,	$C_6H_5\cdot COCl$
Sodium benzoate,	$C_6H_5\cdot COONa$	Benzamide,	$C_6H_5\cdot CO\cdot NH_2$
Ethyl benzoate,	$C_6H_5\cdot COOC_2H_5$	Benzoic anhydride,	$(C_6H_5\cdot CO)_2O$.

When distilled with lime, they are decomposed with loss of carbon dioxide and formation of the corresponding hydrocarbons, just as acetic acid under similar circumstances yields marsh-gas,

$$C_6H_5\cdot COOH = C_6H_6 + CO_2$$
$$C_6H_4(CH_3)\cdot COOH = C_6H_5\cdot CH_3 + CO_2.$$

Benzoic acid, $C_6H_5\cdot COOH$, occurs in the free state in many resins, especially in gum benzoïn and Peru balsam; it is also found in the urine of cows and horses, as hippuric acid or benzoylglycine, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$, to the extent of about 2 per cent.

It may be obtained by subliming gum benzoïn in iron pots, the crude sublimate being purified by recrystallisation from water; or by boiling hippuric acid with hydrochloric acid (Part I. p. 300),

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH + HCl + H_2O = C_6H_5{\cdot}COOH + NH_2{\cdot}CH_2{\cdot}COOH, HCl.$$

Benzoic acid is manufactured by oxidising benzyl chloride (p. 361) with 60 per cent. nitric acid,

$$C_6H_5{\cdot}CH_2Cl + 2O = C_6H_5{\cdot}COOH + HCl,$$

or by heating calcium phthalate with lime at about 350°,

$$2C_6H_4(COO)_2Ca + Ca(OH)_2 = (C_6H_5{\cdot}COO)_2Ca + 2CaCO_3.$$

It may also be prepared by oxidising toluene, benzyl alcohol, or benzaldehyde, and by hydrolysing benzonitrile with caustic soda,

$$C_6H_5{\cdot}CO{\cdot}CN + 2H_2O = C_6H_5{\cdot}COOH + NH_3.$$

Benzoic acid separates from water in glistening crystals, melts at 121·5°, and boils at 249°, but it sublimes very readily even at 100°, and is volatile in steam; it dissolves in 400 parts of water at 15°, but is readily soluble in hot water, alcohol, and ether. Its vapour has a characteristic odour, and an irritating action on the throat, causing violent coughing. Most of the metallic salts of benzoic acid are soluble in water and crystallise well; *calcium benzoate*, $(C_6H_5{\cdot}COO)_2Ca + 3H_2O$, for example, prepared by neutralising benzoic acid with milk of lime, crystallises in needles, and is very soluble in water.

Ethyl benzoate, $C_6H_5{\cdot}COOC_2H_5$, is prepared by saturating a solution of benzoic acid (1 part) in alcohol (3 parts) with hydrogen chloride, and then boiling the solution (with reflux condenser) for about two hours (Part I. p. 191).

The alcohol is then distilled, the oily residue poured into water, and shaken with dilute sodium carbonate until free from acids; the ester is next washed with water, dried with calcium chloride, and distilled. A little ether may be used to dissolve the ester if it does not separate well from the aqueous solutions. It boils at 211°, has a pleasant aromatic odour, and is readily hydrolysed by boiling alcoholic potash.

Benzoyl chloride, $C_6H_5{\cdot}COCl$, is obtained by treating benzoic acid with phosphorus pentachloride.

The dry acid is placed in a distillation flask, and about 5 per cent. more than one molecular proportion of the pentachloride is added; the fumes which are evolved are passed into water or dilute soda (care being taken that the liquid is not sucked into the flask), the whole operation being conducted in the fume cupboard. When the reaction is finished, the mixture of phosphorus oxychloride (b.p. 107°) and benzoyl chloride is submitted to fractional distillation.

It is a colourless oil, possessing a most irritating odour, and boils at 198°; it is gradually decomposed by water, yielding benzoic acid and hydrochloric acid.

Benzoic anhydride, $(C_6H_5{\cdot}CO)_2O$, is produced when benzoyl chloride is treated with sodium benzoate, just as acetic anhydride is formed by the interaction of acetyl chloride and sodium acetate (Part I. p. 163); it is a crystalline substance, melting at 42°, and closely resembles acetic anhydride in ordinary chemical properties.

Benzoyl chloride and benzoic anhydride, more especially the former, are frequently used for the detection of hydroxy- and amido-compounds, as they interact with all such substances, yielding benzoyl-derivatives, the monovalent *benzoyl*-group, $C_6H_5{\cdot}CO-$, taking the place of the hydrogen of the hydroxyl- or amido-group,

$$C_6H_5{\cdot}COCl + C_2H_5{\cdot}OH = \underset{\text{Ethyl Benzoate.}}{C_6H_5{\cdot}O{\cdot}CO{\cdot}C_2H_5} + HCl$$

$$(C_6H_5{\cdot}CO)_2O + C_2H_5{\cdot}OH = C_2H_5{\cdot}O{\cdot}CO{\cdot}C_6H_5 + C_6H_5{\cdot}COOH$$

$$C_6H_5{\cdot}COCl + NH_2{\cdot}C_6H_5 = C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + HCl.$$

As such benzoyl-derivatives usually crystallise much more readily than the corresponding acetyl-derivatives, they are generally prepared in preference to the latter when it is a question of identifying or isolating a substance.

Benzoyl-derivatives may be prepared by heating the hydroxy- or amido-compound with benzoyl chloride or with benzoic anhydride. A more convenient method, however, is that of Baumann and Schotten : it consists in adding benzoyl chloride and 10 per cent. potash alternately, in small quantities at a time, to the compound, which is either dissolved or suspended in water, the mixture being well shaken and kept cool during the operation. Potash alone is then added until the disagreeable smell of benzoyl chloride is no longer noticed, and the solution remains permanently *alkaline;* the product is finally separated by filtration or by extraction with ether. The alkali serves to neutralise the hydrochloric acid which is formed, the interaction taking place much more readily in the neutral or slightly alkaline solution.

Benzamide, $C_6H_5{\cdot}CO{\cdot}NH_2$, may be taken as an example of an aromatic amide; it may be obtained by reactions similar to those employed in the case of acetamide (Part I. p. 164), as, for example, by treating ethyl benzoate with ammonia,

$$C_6H_5{\cdot}COOC_2H_5 + NH_3 = C_6H_5{\cdot}CO{\cdot}NH_2 + C_2H_5{\cdot}OH\,;$$

but it is most conveniently prepared by triturating benzoyl chloride with excess of dry ammonium carbonate in a mortar until the smell of the chloride is barely perceptible, and then purifying the product by recrystallisation from water,

$$C_6H_5{\cdot}COCl + (NH_4)_2CO_3 = C_6H_5{\cdot}CO{\cdot}NH_2 + CO_2 + H_2O + NH_4Cl.$$

It is a crystalline substance, melts at 130°, and is sparingly soluble in cold, but readily soluble in hot, water; like other amides, it is decomposed by boiling alkalies, yielding ammonia and an alkali salt,

$$C_6H_5{\cdot}CO{\cdot}NH_2 + KOH = C_6H_5{\cdot}COOK + NH_3.$$

Benzonitrile, or phenyl cyanide, $C_6H_5{\cdot}CN$, may be obtained by treating benzamide with dehydrating agents, a method similar to that employed in the preparation of fatty nitriles,

$$C_6H_5{\cdot}CO{\cdot}NH_2 = C_6H_5{\cdot}CN + H_2O.$$

Although it cannot be prepared by treating chloro- or bromobenzene with potassium cyanide (the halogen atom being so firmly held that no interaction occurs), it may be obtained by fusing benzenesulphonic acid with potassium cyanide (or with potassium ferrocyanide, which yields the cyanide), just as fatty nitriles may be prepared by heating the alkylsulphuric acids with potassium cyanide,

$$C_6H_5{\cdot}SO_3K + KCN = C_6H_5{\cdot}CN + K_2SO_3$$
$$C_2H_5{\cdot}SO_4K + KCN = C_2H_5{\cdot}CN + K_2SO_4.$$

It is, however, most conveniently prepared from aniline by Sandmeyer's reaction—namely, by treating a solution of diazobenzene chloride with cuprous cyanide (p. 384),

$$C_6H_5{\cdot}N_2Cl + CuCN = C_6H_5{\cdot}CN + CuCl + N_2.$$

Aniline (1 part) is *diazotised* exactly as already described (p. 384), and the solution of the diazo-chloride is then gradually added to a hot solution of cuprous cyanide (see below); the product is separated by steam distillation, &c., just as described in the case of iodobenzene (p. 358).

The solution of cuprous cyanide is prepared by slowly adding a solution of potassium cyanide (3 parts) to a solution of crystallised cupric sulphate (2½ parts), this and the subsequent operations, including steam distillation, being conducted in a good draught cupboard on account of the evolution of cyanogen and hydrogen cyanide,

$$2CuSO_4 + 4KCN = 2CuCN + (CN)_2 + K_2SO_4.$$

Benzonitrile is a colourless oil, boiling at 191°, and smells like nitrobenzene. It undergoes changes exactly similar to those which are characteristic of fatty nitriles, being converted into the corresponding acid on hydrolysis with alkalies or mineral acids,

$$C_6H_5{\cdot}CN + 2H_2O = C_6H_5{\cdot}COOH + NH_3,$$

and into a primary amine on reduction,

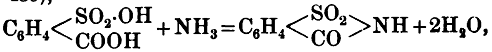
$$C_6H_5{\cdot}CN + 4H = C_6H_5{\cdot}CH_2{\cdot}NH_2.$$

Other aromatic nitriles, such as the three tolunitriles, $C_6H_4(CH_3){\cdot}CN$, are known, also compounds such as phenylacetonitrile (benzyl cyanide, p. 442), $C_6H_5{\cdot}CH_2{\cdot}CN$, which contain the cyanogen group in the side-chain.

Substitution Products of Benzoic Acid.—Benzoic acid is attacked by halogens (although not so readily as the hydrocarbons), the first product consisting of the *meta*-derivative (p. 364); when, for example, benzoic acid is heated with bromine and water at 125°, *m*-bromobenzoic acid, $C_6H_4Br{\cdot}COOH$ (m.p. 155°), is formed. The *o*- and *p*-bromobenzoic acids are obtained by oxidising the corresponding bromotoluenes with dilute nitric or chromic acid; the former melts at 147°, the latter at 251°. Nitric acid, in the presence of sulphuric acid, acts readily on benzoic acid, *m*-nitrobenzoic acid, $C_6H_4(NO_2){\cdot}COOH$ (m.p. 141°), being the principal product; *o*-nitrobenzoic acid (m.p. 147°) and *p*-nitrobenzoic acid (m.p. 238°) are obtained by the oxidation of *o*- and *p*-nitrotoluene respectively (p. 367); when these acids are reduced with tin and hydrochloric acid, they yield the corresponding amidobenzoic acids, $C_6H_4(NH_2){\cdot}COOH$, which, like glycine (Part I. p. 299), form salts both with acids and bases.

Anthranilic acid, or *o*-amidobenzoic acid, was first obtained by oxidising indigo (p. 539); it melts at 144°, and decomposes at higher temperatures, giving aniline and carbon dioxide.

When heated with sulphuric acid, benzoic acid is converted into *m*-sulphobenzoic acid, $C_6H_4(SO_3H){\cdot}COOH$, small quantities of the *p*-acid also being produced. The *o*-acid is obtained by oxidising toluene-*o*-sulphonic acid; when treated with ammonia it yields an imide (p. 439),



$$C_6H_4{<}\begin{matrix}SO_2{\cdot}OH\\COOH\end{matrix} + NH_3 = C_6H_4{<}\begin{matrix}SO_2\\CO\end{matrix}{>}NH + 2H_2O,$$

which is remarkable for possessing an exceedingly sweet taste, and which is known as *saccharin.*

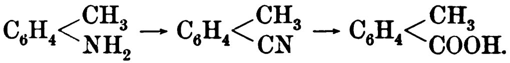
The sulphobenzoic acids are very soluble in water; when fused with potash they yield hydroxy-acids (p. 446), just as benzenesulphonic acid gives phenol,

$$C_6H_4(SO_3K){\cdot}COOK + 2KOH = C_6H_4(OK){\cdot}COOK + K_2SO_3 + H_2O.$$

The three (*o.m.p.*) **toluic acids,** $C_6H_4(CH_3){\cdot}COOH$, may be produced by oxidising the corresponding xylenes with dilute nitric acid,

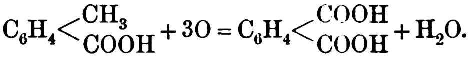
$$C_6H_4(CH_3)_2 + 3O = C_6H_4(CH_3){\cdot}COOH + H_2O,$$

but the *o*- and *p*-acids are best prepared by converting the corresponding toluidines (*m*-toluidine cannot easily be obtained) into the nitriles by Sandmeyer's reaction (p. 384), and then hydrolysing with acids or alkalies,



$$C_6H_4<\begin{matrix}CH_3\\NH_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}CH_3\\CN\end{matrix} \rightarrow C_6H_4<\begin{matrix}CH_3\\COOH.\end{matrix}$$

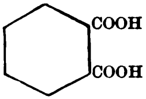
The *o*-, *m*-, and *p*-toluic acids melt at 103°, 110°, and 180° respectively, and resemble benzoic acid very closely, but since they contain a methyl-group, they have also properties which are not shown by benzoic acid; on oxidation, for example, they are converted into the corresponding phthalic acids, just as toluene is transformed into benzoic acid,



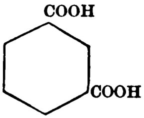
$$C_6H_4<\begin{matrix}CH_3\\COOH\end{matrix} + 3O = C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} + H_2O.$$

Dicarboxylic Acids.

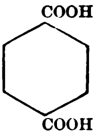
The most important dicarboxylic acids are the three (*o.m.p.*) phthalic acids, or benzenedicarboxylic acids, which are represented by the formulæ,



Phthalic Acid.

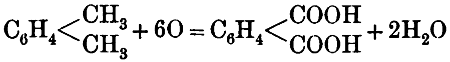


Isophthalic Acid.

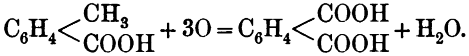


Terephthalic Acid.

These compounds may be prepared by the oxidation of the corresponding dimethylbenzenes with dilute nitric acid, or more conveniently by treating the toluic acids with potassium permanganate in alkaline solution,



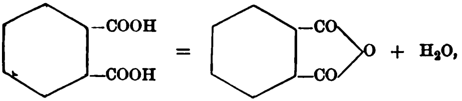
$$C_6H_4<\begin{matrix}CH_3\\CH_3\end{matrix} + 6O = C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} + 2H_2O$$



$$C_6H_4<\begin{matrix}CH_3\\COOH\end{matrix} + 3O = C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} + H_2O.$$

They are colourless, crystalline substances, and have all the ordinary properties of carboxylic acids. They yield normal and hydrogen metallic salts, esters, acid chlorides, amides, &c., which are similarly constituted to, and formed by the same reactions as, those of other dicarboxylic acids (Part I. p. 234).

Phthalic acid, like succinic acid (Part I. p. 240), is converted into its anhydride when strongly heated,



but it is very important to notice that an anhydride of isophthalic acid or of terephthalic acid cannot be produced; it is, in fact, a general rule that the formation of an anhydride from *one* molecule of the acid takes place only when the two carboxyl-groups in the benzene nucleus are in the *o*-position, never when they occupy the *m*- or *p*-position.

When cautiously heated with lime, all these dicarboxylic acids yield benzoic acid (p. 430),

$$C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} = C_6H_5\cdot COOH + CO_2,$$

but if the operation be conducted at a high temperature, both carboxyl-groups are displaced by hydrogen, and benzene is formed,

$$C_6H_4<\begin{matrix}COOH\\COOH\end{matrix} = C_6H_6 + 2CO_2;$$

this behaviour clearly shows that these acids are all dicarboxy-derivatives of benzene.

When a trace of phthalic acid is heated with resorcinol and a drop of sulphuric acid,* fluoresceïn (p. 532) is produced, and the reddish-brown product, when dissolved in soda and poured into a large quantity of water, yields a magnificently fluorescent solution. This reaction is shown by all the *o*-dicarboxylic acids of the benzene series, but not by the *m*- and *p*-dicarboxylic acids; it is also shown by acids of the fatty series, such as succinic acid, which give *internal*

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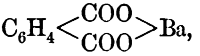
* To convert the acid into its anhydride; sometimes, as in the case of phthalic acid itself, the addition of sulphuric acid is unnecessary.

anhydrides—that is to say, anhydrides formed from *one* molecule of the acid.

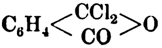
Phthalic acid, $C_6H_4(COOH)_2$ (benzene-*o*-dicarboxylic acid), may be obtained by oxidising *o*-xylene or *o*-toluic acid, but it is usually manufactured by oxidising naphthalene (p. 455) with sulphuric acid in presence of a small quantity of mercury; for laboratory purposes naphthalene tetrachloride, $C_{10}H_8Cl_4$ (p. 463), is oxidised with nitric acid.

Concentrated nitric acid (sp. gr. 1·45, 10 parts) is gradually added to naphthalene tetrachloride (1 part), and the mixture heated until a clear solution is produced. This is then evaporated to dryness, and the residue distilled, the phthalic anhydride (see below), which passes over, being reconverted into phthalic acid by boiling it with caustic soda; the acid is then precipitated by adding a mineral acid, and the crystalline precipitate purified by recrystallisation from boiling water.

Phthalic acid crystallises in colourless prisms, and melts at 184°, with formation of the anhydride, so that, if the melted substance be allowed to solidify, and the melting-point again determined, it will be found to be about 128°, the melting-point of phthalic anhydride.

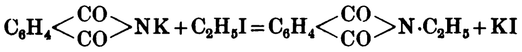
Phthalic acid is readily soluble in hot water, alcohol, and ether, and gives with metallic hydroxides well-characterised salts; the *barium* salt,  $C_6H_4{<}{\substack{COO\\COO}}{>}Ba$, obtained as a white precipitate by adding barium chloride to a neutral solution of the ammonium salt, is very sparingly soluble in water.

Ethyl phthalate, $C_6H_4(COOC_2H_5)_2$, is readily prepared by saturating an alcoholic solution of phthalic acid (or its anhydride) with hydrogen chloride. It is a colourless liquid, boiling at 295°.

Phthalyl chloride, $C_6H_4(COCl)_2$, is prepared by heating phthalic anhydride (1 mol.) with phosphorus pentachloride (1 mol.). It is a colourless oil, boils at 275° (726 mm.), and is slowly decomposed by water, with regeneration of phthalic acid. In many of its reactions it behaves as if it had the constitution represented by the formula  $C_6H_4{<}{\substack{CCl_2\\CO}}{>}O$ (compare succinyl chloride, Part I. p. 242).

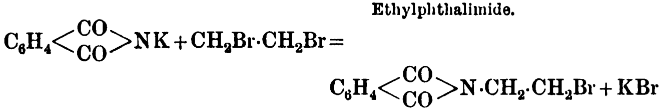
Phthalic anhydride, $C_6H_4<{CO \atop CO}>O$, is formed when phthalic acid is distilled. It sublimes readily in long needles, melts at 128°, boils at 284°, and is only very gradually decomposed by water, but dissolves readily in alkalies, yielding salts of phthalic acid. When heated in a stream of ammonia it is converted into *phthalimide*, $C_6H_4<{CO \atop CO}>NH$, a substance which melts at 229°, and yields a potassium derivative, $C_6H_4<{CO \atop CO}>NK$, on treatment with alcoholic potash. There is thus a great similarity between phthalimide and succinimide (Part I. p. 243).

Potassium phthalimide interacts with various halogen derivatives, as, for example, with ethyl iodide and with ethylene dibromide, giving substituted phthalimides,



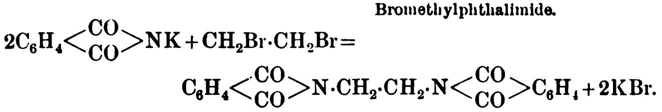
$$C_6H_4<{CO \atop CO}>NK + C_2H_5I = C_6H_4<{CO \atop CO}>N{\cdot}C_2H_5 + KI$$

Ethylphthalimide.



$$C_6H_4<{CO \atop CO}>NK + CH_2Br{\cdot}CH_2Br = C_6H_4<{CO \atop CO}>N{\cdot}CH_2{\cdot}CH_2Br + KBr$$

Bromethylphthalimide.



$$2C_6H_4<{CO \atop CO}>NK + CH_2Br{\cdot}CH_2Br = C_6H_4<{CO \atop CO}>N{\cdot}CH_2{\cdot}CH_2{\cdot}N<{CO \atop CO}>C_6H_4 + 2KBr.$$

Ethylenediphthalimide.

These products are hydrolysed by mineral acids and by alkalies yielding phthalic acid and an amine, or a bromo- or hydroxyamine; *ethylphthalimide*, for example, gives ethylamine, whereas *bromethylphthalimide* gives *bromethylamine*, $NH_2{\cdot}CH_2{\cdot}CH_2Br$, or *amidoethyl alcohol*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, according to the hydrolysing agent used. *Ethylenediphthalimide* yields *ethylene diamine*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$.

Isophthalic acid, $C_6H_4(COOH)_2$ (benzene-*m*-dicarboxylic acid), is produced by oxidising *m*-xylene with nitric acid or chromic acid; or from *m*-toluic acid (p. 435) by oxidation with potassium permanganate in alkaline solution.

It crystallises in needles, melts above 300°, and when strongly heated sublimes unchanged; it is very sparingly soluble in water. *Methyl isophthalate*, $C_6H_4(COOCH_3)_2$, melts at 65°.

Terephthalic acid, $C_6H_4(COOH)_2$ (benzene-*p*-dicarboxylic acid), is formed by the oxidation of *p*-xylene, *p*-toluic acid, and of all di-alkyl substitution-derivatives of benzene, which, like cymene, $CH_3{\cdot}C_6H_4{\cdot}CH(CH_3)_2$, contain the alkyl-groups in the *p*-position. It is best prepared by oxidising *p*-toluic acid (p. 435) in alkaline solution with potassium permanganate.

Terephthalic acid is almost insoluble in water, and, when heated, sublimes without melting; the *methyl* salt, $C_6H_4(COOCH_3)_2$, melts at 140°.

Acids, such as isophthalic acid and terephthalic acid, which have no definite melting-point, or which melt above 300°, are best identified by converting them into their methyl salts, which generally crystallise well, and melt at comparatively low temperatures.

For this purpose a centigram of the acid is warmed in a test tube with about three times its weight of phosphorus pentachloride, and the clear solution, which now contains the chloride of the acid, poured into excess of methyl alcohol. As soon as the vigorous reaction has subsided, the liquid is diluted with water, the crude methyl salt collected, recrystallised, and its melting-point determined.

Phenylacetic Acid, Phenylpropionic Acid, and their Derivatives.

Many cases have already been mentioned in which aromatic compounds have been found to have certain properties similar to those of members of the fatty series, and it has been pointed out that this is due to the presence in the former of groups of atoms (side-chains) which may be considered as fatty radicles; benzyl chloride, for example, has some properties in common with methyl chloride, benzyl alcohol with methyl alcohol, benzylamine with methylamine, and so on, simply because similar groups or radicles in a similar state of combination confer, as a rule, similar properties on the compounds in which they occur. Since, moreover, nearly all fatty compounds may theoretically be converted into aromatic compounds of the same type by the substitution of a phenyl group for hydrogen, it follows that any series of fatty compounds may have its counterpart in the aromatic group. This is well illustrated in the case of the carboxylic acids, because, corresponding with the fatty acids, there is a series of aromatic acids which may be regarded as derived from them in the manner just mentioned.

Formic acid, $H{\cdot}COOH$,
Benzoic acid, $C_6H_5{\cdot}COOH$ (phenylformic acid).
Acetic acid, $CH_3{\cdot}COOH$,
Phenylacetic acid, $C_6H_5{\cdot}CH_2{\cdot}COOH$.
Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$,
Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.
Butyric acid, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$,
Phenylbutyric acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

With the exception of benzoic acid, all the above aromatic acids are derived from the aromatic hydrocarbons by the substitution of carboxyl for hydrogen of the *side-chain.* They have not only the characteristic properties of aromatic compounds in general, but also those of fatty acids, and, like the latter, they may be converted into unsaturated compounds by loss of two or more atoms of hydrogen, giving rise to new series, as the following example will show.

Propionic acid, $CH_3{\cdot}CH_2{\cdot}COOH$,
Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.
Acrylic acid, $CH_2{:}CH{\cdot}COOH$,
Phenylacrylic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$.
Propiolic acid, $CH{\vdots}C{\cdot}COOH$,
Phenylpropiolic acid, $C_6H_5{\cdot}C{\vdots}C{\cdot}COOH$.

Preparation.—Aromatic acids, containing the carboxyl-group in the side-chain, may be prepared by *carefully* oxidising the corresponding alcohols and aldehydes, and by hydrolysing the nitriles with alkalies or mineral acids,

$$C_6H_5{\cdot}CH_2{\cdot}CN + 2H_2O = C_6H_5{\cdot}CH_2{\cdot}COOH + NH_3,$$

but these methods are limited in application, owing to the difficulty of obtaining the requisite substances.

The most important general methods are: (*a*) By the reduction of the corresponding unsaturated acids, compounds which are prepared without much difficulty (p. 444),

$$C_6H_5{\cdot}CH{:}CH{\cdot}COOH + 2H = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH;$$

and (*b*) by treating the sodium compound of ethyl malonate or of ethyl acetoacetate with the halogen derivatives of the aromatic hydrocarbons. As in the latter case the procedure is exactly similar to that employed in preparing fatty acids (Part I. pp. 193, 198, and 203), one example only need be given—namely, the synthesis of phenylpropionic acid.

The sodium compound of ethyl malonate is heated with benzyl chloride, and the ethyl benzylmalonate which is thus produced,

$$C_6H_5{\cdot}CH_2Cl + CHNa(COOC_2H_5)_2 = \underset{\text{Ethyl Benzylmalonate.}}{C_6H_5{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2} + NaCl,$$

is hydrolysed with alcoholic potash. The benzylmalonic acid is then isolated, and heated at 200°, when it is converted into phenylpropionic acid, with loss of carbon dioxide,

$$C_6H_5{\cdot}CH_2{\cdot}CH(COOH)_2 = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + CO_2.$$

It should be remembered that only those halogen derivatives in which the halogen is in the *side-chain* can be employed in such syntheses, because when the halogen is united with the nucleus, as in monochlorotoluene, $C_6H_4Cl{\cdot}CH_3$, for example, no action takes place (compare p. 357).

The properties of two of the most typical acids of this class are described below.

Phenylacetic acid, or α-toluic acid, $C_6H_5{\cdot}CH_2{\cdot}COOH$, is prepared by boiling a solution of benzyl chloride (1 mol.) and potassium cyanide (1 mol.) in dilute alcohol for about three hours; the benzyl cyanide which is thus formed is purified by fractional distillation, and the fraction 220–235° (benzyl cyanide boils at 232°) is hydrolysed by boiling with dilute sulphuric acid, the product being purified by recrystallisation from water,

$$C_6H_5{\cdot}CH_2Cl \longrightarrow C_6H_5{\cdot}CH_2{\cdot}CN \longrightarrow C_6H_5{\cdot}CH_2{\cdot}COOH.$$

Phenylacetic acid melts at 76·5°, boils at 262°, and crystallises from boiling water in glistening plates; it has an agreeable, characteristic smell, and forms salts and derivatives just as do benzoic and acetic acids.

When oxidised with chromic acid it yields benzoic acid, a change very different from that undergone by the isomeric toluic acids (p. 436),

$$C_6H_5{\cdot}CH_2{\cdot}COOH + 3O = C_6H_5{\cdot}COOH + CO_2 + H_2O.$$

Phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ (hydrocinnamic acid), is most conveniently prepared by reducing cinnamic acid (see below) with sodium amalgam and water,

$$C_6H_5{\cdot}CH{:}CH{\cdot}COOH + 2H = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

but may also be obtained from the product of the action of benzyl chloride on the sodium compound of ethyl malonate (p. 442). It crystallises from water in needles, melts at 47°, and distils at 280° without decomposing.

Cinnamic acid, or phenylacrylic acid, $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$, is closely related to phenylpropionic acid, and is one of the best-known *unsaturated* acids of the aromatic series. It occurs in large quantities in storax (*Styrax officinalis*), and may be obtained from this resin by warming it with caustic soda; the filtered aqueous solution of sodium cinnamate is then acidified with hydrochloric acid, and the precipitated cinnamic acid purified by recrystallisation from boiling water.

Cinnamic acid is usually prepared by heating benzaldehyde with acetic anhydride and anhydrous sodium acetate, a reaction which is most simply expressed by the equation,

$$C_6H_5{\cdot}CHO + CH_3{\cdot}COONa = C_6H_5{\cdot}CH{:}CH{\cdot}COONa + H_2O.$$

A mixture of benzaldehyde (3 parts), acetic anhydride (10 parts), and anhydrous sodium acetate (3 parts) is heated to boiling in a flask placed in an oil-bath. After about eight hours' time, the mixture is poured into water, and distilled in steam to separate the unchanged benzaldehyde; the residue is then treated with caustic soda, the hot alkaline solution filtered from oily and tarry impurities, and acidified with hydrochloric acid, the precipitated cinnamic acid being purified by recrystallisation from boiling water.

This method (Perkin's reaction) is a general one for the preparation of unsaturated aromatic acids, as by employing the anhydrides and sodium salts of other fatty acids, homologues of cinnamic acid are obtained. When, for example, benzaldehyde is treated with sodium propionate and propionic anhydride, *phenylmethylacrylic acid* (*a-methylcinnamic acid*), $C_6H_5{\cdot}CH{:}C(CH_3){\cdot}COOH$, is formed; *phenylisocrotonic acid*, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, is not obtained by this reaction, because combination always takes place between the aldehyde oxygen atom and the hydrogen atoms of that $-CH_2-$ group which is directly united with the carboxyl-radicle of the *sodium salt.*

Phenylisocrotonic acid may, however, be prepared by heating benzaldehyde with a mixture of sodium succinate and succinic anhydride, carbon dioxide being eliminated,

$$C_6H_5{\cdot}CHO + COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH = C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH + CO_2 + H_2O.$$

It is a colourless, crystalline substance, melts at 86°, and boils at 302°; at its boiling-point it is gradually converted into *a*-naphthol and water (p. 459).

Other aldehydes which contain the aldehyde-group directly united to the nucleus may be used in the Perkin reaction; the three *toluic aldehydes*, $CH_3{\cdot}C_6H_4{\cdot}CHO$, for example, give with sodium acetate and acetic anhydride the three *methylcinnamic acids*, $CH_3{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COOH$.

Cinnamic acid crystallises from water in needles, and melts at 133°. Its chemical behaviour is in many respects similar to that of acrylic acid and other unsaturated fatty acids; it combines directly with bromine, for example, yielding *phenyl-aβ-dibromopropionic acid*, $C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}COOH$, and with hydrogen bromide, giving *phenyl-β-bromopropionic acid*, $C_6H_5{\cdot}CHBr{\cdot}CH_2{\cdot}COOH$.

A solution of cinnamic acid in sodium carbonate immediately reduces (decolourises) a dilute solution of potassium permanganate at ordinary temperatures; all *unsaturated* acids show this behaviour, and are thus easily detected (Baeyer). On reduction with sodium amalgam and water, cinnamic acid is converted into phenylpropionic acid (p. 443), just as acrylic acid is transformed into propionic acid.

When distilled with lime, cinnamic acid is decomposed into carbon dioxide, and *phenylethylene* or *styrolene*,*

$$C_6H_5\cdot CH:CH\cdot COOH = C_6H_5\cdot CH:CH_2 + CO_2.$$

Concentrated nitric acid converts cinnamic acid into a mixture of about equal quantities of *o*- and *p-nitrocinnamic acids*, $C_6H_4(NO_2)\cdot CH:CH\cdot COOH$, which may be separated by converting them into their ethyl esters, $C_6H_4(NO_2)\cdot CH:CH\cdot COOC_2H_5$ (by means of alcohol and hydrogen chloride), and recrystallising these from alcohol, the sparingly soluble ester of the *p*-acid being readily separated from the readily soluble ethyl *o*-nitrocinnamate. From the pure esters the acids are then regenerated by hydrolysing with dilute sulphuric acid. They resemble cinnamic acid closely in properties, and combine directly with bromine, yielding the corresponding nitrophenyldibromopropionic acids, $C_6H_4(NO_2)\cdot CHBr\cdot CHBr\cdot COOH$.

Phenylpropiolic acid, $C_6H_5\cdot C\vdots C\cdot COOH$, is obtained by treating phenyldibromopropionic acid, or, better, its ethyl ester, with alcoholic potash,

$$C_6H_5\cdot CHBr\cdot CHBr\cdot COOH = C_6H_5\cdot C\vdots C\cdot COOH + 2HBr,$$

a method which is exactly similar to that employed in preparing acetylene by the action of alcoholic potash on ethylene dibromide. It melts at 137°, and at higher temperatures, or when heated with water at 120°, it decomposes into carbon dioxide and *phenylacetylene*, a colourless liquid, which boils at 140°, and is closely related to acetylene in chemical properties,

$$C_6H_5\cdot C\vdots C\cdot COOH = C_6H_5\cdot C\vdots CH + CO_2.$$

o-Nitrophenylpropiolic acid, $C_6H_4(NO_2)\cdot C\vdots C\cdot COOH$, may be similarly prepared from *o*-nitrophenyldibromopropionic acid; it is a substance of great interest, as when treated with reducing agents,

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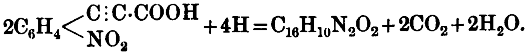
* *Styrolene*, $C_6H_5\cdot CH:CH_2$, may be taken as a typical example of an aromatic hydrocarbon containing an unsaturated side-chain. It is a colourless liquid which boils at 145°, and in chemical properties shows the closest resemblance to ethylene, of which it is the phenyl substitution product. With bromine, for example, it yields a dibrom-additive product, $C_6H_5\cdot CHBr\cdot CH_2Br$ (dibromethylbenzene), and when heated with hydriodic acid, it is reduced to ethylbenzene, $C_6H_5\cdot CH_2\cdot CH_3$.

such as hydrogen sulphide, or grape-sugar and potash, it is converted into indigo-blue (Baeyer),



$$2C_6H_4{<}\begin{matrix}C{:}C\cdot COOH\\ NO_2\end{matrix} + 4H = C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O.$$

This method of preparation, however, is not of technical value, owing to the high price of phenylpropiolic acid (compare p. 540).

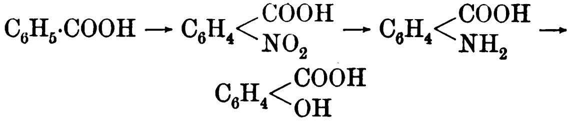
CHAPTER XXX.

HYDROXYCARBOXYLIC ACIDS.

The hydroxy-acids of the aromatic series are derived from benzoic acid and its homologues, by the substitution of hydroxyl-groups for hydrogen atoms, just as glycollic acid, for example, is derived from acetic acid (Part I. p. 229); like the simple hydroxy-derivatives of the hydrocarbons, they may be divided into two classes, according as the hydroxyl-group is united with carbon of the nucleus or of the side-chain. In the first case the hydroxyl-group has the same character as in phenols, and consequently hydroxy-acids of this class, as, for example, the three (*o.m.p.*) *hydroxybenzoic acids*, $C_6H_4(OH)\cdot COOH$, are both phenols and carboxylic acids; in the second case, however, the hydroxyl-group has the same character as in alcohols, so that the compounds of this class, such as *mandelic acid*, $C_6H_5\cdot CH(OH)\cdot COOH$, have properties closely resembling those of the fatty hydroxy-acids; in other words, the differences between the two classes of aromatic hydroxy-acids are practically the same as those between phenols and alcohols.

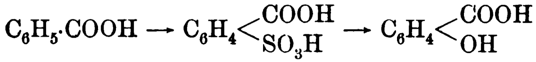
As those acids which contain the hydroxyl-group united with carbon of the nucleus form by far the more important class, they will be described first, and the following statements refer to them only, except where stated to the contrary.

Preparation.—The hydroxy-acids may be prepared from the simple carboxylic acids, by reactions exactly similar to those employed in the preparation of phenols from hydrocarbons; that is to say, the acids are converted into nitro-compounds, then into amido-compounds, and the latter are treated with nitrous acid in the usual manner,



$$C_6H_5{\cdot}COOH \rightarrow C_6H_4<^{COOH}_{NO_2} \rightarrow C_6H_4<^{COOH}_{NH_2} \rightarrow C_6H_4<^{COOH}_{OH}$$

or, the acids are heated with sulphuric acid, and the sulphonic acids obtained in this way are fused with potash,

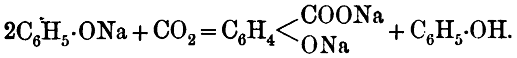


$$C_6H_5{\cdot}COOH \rightarrow C_6H_4<^{COOH}_{SO_3H} \rightarrow C_6H_4<^{COOH}_{OH}$$

It must be borne in mind, however, that as the carboxyl-group of the acid determines the position taken up by the nitro- and sulphonic-groups (p. 364), only the *meta*-hydroxy-compounds are conveniently prepared in this way directly from the carboxylic acids.

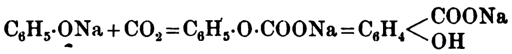
The *ortho*-hydroxy-acids, and in some cases the meta- and para-compounds, are most conveniently prepared from the phenols by one of the following methods.

The dry sodium compound of the phenol is heated at about 200° in a stream of carbon dioxide,



$$2C_6H_5{\cdot}ONa + CO_2 = C_6H_4<^{COONa}_{ONa} + C_6H_5{\cdot}OH.$$

Under these conditions half the phenol distils over and is recovered; but if the sodium compound be first saturated with carbon dioxide under pressure, it is converted into an aromatic derivative of carbonic acid, which, when heated at about 130° under pressure, is completely transformed into a salt of the hydroxy-acid by intramolecular change,

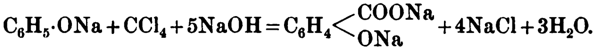


$$C_6H_5{\cdot}ONa + CO_2 = C_6H_5{\cdot}O{\cdot}COONa = C_6H_4<^{COONa}_{OH}$$

Sodium Phenylcarbonate.

Many dihydric and trihydric phenols may be converted into the corresponding hydroxy-acids, simply by heating them with ammonium carbonate or potassium bicarbonate; when resorcinol, for example, is treated in this way, it yields a mixture of isomeric *resorcylic acids*, $C_6H_3(OH)_2\cdot COOH$.

The second general method of preparing hydroxy-acids from phenols consists in boiling a strongly alkaline solution of the phenol with carbon tetrachloride; the principal product is the *ortho*-acid, but varying proportions of the *para*-acid are also formed,



$$C_6H_5\cdot ONa + CCl_4 + 5NaOH = C_6H_4<\begin{matrix}COONa\\ ONa\end{matrix} + 4NaCl + 3H_2O.$$

After the substances have been heated together for some hours, the unchanged carbon tetrachloride is distilled off, the residue acidified, and the solution extracted with ether; the crude acid obtained on evaporating the ethereal solution is then separated from unchanged phenol by dissolving it in sodium carbonate, re-precipitated with a mineral acid, and purified by recrystallisation.

The above method is clearly analogous to Reimer's reaction (p. 421), and the changes which occur during the process may be assumed to take place in various stages as indicated below,

$$C_6H_5\cdot OH \longrightarrow C_6H_4<\begin{matrix}CCl_3\\ OH\end{matrix} \longrightarrow C_6H_4<\begin{matrix}C(OH)_3\\ OH\end{matrix} \longrightarrow C_6H_4<\begin{matrix}COOH\\ OH\end{matrix}$$

Properties.—The hydroxy-acids are colourless, crystalline substances, more readily soluble in water and less volatile than the acids from which they are derived; many of them undergo decomposition when heated strongly, carbon dioxide being evolved; when heated with lime they are decomposed, with formation of phenols,

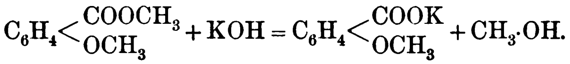
$$C_6H_4(OH)\cdot COOH = C_6H_5\cdot OH + CO_2$$
$$C_6H_3(OH)_2\cdot COOH = C_6H_4(OH)_2 + CO_2.$$

The *o*-acids, as, for example, salicylic acid, give, in neutral solution, a violet colouration with ferric chloride, whereas the *m*- and *p*-hydroxy-acids, such as the *m*- and *p*-hydroxybenzoic acids, give no colouration.

The chemical properties of the hydroxy-acids will be readily understood when it is remembered that they are both phenols and carboxylic acids. As carboxylic acids they form salts by the displacement of the hydrogen atom of the carboxyl-group, such salts being obtained on treating with *carbonates* or with the calculated quantity of the metallic hydroxide; when, however, excess of *alkali hydroxide* is employed, the hydrogen of the phenolic hydroxyl-group is also displaced, just as in phenol itself. It is clear, therefore, that hydroxy-acids form both mono- and di-metallic salts; salicylic acid, for example, yielding the two sodium salts, $C_6H_4(OH){\cdot}COONa$ and $C_6H_4(ONa){\cdot}COONa$.

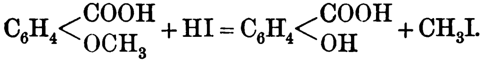
The di-metallic salts are decomposed by carbonic acid, with formation of mono-metallic salts, just as the phenates are resolved into the phenols; the metal in combination with the carboxyl-group, however, cannot be displaced in this way.

The esters of the hydroxy-acids are prepared in the usual manner—namely, by saturating a solution of the acid in the alcohol with hydrogen chloride (Part I. p. 191); by this treatment the hydrogen of the carboxyl-group only is displaced, ordinary esters, such as *methyl salicylate*, $C_6H_4(OH){\cdot}COOCH_3$, being formed; these compounds have still phenolic properties, and dissolve in caustic alkalies, forming metallic derivatives, such as *methyl potassiosalicylate*, $C_6H_4(OK){\cdot}COOCH_3$, which, when heated with alkyl halogen compounds, yield alkyl-derivatives, such as *methyl methylsalicylate*, $C_6H_4(OCH_3){\cdot}COOCH_3$. On hydrolysing di-alkyl compounds of this kind with alcoholic potash, only the alkyl of the carboxyl-group is removed, methyl methylsalicylate, for example, yielding the potassium salt of *methylsalicylic acid*,



$$C_6H_4{<}\begin{matrix}COOCH_3\\OCH_3\end{matrix} + KOH = C_6H_4{<}\begin{matrix}COOK\\OCH_3\end{matrix} + CH_3{\cdot}OH.$$

The other alkyl-group is not eliminated even on boiling with alkalies, a behaviour which corresponds with that of the alkyl-group in derivatives of phenols, such as anisole, $C_6H_5{\cdot}OCH_3$ (p. 405); just, however, as anisole is decomposed into phenol and methyl iodide when heated with hydriodic acid, so methylsalicylic acid under similar conditions yields the hydroxy-acid,



$$C_6H_4\begin{matrix}<\end{matrix}\begin{matrix}COOH\\OCH_3\end{matrix} + HI = C_6H_4\begin{matrix}<\end{matrix}\begin{matrix}COOH\\OH\end{matrix} + CH_3I.$$

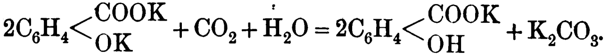
Salicylic acid, or *o*-hydroxybenzoic acid, $C_6H_4(OH)\cdot COOH$, occurs in the blossom of *Spiræa ulmaria*, and is also found in considerable quantities, as methyl salicylate, in oil of wintergreen (*Gaultheria procumbens*). It used to be prepared, especially for pharmaceutical purposes, by hydrolysing this oil with potash; after boiling off the methyl alcohol (Part I. p. 89), the solution is acidified with dilute sulphuric acid, and the precipitated salicylic acid purified by recrystallisation from water.

Salicylic acid may be obtained by oxidising salicylaldehyde (p. 422), or salicylic alcohol (saligenin, p. 416), with chromic acid, by treating *o*-amidobenzoic acid (anthranilic acid, p. 435) with nitrous acid, and also by boiling phenol with caustic soda and carbon tetrachloride.

It is now prepared on the large scale by treating sodium phenate with carbon dioxide under pressure, and then heating the *sodium phenylcarbonate*, $C_6H_5\cdot O\cdot COONa$, which is thus formed, at 120–140° under pressure, when it undergoes intramolecular change into sodium salicylate (p. 447).

Salicylic acid is sparingly soluble in cold (1 in 400 parts at 15°), but readily in hot, water, from which it crystallises in needles, melting at 156°; its neutral solutions give with ferric chloride an intense violet colouration. When rapidly heated it sublimes, and only slight decomposition occurs; but when distilled slowly, a large proportion decomposes into phenol and carbon dioxide, this change being complete if the acid be distilled with lime.

Salicylic acid is a powerful antiseptic, and, as it has no smell, it is frequently used as a disinfectant instead of phenol; it is also extensively employed in medicine and as a food preservative. The mono-metallic salts of salicylic acid, as, for example, *potassium salicylate*, $C_6H_4(OH)\cdot COOK$, and *calcium salicylate*, $\{C_6H_4(OH){\cdot}COO\}_2Ca$, are prepared by neutralising a hot aqueous solution of the acid with metallic *carbonates;* they are, as a rule, soluble in water. The di-metallic salts, such as $C_6H_4(OK){\cdot}COOK$ and $C_6H_4{<}\begin{matrix}-O-\\COO\end{matrix}{>}Ba$, are obtained in a similar manner, employing excess of the metallic *hydroxides;* with the exception of the salts of the alkali metals, these di-metallic compounds are insoluble; they are all decomposed by carbonic acid, with formation of the mono-metallic salts,



$$2C_6H_4{<}\begin{matrix}COOK\\OK\end{matrix} + CO_2 + H_2O = 2C_6H_4{<}\begin{matrix}COOK\\OH\end{matrix} + K_2CO_3.$$

Methyl salicylate, $C_6H_4(OH){\cdot}COOCH_3$, prepared in the manner described (p. 449), or by distilling a mixture of salicylic acid, methyl alcohol, and sulphuric acid (Part I. p. 191), is an agreeably-smelling oil, boiling at 224°; *ethyl salicylate*, $C_6H_4(OH){\cdot}COOC_2H_5$, boils at 223°.

Methyl methylsalicylate, $C_6H_4(OCH_3){\cdot}COOCH_3$, is formed when methyl salicylate is heated with methyl iodide and potash (1 mol.) in alcoholic solution; it is an oil boiling at 228°.

Methylsalicylic acid, $C_6H_4(OCH_3){\cdot}COOH$, is obtained when its methyl salt is hydrolysed with potash; it is a crystalline substance, melting at 98·5°, and when heated with hydriodic acid it is decomposed, giving salicylic acid and methyl iodide; the other halogen acids have a similar action.

m-Hydroxybenzoic acid is prepared by fusing *m*-sulphobenzoic acid with potash, and also by the action of nitrous acid on *m*-amidobenzoic acid. It melts at 200°, does not give a colouration with ferric chloride, and when distilled with lime it is decomposed into phenol and carbon dioxide.

p-Hydroxybenzoic acid is formed, together with salicylic acid, by the action of carbon tetrachloride and soda on phenol; it may also be obtained from *p*-sulphobenzoic acid by fusing with potash, or by the action of nitrous acid on *p*-amidobenzoic acid.

It is prepared by heating potassium phenate in a stream of carbon dioxide at 220° as long as phenol distils over; if, however, the temperature be kept below 150°, potassium salicylate is formed. The residue is dissolved in water, the acid precipitated from the filtered solution by adding hydrochloric acid, and purified by recrystallisation from water. *p*-Hydroxybenzoic acid melts at 210°, and is completely decomposed on distillation into phenol and carbon dioxide; its aqueous solution gives no colouration with ferric chloride.

Anisic acid, *p*-methoxybenzoic acid, $C_6H_4(OCH_3)\cdot COOH$, is obtained by oxidising *anethole*, $C_6H_4(OCH_3)\cdot CH{:}CH\cdot CH_3$ (the principal constituent of oil of aniseed) with chromic acid, when the group $-CH{:}CH\cdot CH_3$ is converted into $-COOH$; it may also be prepared from *p*-hydroxybenzoic acid by means of reactions analogous to those employed in the formation of methylsalicylic acid from salicylic acid (p. 451).

Anisic acid melts at 185°, and when distilled with lime it is decomposed, with formation of anisole (p. 405); when heated with fuming hydriodic acid, it yields *p*-hydroxybenzoic acid and methyl iodide.

There are six *dihydroxybenzoic acids*, $C_6H_3(OH)_2\cdot COOH$, two of which are derived from catechol, three from resorcinol, and one from hydroquinone; the most important of these is **protocatechuic acid**, [OH:OH:COOH = 1:2:4], one of the two isomeric catecholcarboxylic acids. This compound is formed on fusing many resins, such as catechu and gum benzoïn, and also certain alkaloids, with potash, and it may be prepared synthetically by heating catechol with water and ammonium carbonate at 140°.

It crystallises from water, in which it is very soluble, in needles, melts at 199°, and when strongly heated it is decomposed into catechol and carbon dioxide; its aqueous solution gives with ferric chloride a green solution, which becomes violet and then red on the addition of sodium bicarbonate.

Gallic acid, or pyrogallolcarboxylic acid,

$$C_6H_2(OH)_3\cdot COOH, [OH{:}OH{:}OH{:}COOH = 1{:}2{:}3{:}5],$$

is a trihydroxybenzoic acid; it occurs in gall-nuts, tea, and many other vegetable products, and is best prepared by boiling *tannin* (see below) with dilute acids. It crystallises in needles, and melts at 220°, being at the same time resolved into pyrogallol (p. 412) and carbon dioxide; it is readily soluble in water, and its aqueous solution gives with ferric chloride a bluish-black precipitate. Gallic acid is a strong reducing agent, and precipitates gold, silver, and platinum from solutions of their salts.

Tannin, digallic acid, or tannic acid, $C_{14}H_{10}O_9$, occurs in large quantities in gall-nuts, and in all kinds of bark, from which it may be extracted with boiling water. It is an almost colourless, amorphous substance, and is readily soluble in water; its solutions possess a very astringent taste, and give with ferric chloride an intense dark-blue solution, for which reason tannin is largely used in the manufacture of inks.

When boiled with dilute sulphuric acid, tannin is completely converted into gallic acid, a fact which shows that it is the anhydride of this acid,

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$

Tannin is used largely in dyeing as a mordant, owing to its property of forming insoluble coloured compounds with many dyes. It is also extensively employed in 'tanning;' when animal skin or membrane, after suitable preliminary operations, is placed in a solution of tannin, or in contact with moist bark containing tannin, it absorbs and combines with the tannin, and is converted into a much tougher material; such tanned skins constitute leather.

Mandelic acid, $C_6H_5{\cdot}CH(OH){\cdot}COOH$ (phenylglycollic acid), is an example of an aromatic hydroxy-acid containing the hydroxyl-group in the *side-chain.* It may be obtained by boiling amygdalin (which yields benzaldehyde, hydrogen cyanide, and glucose, p. 418) with hydrochloric acid, but it is usually prepared by treating benzaldehyde with hydrocyanic acid and hydrolysing the resulting hydroxycyanide, a method analogous to that employed in the synthesis of lactic acid from aldehyde (Part I. p. 234),

$$C_6H_5{\cdot}CHO + HCN = C_6H_5{\cdot}CH(OH){\cdot}CN$$
$$C_6H_5{\cdot}CH(OH){\cdot}CN + 2H_2O = C_6H_5{\cdot}CH(OH){\cdot}COOH + NH_3.$$

Mandelic acid melts at 133°, is moderately soluble in water, and shows in many respects the greatest resemblance to lactic acid (methylglycollic acid); when heated with hydriodic acid, for example, it is reduced to phenylacetic acid (p. 442), just as lactic acid is reduced to propionic acid (Part I. p. 232),

$$C_6H_5{\cdot}CH(OH){\cdot}COOH + 2HI = C_6H_5{\cdot}CH_2{\cdot}COOH + I_2 + H_2O.$$

The character of the hydroxyl-group in mandelic acid is, in fact, quite similar to that of the hydroxyl-group in the fatty hydroxy-acids and in the alcohols, so that there are many points of difference between mandelic acid and acids, such as salicylic acid, which contain the hydroxyl-group united with carbon of the nucleus; when, for example, *ethyl mandelate*, $C_6H_5{\cdot}CH(OH){\cdot}COOC_2H_5$, is treated with caustic alkalies, it does not yield an alkali derivative, although the hydrogen of the hydroxyl-group is displaced on treating with sodium or potassium.

Mandelic acid, like lactic acid, exists in three optically different forms. The synthetical acid is optically inactive, but the acid prepared from amygdalin is levo-rotatory.

CHAPTER XXXI.

NAPHTHALENE AND ITS DERIVATIVES.

All the aromatic hydrocarbons hitherto described, with the exception of diphenyl, diphenylmethane, and triphenylmethane (p. 350), contain only *one* closed-chain of six carbon atoms, and are very closely and directly related to benzene; most of them may be prepared from benzene by comparatively simple reactions, and reconverted into this hydrocarbon, perhaps even more readily, so that they may all be classed as simple benzene derivatives. The exceptions just mentioned are also, strictly speaking, derivatives of benzene, although at the same time they may be regarded as hydrocarbons of quite another class, since diphenyl and diphenylmethane contain two, and triphenylmethane three, closed-chains of six carbon atoms. There are, in fact, numerous classes or types of aromatic hydrocarbons, and, just as benzene is the parent substance of a vast number of derivatives, so also these other hydrocarbons form the starting-points of new homologous series and of derivatives of a different type.

The hydrocarbons *naphthalene* and *anthracene*, which are now to be described, are perhaps second only to benzene in importance; each forms the starting-point of a great number of compounds, many of which are extensively employed in the manufacture of dyes.

Naphthalene, $C_{10}H_8$, occurs in coal-tar in larger quantities than any other hydrocarbon, and is easily isolated from this source in a pure condition; the crystals of crude naphthalene, which are deposited on cooling from the fraction of coal-tar passing over between 170 and 230° (p. 307), are first pressed to get rid of liquid impurities, and then warmed with a small quantity of concentrated sulphuric acid, which converts most of the foreign substances into non-volatile sulphonic acids; the naphthalene is then distilled in steam, or sublimed, and is thus obtained almost chemically pure.

Naphthalene crystallises in large, lustrous plates, melts at 79°, and boils at 218°. It has a highly characteristic smell, and is extraordinarily volatile, considering its high molecular weight—so much so, in fact, that only part of the naphthalene in crude coal-gas is deposited in the condensers (p. 305), the rest being carried forward into the purifiers, and even into the gas-mains, in which it is deposited in crystals in cold weather, principally at the bends of the pipes, frequently causing stoppages. It is insoluble in water, but dissolves freely in hot alcohol and ether, from either of which it may be crystallised. Like many other aromatic hydrocarbons, it combines with picric acid, when the two substances are dissolved together in alcohol, forming *naphthalene picrate*, a yellow crystalline compound of the composition,

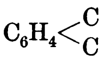
$$C_{10}H_8,C_6H_2(NO_2)_3 \cdot OH,$$

which melts at 149°.

As the vapour of naphthalene burns with a highly luminous flame, the hydrocarbon is used to some extent for carburetting coal-gas—that is to say, for increasing its illuminating power; for this purpose the gas is passed through a vessel which contains coarsely-powdered naphthalene, gently heated by the gas flame, so that the hydrocarbon volatilises and burns with the gas. The principal use of naphthalene, however, is for the manufacture of a number of derivatives which are employed in the colour industry.

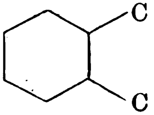
Constitution.—Naphthalene has the characteristic properties of an aromatic compound—that is to say, its behaviour under various conditions is similar to that of benzene and its derivatives, and different from that of fatty compounds; when treated with nitric acid, for example, it yields nitro-derivatives, and with sulphuric acid it gives sulphonic acids. This similarity between benzene and naphthalene at once suggests a resemblance in constitution, a view which is confirmed by the fact that naphthalene, like benzene, is a very stable compound, and is resolved into simpler substances only with difficulty. When, however, naphthalene is boiled with dilute nitric or chromic acid, or heated with sulphuric acid (p. 438), it is slowly oxidised, yielding carbon dioxide and (*ortho*)-phthalic acid, $C_6H_4(COOH)_2$.

Now the formation of phthalic acid in this way is a fact of very great importance, since it is a proof that naphthalene contains the group,



$$C_6H_4{<}\begin{matrix}C\\C\end{matrix}$$

or

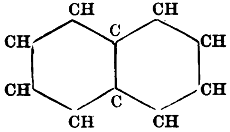


that is to say, that it contains a benzene nucleus to which two carbon atoms are united in the *ortho*-position to one another. This fact alone, however, is insufficient to establish the constitution of the hydrocarbon, since there are still two carbon and four hydrogen atoms to be accounted for, and there are many different ways in which these might be united with the $C_6H_4{<}\begin{smallmatrix}C\\C\end{smallmatrix}$ group.

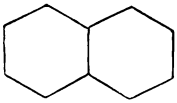
Clearly, therefore, it is important to ascertain the structure of that part of the naphthalene molecule which has been oxidised to carbon dioxide and water—to obtain, if possible, some decomposition product of known constitution in which these carbon and hydrogen atoms are retained in their original state of combination.

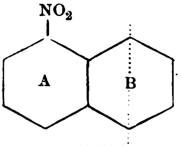
Now this can be done in the following way: When nitronaphthalene, $C_{10}H_7{\cdot}NO_2$, a simple mono-substitution product of the hydrocarbon, is boiled with dilute nitric acid, it yields nitrophthalic acid, $C_6H_3(NO_2)(COOH)_2$; therefore, again, naphthalene contains a benzene nucleus, and the nitro-group in nitronaphthalene is combined with this nucleus. If, however, the *same* nitronaphthalene be reduced to amidonaphthalene, $C_{10}H_7{\cdot}NH_2$, and the latter oxidised, phthalic acid (and not amidophthalic acid) is obtained; this last fact can only be explained by assuming, either that the benzene nucleus, which is known to be united with the amido-group, has been destroyed, or that the amido-group has been displaced by hydrogen during oxidation. Since, however, the latter alternative is contrary to all experience, the former must be accepted, and it must be concluded that the benzene nucleus, which is contained in the oxidation product of amidonaphthalene, is *not the same* as that present in the oxidation product of nitronaphthalene; in other words, different parts of the naphthalene molecule have been oxidised to carbon dioxide and water in the two cases, and yet in both the group $C_6H_4{<}\begin{smallmatrix}C\\C\end{smallmatrix}$ remains.

The constitution of naphthalene must therefore be expressed by the formula,

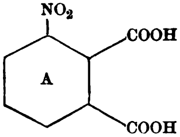


This will be evident if the above changes be represented with the aid of this formula. When nitronaphthalene is oxidised, the nucleus B (see below), which does not contain the nitro-group, is destroyed, as indicated by the dotted lines, the product being nitrophthalic acid; when, on the other hand, amidonaphthalene is oxidised, the nucleus A, combined with the amido-group, is attacked in preference to the other, and phthalic acid is formed,

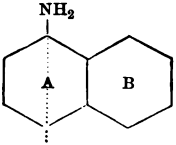

Naphthalene.



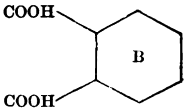
Nitronaphthalene.



Nitrophthalic Acid.



Amidonaphthalene.



Phthalic Acid.

The constitution of naphthalene was first established in this way by Graebe in 1880, although the above formula had been suggested by Erlenmeyer as early as 1866; that the hydrocarbon is composed of two closed-chains of six carbon atoms *condensed* * together in the *o*-position, as shown above, has since been confirmed by syntheses of

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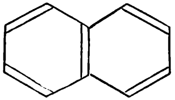
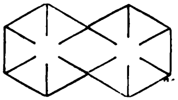
* The term *condensed* used in this and in similar cases signifies that certain carbon atoms are contained in, or are common to, both nuclei.

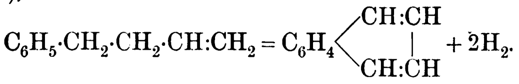
its derivatives, but even more conclusively by the study of the isomerism of its substitution products.

The difficulty of determining and of expressing the actual state or disposition of the fourth affinity of each of the carbon atoms in naphthalene is just as great as in the case of benzene. If the carbon atoms be represented as united by alternate double linkings, as in the formula on the left-hand side (see below), there is the objection that they do not show, as indicated, the behaviour of carbon atoms in fatty unsaturated compounds, as explained more fully in the case of benzene. For this reason the formula on the right-hand side (see below) has been suggested as perhaps preferable, the lines drawn towards the centres of the nuclei having the same significance as in the centric formula for benzene (p. 317). The simple, double-hexagon formula given above is usually employed for the sake of convenience.





Naphthalene may be obtained synthetically by passing the vapour of phenylbutylene, $C_6H_5\cdot CH_2\cdot CH_2\cdot CH:CH_2$* (or of phenylbutylene dibromide, $C_6H_5\cdot CH_2\cdot CH_2\cdot CHBr\cdot CH_2Br$), over red-hot lime, the change involving loss of hydrogen, as in the formation of other aromatic from fatty hydrocarbons (p. 310),



$$C_6H_5\cdot CH_2\cdot CH_2\cdot CH:CH_2 = C_6H_4\left\langle\begin{matrix}CH:CH\\ |\\ CH:CH\end{matrix}\right. + 2H_2.$$

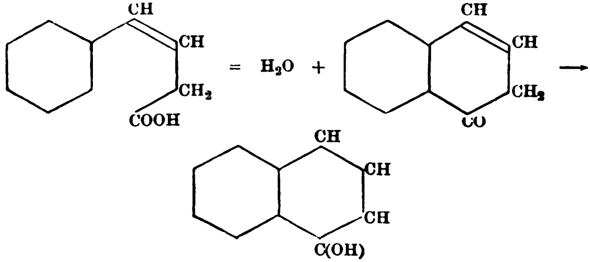
A most important synthesis of naphthalene was accomplished by Fittig, who showed that α-naphthol (α-hydroxynaphthalene) is formed on boiling phenylisocrotonic acid (p. 444) with water. This change probably takes place in two stages, the first product being a keto-derivative of

* *Phenylbutylene* is obtained by treating a mixture of benzyl chloride and allyl iodide with sodium,

$$C_6H_5\cdot CH_2Cl + CH_2I\cdot CH:CH_2 + 2Na = C_6H_5\cdot CH_2\cdot CH_2\cdot CH:CH_2 + NaCl + NaI.$$

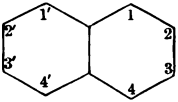
It is a liquid, boiling at 178°, and, like butylene, it combines directly with one molecule of bromine, yielding the dibromide.

naphthalene, which passes into α-naphthol by intramolecular change (compare Part I. p. 200),

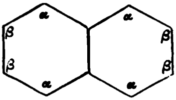


The α-naphthol thus obtained may be converted into naphthalene by distillation with zinc-dust, just as phenol may be transformed into benzene (p. 341).

Isomerism of Naphthalene Derivatives.—As in the case of benzene, the study of the isomerism of the substitution products affords the most convincing evidence that the accepted constitutional formula of naphthalene is correct. In the first place, naphthalene differs from benzene in yielding *two* isomeric mono-substitution products; there are, for example, two monochloronaphthalenes, two monohydroxynaphthalenes, two mononitronaphthalenes, &c. This fact is readily accounted for; on considering the constitutional formula of naphthalene, which may be conveniently written,



or



numbered or lettered as shown (the symbols C and H being omitted for the sake of simplicity), it will be evident that the eight hydrogen atoms are not all similarly situated relatively to the rest of the molecule. If, for example, the hydrogen atom (1) were displaced by chlorine or hydroxyl, the substitution product would be isomeric, but not identical with that produced by the displacement of the hydrogen atom (2). In the first case the substituting atom or group would be united with a carbon atom which is itself directly united with a carbon atom common to both nuclei, whereas in the other case this would not be so. Clearly, then, the fact that the mono-substitution products of naphthalene exist in two isomeric forms is in accordance with the above constitutional formula. Further, it will be seen that no more than two such isomerides could be obtained, because the positions 1.4.1′.4′ (the four α-positions) are identical, and so also are the positions 2.3.2′.3′ (the four β-positions); the isomeric mono-substitution products are, therefore, usually distinguished by using the letters α and β.

When *two* hydrogen atoms in naphthalene are displaced by two identical groups or atoms, *ten* isomeric di-derivatives may be obtained. Denoting the positions of the substituents by the system of numbering already used, these isomerides would be,

1:2, 1:3, 1:4, 1:4′, 1:3′, 1:2′, 1:1′, 2:3, 2:3′, 2:2′,

all other possible positions being identical with one of these; 2:4′, for example, is the same as 1:3′, 2′:4 and 3:1′, and 1′:4 is identical with 1:4′. The constitution of such a di-derivative is usually expressed with the aid of numbers in this manner, as it is necessary to show whether the substituents are combined with the same or with different nuclei.

When the two atoms or groups are present in one and the same nucleus, their relative position is similar to that of groups in the *o*-, *m*-, or *p*-position in benzene. The positions 1:2, 2:3, and 3:4 correspond with the *ortho*-, 1:3 and 2:4 with the *meta*-, and 1:4 with the *para*-position, and similarly in the case of the other nucleus. The position 1:1′ or 4:4′, however, is different from any of these, and is termed the *peri*-position; groups thus situated behave in much the same way as those in the *o*-position in the benzene and naphthalene nuclei.

Derivatives of Naphthalene.

The *homologues of naphthalene*—that is to say, its *alkyl substitution products*, are of comparatively little importance, but it may be mentioned that they may be prepared from the parent hydrocarbon by methods similar to those employed in the case of the corresponding benzene derivatives, as, for example, by treating naphthalene with alkyl halogen compounds and aluminium chloride,

$$C_{10}H_8 + C_2H_5I = C_{10}H_7 \cdot C_2H_5 + HI,$$

and by treating the bromonaphthalenes with an alkyl halogen compound and sodium,

$$C_{10}H_7Br + CH_3Br + 2Na = C_{10}H_7 \cdot CH_3 + 2NaBr.$$

a-Methylnaphthalene, $C_{10}H_7 \cdot CH_3$, is a colourless liquid, boiling at 240–242°, but *β-methylnaphthalene* is a solid, melts at 32°, and boils at 242°; both these hydrocarbons occur in coal-tar.

The *halogen mono-substitution products* of naphthalene are also of little importance. They may be obtained by treating the hydrocarbon, at its boiling-point, with the halogens (chlorine and bromine), but only the *a*-derivatives are formed in this way. Both the *a*- and the *β*-compounds may be obtained by treating the corresponding naphthols (p. 466), or, better, the naphthalenesulphonic acids (p. 467) with pentachloride or pentabromide of phosphorus,

$$C_{10}H_7 \cdot SO_2Cl + PCl_5 = C_{10}H_7Cl + POCl_3 + SOCl_2,$$

or by converting the naphthylamines (p. 465) into the corresponding diazo-compounds, and decomposing the latter with a halogen cuprous salt (pp. 383–384),

$$C_{10}H_7 \cdot NH_2 \longrightarrow C_{10}H_7 \cdot N_2Cl \longrightarrow C_{10}H_7Cl.$$

All these methods correspond with those described in the case of the halogen derivatives of benzene, and are carried out practically in a similar manner.

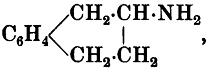
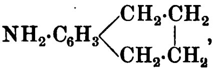
a-Chloronaphthalene, $C_{10}H_7Cl$, is a liquid, boiling at about

263°, but the *β-derivative* is a crystalline substance, melting at 56°, and boiling at 265°.

a-Bromonaphthalene, $C_{10}H_7Br$, is also a liquid at ordinary temperatures, and boils at 279°, but the *β-derivative* is crystalline, and melts at 59°.

The chemical properties of these, and of other halogen derivatives of naphthalene, are similar to those of the halogen derivatives of benzene; the halogen atoms are very firmly combined, and are not displaced by hydroxyl-groups on boiling with alkalies, &c.

Naphthalene tetrachloride, $C_{10}H_8Cl_4$, is an important halogen *additive product*, which is produced on passing chlorine into a vessel containing coarsely-powdered naphthalene, at ordinary temperatures. It forms large colourless crystals, melts at 182°, and is converted into *dichloronaphthalene*, $C_{10}H_6Cl_2$ (a substitution product of naphthalene), when heated with alcoholic potash; it is readily oxidised by nitric acid, yielding phthalic and oxalic acids, a fact which shows that all the chlorine atoms are present in one and the same nucleus; the constitution of the compound is therefore expressed by the formula  $C_6H_4\left\langle\begin{matrix}CHCl\cdot CHCl\\ CHCl\cdot CHCl\end{matrix}\right\rangle$.

The formation of this additive product shows that naphthalene, like benzene, is not really a saturated compound, although it usually behaves as such; many other compounds, formed by the addition of four atoms of hydrogen to naphthalene, or to a naphthalene derivative, are known, and it has been found that when one of the nuclei is thus fully reduced, the atoms or groups directly united to it acquire the character which they have in fatty compounds, whereas those united to the unreduced nucleus retain the character which they have in simple substitution products of benzene. The amido-group in the *tetrahydro-β-naphthylamine* of the constitution  $C_6H_4\left\langle\begin{matrix}CH_2\cdot CH\cdot NH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\right.$, for example, has the same character as that in fatty amines, whereas in the case of the isomeric *tetrahydro-β-naphthylamine*,  $NH_2\cdot C_6H_3\left\langle\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\right.$, the amido-group has the same properties as that in aniline, because it is combined with the unreduced nucleus. Such tetrahydro-derivatives of naphthalene are termed *aromatic* (ar.-) or *alicyclic* (ac.-), according as the substituent is contained in the unreduced or in the reduced nucleus.

Nitro-derivatives.—Naphthalene, like benzene, is readily acted on by concentrated nitric acid, yielding nitro-derivatives, one, two, or more atoms of hydrogen being displaced according to the concentration of the acid and the temperature at which the reaction is carried out; the presence of sulphuric acid facilitates nitration for reasons already mentioned. The chemical properties of the nitro-naphthalenes are in nearly all respects similar to those of the nitro-benzenes.

α-**Nitronaphthalene,** $C_{10}H_7{\cdot}NO_2$, is best prepared in small quantities by dissolving naphthalene in acetic acid, adding concentrated nitric acid, and then heating on a water-bath for half-an-hour; the product is poured into water, and the nitronaphthalene purified by recrystallisation from alcohol. On the large scale it is prepared by treating naphthalene with nitric and sulphuric acids, the method being similar to that employed in the case of nitrobenzene (p. 365). It crystallises in yellow prisms, melts at 61°, and boils at 304°; on oxidation with nitric acid it yields nitrophthalic acid (p. 458).

β-**Nitronaphthalene** is not formed on nitrating naphthalene, but it may be prepared by dissolving β-nitro-α-naphthylamine (a compound obtained on treating α-naphthylamine with *dilute* nitric acid) in an alcoholic solution of hydrogen chloride, adding finely-divided sodium nitrite, and then heating the solution of the diazo-compound (compare p. 383),

$$C_{10}H_6(NO_2){\cdot}N_2Cl + C_2H_5{\cdot}OH = C_{10}H_7{\cdot}NO_2 + N_2 + HCl + C_2H_4O.$$

It crystallises in yellow needles, melting at 79°.

The **amido-derivatives** of naphthalene are very similar in properties to the corresponding benzene derivatives, except that even the monamido-compounds are crystalline solids; they have a neutral reaction to litmus, and yet are distinctly basic in character, since they neutralise acids, forming salts, which, however, are decomposed by the hydroxides and carbonates of the alkalies. These amido-compounds, moreover, may be converted into diazo-compounds, amidoazo-compounds, &c., by reactions similar to those employed in the case of the amido-benzenes, and many of the substances obtained in this way, as well as the amido-compounds themselves, are extensively employed in the manufacture of dyes.

α-**Naphthylamine,** $C_{10}H_7 \cdot NH_2$, may be obtained by heating α-naphthol with ammonio-zinc chloride or ammonio-calcium chloride at 250°,*

$$C_{10}H_7 \cdot OH + NH_3 = C_{10}H_7 \cdot NH_2 + H_2O,$$

but it is best prepared by reducing α-nitronaphthalene with iron-filings and acetic acid,

$$C_{10}H_7 \cdot NO_2 + 6H = C_{10}H_7 \cdot NH_2 + 2H_2O.$$

It is a colourless, crystalline substance, melting at 50°, and boiling at 300°; it has a disagreeable smell, turns red on exposure to the air, and its salts give a blue precipitate with ferric chloride and other oxidising agents. On oxidation with a boiling solution of chromic acid, it is converted into α-naphthaquinone (p. 468).

β-**Naphthylamine** is not prepared from β-nitronaphthalene (as this substance is itself only obtained with difficulty), but from β-naphthol, as described in the case of the α-compound. It crystallises in colourless plates, melts at 112°, and boils at 294°; it differs markedly from α-naphthylamine in being odourless, and its salts give no colouration with ferric chloride. On oxidation with potassium permanganate, it yields phthalic acid.

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* Prepared by passing ammonia over anhydrous zinc or calcium chloride. These compounds decompose when heated, evolving ammonia, and are, therefore, conveniently employed in many reactions requiring the presence of ammonia at high temperatures; the zinc or calcium chloride resulting from their decomposition also favours the reaction in those cases in which water is formed, as both substances are powerful dehydrating agents. Ammonium acetate may be employed for a similar purpose, as it dissociates at comparatively low temperatures, but its action is less energetic.

The two **naphthols**, or monohydroxy-derivatives of naphthalene, correspond with the monohydric phenols, and are compounds of considerable importance, as they are extensively employed in the colour industry. They both occur in coal-tar, but only in small quantities, and are, therefore, prepared either by diazotising the corresponding naphthylamines,

$$C_{10}H_7{\cdot}NH_2 \rightarrow C_{10}H_7{\cdot}N_2Cl \rightarrow C_{10}H_7{\cdot}OH,$$

or by fusing the corresponding sulphonic acids with potash (compare p. 400),

$$C_{10}H_7{\cdot}SO_3K + KOH = C_{10}H_7{\cdot}OH + K_2SO_3.$$

Their properties are, on the whole, very similar to those of the phenols, and, like the latter, they dissolve in caustic alkalies, yielding metallic derivatives, which are decomposed by carbonic acid; the hydrogen of the hydroxyl-group in the naphthols may also be displaced by an acetyl-group or by an alkyl-group, just as in phenols, and on treatment with pentachloride or pentabromide of phosphorus, a halogen atom is substituted for the hydroxyl-group. The naphthols further resemble the phenols in giving colour reactions with ferric chloride.

In a few respects, however, there are certain differences between the chemical properties of the naphthols and phenols, inasmuch as the hydroxyl-groups in the former more readily undergo change; when, for example, a naphthol is heated with ammonio-zinc chloride at 250°, it is converted into the corresponding amido-compound (see above), whereas the conversion of phenol into aniline requires a temperature of 300–350°, other conditions remaining the same. Again, when a naphthol is heated with an alcohol and hydrogen chloride, it is converted into an alkyl-derivative, whereas alkyl-derivatives of phenols cannot, as a rule, be obtained in this way. In some respects the naphthols form, as it were, a connecting-link between the phenols and the alcohols.

a-**Naphthol,** $C_{10}H_7{\cdot}OH$, is formed, as previously stated (p. 459), on boiling phenylisocrotonic acid with water, an important synthesis, which proves that the hydroxyl-group is in the *a*-position; it is prepared from *a*-naphthylamine or from naphthalene-*a*-sulphonic acid (p. 468). It is a colourless, crystalline substance, melting at 94°, and boiling at 280°; it has a faint smell, recalling that of phenol, and it dissolves freely in alcohol and ether, but is only sparingly soluble in hot water. Its aqueous solution gives with ferric chloride a violet, flocculent precipitate, consisting probably of an iron compound of *a-di-naphthol*, $OH \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot OH$, an oxidation product of the naphthol.

a-Naphthol, like phenol, is very readily acted on by nitric acid, yielding a *dinitro*-derivative, $C_{10}H_5(NO_2)_2 \cdot OH$, which crystallises in yellow needles, and melts at 138°; this nitro-compound, like picric acid, has a much more strongly marked acid character than the hydroxy-compound from which it is derived, and decomposes carbonates, forming deep-yellow salts which dye silk a beautiful golden yellow; its sodium derivative, $C_{10}H_5(NO_2)_2 \cdot ONa + H_2O$, is known commercially as *Martius' yellow*, or *naphthalene yellow*. Another dye obtained from *a*-naphthol is *naphthol yellow* (p. 538), the potassium salt of dinitro-*a*-naphtholsulphonic acid, $C_{10}H_4(NO_2)_2(OK) \cdot SO_3K$; the acid itself is manufactured by nitrating *a*-naphtholtrisulphonic acid (prepared by heating *a*-naphthol with anhydrosulphuric acid), in which process two of the sulphonic groups are displaced by nitro-groups.

β-**Naphthol,** prepared by fusing naphthalene-*β*-sulphonic acid with potash, melts at 122°, and boils at 286°; it is a colourless, crystalline compound, readily soluble in hot water, and, like the *a*-derivative, it has a faint phenol-like smell. Its aqueous solution gives, with ferric chloride, a green colouration and a flocculent precipitate of *β*-di-naphthol, $OH \cdot C_{10}H_6 \cdot C_{10}H_6 \cdot OH$.

Sulphonic Acids.—Perhaps the most important derivatives of naphthalene, from a commercial point of view, are the various mono- and di-sulphonic acids, which are obtained from the hydrocarbon itself, from the naphthylamines, and from the naphthols, and used in large quantities in the manufacture of dyes. It would be of little use to describe here the very numerous compounds of this class, but some indication of their properties may be afforded by a brief statement of the more important points.

Naphthalene is readily sulphonated, yielding two *monosulphonic acids*, $C_{10}H_7 \cdot SO_3H$, namely, the α- and β-compounds, both of which are formed when the hydrocarbon is heated with concentrated sulphuric acid at 80°; if, however, the operation be carried out at 160°, only the β-acid is obtained, because at this temperature the α-acid is converted into the β-acid by intramolecular change, just as phenol-*o*-sulphonic acid is transformed into the *p*-acid by heating. The two naphthalenesulphonic acids are crystalline hygroscopic substances, and show all the characteristic properties of acids of this class.

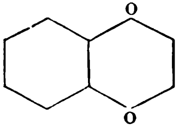
Di-sulphonic acids may be obtained by strongly heating naphthalene with sulphuric or anhydrosulphuric acid.

Fourteen isomeric *naphthylaminemonosulphonic acids*, $C_{10}H_6(NH_2) \cdot SO_3H$, may theoretically be obtained—namely, seven from α-naphthylamine, and seven from the β-base; as a matter of fact, nearly all these acids are known. One of the most important, perhaps, is 1:4-naphthylaminemonosulphonic acid, or *naphthionic acid*, which is the sole product of the action of sulphuric acid on α-naphthylamine; it is a crystalline compound, very sparingly soluble in cold water, and is used in the manufacture of Congo-red (p. 537) and other dyes.

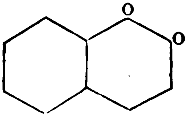
The *naphtholmonosulphonic acids* correspond in number with the naphthylaminemonosulphonic acids, and are also extensively used in the colour industry.

α-**Naphthaquinone,** $C_{10}H_6O_2$, is a derivative of naphthalene corresponding with (benzo)quinone, and, like the latter, it is formed on oxidising various mono- and di-substitution products of the hydrocarbon with sodium dichromate and sulphuric acid, but only those in which the substituting groups occupy the α-positions; α-naphthylamine, 1:4-amidonaphthol, and 1:4-diamidonaphthalene, for example, may be employed. As a rule, however, naphthalene itself is oxidised with a boiling solution of chromic acid in acetic acid (a method not applicable for the preparation of quinone from benzene), as the product is then easily obtained in a state of purity.

α-Naphthaquinone crystallises from alcohol in deep-yellow needles, melting at 125°; it resembles quinone in colour, in having a curious pungent smell, and in being very volatile, subliming readily even at 100°, and distilling rapidly in steam. Unlike quinone, it is not reduced by sulphurous acid, but some reducing agents convert it into 1:4-dihydroxynaphthalene, $C_{10}H_6(OH)_2$, just as quinone is transformed into hydroquinone (p. 426). This close similarity in properties clearly points to a similarity in constitution, so that α-naphthaquinone may be represented by the formula,



β-Naphthaquinone, $C_{10}H_6O_2$, isomeric with the α-compound, is formed when α-amido-β-naphthol is oxidised with potassium dichromate and dilute sulphuric acid, or with ferric chloride; it crystallises in red needles, decomposes at about 115° without melting, and on reduction with sulphurous acid, is converted into 1:2-dihydroxynaphthalene. It differs from α-naphthaquinone and from quinone in colour, in having no smell, and in being non-volatile, properties which, though apparently insignificant, are really of some importance, as showing the difference between *ortho*-quinones and *para*-quinones; the latter are generally deep-yellow, volatile compounds, having a pungent odour, whereas the former are red, non-volatile, and odourless. β-Naphthaquinone is an example of an ortho-quinone, and its constitution may be represented by the formula,



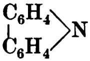
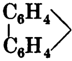
Both *α*- and *β*-naphthaquinone are oxidised by nitric acid, giving *o*-phthalic acid, a proof that in both compounds the two oxygen atoms are united with only one nucleus; that the one is a *para*-, the other an *ortho*-quinone is also established, but, for reasons similar to those stated more fully in the case of quinone, the exact disposition of the various carbon affinities is unknown.

The above description of some of the more important naphthalene derivatives will be sufficient to show the close relationship which these compounds bear to the corresponding derivatives of benzene; although the former exist in a larger number of isomeric forms, they are, as a rule, prepared by the same methods as their analogues of the benzene series, and resemble them closely in chemical properties. It may, in fact, be stated that, as a rule, all general reactions and generic properties of benzene derivatives are met with again in studying naphthalene derivatives.

CHAPTER XXXII.

ANTHRACENE AND PHENANTHRENE.

Anthracene, $C_{14}H_{10}$, is a hydrocarbon of great commercial importance, as it is the starting-point in the manufacture of alizarin, the colouring matter employed in producing Turkey-red dye; it is prepared exclusively from coal-tar. The crude mixture of hydrocarbons and other substances known as '50 per cent. anthracene' (p. 308) is first distilled with one-third of its weight of potash from an iron retort; the distillate, which consists almost entirely of anthracene and phenanthrene, is then digested with carbon disulphide, when the phenanthrene dissolves, leaving the anthracene, which is further purified by crystallisation from benzene.

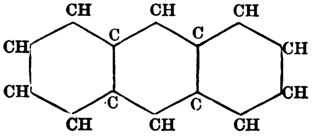
Crude anthracene contains considerable quantities of carbazole,  $\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>\!NH$, a colourless, crystalline substance, melting at 238°, and boiling at 355°. On treatment with potash this substance is converted into a potassium derivative,  $\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>\!NK$, which remains in the retort, or is decomposed on heating; many other impurities, which cannot readily be separated by crystallisation, are also got rid of in this way.

Anthracene crystallises from benzene in colourless, lustrous plates, which show a beautiful blue fluorescence; it melts at 213°, boils at 351°, and dissolves freely in boiling benzene, but is only sparingly soluble in alcohol and ether. On mixing saturated alcoholic solutions of anthracene and picric acid, *anthracene picrate*, $C_{14}H_{10},C_6H_2(NO_2)_3 \cdot OH$, is deposited in ruby-red needles, which melt at 138°; this compound is resolved into its components when treated with a large quantity of alcohol (distinction from phenanthrene picrate, p. 481).

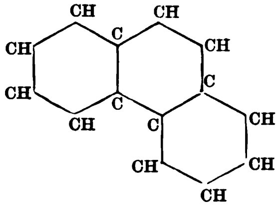
Constitution.—The behaviour of anthracene towards chlorine and bromine is, on the whole, similar to that of benzene and naphthalene—that is to say, it yields additive or substitution products according to the conditions employed; towards concentrated sulphuric acid, also, it behaves like other aromatic compounds, and is converted into sulphonic acids. When treated with nitric acid, however, instead of yielding a nitro-derivative, as was to be expected from the molecular formula of the hydrocarbon (which, from the relatively small proportion of hydrogen, clearly indicates the presence of one or more closed-chains), it is oxidised to anthraquinone, $C_{14}H_8O_2$, two atoms of hydrogen being displaced by two atoms of oxygen; this change always takes place, even when dilute nitric acid, or some other oxidising agent, is employed, and as it is closely analogous to that which occurs in the conversion of naphthalene, $C_{10}H_8$, into *a*-naphthaquinone, $C_{10}H_6O_2$ (p. 468), it is an indication of the presence of a closed-chain, oxidation processes of this kind (namely, the substitution of oxygen atoms for an *equal* number of hydrogen atoms) being unknown in the case of fatty (open-chain) hydrocarbons. Another highly important fact, owing to its bearing on the constitution of anthracene, is this, that, although the hydrocarbon and most of its derivatives are resolved into simpler substances only with very great difficulty, when this does occur one of the products is always some benzene derivative, usually phthalic acid.

Now, if the molecule of anthracene contained only one benzene nucleus, or even if, like naphthalene, it contained two condensed nuclei, there would still be certain carbon and hydrogen atoms to be accounted for, and this could only be done by assuming the presence of *unsaturated* side-chains; as, however, all experience has shown that such side-chains in benzene and in naphthalene are oxidised to carboxyl (compare p. 452) with the utmost facility, it is impossible to assume their presence in anthracene, a compound which is always oxidised to the neutral substance anthraquinone, without loss of carbon. Arguments of this kind lead, therefore, to the conclusion that the molecule of anthracene is composed only of combined or condensed nuclei; as, moreover, the hydrocarbon may be indirectly converted into phthalic acid, it must be assumed that two of these nuclei are condensed together in the *o*-position, as in naphthalene.

If, now, an attempt be made to deduce a constitutional formula for anthracene on this basis, and it be further assumed that all the closed-chains are composed of six carbon atoms, as in naphthalene, the following formulæ suggest themselves as the most probable,



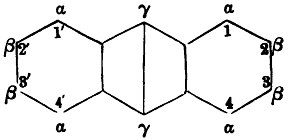
I.



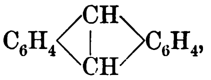
II.

although, of course, neither could be accepted as final without further evidence.

Experience has shown, however, that formula I. must be taken as representing the constitution of anthracene (formula II. expressing that of phenanthrene, p. 481), because it accounts satisfactorily for all known facts—amongst others, for a number of important syntheses of the hydrocarbon (see below), for the relation of anthracene to anthraquinone, and for the isomerism of the anthracene derivatives. It is, nevertheless, just as difficult to determine and to express the actual disposition of the fourth affinity of each carbon atom in anthracene as in the cases of benzene and naphthalene; as, however, there are reasons for supposing that the state of combination of the two central CH groups (that is, those which form part of the central nucleus only) is different from that of all the others (inasmuch as they are generally attacked first), and that the two carbon atoms of these groups are directly united, the above formula (I.) is usually written,



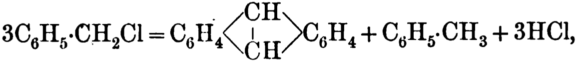
or



$C_6H_4{<}\begin{matrix}CH\\|\\CH\end{matrix}{>}C_6H_4$,

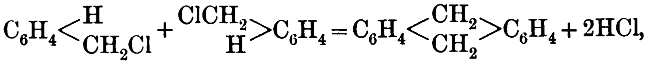
the disposition of the fourth affinities of the carbon atoms in the two $C_6H_4<$ groups being taken to be the same as in the centric formula for benzene.*

Anthracene may be obtained synthetically in various ways. It is produced when benzyl chloride is heated with aluminium chloride,



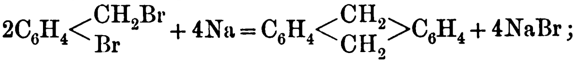
$$3C_6H_5{\cdot}CH_2Cl = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + C_6H_5{\cdot}CH_3 + 3HCl,$$

the hydranthracene (p. 475), which is formed as an intermediate-product,



$$C_6H_4<\begin{matrix}H\\CH_2Cl\end{matrix} + \begin{matrix}ClCH_2\\H\end{matrix}>C_6H_4 = C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_4 + 2HCl,$$

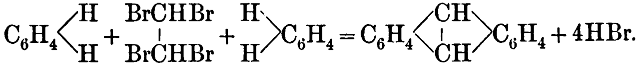
being converted into anthracene by loss of hydrogen, which reduces part of the benzyl chloride to toluene, as shown in the first equation. Anthracene is also formed, together with hydranthracene and phenanthrene (p. 481), when *ortho*-bromobenzyl bromide (prepared by brominating *boiling* *o*-bromotoluene, $C_6H_4Br{\cdot}CH_3$) is treated with sodium,



$$2C_6H_4<\begin{matrix}CH_2Br\\Br\end{matrix} + 4Na = C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_4 + 4NaBr;$$

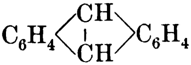
here, again, hydranthracene is the primary product, and from it anthracene is formed by loss of hydrogen.

Another interesting synthesis may be mentioned—namely, the formation of anthracene on treating a mixture of tetrabromethane and benzene with aluminium chloride,



$$C_6H_4\left\langle\begin{matrix}H\\H\end{matrix}\right. + \begin{matrix}BrCHBr\\|\\BrCHBr\end{matrix} + \left.\begin{matrix}H\\H\end{matrix}\right\rangle C_6H_4 = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + 4HBr.$$

All these methods of formation are accounted for in a simple manner with the aid of the above constitutional formula, the last one especially indicating that the two central carbon atoms are directly united; the formula $C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4$ will, therefore, be employed in describing the anthracene derivatives.



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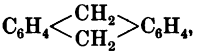
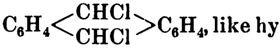
* The letters or numbers serve to denote the constitution of the anthracene derivatives (p. 475).

Isomerism of Anthracene Derivatives.—Further evidence in support of the above constitutional formula is afforded by the study of the isomerism of the substitution products of anthracene, although, in most cases, all the isomerides theoretically possible have not yet been prepared.

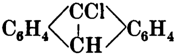
When one atom of hydrogen is displaced, *three* isomerides may be obtained, since there are three hydrogen atoms (α,β,γ), all of which are differently situated relatively to the rest of the molecule; these mono-substitution products are usually distinguished by the letters α, β, γ, according to the position of the substituent (compare formula p. 473). When two atoms of hydrogen are displaced by similar atoms or groups, fifteen isomeric di-substitution products may be obtained.

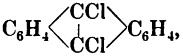


Hydranthracene, $C_6H_4\left<\begin{array}{c}CH_2\\CH_2\end{array}\right>C_6H_4$, a substance of little importance, is formed on reducing anthracene with boiling concentrated hydriodic acid, or with sodium amalgam and water. It is a colourless, crystalline compound, melting at 106–108°, and when heated with sulphuric acid it is converted into anthracene, the acid being reduced to sulphur dioxide.



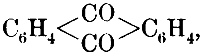
Anthracene dichloride, $C_6H_4\left<\begin{array}{c}CHCl\\CHCl\end{array}\right>C_6H_4$, like hydranthracene, is an additive product of the hydrocarbon; it is obtained when chlorine is passed into a *cold* solution of anthracene in carbon disulphide, whereas at 100° substitution takes place, *monochloranthracene* and *dichloranthracene*,





$$C_6H_4\left<\begin{array}{c}CCl\\|\\CH\end{array}\right>C_6H_4 \quad \text{and} \quad C_6H_4\left<\begin{array}{c}CCl\\|\\CCl\end{array}\right>C_6H_4,$$

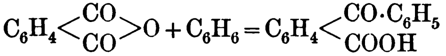
being formed; these substitution products crystallise in yellow needles, melting at 103° and 209° respectively, and they are both converted into anthraquinone on oxidation, a fact which shows the positions of the chlorine atoms.



Anthraquinone, $C_6H_4\left<\begin{array}{c}CO\\CO\end{array}\right>C_6H_4$, is formed, as already mentioned, on oxidising anthracene with chromic or nitric acid. It is conveniently prepared by dissolving anthracene (1 part) in boiling glacial acetic acid, and gradually adding a concentrated solution of chromic acid (2 parts) in glacial acetic acid. As soon as oxidation is complete the product is allowed to cool, and the anthraquinone, which separates in long needles, is collected and purified either by sublimation or by recrystallisation from acetic acid.

Anthraquinone is manufactured by oxidising finely-divided '50 per cent. anthracene,' suspended in water, with sodium dichromate and sulphuric acid. The crude anthraquinone is collected on a filter, washed, dried, and heated at 100° with 2–3 parts of concentrated sulphuric acid, by which means the impurities are converted into soluble sulphonic acids, whereas the anthraquinone is not acted on. The almost black product is now allowed to stand in a damp place, when the anthraquinone gradually separates in crystals as the sulphuric acid becomes dilute; water is then added, and the anthraquinone collected, washed, dried, and sublimed.

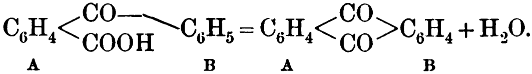
Anthraquinone may be produced synthetically by treating a solution of phthalic anhydride (p. 439) in benzene, with a strong dehydrating agent, such as aluminium chloride, the reaction taking place in two stages; *o*-benzoylbenzoic acid is first produced,



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O + C_6H_6 = C_6H_4<\begin{matrix}CO\cdot C_6H_5\\COOH\end{matrix}$$

o-Benzoylbenzoic Acid.

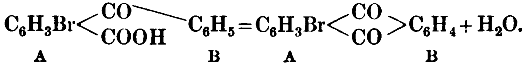
but by the further action of the aluminium chloride (or when treated with sulphuric acid), this substance is converted into anthraquinone with loss of 1 molecule of water,



$$\underset{A}{C_6H_4}<\begin{matrix}CO—\\COOH\end{matrix}\underset{B}{C_6H_5} = \underset{A}{C_6H_4}<\begin{matrix}CO\\CO\end{matrix}>\underset{B}{C_6H_4} + H_2O.$$

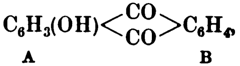
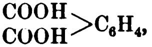
Anthraquinone contains, therefore, two $C_6H_4<$ groups, united by two $CO<$ groups.

That the two $CO<$ groups occupy the *o*-position in the one benzene ring (A) is known, because they do so in phthalic acid; that they occupy the *o*-position in the second benzene ring (B) has been proved, as follows: When bromophthalic anhydride is treated with benzene and aluminium chloride, bromobenzoylbenzoic acid is produced, and this, when treated with sulphuric acid, yields bromanthraquinone,

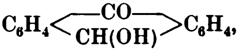
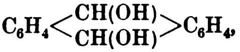
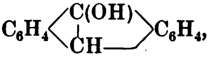


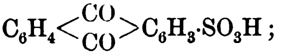
$$\underset{A}{C_6H_3Br}<\begin{matrix}CO—\\COOH\end{matrix}\underset{B}{C_6H_5} = \underset{A}{C_6H_3Br}<\begin{matrix}CO\\CO\end{matrix}>\underset{B}{C_6H_4} + H_2O.$$

The formation of this substance from bromophthalic acid proves, as before, that the two CO< groups are united to the ring A in the *o*-position.

Now, when bromanthraquinone is heated with potash at 160°, it is converted into hydroxyanthraquinone,  $\underset{A}{C_6H_3(OH)}<\begin{matrix}CO\\CO\end{matrix}>\underset{B}{C_6H_4}$, and this, with nitric acid, yields phthalic acid,  $\begin{matrix}COOH\\COOH\end{matrix}>C_6H_4$, the group A being oxidised; therefore the two CO< groups are attached to B, as well as to A, in the *o*-position, and anthraquinone has the constitution represented above, a conclusion which affords strong support to the above views regarding the constitution of anthracene.

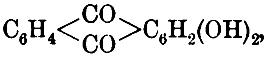
Anthraquinone crystallises from glacial acetic acid in pale-yellow needles, melts at 285°, and sublimes at higher temperatures; it is exceedingly stable, and is only with difficulty attacked by oxidising agents, by sulphuric acid, or by nitric acid. In all those properties which are connected with the presence of the two carbonyl-groups, anthraquinone resembles the aromatic ketones much more closely than it does the quinones. It has no smell, is by no means readily volatile, and is not reduced when treated with sulphurous acid; unlike quinone, therefore, it is not an oxidising agent.

When treated with more powerful reducing agents, however, it is converted into *oxanthranol*,  $C_6H_4<\begin{matrix}CO\\CH(OH)\end{matrix}>C_6H_4$, one of the CO< groups becoming >CH·OH, just as in the reduction of ketones; on further reduction the other CO< group undergoes a similar change, but the product,  $C_6H_4<\begin{matrix}CH(OH)\\CH(OH)\end{matrix}>C_6H_4$, loses one molecule of water, yielding *anthranol*,  $C_6H_4<\begin{matrix}C(OH)\\|\\CH\end{matrix}>C_6H_4$, which is finally reduced to hydranthracene; when anthraquinone is distilled with zinc-dust, anthracene is produced.

Anthraquinone is only slowly acted on by ordinary sulphuric acid even at 250°, yielding anthraquinone-β-monosulphonic acid,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3{\cdot}SO_3H$; but when heated with a large excess of anhydrosulphuric acid at 160–170°, it yields a mixture of isomeric disulphonic acids, $C_{14}H_6O_2(SO_3H)_2$.

Sodium anthraquinone-β-monosulphonate, which is used in such large quantities in the manufacture of alizarin (see below), is prepared by heating anthraquinone with an equal weight of anhydrosulphuric acid (containing 50 per cent. of SO_3) in enamelled iron pots at 160°. The product is diluted with water, filtered from unchanged anthraquinone, and neutralised with soda; on cooling, sparingly soluble sodium anthraquinone-monosulphonate separates in glistening plates, and is collected in filter-presses. The more soluble sodium salts of the anthraquinone-disulphonic acids, which are always formed at the same time, remain in solution.

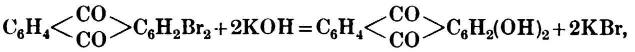
Test for Anthraquinone.—When a trace of finely-divided anthraquinone is mixed with dilute soda, a little zinc-dust added, and the mixture heated to boiling, an intense red colouration is produced, but on shaking in contact with air, the solution is decolourised; in this reaction oxanthranol (p. 477) is formed, and this substance dissolves in the alkali, forming a deep-red solution; on shaking with air, however, it is oxidised to anthraquinone, which separates as a flocculent precipitate.



Alizarin, $C_6H_4<\substack{CO\\CO}>C_6H_2(OH)_2$, or 1:2-dihydroxyanthraquinone, occurs in madder (the root of *Rubia tinctorum*), a substance which has been used from the earliest times for dyeing purposes, and which owes its tinctorial properties to two substances, alizarin and purpurin (see below), both of which are present in the root in the form of glucosides. *Ruberythric acid*, the glucoside of alizarin, is decomposed when boiled with acids, or when the madder extract is allowed to undergo fermentation, with formation of alizarin and two molecules of glucose,

$$\underset{\text{Ruberythric Acid.}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{Alizarin.}}{C_{14}H_8O_4} + 2C_6H_{12}O_6.$$

A dye of such great importance as alizarin naturally attracted the attention of chemists, and many attempts were made to prepare it synthetically. This was first accomplished in 1868 by Graebe and Liebermann, who found that alizarin could be produced by fusing 1:2-dibromanthraquinone* with potash,

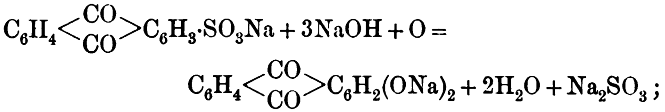


$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6H_2Br_2+2KOH=C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6H_2(OH)_2+2KBr},$$

but the process was not a commercial success.

At the present day, however, madder is no longer used, and the whole of the alizarin of commerce is made from (coal-tar) anthracene in the following manner.

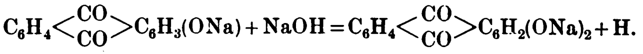
Anthracene is first oxidised to anthraquinone, and the latter is converted into anthraquinone-β-sulphonic acid by the method already described (p. 477); the sodium salt of this acid is then heated with soda and a little potassium chlorate, and is thus converted into the sodium derivative of alizarin,



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6H_3{\cdot}SO_3Na+3NaOH+O=}$$
$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6H_2(ONa)_2+2H_2O+Na_2SO_3};$$

from this sodium salt alizarin is obtained by adding acid.

When anthraquinonesulphonic acid is fused with soda, the $-\mathrm{SO_3H}$ group is displaced by $-\mathrm{ONa}$ in the usual manner, but the *hydroxyanthraquinone* (sodium derivative) thus produced is further acted on by the soda, giving alizarin (sodium derivative) and hydrogen,



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6H_3(ONa)+NaOH=C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C_6H_2(ONa)_2+H}.$$

The oxidising agent ($\mathrm{KClO_3}$) is added in order to prevent the nascent hydrogen reducing the still unchanged hydroxyanthraquinone to anthraquinone, the operation being conducted as follows.

Sodium anthraquinonesulphonate (100 parts) is heated in a closed iron cylinder, fitted with a stirrer, with soda (300 parts) and potassium chlorate (14 parts), for two days at 180°. The dark-violet product, which contains the sodium salt of alizarin, is dissolved in water, the solution filtered if necessary, and the alizarin precipitated by the addition of hydrochloric acid. The yellowish crystalline precipitate is collected in filter-presses, washed well with

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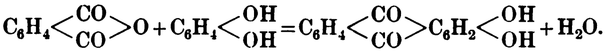
* Obtained by heating anthraquinone with bromine and a trace of iodine in a sealed tube at 160°.

water, and sent into the market in the form of a 10 or 20 per cent. paste. From this product alizarin is obtained in a pure state by recrystallisation from toluene, or by sublimation.

Alizarin crystallises and sublimes in dark-red prisms, which melt at 290°, and are almost insoluble in water, but moderately soluble in alcohol. It is a dihydroxy-derivative of anthraquinone, and has therefore the properties of a dihydric phenol; it dissolves in potash and soda, forming metallic derivatives of the type $C_6H_4 < \begin{array}{c} CO \\ CO \end{array} > C_6H_2(OM)_2$, which are soluble in water, yielding intensely purple solutions. With acetic anhydride it gives a *diacetate*, $C_{14}H_6O_2(C_2H_3O_2)_2$, melting at 180°, and when distilled with zinc-dust it is reduced to anthracene.

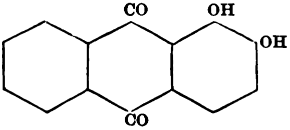
The value of alizarin as a dye lies in the fact that it yields coloured, insoluble compounds ('lakes,' p. 518) with certain metallic oxides; the ferric compound, for example, is violet black, the lime compound blue, and the tin and aluminium compounds different shades of red (Turkey-red). A short account of the methods used in dyeing with alizarin is given later (p. 516).

Constitution of Alizarin.—Alizarin may be prepared by heating a mixture of phthalic anhydride and catechol with sulphuric acid at 150°,

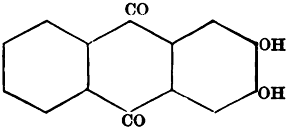


$$C_6H_4 < \begin{array}{c} CO \\ CO \end{array} > O + C_6H_4 < \begin{array}{c} OH \\ OH \end{array} = C_6H_4 < \begin{array}{c} CO \\ CO \end{array} > C_6H_2 < \begin{array}{c} OH \\ OH \end{array} + H_2O.$$

As catechol is *o*-dihydroxybenzene, it follows that the two hydroxyl-groups in alizarin must be in the *o*-position to one another, and this substance must, therefore, be represented by one of the following formulæ,



I.



II.

Now, alizarin yields two isomeric *mono*-nitro-derivatives, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H(OH)_2\cdot NO_2$, both of which contain the nitro-group in the same nucleus as the two hydroxyl-groups; its constitution must, therefore, be represented by formula I., as a substance having the constitution II. could only yield one such nitro-derivative.

Besides alizarin, several other dihydroxy- and also trihydroxy-anthraquinones have been obtained, but only those are of value as dyes which contain two hydroxyl-groups in the same positions as in alizarin; two such derivatives, which possess very valuable dyeing properties, may be mentioned.

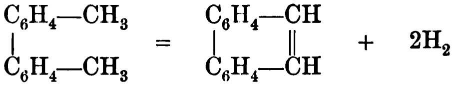
Purpurin, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H(OH)_3$, or 1:2:4-trihydroxyanthraquinone, is contained in madder, in the form of a glucoside, and may be prepared by oxidising alizarin with manganese dioxide and sulphuric acid. It crystallises in deep-red needles, melts at 253°, and gives, with aluminium mordants, a much yellower shade of red than alizarin, and is now used on the large scale for the production of brilliant reds.

Anthrapurpurin, $C_6H_3(OH)<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2<\genfrac{}{}{0pt}{}{OH(1)}{OH(2)}$, is isomeric with purpurin, and is manufactured by fusing anthraquinone-disulphonic acid, $C_6H_3(SO_3H)<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_3\cdot SO_3H$, with soda and potassium chlorate (see alizarin, p. 479). It crystallises in yellowish-red needles, melts at 330°, and is very largely employed in dyeing yellow shades of Turkey-red.

Phenanthrene, $C_{14}H_{10}$, an isomeride of anthracene, is a hydrocarbon of considerable theoretical interest, although it has no commercial value. It occurs in large quantities in '50 per cent. anthracene,' from which it may be extracted as already described (p. 470). The resulting crude phenanthrene is converted into the picrate, which is first recrystallised from alcohol, to free it from anthracene picrate, and then decomposed by ammonia, the hydrocarbon being finally purified by recrystallisation.

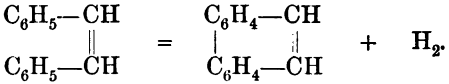
Phenanthrene crystallises in glistening needles, melts at 99°, and distils at about 340°; it is readily soluble in alcohol, ether, and benzene. When oxidised with chromic acid, it is first converted into *phenanthraquinone*, $C_{14}H_8O_2$, isomeric with anthraquinone, and then into *diphenic acid*, $C_{14}H_{10}O_4$. This acid is decomposed on distillation with lime, yielding carbon dioxide and *diphenyl* (p. 350); it is therefore *diphenyldicarboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}COOH$, and its formation from phenanthrene shows that the latter contains *two* benzene nuclei.

Further evidence as to the constitution of phenanthrene is obtained by studying its methods of formation. It is formed, for example, on passing *o-ditolyl* (prepared by treating *o*-bromotoluene with sodium) or *stilbene** through a red-hot tube; since these two hydrocarbons give the *same* product, the reactions must be expressed as follows,



$$\begin{array}{l} C_6H_4-CH_3 \\ | \\ C_6H_4-CH_3 \end{array} = \begin{array}{l} C_6H_4-CH \\ |\qquad\ \ \| \\ C_6H_4-CH \end{array} + 2H_2$$

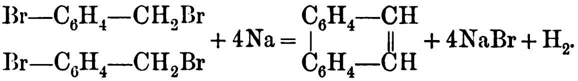
o-Ditolyl. Phenanthrene.



$$\begin{array}{l} C_6H_5-CH \\ \qquad\quad\ \ \| \\ C_6H_5-CH \end{array} = \begin{array}{l} C_6H_4-CH \\ |\qquad\ \ \| \\ C_6H_4-CH \end{array} + H_2.$$

Stilbene. Phenanthrene.

Again, phenanthrene is formed, together with anthracene, by the action of sodium on *o*-bromobenzyl bromide (p. 474),



$$\begin{array}{l} Br-C_6H_4-CH_2Br \\ Br-C_6H_4-CH_2Br \end{array} + 4Na = \begin{array}{l} C_6H_4-CH \\ |\qquad\ \ \| \\ C_6H_4-CH \end{array} + 4NaBr + H_2.$$

---

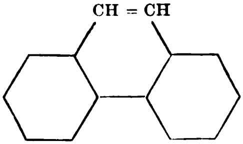
* *Stilbene*, or *diphenylethylene*, $C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5$, may be prepared by acting on benzal chloride (p. 362) with sodium,

$$2C_6H_5{\cdot}CHCl_2 + 4Na = C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5 + 4NaCl.$$

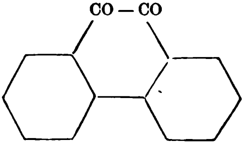
It crystallises in colourless needles, melts at 120°, and, like ethylene, combines with two atoms of bromine, forming *stilbene dibromide*,

$$C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_5 \text{ (m.p. } 237^\circ).$$

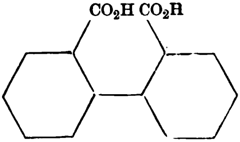
For these and many other reasons, the constitution of phenanthrene is expressed by the formula,



When the hydrocarbon is oxidised to phenanthraquinone, the group $-CH=CH-$ becomes $-CO—CO-$, and, on further oxidation to diphenic acid, each carbonyl-group is converted into a carboxyl-group,



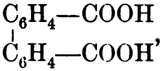
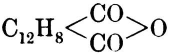
Phenanthraquinone.



Diphenic Acid.

Phenanthraquinone, $\begin{array}{l}C_6H_4—CO\\ \mid \qquad\;\; \mid \\ C_6H_4—CO\end{array}$, like anthraquinone, is formed by oxidising the hydrocarbon with chromic acid. It crystallises from alcohol in orange needles, and melts at 198°. In chemical properties it shows little resemblance to quinone or to α-naphthaquinone, but is closely related to β-naphthaquinone (p. 469), and is, like the latter, an ortho-diketone (ortho-quinone); it has no smell, and does not volatilise except when strongly heated, but it is readily reduced by sulphurous acid to *dihydroxyphenanthrene*, $C_{14}H_8(OH)_2$, and it combines with sodium bisulphite, forming a soluble *bisulphite* compound, $C_{14}H_8O_2, NaHSO_3+2H_2O$; with hydroxylamine it yields a *dioxime*, $C_{12}H_8(C:NOH)_2$. The hydroxy-derivatives of phenanthraquinone, unlike those of anthraquinone, possess no tinctorial properties.

Phenanthraquinone may be readily detected by dissolving a small quantity (0·1 gram) in glacial acetic acid (20 c.c.), adding a few drops of commercial toluene, and then mixing the well-cooled solution with sulphuric acid (1 c.c.). After standing for a few minutes, the bluish-green liquid is poured into water and shaken with ether, when the ether acquires an intense reddish-violet colouration (Laubenheimer's reaction). Like the indophenin reaction, this test depends on the formation of a colouring matter containing sulphur, produced by the condensation of the phenanthraquinone with the *thiotolene*, $C_4H_3S(CH_3)$, which is contained in crude toluene (p. 344).

Diphenic acid,  $\begin{array}{l}C_6H_4\text{—}COOH\\ |\\ C_6H_4\text{—}COOH\end{array}$, obtained by the oxidation of phenanthrene or of phenanthraquinone with chromic acid, crystallises from water in needles, and melts at 229°. When heated with acetic anhydride it is converted into *diphenic anhydride*,  $C_{12}H_8{<}\begin{array}{c}CO\\ CO\end{array}{>}O$ (m.p. 217°).

This fact is remarkable, because it shows that in the case of derivatives of hydrocarbons which are composed of *condensed* benzene nuclei, the ortho-position is not the only one which allows of the formation of an anhydride. Naphthalic acid, $C_{10}H_6(COOH)_2$, a derivative of naphthalene in which the carboxyl-groups are in the 1:1′- or peri-position, also forms an anhydride.

CHAPTER XXXIII.

PYRIDINE, QUINOLINE, AND ISOQUINOLINE.

Pyridine, quinoline, and isoquinoline are three very interesting aromatic bases, which, together with their numerous derivatives, form a group of great theoretical interest, and of scarcely less importance than that of the aromatic hydrocarbons; many of these derivatives occur in nature, and belong to the well-known and important class of compounds known as 'alkaloids.'

Coal-tar, though consisting principally of hydrocarbons and phenols, contains also small quantities of pyridine and its homologues, quinoline, isoquinoline, and numerous other basic substances, such as aniline; all these bases are dissolved, in the form of sulphates, in the purification of the hydrocarbons, &c., by treatment with sulphuric acid (compare p. 307), and, if the dark acid liquor be afterwards treated with excess of soda, they separate again at the surface of the liquid in the form of a dark-brown oil. By repeated fractional distillation a partial separation of the various constituents of this oil may be effected, and crude pyridine, quinoline, &c., may be obtained; on further purification by crystallisation of their salts, or in other ways, some of these bases may be prepared in a state of purity.

Another important source of these compounds is *bone-tar* or *bone-oil*, a dark-brown, unpleasant-smelling liquid formed during the dry distillation of bones in the preparation of bone-black (animal charcoal); this oil contains considerable quantities of pyridine and quinoline, and their homologues, as well as other bases, and these compounds may be extracted from it with the aid of sulphuric acid, and then separated in the manner mentioned above. Bone-oil, purified by distillation, was formerly used in medicine under the name of *Dippel's oil.*

Pyridine and its Derivatives.

Pyridine, C_5H_5N, is formed during the destructive distillation of a great variety of nitrogenous organic substances; hence its presence in coal-tar and in bone-oil.

Pure pyridine is conveniently prepared in small quantities by distilling nicotinic acid (p. 492), or other pyridinecarboxylic acid, with lime, just as pure benzene may be prepared from benzoic and phthalic acids in a similar manner,

$$C_5H_4N{\cdot}COOH = C_5H_5N + CO_2$$

$$C_5H_3N(COOH)_2 = C_5H_5N + 2CO_2.$$

For commercial purposes it is usually prepared by the repeated fractional distillation of the basic mixture, which is separated from bone-oil or coal-tar as already described; the product consists of pyridine, together with small quantities of its homologues.

Pyridine is a colourless, mobile liquid of sp. gr. 1·003 at 0°; it boils at 115°, is miscible with water in all proportions, and possesses a pungent and very characteristic odour. It is an exceedingly stable substance, as it is not attacked by boiling nitric or chromic acid, and only with difficulty by halogens; in the latter case *substitution* products such as *monobromopyridine*, C_5H_4BrN, and *dibromopyridine*, $C_5H_3Br_2N$, are formed. If, however, a solution of pyridine in hydrochloric acid be treated with bromine, a crystalline, unstable *additive* product, $C_5H_5NBr_2$, is precipitated, even from very dilute solutions, and the formation of this substance is sometimes used as a test for pyridine.

When dissolved in alcohol and treated with sodium, pyridine is readily reduced, *piperidine* or *hexahydropyridine* (p. 489) being formed,

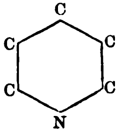
$$C_5H_5N + 6H = C_5H_{11}N.$$

Pyridine is a strong base; like the amines, it turns red litmus blue, and combines with acids to form crystalline salts, such as the *hydrochloride*, C_5H_5N,HCl, and the *sulphate*, $(C_5H_5N)_2,H_2SO_4$. The *platinichloride*, $(C_5H_5N)_2,H_2PtCl_6$, crystallises in orange-yellow needles, and is readily soluble in water; when, however, its solution is boiled, a very sparingly soluble yellow salt, $(C_5H_5N)_2PtCl_4$, separates, a fact which may be made use of for the detection of pyridine even when only small quantities of the base are available. Another test for pyridine (and its homologues) consists in heating a few drops of the base in a test tube with methyl iodide, when a vigorous reaction takes place, and a yellowish additive product, *pyridine methiodide*, C_5H_5N,CH_3I, is produced; if a piece of solid potash be now added, and the contents of the tube again heated, a most pungent and exceedingly disagreeable smell is at once noticed.

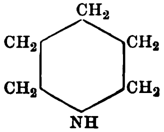
Constitution.—Pyridine is a strong base, has a pungent odour, and turns red litmus blue, properties which at once suggest some relation to the *amines*. It is not, however, a primary amine, because it does not give the carbylamine reaction; nor is it a secondary amine, because it is not acted on by nitrous acid; the necessary conclusion that pyridine is a *tertiary* base is further borne out by its behaviour towards methyl iodide. But since pyridine has the molecular formula, C_5H_5N, it is obvious that it cannot be an *open-chain* tertiary base, because no reasonable constitutional formula based on this view could be constructed. If, moreover, it be borne in mind that pyridine is extremely stable, the probability of its being a fatty (open-chain) compound at all seems very remote, because if it were it would be highly unsaturated, and should be readily oxidised and resolved into simpler substances. The grounds for doubting its relation to any fatty compound are, in fact, much the same as those which led to the conclusion that the constitution of benzene is totally different from that of dipropargyl (p. 314).

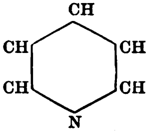
Comparing now the properties of pyridine with those of aromatic compounds, a general analogy is at once apparent; in spite of its great stability, pyridine shows, under certain conditions, the behaviour of an unsaturated compound, and, like benzene, naphthalene, and other closed-chain compounds, yields *additive* products, such as piperidine.

Considerations such as these led to the conclusion, suggested by Körner in 1869, that pyridine, like benzene, contains a closed-chain or nucleus, as represented by the following formula,



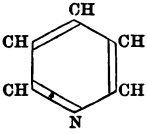
and this view has since been confirmed in a great many ways, notably in the following manner: Piperidine, or hexahydropyridine, the compound which is formed by the reduction of pyridine, and which is reconverted into the latter on oxidation with sulphuric acid (p. 490), has been prepared synthetically by a method (p. 490) which shows it to have the constitution (I.); pyridine, therefore, has the constitution (II.), the relation between the two compounds being the same as that between benzene and hexahydrobenzene,

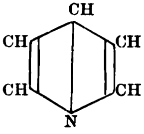

Piperidine (I.).

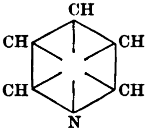

Pyridine (II.).

That the constitution of pyridine is represented by this formula (II.) is also established by a study of the isomerism of pyridine derivatives, and by its relation to quinoline (p. 493); it must, therefore, be regarded as derived from benzene by the substitution of trivalent nitrogen $N<$ for one of the $CH<$ groups.

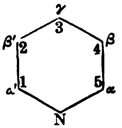
The exact nature of the union of the nitrogen and carbon atoms is not known, and, as in the case of benzene, several methods of representation (some of which are shown below) have been suggested; of these, the centric formula is perhaps the best, for reasons similar to those already mentioned in discussing the constitution of benzene (pp. 316–317).


Körner.

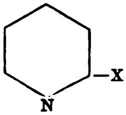

Dewar.

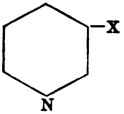

Centric Formula.

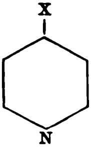
Isomerism of Pyridine Derivatives.—The *mono*-substitution products of pyridine, as, for example, the methylpyridines, exist in *three* isomeric forms; this fact is clearly in accordance with the accepted constitutional formula for pyridine, in which, for the sake of reference, the carbon atoms may be numbered or lettered[*] in the following manner, the symbols C and H being omitted as usual,



These substitution products being formed by the displacement of any one of the five hydrogen atoms, it is evident that the following three, but not more than three, isomerides may be obtained,







The positions $\alpha\alpha'$ are identical, and so also are the positions $\beta\beta'$, but the position γ is different from any of the others.

The *di*-substitution products exist theoretically in *six* isomeric forms, the positions of the substituents in the several isomerides being as follows,

$$\alpha\beta,\ \alpha\gamma,\ \alpha\beta',\ \alpha\alpha',\ \beta\beta',\ \beta\gamma.$$

All other positions are identical with one of these; $\alpha\beta$, for example, is the same as $\alpha'\beta'$, and $\beta\gamma$ is identical with $\beta'\gamma$.

As regards the isomerism of its derivatives, pyridine may be conveniently compared with a mono-substitution product of benzene—aniline, for example—the effect of substituting a nitrogen atom for one of the $\mathrm{CH}\leqslant$ groups in benzene being the same, in this respect, as that of displacing one of the hydrogen atoms by some substituent.

Derivatives of Pyridine.—**Piperidine**, or hexahydropyridine, $C_5H_{10}NH$, is formed, as already stated, when pyridine is reduced with sodium and alcohol; it is usually prepared

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[*] In the pyridine derivatives letters are generally used instead of numerals, the latter being conveniently reserved for benzene derivatives.

from pepper, which contains the alkaloid *piperine* (p. 503), a substance which is decomposed by boiling alkalies yielding piperidine and piperic acid.

Powdered pepper is extracted with alcohol, the filtered solution evaporated, and the residue distilled with potash; after neutralising with hydrochloric acid, the distillate is evaporated to dryness, and the residue extracted with hot alcohol to separate the piperidine hydrochloride from the ammonium chloride which is always present. The filtered alcoholic solution is then evaporated, the residue distilled with solid potash, and the crude piperidine purified by fractional distillation over potash.

Piperidine is a colourless liquid, boiling at 106°, and is miscible with water in all proportions, heat being developed; it has a very penetrating odour, recalling that of pepper. Like pyridine, it is a very strong base, turns red litmus blue, and combines with acids forming crystalline salts; when heated with concentrated sulphuric acid at 300° it loses six atoms of hydrogen, and is converted into pyridine, part of the sulphuric acid being reduced to sulphur dioxide.

Piperidine behaves like a secondary amine towards nitrous acid, and yields *nitroso-piperidine*, $C_5H_{10}N{\cdot}NO$, an oil, boiling at 218°; like secondary amines, moreover, it interacts with methyl iodide, giving *methylpiperidine*, $C_5H_{10}N{\cdot}CH_3$; it is, therefore, a secondary base (compare p. 496).

The important synthesis of piperidine, which has already been referred to as establishing the constitution of the base, and also that of pyridine, was accomplished by Ladenburg in the following way. *Trimethylene bromide** is heated with potassium cyanide in alcoholic solution, and thus converted into *trimethylene cyanide*,

$$Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Br + 2KCN = CN{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN + 2KBr,$$

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* *Trimethylene bromide*, $C_3H_6Br_2$, is prepared by treating allyl bromide (Part I. p. 262) with concentrated hydrobromic acid,

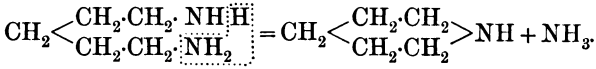
$$CH_2Br{\cdot}CH{:}CH_2 + HBr = CH_2Br{\cdot}CH_2{\cdot}CH_2Br;$$

it is a heavy, colourless oil, and boils at 164°.

a substance which, on reduction with sodium and alcohol, yields *pentamethylene diamine*, just as methyl cyanide under similar conditions yields ethylamine,

$$CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN + 8H = NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2;$$

during this reduction process some of the pentamethylene diamine is decomposed into piperidine and ammonia, and the same change occurs, but much more completely, when the hydrochloride of the diamine is distilled,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot NH\boxed{H}\\ CH_2\cdot CH_2\cdot \boxed{NH_2}\end{matrix} = CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>NH + NH_3.$$

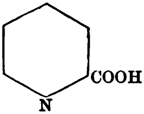
Homologues of Pyridine.—The alkyl-derivatives of pyridine occur in coal-tar and bone-oil, and are therefore present in the crude pyridine obtained from the mixture of bases in the manner already referred to; they can only be isolated by repeated fractional distillation and subsequent crystallisation of their salts. The three (α, β, γ) isomeric *methylpyridines* or *picolines*, $C_5H_4N\cdot CH_3$, the six isomeric *dimethylpyridines* or *lutidines*, $C_5H_3N(CH_3)_2$, and the *trimethylpyridines* or *collidines*, $C_5H_2N(CH_3)_3$, resemble the parent base in most ordinary properties, but, unlike the latter, they undergo oxidation more or less readily on treatment with nitric acid or potassium permanganate, and are converted into pyridinecarboxylic acids, just as the homologues of benzene yield benzenecarboxylic acids, the alkyl-groups or side-chains being oxidised to carboxyl-groups,

$$C_5H_4N\cdot CH_3 + 3O = C_5H_4N\cdot COOH + H_2O$$
$$C_5H_3N(CH_3)_2 + 6O = C_5H_3N(COOH)_2 + 2H_2O.$$

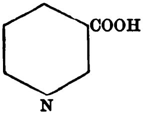
This behaviour is of great use in determining the positions of the alkyl-groups in these homologues of pyridine, because the carboxylic acids into which they are converted are easily isolated, and are readily identified by their melting-points and other properties.

The *pyridinecarboxylic acids* are perhaps, as a class, the most important derivatives of pyridine, chiefly because they are obtained as decomposition products on oxidising many of the alkaloids.

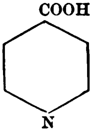
The three (α, β, γ) *monocarboxylic* acids may be prepared by oxidising the corresponding picolines or methylpyridines (see above) with potassium permanganate. The α-carboxylic acid is usually known as *picolinic acid*, because it was first prepared from α-picoline (α-methylpyridine), whereas the β-compound is called *nicotinic acid*, because it was first obtained by the oxidation of nicotine (p. 502); the third isomeride—namely, the γ-carboxylic acid—is called *isonicotinic acid*, and is the oxidation product of γ-picoline.



Picolinic Acid, or
Pyridine-α-carboxylic Acid
(m.p. 136°).



Nicotinic Acid, or
Pyridine-β-carboxylic Acid
(m.p. 229°).



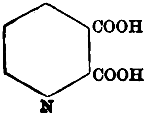
Isonicotinic Acid, or
Pyridine-γ-carboxylic Acid
(sublimes without melting).

These monocarboxylic acids are all crystalline and soluble in water; they have both basic and acid properties, and form salts with mineral acids as well as with bases, a behaviour which is similar to that of glycine (Part I. p. 299).

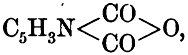
The α-carboxylic acid, and all other pyridinecarboxylic acids which contain a carboxyl-group in the α-position (but only such), give a red or yellowish-red colouration with ferrous sulphate, a reaction which is of great value in determining the positions of the carboxyl-groups in such compounds.

A carboxyl-group in the α-position, moreover, is usually very readily eliminated on heating; picolinic acid, for example, is much more readily converted into pyridine than nicotinic or isonicotinic acid.

Quinolinic acid, $C_5H_3N(COOH)_2$ (pyridine-$\alpha\beta$-dicarboxylic acid),



a compound produced by the oxidation of quinoline with potassium permanganate, is the most important of the six isomeric dicarboxylic acids. It crystallises in colourless prisms, is only sparingly soluble in water, and gives, with ferrous sulphate, an orange colouration, one of the carboxyl-groups being in the α-position. When heated at 190° it decomposes into carbon dioxide and nicotinic acid, a fact which shows that the second carboxyl-group is in the β-position. On distillation with lime, quinolinic acid, like all pyridinecarboxylic acids, is converted into pyridine.

In its behaviour when heated alone, quinolinic acid differs in a marked manner from phthalic acid—the corresponding benzenedicarboxylic acid—as the latter is converted into its anhydride (p. 439); nevertheless, when heated with acetic anhydride, quinolinic acid gives an anhydride,  $C_5H_3N<^{CO}_{CO}>O$, a colourless, crystalline substance, melting at 134°. This fact shows that the carboxyl-groups are united with carbon atoms, which are themselves directly united (as in the case of phthalic acid), and is further evidence in support of the constitutional formula given above.

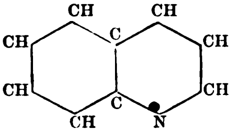
Quinoline.

Quinoline, C_9H_7N, occurs, together with isoquinoline, in that fraction of coal-tar and bone-oil bases (p. 485) which is collected between 236° and 243°; as, however, it is difficult to obtain the pure substance from this mixture, quinoline is usually prepared synthetically, by a method devised by Skraup—namely, by heating a mixture of aniline and glycerol with sulphuric acid and nitrobenzene.

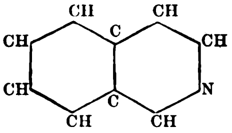
Concentrated sulphuric acid (100 parts) is gradually added to a mixture of aniline (38 parts), nitrobenzene (24 parts), and glycerol (120 parts), and the mixture is then very cautiously heated in a large flask (with reflux apparatus) on a sand-bath; after the very violent reaction which soon sets in has subsided, the liquid is kept boiling for about four hours. It is then cooled, diluted with water, and the unchanged nitrobenzene separated by distillation in steam; soda is then added in excess to liberate the quinoline and the unchanged aniline from their sulphates, and the mixture is again steam-distilled. As these two bases cannot well be separated by fractional distillation, the whole of the aqueous distillate is acidified with sulphuric acid, and sodium nitrite added until nitrous acid is present after shaking well (p. 385); after heating, to convert the diazo-salt into phenol, the solution is rendered alkaline with soda and again submitted to distillation in steam. The quinoline in the receiver is finally separated with the aid of a funnel, dried over solid potash, and purified by fractional distillation.

Quinoline is a colourless, highly refractive oil, of sp. gr. 1·095 at 20°, and boils at 239°. It has a peculiar characteristic smell, and is sparingly soluble in water, but it dissolves freely in dilute acids, forming crystalline salts, such as the *hydrochloride*, C_9H_7N,HCl, the *sulphate*, $(C_9H_7N)_2,H_2SO_4$, &c. It also forms double salts, of which the *platinichloride*, $(C_9H_7N)_2,H_2PtCl_6+2H_2O$, and the *dichromate*, $(C_9H_7N)_2,H_2Cr_2O_7$, may be mentioned; the latter, prepared by adding potassium dichromate to a solution of quinoline hydrochloride, crystallises from water, in which it is only sparingly soluble, in glistening yellow needles, melting at 165°.

Constitution.—Quinoline is alkaline to litmus, but it does not give the reactions of a primary nor those of a secondary base; on the other hand, it combines with methyl iodide to form the additive product, *quinoline methiodide*, C_9H_7N,CH_3I, and in this and other respects shows the behaviour of a *tertiary* base. Now, as the relation between pyridine, C_5H_5N, and quinoline, C_9H_7N, on the one hand, is much the same as that between benzene, C_6H_6, and naphthalene, $C_{10}H_8$, on the other, both as regards molecular composition (the difference being C_4H_2 in both cases) and chemical behaviour, and as, consequently, quinoline cannot be an *open-chain* compound, it might be assumed that quinoline is derived from pyridine, just as naphthalene is derived from benzene; its constitution would then be expressed by one of the following formulæ,



I.



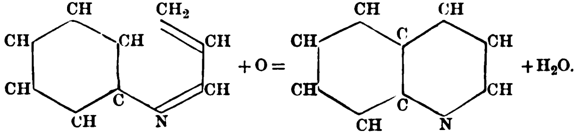
II.

Now, quinoline differs from pyridine, just as naphthalene differs from benzene, in being much more readily oxidised, and when heated with an alkaline solution of potassium permanganate it yields quinolinic acid, $C_5H_3N(COOH)_2$, a derivative of pyridine (p. 492); this fact proves that quinoline contains a pyridine nucleus; but it also contains a benzene nucleus, as is shown by its formation from aniline by Skraup's method. Its constitution, therefore, must be expressed by one of the above formulæ, as these facts admit of no other interpretation. As, moreover, the carboxyl-groups in quinolinic acid are in the $\alpha\beta$-position (compare p. 493), formula II. is inadmissible, a conclusion which is obviously necessary to explain the formation of quinoline from aniline. For these and other reasons, the constitution of quinoline is represented by formula I. (the other expressing that of isoquinoline).

The formation of quinoline from aniline and glycerol may be explained as follows: The glycerol and sulphuric acid first interact, yielding acroleïn (Part I. p. 262), which then condenses with aniline (as do all aldehydes), forming *acrylaniline*,

$$C_6H_5 \cdot NH_2 + CHO \cdot CH:CH_2 = C_6H_5 \cdot N:CH \cdot CH:CH_2 + H_2O;$$

this substance, under the oxidising action of the nitrobenzene,* loses two atoms of hydrogen, and is converted into quinoline,



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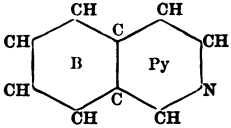
* Nitrobenzene is often employed as a mild oxidising agent, as in presence of an oxidisable substance it is reduced to aniline,

$$C_6H_5 \cdot NO_2 + 6H = C_6H_5 \cdot NH_2 + 2H_2O.$$

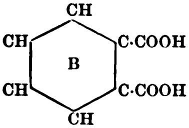
Many derivatives of quinoline may be obtained by Skraup's reaction, using derivatives of aniline instead of the base itself; when, for example, one of the three toluidines (p. 376) is employed, a *methylquinoline* is formed, the position of the methyl-group—which is, of course, united with the benzene, and not with the pyridine nucleus—depending on which of the toluidines is taken.

Isoquinoline, C_9H_7N, occurs in coal-tar quinoline, and may be isolated by converting the fraction of the mixed bases, boiling at 236–243°, into the acid sulphates, C_9H_7N,H_2SO_4, and recrystallising these salts from alcohol (88 per cent.) until the crystals melt at 205°. The sulphate of isoquinoline thus obtained is decomposed by potash, and the base purified by distillation. Isoquinoline is very like quinoline in chemical properties, but it is solid, and melts at 23°; its boiling-point, 241°, is also slightly higher than that of quinoline (239°).

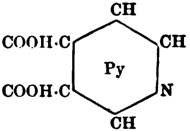
The constitution of isoquinoline is very clearly proved by its behaviour on oxidation with permanganate, when it yields both phthalic acid and *cinchomeronic acid*, $C_5H_3N(COOH)_2$, or pyridine-$\beta\gamma$-dicarboxylic acid; oxidation takes place, therefore, in two directions, in the one case the pyridine (Py), in the other the benzene (B), nucleus being broken up,



Isoquinoline.



Phthalic Acid.



Cinchomeronic Acid.

Aromatic Bases.—It will be seen from the above description of piperidine, pyridine, and quinoline that aromatic bases which owe their basic character to the group $>NH$ or $\geqslant N$ forming *part of a closed-chain* show the same chemical behaviour as *open-chain*, secondary, or tertiary bases respectively, as far as these particular groups are concerned.

The *secondary* bases, such as piperidine, which contain the

$>$NH-group, yield nitroso-derivatives, and when warmed with an alkyl halogen compound they are converted into alkyl-derivatives by the *substitution* of an alkyl-group for the hydrogen atom of the $>$NH-group,

$$>NH + CH_3I = >N{\cdot}CH_3,HI,$$

just as diethylamine, for example, interacts with ethyl iodide, giving triethylamine,

$$(C_2H_5)_2NH + C_2H_5I = (C_2H_5)_2N{\cdot}C_2H_5,HI.$$

These alkyl-derivatives of the secondary bases are themselves tertiary bases, and have the property of forming *additive* products with alkyl halogen compounds, giving salts corresponding with the quaternary ammonium salts (Part I. pp. 209, 210),

$$>N{\cdot}CH_3 + CH_3I = >N{\cdot}CH_3,CH_3I, \text{ or } >N(CH_3)_2I.$$

The hydrogen atom of the $>$NH-group in secondary bases of this kind is also displaceable by the acetyl-group and by other acid radicles.

The *tertiary* bases, such as pyridine and quinoline, in which the nitrogen atom is not directly united with hydrogen, do not yield nitroso- or acetyl-derivatives, but they unite with one molecule of an alkyl halogen compound giving *additive* compounds, corresponding with the quaternary ammonium salts.

CHAPTER XXXIV.

ALKALOIDS.

The term *alkaloid* is generally applied to those *basic nitrogenous substances* which occur in plants, irrespective of any similarity in properties or constitution; as, however, most substances of this kind have some important physiological action, the use of the word may be restricted in this sense.

Most alkaloids are composed of carbon, hydrogen, oxygen, and nitrogen, have a high molecular weight, and are crystalline and non-volatile, but a few, notably coniine and nicotine, are composed of carbon, hydrogen, and nitrogen only, and are volatile liquids; with the exception of these liquid compounds, which are readily soluble, the alkaloids are usually sparingly soluble in water, but dissolve much more readily in alcohol, chloroform, ether, and other organic solvents; they are all soluble in acids, with which they usually form well-defined, crystalline salts. Many alkaloids have a very bitter taste, and are excessively poisonous; many, moreover, are extensively used in medicine, and their value in this respect can hardly be overrated.

Generally speaking, the alkaloids are tertiary aromatic bases, but the constitutions of many of them have not yet been established in detail, owing partly to their complexity, partly to the difficulties which are experienced in resolving them into simpler compounds which throw any light on the structure of their molecules. It is known, however, that many alkaloids are derivatives of pyridine, quinoline, or isoquinoline.

It is a remarkable fact that by far the greater number of alkaloids contain one or two, sometimes three or more, methoxy-groups ($-O\cdot CH_3$), united with a benzene nucleus (as in anisole, $C_6H_5\cdot O\cdot CH_3$, p. 405), and the determination of the number of such groups in the molecule is of the greatest importance as a step in establishing the constitution of an alkaloid, because in this way some of the carbon, oxygen, and hydrogen atoms are at once disposed of. The method employed for this purpose depends on the fact that all substances containing methoxy-groups are decomposed by hydriodic acid, yielding methyl iodide and a hydroxy-compound (compare anisole) in accordance with the general equation,

$$n(-O\cdot CH_3) + nHI = n(-OH) + nCH_3I;$$

by estimating the methyl iodide obtained from a given quantity of a compound of known molecular weight, it is easy, therefore, to determine the number of methoxy-groups in the molecule; ethoxy-groups may also be determined in a similar manner.

This method was first applied by Zeisel, and is of general application, as it affords a means of accurately determining the number of methoxy-groups, not only in alkaloids, but in any other substances in which they occur; it is carried out as follows:

A distilling flask of about 35 c.c. capacity (*a*, fig. 24), with the side-tube bent as shown, and suspended in a beaker of glycerol, is fixed to the condenser (*b*) by means of a cork, and connected with an apparatus for generating carbon dioxide.

The condenser, through which water at 50° circulates from the bottle (*c*), is attached to the 'potash bulbs,' which contain water and about 0·5 gram of amorphous phosphorus; the bulbs are suspended in a beaker of water kept at 60°, and connected, as shown, with two flasks (*d*, *e*), containing respectively 50 c.c. and 25 c.c. of an alcoholic solution of silver nitrate (prepared by adding 100 c.c. of absolute alcohol to a solution of 5 grams of silver nitrate in 12 c.c. of water).

About 0·3 gram of the substance under examination is placed in the flask (*a*), together with 10 c.c. of distilled hydriodic acid (free from sulphur compounds), and the temperature of the glycerol bath is gradually raised, until the acid just boils, carbon dioxide, at the rate of about 3 bubbles in 2 seconds, being passed all the time.

The methyl iodide is carried forward through the 'potash bulbs,' where it is freed from hydriodic acid and small quantities of iodine, and then into the alcoholic silver nitrate, where it is decomposed with separation of silver iodide. The operation, which occupies about two hours, is at an end when the precipitate in the flask settles, and leaves a clear, supernatant liquid.

The contents of flask *e* are poured into 5 vols. of water and gently warmed; if, as is usually the case, no precipitation take place after five minutes, the solution is neglected; if, however, a precipitate form, it must be collected and added to that contained in flask *d*. The alcoholic liquid in flask *d* is decanted from the precipitate, mixed with water (300 c.c.) and a few drops of nitric acid, and heated to boiling until free from alcohol; any precipitate is then added to the main quantity, the whole digested for a few minutes with dilute nitric acid, collected, dried, and weighed.

Example.—0·3726 gram of substance gave 0·8164 gram of silver iodide, which corresponds with 28·9 per cent. of $-OCH_3$; the substance was $C_8H_4O_3(OCH_3)_2$.

The extraction of alkaloids from plants, and their subsequent purification, are frequently matters of considerable difficulty, partly because in many cases a number of alkaloids

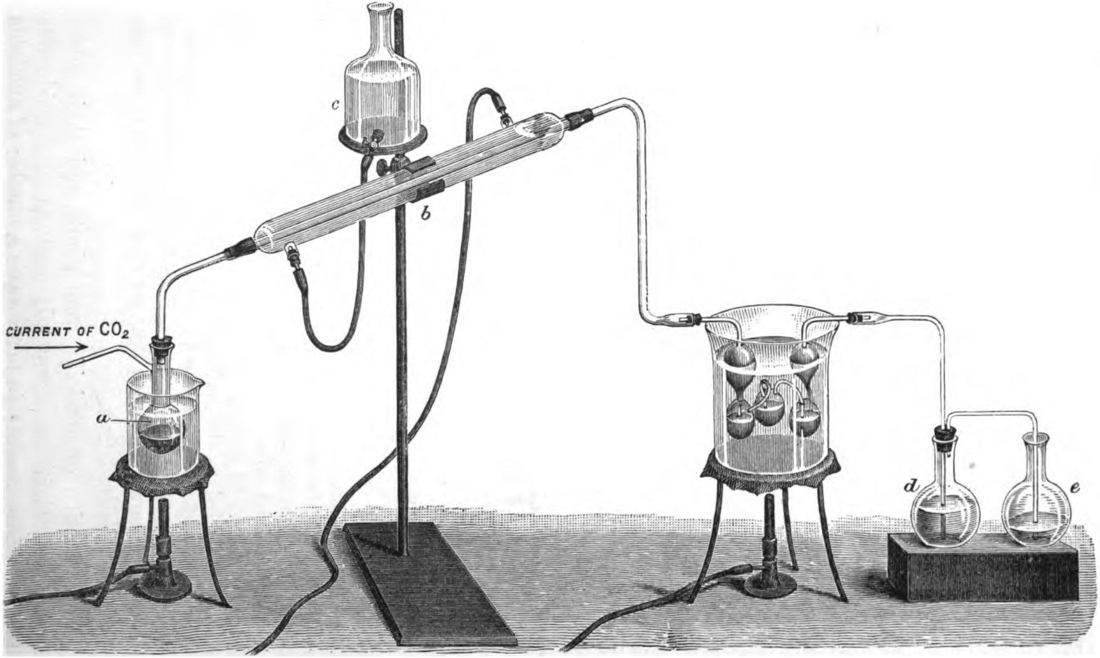


Fig. 24.

occur together, partly because of the neutral and acid substances, such as the glucosides, sugars, tannic acid, malic acid, &c., which are often present in large quantities. Generally speaking, they may be extracted by treating the macerated plant or vegetable product with dilute acids, which dissolve out the alkaloids in the form of salts; the filtered solution may then be treated with soda to liberate the alkaloids, which, being sparingly soluble, are usually precipitated, and may be separated by filtration; if not, the alkaline solution is extracted with ether, chloroform, &c. The products are finally purified by recrystallisation, or in some other manner.

Most alkaloids give insoluble precipitates with a solution of tannic, picric, phosphomolybdic, or phosphotungstic acid, and with a solution of mercuric iodide in potassium iodide,* &c.; these reagents, therefore, are often used for their detection and isolation.

Only the more important alkaloids are described in the following pages.

Alkaloids derived from Pyridine.

Coniine, $C_8H_{17}N$, one of the simplest known alkaloids, is contained in the seeds of the spotted hemlock (*Conium maculatum*), from which it may be prepared by distillation with soda.

It is a colourless oil, boiling at 167°, and is readily soluble in water; it has a most penetrating odour, and turns brown on exposure to air. Coniine is a strong base, and combines with acids to form salts, such as the *hydrochloride*, $C_8H_{17}N,HCl$, which are readily soluble in water; both the base and its salts are exceedingly poisonous, a few drops of the pure substance causing death in a short time by paralysing the muscles of respiration.

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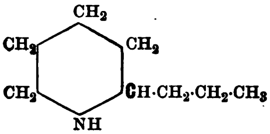
* In cases of alkaloid poisoning it is usual, after using the stomach-pump, to wash out the stomach with dilute tannic acid, or to administer strong tea (which contains tannin), in order to render the alkaloids insoluble, and therefore harmless.

Ladenburg has shown that coniine is dextrorotatory *a-propylpiperidine,*



and has succeeded in preparing it synthetically, the first instance of the synthesis of an optically active alkaloid.

a-Propylpiperidine contains an asymmetric carbon atom (shown in heavy type—compare p. 544), and therefore, like lactic acid, it exists in three modifications; the inactive modification, which is obtained by synthesis, may be resolved into its two optically active components by crystallisation of its tartrate (compare p. 557).

Nicotine, $C_{10}H_{14}N_2$, is present in the leaves of the tobacco-plant (*Nicotiana tabacum*), combined with malic or citric acid.

Tobacco-leaves are extracted with boiling water, the extract concentrated, mixed with milk of lime, and distilled; the distillate is acidified with oxalic acid, evaporated to a small bulk, decomposed with potash, and the free nicotine extracted with ether. The ethereal solution, on evaporation, deposits the crude alkaloid, which is purified by distillation in a stream of hydrogen.

It is a colourless oil, which boils at 241°, possesses a very pungent odour, and rapidly turns brown on exposure to air; it is readily soluble in water and alcohol. It is a strong di-acid base, and forms crystalline salts, such as the *hydrochloride,* $C_{10}H_{14}N_2,2HCl$; it combines directly with two molecules of methyl iodide, yielding *nicotine dimethiodide,* $C_{10}H_{14}N_2,2CH_3I$, a fact which shows that it is a di-tertiary base (p. 497). When oxidised with chromic acid it yields nicotinic acid (pyridine-β-carboxylic acid, p. 492); it is, therefore, a pyridine-derivative, but its constitution cannot be fully discussed here.

Nicotine is exceedingly poisonous, two or three drops taken into the stomach being sufficient to cause death in a few minutes. It shows no very characteristic reactions, but its presence may be detected by its extremely pungent odour (which recalls that of a foul tobacco-pipe).

Piperine, $C_{17}H_{19}NO_3$, occurs to the extent of about 8–9 per cent. in pepper, especially in black pepper (*Piper. nigrum*), from which it is easily extracted.

The pepper is powdered and warmed with milk of lime for fifteen minutes; the mixture is then evaporated to dryness on a water-bath, extracted with ether, the ethereal solution evaporated, and the residual crude piperine purified by recrystallisation from alcohol.

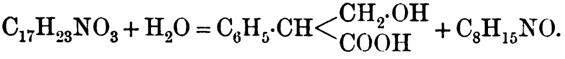
It crystallises in prisms, melts at 128°, and is almost insoluble in water; it is only a very weak base, and when heated with alcoholic potash it is decomposed into piperidine (p. 489) and piperic acid,

$$C_{17}H_{19}NO_3 + H_2O = \underset{\text{Piperidine.}}{C_5H_{11}N} + \underset{\text{Piperic Acid.}}{C_{12}H_{10}O_4}.$$

Atropine, or daturine, $C_{17}H_{23}NO_3$, does not occur in nature, although it is prepared from the deadly nightshade (*Atropa belladonna*). This plant contains two isomeric and closely related alkaloids, *hyoscyamine* and *hyoscine*, and the former readily undergoes intramolecular change into atropine on treatment with bases.

The plant is pressed, the juice mixed with potash, and extracted with chloroform (1 litre of juice requires 4 grams of potash and 30 grams of chloroform); the chloroform is then evaporated, the atropine extracted from the residue with dilute sulphuric acid, the solution treated with potassium carbonate, and the precipitated alkaloid recrystallised from alcohol.

It crystallises from dilute alcohol in glistening prisms, and melts at 115°; it is readily soluble in alcohol, ether, and chloroform, but almost insoluble in water. When boiled with baryta water it is readily hydrolysed, yielding *tropic acid* and a base called *tropine*, which is a derivative of piperidine,



$$C_{17}H_{23}NO_3 + H_2O = \underset{\text{Tropic Acid.}}{C_6H_5{\cdot}CH{<}\begin{matrix}CH_2{\cdot}OH\\ COOH\end{matrix}} + \underset{\text{Tropine.}}{C_8H_{15}NO}.$$

Atropine is a strong base, and forms well-characterised salts, of which the *sulphate*, $(C_{17}H_{23}NO_3)_2,H_2SO_4$, is readily soluble, and, therefore, most commonly used in medicine; both the base and its salts are excessively poisonous, 0·05–0·2 gram causing death. Atropine sulphate is largely used in ophthalmic surgery, owing to the remarkable property which it possesses of dilating the pupil when its solution is placed on the eye.

Test for Atropine.—If a trace of atropine be moistened with fuming nitric acid, and evaporated to dryness on a water-bath, it yields a yellow residue, which, on the addition of alcoholic potash, gives an intense violet solution, the colour gradually changing to red.

Cocaïne, $C_{17}H_{21}NO_4$, and several other alkaloids of less importance, are contained in coca-leaves (*Erythroxylon coca*).

The coca-leaves are extracted with hot water (80°), the solution mixed with lead acetate (in order to precipitate tannin, &c.), filtered, and the lead in the filtrate precipitated with sodium sulphate; the solution is then rendered alkaline with soda, the cocaïne extracted with ether, and purified by recrystallisation from alcohol.

Cocaïne crystallises in colourless prisms, melts at 98°, and is sparingly soluble in water; it forms well-characterised salts, of which the *hydrochloride*, $C_{17}H_{21}NO_4,HCl$, is most largely used in medicine. Cocaïne is a very valuable local anæsthetic, and is used in minor surgical operations, as its local application takes away all sensation of pain; it is, however, poisonous, one grain injected subcutaneously having been attended with fatal results.

When heated with acids or alkalies, cocaïne is readily hydrolysed with formation of benzoic acid, methyl alcohol, and ecgonine,

$$C_{17}H_{21}NO_4 + 2H_2O = C_6H_5{\cdot}COOH + CH_3{\cdot}OH + C_9H_{15}NO_3.$$

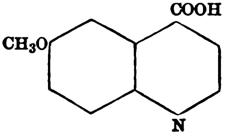
Alkaloids derived from Quinoline.

Quinine, $C_{20}H_{24}N_2O_2$, cinchonine (see below), and several other allied alkaloids occur in all varieties of cinchona-bark, some of which contain as much as 3 per cent. of quinine. The alkaloids are contained in the bark, combined with tannic and quinic acids.*

The powdered bark is extracted with dilute sulphuric acid, and the solution of the sulphates precipitated with soda. The crude mixture of alkaloids thus obtained is dissolved in alcohol, the solution neutralised with sulphuric acid, and the sulphates which are deposited repeatedly recrystallised from water. Quinine sulphate is the least soluble, and separates out first, the sulphates of cinchonine and the other alkaloids remaining in solution; from the pure sulphate, quinine may be obtained as an amorphous powder by adding ammonia.

Quinine crystallises with 3 mols. H_2O, melts at 177° when anhydrous, and is only very sparingly soluble in water; it is only a feeble di-acid base, and generally forms hydrogen salts, such as the *sulphate*, $(C_{20}H_{24}N_2O_2)_2,H_2SO_4 + 8H_2O$; many of its salts are soluble in water, and much used in medicine as tonics, and for lowering the temperature in cases of fever, &c.

Quinine is a di-tertiary base, because it combines with methyl iodide to form *quinine dimethiodide*, $C_{20}H_{24}N_2O_2,(CH_3I)_2$; it is a derivative of quinoline, because on oxidation with chromic acid it yields *quininic acid* (methoxyquinoline-γ-carboxylic acid),



Quinine contains one methoxy-group, as has been demonstrated by Zeisel's method (p. 498), and it is a methoxy-cinchonine, because on oxidation it yields the methoxy-derivative of quinoline-γ-carboxylic acid (see below).

Tests for Quinine.—If a solution of a salt of quinine be mixed with chlorine- or bromine-water, and then ammonia

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* *Quinic acid*, $C_6H_7(OH)_4{\cdot}COOH$, crystallises in prisms, and melts at 162°. It is a derivative of benzoic acid, being, in fact, tetrahydroxyhexahydrobenzoic acid.

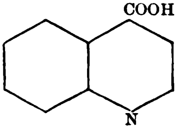
added, a highly characteristic emerald-green colouration is produced; quinine is also characterised by the fact that *dilute* solutions of its salts show a beautiful light-blue fluorescence.

Cinchonine, $C_{19}H_{22}N_2O$, accompanies quinine in almost all the cinchona-barks, and is present in some kinds (in the bark, *Cinchona Huanaco*) to the extent of 2·5 per cent.

In order to prepare cinchonine, the mother-liquors from the crystals of quinine sulphate (see above) are treated with soda, and the precipitate dissolved in the smallest possible quantity of boiling alcohol; the crude cinchonine, which separates on cooling, is further purified by converting into the sulphate, and crystallising this salt from water.

Cinchonine crystallises in colourless prisms, melts at 255°, and resembles quinine in ordinary properties; its salts, for example, are antipyretics, but are much less active than those of quinine.

Oxidising agents, such as nitric acid and potassium permanganate, readily attack cinchonine, converting it into a variety of substances, one of the most important of which is *cinchoninic acid*, or quinoline-γ-carboxylic acid,



The formation of this acid proves that cinchonine is a quinoline-derivative.

Strychnine, $C_{21}H_{22}N_2O_2$, and brucine, two highly poisonous alkaloids, are contained in the seeds of *Strychnos nux vomica* and of *Strychnos Ignatii* (Ignatius' beans), but they are usually extracted from the former.

Powdered nux vomica is boiled with dilute alcohol, the filtered solution evaporated to expel the alcohol, and treated with lead acetate to precipitate tannin, &c. The filtrate is then treated with hydrogen sulphide to precipitate the lead, and the filtered solution mixed with magnesia and allowed to stand. The precipitated alkaloids are separated, and warmed with a little alcohol, which dissolves out the brucine; the residual *strychnine* is further purified by recrystallisation from alcohol.

The alcoholic solution of the brucine—which still contains strychnine—is evaporated, and the residue dissolved in dilute acetic acid; this solution is now evaporated to dryness on a water-bath, during which process the strychnine acetate decomposes, with loss of acetic acid and separation of the free base. The stable brucine acetate is dissolved again by adding water, the filtered solution treated with soda, and the precipitated *brucine* purified by recrystallisation from dilute alcohol.

Strychnine crystallises in beautiful rhombic prisms, and melts at 284°; although it is very sparingly soluble in water (1 part in 4000 at 15°), its solution possesses an intensely bitter taste, and is very poisonous. Strychnine is, in fact, one of the most poisonous alkaloids, half a grain of the sulphate having caused death in twenty minutes.

Although strychnine contains two atoms of nitrogen, it is, like brucine, only a mon-acid base, forming salts, such as the *hydrochloride*, $C_{21}H_{22}N_2O_2,HCl$; many of the salts are soluble in water. It is a tertiary base, because it combines with methyl iodide to form *strychnine methiodide*, $C_{21}H_{22}N_2O_2,CH_3I$.

When distilled with potash, strychnine yields, among other products, quinoline; probably, therefore, it is a derivative of this base.

Test for Strychnine.—Strychnine is very readily detected, as it shows many characteristic reactions, of which the following is the most important: When a small quantity of powdered strychnine is placed in a porcelain basin, a little concentrated sulphuric acid added, and then a little powdered potassium dichromate dusted over the liquid, an intense violet solution, which gradually becomes bright-red, and then yellow, is produced.

Brucine, $C_{23}H_{26}N_2O_4$, crystallises in colourless prisms, with 4 mols. H_2O, and melts, when anhydrous, at 178°. It is more readily soluble in water and in alcohol than strychnine, and, although very poisonous, it is not nearly so deadly as the latter (its physiological effect being only about $\frac{1}{24}$th of that of strychnine). Although it contains two atoms of nitrogen, brucine, like strychnine, is a monacid base. The *hydrochloride*, for example, has the composition $C_{23}H_{26}N_2O_4,HCl$; it is also a tertiary base, because it combines with methyl iodide to form *brucine methiodide*, $C_{23}H_{26}N_2O_4,CH_3I$.

Test for Brucine.—When a solution of a brucine salt is treated with nitric acid, a deep brownish-red colouration is obtained, and, on warming, the solution becomes yellow; if now stannous chloride be added, an intense violet colouration is produced.

This colour reaction serves as a delicate test, both for brucine and for nitric acid, as it may be carried out with very small quantities.

Alkaloids contained in Opium.

The juice of certain kinds of poppy-heads (*Papaver somniferum*) contains a great variety of alkaloids, of which *morphine* is the most important, but *codeïne*, *narcotine*, *thebaïne*, and *papaverine* may also be mentioned. All these compounds are present in the juice in combination with *meconic acid*,* and partly also with sulphuric acid. When incisions are made in the poppy-heads, and the juice which exudes is collected and left to dry, it assumes a pasty consistency, and is called *opium*. An alcoholic tincture of opium, containing about 1 grain of opium in 15 minims, is known as *laudanum*.

Preparation of Morphine.—Opium is extracted with hot water, the extract boiled with milk of lime, and filtered from the precipitate, which contains the meconic acid, and all the alkaloids,

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* *Meconic acid*, $C_5HO_2(OH)(COOH)_2$, is a hydroxydicarboxylic acid belonging to the aliphatic series. It crystallises with three molecules of water, and gives, with ferric chloride, an intense dark-red colouration. In cases of suspected opium-poisoning this acid is always tested for, owing to the ease with which it can be detected by this colour reaction.

except morphine. The filtrate is then concentrated, digested with ammonium chloride until ammonia ceases to be evolved (to convert any lime present into soluble calcium chloride), and allowed to stand for some days; the morphine, which separates, is collected and purified by recrystallisation from fusel oil (Part I. p. 107).

Morphine, $C_{17}H_{19}NO_3$, crystallises in colourless prisms, with 1 mol. H_2O, and is only slightly soluble in water and cold alcohol, but dissolves readily in potash and soda, from which it is reprecipitated on the addition of acids; it has, in fact, the properties of a phenol. At the same time, it is a mon-acid base, and forms well-characterised salts with acids; the *hydrochloride*, $C_{17}H_{19}NO_3,HCl + 3H_2O$, crystallises from water in needles, and is the salt most commonly employed in medicine. Morphine is a tertiary base, and when treated with methyl iodide it yields *morphine methiodide*, $C_{17}H_{19}NO_3,CH_3I$.

Morphine has a bitter taste, and is excessively poisonous, one grain of the hydrochloride having been found sufficient to cause death; on the other hand, the system may become so accustomed to the habitual use of opium that, after a time, very large quantities may be taken daily without fatal effects. Morphine is extensively used in medicine as a soporific, especially in cases of intense pain.

Tests for Morphine.—Morphine has the property of liberating iodine from a solution of iodic acid. If a little iodic acid be dissolved in water, and a few drops of a solution of morphine hydrochloride added, a brownish colouration is at once produced, owing to the liberation of iodine, and on adding some of the solution to starch-paste, the well-known deep-blue colouration is obtained.

A solution of morphine, or of a morphine salt, gives a deep-blue colouration with ferric chloride, but perhaps the most delicate test for the alkaloid is the following: If a trace of morphine be dissolved in concentrated sulphuric acid, the solution kept for 15 hours, and then treated with nitric acid, it gives a bluish-violet colour, which changes to blood-red. This reaction is very delicate, and is well shown by 0·01 milligramme of morphine.

Morphine contains two hydroxyl-groups, one of which is phenolic, the other alcoholic; it is to the presence of the phenolic hydroxyl-group that morphine owes its property of dissolving in alkalies, and giving a blue colour with ferric chloride.

If the base be heated with potash and methyl iodide, *methylmorphine*, $C_{17}H_{17}NO(OCH_3)\cdot OH$, is produced, a substance which is identical with *codeïne*, an alkaloid which accompanies morphine in opium. Codeïne is insoluble in alkalies, and is, therefore, not a phenol; it behaves, however, like an alcohol, and gives, with acetic anhydride, *acetylcodeïne*, $C_{17}H_{17}NO(OCH_3)\cdot C_2H_3O_2$.

It is very remarkable that morphine seems to be a derivative of phenanthrene, as derivatives of this hydrocarbon are very seldom met with in nature. If morphine be distilled with zinc-dust, a considerable quantity of this hydrocarbon is obtained, together with pyridine, quinoline, and other substances.

Alkaloids related to Uric Acid.

Caffeïne, theïne, or methyltheobromine, $C_8H_{10}N_4O_2$, occurs in coffee-beans ($\frac{1}{2}$ per cent.), in tea (2 to 4 per cent.), in kola-nuts (2·5 per cent.), and in other vegetable products.

Tea (1 part) is macerated with hot water (4 parts), milk of lime (1 part) added, and the whole evaporated to dryness on a water-bath; the caffeïne is then extracted from the residue by means of chloroform, the extract evaporated, and the crude base purified by recrystallisation from water.

Caffeïne crystallises in long, colourless needles, with 1 mol. H_2O, melts at 225°, and at higher temperatures sublimes undecomposed; it has a bitter taste, and is sparingly soluble in cold water and alcohol. Caffeïne is a feeble base, and forms salts only with strong acids; the *hydrochloride*, $C_8H_{10}N_4O_2,HCl$, is at once decomposed on treatment with water, with separation of the base.

The constitution of caffeïne has been determined by E. Fischer, who has shown that this substance and uric acid are very closely allied.

Tests for Caffeïne.—If a trace of caffeïne be evaporated with concentrated nitric acid, it gives a yellow residue (amalinic acid), which on the addition of ammonia becomes intensely violet (murexide reaction); this reaction is also shown by uric acid (Part I. p. 303). A solution of caffeïne in chlorine water yields, on evaporation, a yellowish-brown residue, which dissolves in dilute ammonia, with a beautiful violet-red colouration.

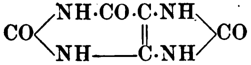
Theobromine, $C_7H_8N_4O_2$, occurs in cocoa-beans, from which it may be obtained by treatment with lime, and extraction with alcohol. It crystallises from water, and shows the greatest resemblance to caffeïne in properties; the latter is, in fact, methyltheobromine, and may be obtained directly from theobromine in the following way:

Theobromine contains an $>NH$ group, the hydrogen of which is readily displaced by metals (as in succinimide, Part I. p. 243), and when treated with an ammoniacal silver nitrate solution it yields *silver theobromine.* This substance interacts readily with methyl iodide with formation of caffeïne,

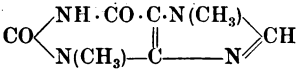
$$C_7H_7N_4O_2Ag + CH_3I = C_7H_7N_4O_2{\cdot}CH_3 + AgI.$$

Silver Theobromine. Caffeïne.

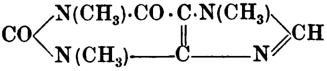
The relationship between uric acid, theobromine, and caffeïne is expressed by the following graphic formulæ,



Uric Acid.



Theobromine.



Caffeïne.

Antipyrine, $C_{11}H_{12}N_2O$, does not occur in nature, and is briefly described here as an example of what may be termed an 'artificial alkaloid;' it was first obtained by Knorr by treating ethyl acetoacetate (Part I. p. 193) with phenylhydrazine (p. 388), and then heating the product (*phenylmethylpyrazolone*) with methyl iodide,

$$C_6H_{10}O_3 + C_6H_5{\cdot}NH{\cdot}NH_2 = C_{10}H_{10}N_2O + C_2H_5{\cdot}OH + H_2O$$
$$C_{10}H_{10}N_2O + CH_3I = C_{11}H_{12}N_2O,HI.$$

It is a colourless, crystalline compound, melts at 113°, and is readily soluble in water and alcohol; it is a strong mon-acid base, and its salts dissolve freely in water. Its aqueous solution gives a deep-red colouration with ferric chloride, and a bluish-green colouration with nitrous acid. Antipyrine is employed in medicine, as a substitute for quinine, for lowering the body temperature in cases of fever.

Antifebrin, or acetanilide, another important febrifuge, has already been described (p. 374).

Choline, Betaïne, Neurine, and Taurine.

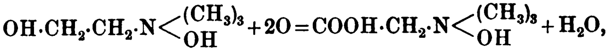
Certain nitrogenous substances which occur in the animal kingdom may also be referred to in this chapter, because they are basic compounds of great physiological importance; they really belong, however, to different classes of the fatty series.

Choline, or hydroxyethyltrimethylammonium hydroxide, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3{\cdot}OH$, occurs in the blood, bile, brain-substance, yolk of egg, and in other parts of animal organisms, usually in the form of *lecithin* (a compound of choline, glycerol, phosphoric acid, and various fatty acids); it also occurs in mustard and in hops. It may be prepared synthetically by warming trimethylamine with ethylene oxide in aqueous solution,

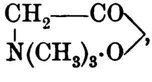
$$N(CH_3)_3 + C_2H_4O + H_2O = C_5H_{15}NO_2.$$

It is a crystalline, very hygroscopic, strongly basic substance, its aqueous solution having an alkaline reaction, and absorbing carbon dioxide from the air; with hydrochloric acid it yields the corresponding chloride, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_3Cl$, but when boiled with water it is decomposed into glycol and trimethylamine.

Betaïne, $C_5H_{11}NO_2$, is formed when choline undergoes mild oxidation; the acid, which is first produced by the conversion of the $-CH_2{\cdot}OH$ group into carboxyl,



$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}N{<}\begin{matrix}(CH_3)_3\\ OH\end{matrix} + 2O = COOH{\cdot}CH_2{\cdot}N{<}\begin{matrix}(CH_3)_3\\ OH\end{matrix} + H_2O,$$

loses one molecule of water, forming betaïne, , a salt-like compound, which has a neutral reaction, a somewhat sweet taste, and crystallises from dilute alcohol with 1 mol. H_2O.

When treated with hydrochloric acid, betaïne is converted into the *chloride*, $COOH{\cdot}CH_2{\cdot}N(CH_3)_3Cl$, and this compound may also be obtained synthetically by heating trimethylamine with chloracetic acid. Betaïne occurs in beet-juice, and is present in large quantities in the mother-liquors obtained in the preparation of beet-sugar.

Neurine, $CH_2{:}CH{\cdot}N(CH_3)_3{\cdot}OH$ (vinyltrimethylammonium hydroxide), can be obtained by heating choline with hydriodic acid, and then treating the product with silver hydroxide,

$$CH_2I{\cdot}CH_2{\cdot}N(CH_3)_3I + 2AgOH = CH_2{:}CH{\cdot}N(CH_3)_3{\cdot}OH + 2AgI + H_2O\,;$$

it is formed, together with choline and numerous other bases, during the putrefaction of animal albuminoid matter.*

Neurine is only known in solution as a strongly basic, very soluble, and exceedingly poisonous substance, but some of its salts, as, for example, the *chloride*, $CH_2{:}CH{\cdot}N(CH_3)_3Cl$, are crystalline.

Taurine, or amidoethylsulphonic acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$, occurs in the combined state in ox-gall and in many other animal secretions. It crystallises in colourless prisms, melts and decomposes at about 240°, and is readily soluble in water, but insoluble in alcohol; it has a neutral reaction, and is only a feeble acid, because the presence of the amido-group neutralises the effect of the sulphonic group to such an extent that it forms salts only with strong bases. When treated with nitrous acid, the amido-group is displaced by hydroxyl, just as in the case of primary amines, and *hydroxyethylsulphonic acid* (isethionic acid) is formed,

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H + HO{\cdot}NO = OH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H + N_2 + H_2O.$$

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* The bases produced during the putrefaction of animal albuminoid matter are known collectively as *ptomaïnes*, and many of them are highly poisonous.

CHAPTER XXXV.

DYES AND THEIR APPLICATION.

Although most organic compounds are colourless, some, especially certain classes of the aromatic series, are intensely coloured substances amongst which representatives of almost every shade occur; most of the principal dyes used at the present day are, in fact, aromatic compounds, the primary source of which is coal-tar—hence the well-known expression 'coal-tar colours.'

That a dye must be a coloured substance is, of course, obvious, but a coloured substance is not necessarily a dye, in the ordinary sense of the word, unless it is also capable of fixing itself, or of being fixed, in the fabric to be dyed, in such a way that the colour is not removed by rubbing or by washing with water; azobenzene, for example, is intensely coloured, but it would not be spoken of as a dye, because it does not fulfil the second condition.

Again, if a piece of *silk* or *wool* be dipped into a solution of picric acid it is dyed yellow, and the colour is not removed on subsequently washing with water, but is fixed in the fibre. If, however, a piece of *calico* or other *cotton* material be treated in the same way, the picric acid does not fix itself, but may be removed by washing with water. A given substance may, therefore, be a dye for certain materials, but not for others; the animal fabrics, silk and wool, fix picric acid, and are dyed by it, but the vegetable fabric, cotton, does not—a behaviour which is repeatedly met with in the case of other colouring matters.

Now, since picric acid is soluble in water, it is evident that it must have undergone some change when brought into contact with the silk or wool, otherwise it would be dissolved out of the fabric on washing with water. Materials such as wool, cotton, silk, &c., consist of minute fibres, which may be very roughly described as long, cylindrical, or flattened tubes (except in the case of silk, the fibres of which are solid), the walls of which, like parchment paper and animal membrane, allow of the passage of water and of dissolved crystalloids by diffusion, but not that of colloid substances, or, of course, of matter in suspension. If, therefore, the picric acid were present in the fibre, *as* picric acid, it would, on washing, rapidly pass into the water by diffusion; as this is not the case, it must be assumed that it has actually combined with some substance in the silk or wool, and has been converted into a yellow compound, which is either insoluble or a colloid.

The nature of the insoluble compound formed when a material is dyed in this way is not known, but there are reasons for supposing that certain constituents of the fibre unite with the dye to form an insoluble salt. This seems probable, from the fact that nearly all dyes which thus fix themselves directly on the fabric are, to some extent, either basic or acid in character. Azobenzene, as already mentioned, is not a dye, probably, because it is a neutral substance; if, however, some group, such as an amido-, hydroxyl-, or sulphonic-group, which confers basic or acid properties, be introduced into the molecule of azobenzene, then the resulting derivative is a dye, because it has the property of combining directly with the fibres of certain materials.

Another fact which leads to the same conclusion may be quoted. Certain dyes—as, for example, rosaniline—are salts of bases which are themselves colourless, and yet some materials may be dyed simply by immersion in *colourless* solutions of these bases, the same colour being obtained as with the coloured salt (that is, the dye itself); this can only be explained by assuming that some constituent of the fibre combines with the colourless base, forming with it a salt of the same colour as the dye.

Some fibres, especially silk and wool, seem to contain both acid and basic constituents, as they are often dyed directly both by basic and by acid dyes; cotton, on the other hand, seems to be almost free from both, as, except in rare cases, it does not combine with colouring matters.

Granting, then, that the fixing of a dye within the fibre is the result of its conversion into some insoluble compound, it seems reasonable to suppose that, even if a colouring matter be incapable of fixing itself in the fibre of the material, it might still be employed as a dye, provided that, after it had once passed through the walls of the fibre, it could be there converted into some insoluble compound by other means; this principle is applied in the case of many dyes, and the substances used to fix them in the material are termed *mordants.*

Dyes, therefore, may be roughly divided into two classes with respect to their behaviour with a *given* fabric: (*a*) Those which fix themselves on the fabric, and (*b*) those which do so only with the aid of a mordant.

Mordants are substances which (usually after first undergoing some preliminary change) combine with dyes, forming insoluble coloured compounds; the colour of the dyed fabric in such cases depends, of course, on that of the compound thus produced, and not on that of the dye itself, so that by using different mordants, different shades or colours are often obtained.

As an example of dyes of the second class, alizarin may be taken, as it illustrates very clearly the use of mordants.

If a piece of calico be dipped into an aqueous solution of alizarin it is coloured *yellow*, but the colour is not fixed, and is easily got rid of on washing with soap and water; if, however, a piece of calico which has been previously mordanted with a suitable aluminium salt (in the manner described below) be treated in the same way, it is dyed a fast *red*, the alizarin having combined with the aluminium compound in the fibre to form a red insoluble substance; if, again, the calico had been mordanted with a ferric salt instead, it would have been dyed a fast *dark purple.**

Substances very frequently employed as mordants are certain salts of iron, aluminium, chromium, and tin, more

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* A colouring matter such as alizarin, which can thus be used for the production of different colours, is sometimes termed 'polygenetic;' a dye which gives only one colour is then named 'monogenetic.'

especially those, such as the acetates, thiocyanates, and alums, which undergo decomposition on treatment with water or with steam, yielding either an insoluble metallic hydroxide or an insoluble basic salt.

The process of mordanting usually involves two operations: firstly, the fabric is passed through, or soaked in, a solution of the mordant, in order that its fibres may become impregnated with the metallic salt; secondly, the fabric is treated in such a way that the salt is decomposed within the fibres, and there converted into some insoluble compound.

The second operation, the fixing of the mordant so that it will not be washed out when the fabric is brought into the dye-bath, is accomplished in many ways. One of the simplest is to pass the mordanted material through a solution of some weak alkali (ammonia, sodium carbonate, lime) or of some salt, such as sodium phosphate or arsenate, which interacts with the metallic salt in the fibre, forming an insoluble metallic hydroxide, phosphate, arsenate, &c. Another method, applicable more especially in the case of mordants which are salts of *volatile acids*, consists in exposing the fabric to the action of steam, at a suitable temperature; under these conditions the metallic salt dissociates, the acid volatilises with the steam, and an insoluble hydroxide or basic salt remains in the fibre.

In the case of silk and woollen fabrics, the operations of mordanting and fixing the mordant may often be carried out simultaneously, by merely soaking the materials in a boiling dilute solution of the mordant; under these conditions the metallic salt is partially dissociated, and deposited in the fibre in an insoluble form; silk may sometimes be simply soaked in a cold, concentrated solution of the mordant, and then washed with water to cause the dissociation of the metallic salt.

In cases where only parts of the fabric are to be dyed, as, for example, in *calico-printing*, a solution of a suitable mordant may be mixed with the dye, and with some thickening substance, such as starch, dextrin, gum, &c., and printed on the fabric in the required manner, the thickening being used to prevent the mordant spreading to other parts; the material is then submitted to a steaming process, when the metallic hydroxide which is produced combines with and fixes the dye.

All these processes are identical in principle, the object being to deposit some insoluble metallic compound within the fibre; when, now, the mordanted material is treated with a solution of a suitable dye, the latter unites with the metallic hydroxide, forming a coloured compound which is fixed in the fibre. The coloured substances produced by the combination of a dye with a metallic hydroxide are termed *lakes*, and those dyes which form lakes are called *acid* dyes.

Tannin (p. 453) is an example of a different class of mordants—namely, of those which are employed with *basic dyes*, such as malachite green (p. 521) and rosaniline (p. 525): its use depends on the fact that, being an acid, it combines with dyes of a basic character, forming with them insoluble coloured salts (tannates), which are thus fixed in the fibre. The fabric is mordanted by first passing it through a solution of tannin, and then through a weak solution of tartar emetic, or stannic chloride, which converts the tannin into an insoluble antimony or tin tannate, and thus fixes it in the fibre.

All colouring matters are converted into colourless compounds on reduction; in the case of some dyes, the reduction product cannot be directly reconverted into the dye by oxidation, as, for example, in that of amidoazobenzene, which, when treated with *powerful* reducing agents, yields aniline and *p*-phenylenediamine,

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2 + 4H = C_6H_5{\cdot}NH_2 + NH_2{\cdot}C_6H_4{\cdot}NH_2.$$

When, however, the colourless reduction product differs from the dye in such a way that it may be readily reconverted into the dye by oxidising agents, the reduction product is called a *leuco-compound*.

Amidoazobenzene, for example, the hydrochloride or oxalate of which is the dye *aniline yellow* (p. 535), on treatment with *mild* reducing agents, such as zinc-dust and acetic acid, yields amidohydrazobenzene, which is only slightly coloured,

$$C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NH_2 + 2H = C_6H_5\cdot NH\cdot NH\cdot C_6H_4\cdot NH_2.$$

The last-named substance is readily oxidised to amidoazobenzene on shaking its alcoholic solution with precipitated (yellow) mercuric oxide, and is, therefore, *leuco*-amidoazobenzene; many examples of leuco-compounds will be met with in the following pages.

When an insoluble dye yields a soluble leuco-compound, which is very readily reconverted into the dye on oxidation, it may be applied to fabrics in a special manner, as, for example, in the case of indigo-blue. Indigo-blue, $C_{16}H_{10}N_2O_2$ (p. 539), is insoluble in water, but on reduction it is converted into a readily soluble leuco-compound, $C_{16}H_{12}N_2O_2$, known as *indigo-white:* in dyeing with indigo, a solution of indigo-white is prepared by reducing indigo, suspended in water, with grape-sugar and sodium hydroxide, or ferrous sulphate and sodium hydroxide, and the fabric is then passed through this solution, whereupon the indigo-white diffuses through the walls into the fibres; on subsequent exposure to the air the indigo-white is reconverted into indigo-blue by oxidation, and the insoluble dye is thus fixed in the fabric.

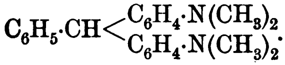
Some of the more important dyes will now be described: as, however, it would be impossible to discuss fully the constitutions of these compounds, it must be understood that the formulæ employed in the following pages are those commonly accepted, and that most of them have been satisfactorily established.

Derivatives of Triphenylmethane.

Triphenylmethane, $C_6H_5\cdot CH(C_6H_5)_2$ (p. 351), or, more strictly speaking, triphenyl carbinol, $C_6H_5\cdot C(C_6H_5)_2\cdot OH$, is the parent substance of a number of dyes, which are of very great technical importance on account of their brilliancy; as examples, *malachite green*, *pararosaniline*, and *rosaniline* may be described.

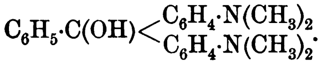
Three distinct classes of substances are constantly met with in studying the triphenylmethane group of colouring matters—namely, the **leuco-base**, the **colour-base**, and the **dye** itself.

The *leuco-base* (p. 518) is an amido-derivative of triphenylmethane; in the case of malachite green, for example, the leuco-base is tetramethyldiamidotriphenylmethane,



$$C_6H_5{\cdot}CH{<}\begin{array}{l}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\end{array}.$$

The *colour-base* is an amido-derivative of triphenyl carbinol, and is produced from the leuco-base by oxidation, just as triphenyl carbinol results from the oxidation of triphenylmethane (p. 351); the colour-base of malachite green, for example, is tetramethyldiamidotriphenyl carbinol,

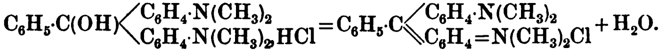


$$C_6H_5{\cdot}C(OH){<}\begin{array}{l}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\end{array}.$$

Both the leuco-base and the colour-base are usually colourless, and the latter also yields colourless, or only slightly coloured, salts on treatment with *cold* acids; when *warmed* with acids, however, the colour-base gives highly coloured salts, which constitute the dye, water being eliminated,

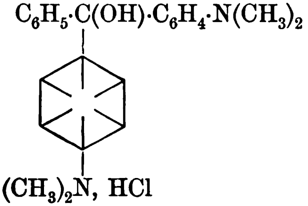
$$\underset{\text{Malachite Green Base.}}{C_{23}H_{26}N_2O} + HCl = \underset{\text{Chloride of Malachite Green.}}{C_{23}H_{25}N_2Cl} + H_2O.$$

This loss of water is probably due to combination taking place between the hydroxyl-group and the hydrogen atom of the acid employed, and the conversion of the colourless into the coloured salt may be expressed as follows,

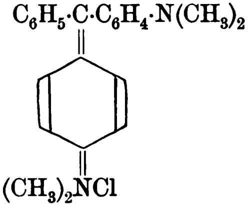


$$C_6H_5{\cdot}C(OH){<}\begin{array}{l}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2,HCl\end{array} = C_6H_5{\cdot}C{<}\begin{array}{l}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{=}N(CH_3)_2Cl\end{array} + H_2O.$$

This change—namely, the elimination of two univalent atoms or groups—resembles the conversion of colourless hydroquinone into highly coloured quinone (p. 426), and also that of *p*-amidophenol into quinone-chlorimide (p. 428), and may be represented in a similar manner,



Hydrochloride of Colour-base.

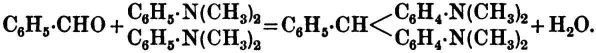


Chloride of Malachite Green.

Exactly similar changes may be assumed to take place in the formation of the pararosaniline and rosaniline dyes, and, in fact, most colouring matters may be regarded as derivatives of quinones.

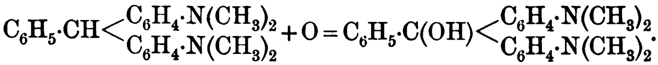
Malachite green (of commerce) is a double salt, formed by the combination of the chloride of tetramethyldiamidotriphenyl carbinol with zinc chloride, and the first step in its manufacture is the preparation of *leuco-malachite green* or *tetramethyl-p-diamidotriphenylmethane*, $C_6H_5{\cdot}CH{<}\begin{smallmatrix}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\end{smallmatrix}$.

Leuco-malachite green is manufactured by heating a mixture of benzaldehyde (1 mol.) and dimethylaniline (2 mols.) with hydrochloric acid,



$$C_6H_5{\cdot}CHO+\begin{matrix}C_6H_5{\cdot}N(CH_3)_2\\C_6H_5{\cdot}N(CH_3)_2\end{matrix}=C_6H_5{\cdot}CH{<}\begin{matrix}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\end{matrix}+H_2O.$$

It is a colourless, crystalline substance, which, when treated with oxidising agents, such as manganese dioxide and sulphuric acid, or lead dioxide and hydrochloric acid, yields *tetramethyldiamidotriphenyl carbinol*, just as triphenylmethane, under similar circumstances, yields triphenyl carbinol,



$$C_6H_5{\cdot}CH{<}\begin{matrix}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\end{matrix}+O=C_6H_5{\cdot}C(OH){<}\begin{matrix}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\end{matrix}.$$

This oxidation product is a colourless base, and dissolves in *cold* acids, yielding colourless solutions of its salts; when, however, such solutions are warmed, the colourless salts lose one molecule of water, intensely green solutions being obtained; the formation of the chloride, for example, is expressed by the equation,

$$C_{23}H_{26}N_2O + HCl = C_{23}H_{25}N_2Cl + H_2O,$$

and its double salt with zinc chloride (or the oxalate of the base), constitutes the malachite green (Victoria green, benzaldehyde green) of commerce.

Preparation of Malachite Green.—Dimethylaniline (10 parts) and benzaldehyde (4 parts) are heated with zinc chloride (4 parts) in a porcelain basin or enamelled iron pot for two days at 100°, with constant stirring; the product is then submitted to distillation in steam, to get rid of the unchanged dimethylaniline, and after cooling, the insoluble leuco-compound is separated. This product is washed with water, dissolved in as little hydrochloric acid as possible, the solution diluted considerably, and the calculated quantity of freshly precipitated lead dioxide added. The filtered dark-green solution is then mixed with sodium sulphate, to precipitate any lead, again filtered, and the colouring matter precipitated in the form of its zinc double salt, $3C_{23}H_{25}N_2Cl,2ZnCl_2+2H_2O$, by the addition of zinc chloride and common salt; this salt is finally purified by recrystallisation.

Malachite green, and other salts of the base, such as the oxalate, $2C_{23}H_{24}N_2,3C_2H_2O_4$, form deep-green crystals, and are readily soluble in water; they are decomposed by alkalies, with separation of the *colour-base*, tetramethyldiamidotriphenyl carbinol.

Malachite green dyes silk and wool directly an intense dark-bluish green, but cotton must first be mordanted with tannin and tartar emetic (p. 518), and then dyed in a bath gradually raised to 60°.

Many other dyes, closely allied to malachite green, are prepared by condensing benzaldehyde with tertiary alkylanilines (p. 377). *Brilliant green*, for example, is finally obtained when diethylaniline is employed instead of dimethylaniline in the above-described process, whereas *acid green* is obtained from benzaldehyde and ethylbenzylaniline,* $C_6H_5{\cdot}N(C_2H_5){\cdot}C_7H_7$, in a similar manner. The salts of these two colouring matters are very sparingly soluble in water, and therefore of little use as dyes;

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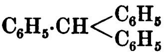
* Produced by treating aniline with benzylchloride and ethyl bromide successively.

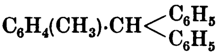
for this reason, the bases are treated with anhydrosulphuric acid, and thus converted into a mixture of readily soluble sulphonic acids, the sodium salts of which constitute the commercial dyes. Silk and wool are dyed in a bath acidified with sulphuric acid (hence the name acid green), and very bright greens are obtained, but these dyes are not suitable for cotton.

Pararosaniline and *rosaniline* are exceedingly important dyes, which, like malachite green, are derived from triphenylmethane. Whereas, however, malachite green is a derivative of *diamido*-triphenylmethane, the rosanilines are all *triamido*-triphenylmethane derivatives, as will be seen from the following formulæ,



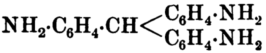
$$C_6H_5\cdot CH<\begin{array}{l}C_6H_5\\C_6H_5\end{array}$$

Triphenylmethane.



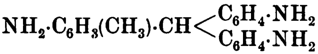
$$C_6H_4(CH_3)\cdot CH<\begin{array}{l}C_6H_5\\C_6H_5\end{array}$$

Tolyldiphenylmethane
(Methyltriphenylmethane).



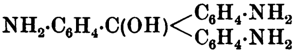
$$NH_2\cdot C_6H_4\cdot CH<\begin{array}{l}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{array}$$

Leuco-pararosaniline
(Paraleucaniline).
Triamidotriphenylmethane.



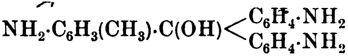
$$NH_2\cdot C_6H_3(CH_3)\cdot CH<\begin{array}{l}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{array}$$

Leuco-rosaniline
(Leucaniline).
Triamidotolyldiphenylmethane.



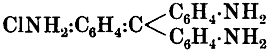
$$NH_2\cdot C_6H_4\cdot C(OH)<\begin{array}{l}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{array}$$

Pararosaniline Base.
Triamidotriphenyl Carbinol.



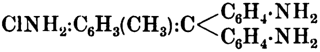
$$NH_2\cdot C_6H_3(CH_3)\cdot C(OH)<\begin{array}{l}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{array}$$

Rosaniline Base.
Triamidotolyldiphenyl Carbinol.



$$ClNH_2{:}C_6H_4{:}C<\begin{array}{l}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{array}$$

Pararosaniline Chloride.

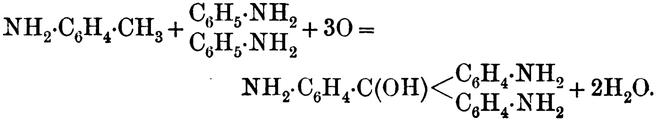


$$ClNH_2{:}C_6H_3(CH_3){:}C<\begin{array}{l}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{array}$$

Rosaniline Chloride.

In all these compounds the amido-groups are in the *para*-position to the methane carbon atom.

Pararosaniline (of commerce) is the chloride of triamidotriphenyl carbinol, a base which is most conveniently prepared by oxidising a mixture of *p*-toluidine (1 mol.) and aniline (2 mols.) with arsenic acid, or nitrobenzene (compare rosaniline, p. 525),



$$NH_2\cdot C_6H_4\cdot CH_3+\begin{array}{l}C_6H_5\cdot NH_2\\C_6H_5\cdot NH_2\end{array}+3O=$$
$$NH_2\cdot C_6H_4\cdot C(OH)<\begin{array}{l}C_6H_4\cdot NH_2\\C_6H_4\cdot NH_2\end{array}+2H_2O.$$

Probably the *p*-toluidine is first oxidised to *p*-amidobenzaldehyde, $NH_2{\cdot}C_6H_4{\cdot}CHO$, which then condenses with the aniline (as in the case of the formation of leuco-malachite green) to form leuco-pararosaniline; this compound is then converted into the pararosaniline base by further oxidation.

The salts of pararosaniline have a deep-magenta colour, and are soluble in warm water; they dye silk, wool, and cotton, under the same conditions as described in the case of malachite green; pararosaniline is, however, not so largely used as rosaniline.

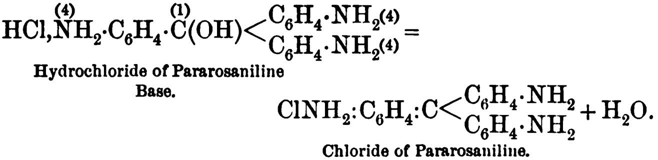
Triamidotriphenyl carbinol, the pararosaniline colour-base, is obtained, as a colourless precipitate, on adding alkalies to a solution of the chloride, or of some other salt; it crystallises from alcohol in colourless needles, and, when treated with acids, gives the intensely coloured pararosaniline salts.

Leuco-pararosaniline, paraleucaniline or triamidotriphenylmethane, $NH_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2$, is prepared by reducing triamidotriphenyl carbinol with zinc-dust and hydrochloric acid,

$$NH_2{\cdot}C_6H_4{\cdot}C(OH)(C_6H_4{\cdot}NH_2)_2 + 2H = NH_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2 + H_2O.$$

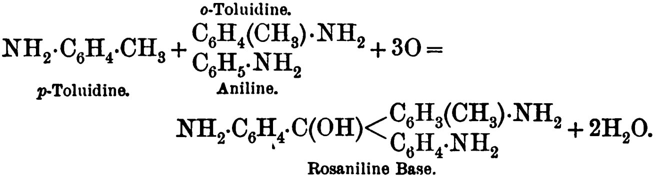
It crystallises in colourless plates, melts at 148°, and forms salts, such as the hydrochloride, $C_{19}H_{19}N_3,3HCl$, with three equivalents of an acid. When the hydrochloride is treated with nitrous acid it is converted into a tri-diazo-compound, $CH(C_6H_4{\cdot}N_2Cl)_3$, which, when boiled with water, yields *aurin*, $C_{19}H_{14}O_3$ (p. 530), and when heated with alcohol, is converted into triphenylmethane, just as diazobenzene chloride, under similar conditions, yields phenol or benzene.

Constitution of Pararosaniline.—Since triphenylmethane can be obtained from pararosaniline in this way, the latter is a derivative of this hydrocarbon (an important fact, first established by E. and O. Fischer in 1878); moreover, pararosaniline may be prepared from triphenylmethane, as follows: Triphenylmethane is converted into trinitrotriphenylmethane, $NO_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NO_2)_2$—a compound in which it has been shown that all the nitro-groups are in the *p*-position to the methane carbon atom—with the aid of fuming nitric acid; this nitro-compound, on reduction, yields a substance which is identical with leuco-pararosaniline, and which, on oxidation, is readily converted into the colour-base, triamidotriphenyl carbinol; this base, when treated with acids, yields salts of pararosaniline, with elimination of water,



$$\mathrm{HCl,\overset{(4)}{N}H_2\cdot C_6H_4\cdot \overset{(1)}{C}(OH)<\begin{matrix}C_6H_4\cdot NH_{2(4)}\\ C_6H_4\cdot NH_{2(4)}\end{matrix}} = \mathrm{ClNH_2{:}C_6H_4{:}C<\begin{matrix}C_6H_4\cdot NH_2\\ C_6H_4\cdot NH_2\end{matrix} + H_2O.}$$

Rosaniline (of commerce), fuchsine, or magenta, is the chloride (or acetate) of triamidotolyldiphenyl carbinol, a base which is produced by the oxidation of equal molecular proportions of aniline, *o*-toluidine, and *p*-toluidine (with nitrobenzene, arsenic acid, mercuric nitrate, &c.), the reaction being similar in all respects to the formation of the pararosaniline base from aniline (2 mols.) and *p*-toluidine (1 mol.),



$$\mathrm{NH_2\cdot C_6H_4\cdot CH_3 + \begin{matrix}C_6H_4(CH_3)\cdot NH_2\\ C_6H_5\cdot NH_2\end{matrix} + 3O} = \mathrm{NH_2\cdot C_6H_4\cdot C(OH)<\begin{matrix}C_6H_3(CH_3)\cdot NH_2\\ C_6H_4\cdot NH_2\end{matrix} + 2H_2O.}$$

Rosaniline is usually manufactured at the present time by what is termed the '*nitrobenzene process*,' or the '*arsenic acid process*.'

To the requisite mixture of aniline, *o*-toluidine, and *p*-toluidine* (38 parts), hydrochloric acid (20 parts) and nitrobenzene (20 parts) are added, and the whole is gradually heated to 190°, small quantities of iron-filings (3–5 parts) being added from time to time (see below). At the end of five hours the reaction is complete,

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* Crude 'aniline-oil,' a mixture of these three bases, has sometimes been used instead of the pure compounds.

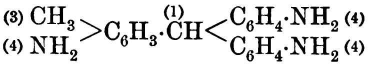
and steam is then led through the mass to drive off any unchanged aniline, toluidine, or nitrobenzene, after which the residue is powdered and extracted with boiling water, under pressure; lastly, the extract is mixed with salt, and the crude rosaniline chloride which separates purified by recrystallisation.

In this reaction the nitrobenzene acts only indirectly as the oxidising agent; the ferrous chloride, produced by the action of the hydrochloric acid on the iron, is oxidised by the nitrobenzene to ferric chloride, which in its turn oxidises the mixture of aniline and toluidines to rosaniline, and is itself again reduced to ferrous chloride; the action is therefore continuous, and only a small quantity of iron is necessary.

The salts of the rosaniline base with one equivalent of acid, as, for example, the chloride, $C_{20}H_{20}N_3Cl$, form magnificent crystals, which show an intense green metallic lustre; they dissolve in warm water, forming deep-red solutions, and dye silk, wool, and cotton a brilliant magenta colour, the conditions of dyeing being the same as in the case of malachite green.

The addition of alkalies to the saturated solution of the chloride of rosaniline destroys the colour, and causes the precipitation of the colour-base, *triamidotolyldiphenyl carbinol*, $C_{20}H_{20}N_3{\cdot}OH$ (p. 523), which crystallises in colourless needles, and on warming with acids is at once reconverted into the intensely coloured salts. When reduced with tin and hydrochloric acid, the rosaniline salts yield *leuco-rosaniline*, $C_{20}H_{21}N_3$ (p. 523), a colourless, crystalline substance, which, when treated with oxidising agents, is again converted into rosaniline.

The *constitution of rosaniline* has been deduced in the same way as that of pararosaniline (p. 524), since, by means of the diazo-reaction, leuco-rosaniline has been converted into diphenyl-*m*-tolylmethane, $CH_3{\cdot}C_6H_4{\cdot}CH(C_6H_5)_2$; leuco-rosaniline has, therefore, the constitution,

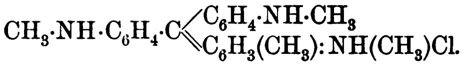


$$\begin{matrix}(3)\ CH_3\\ (4)\ NH_2\end{matrix}\!>C_6H_3{\cdot}\overset{(1)}{C}H<\!\begin{matrix}C_6H_4{\cdot}NH_2\ (4)\\ C_6H_4{\cdot}NH_2\ (4)\end{matrix}$$

and the rosaniline salts are derived from this base, just as those of pararosaniline and of malachite green are derived from leuco-pararosaniline and leuco-malachite green respectively.

Derivatives of Pararosaniline and Rosaniline.

The hydrogen atoms of the three amido-groups in pararosaniline and rosaniline may be displaced by methyl- or ethyl-groups, by heating the dye with methyl or ethyl iodide (chloride or bromide); under these conditions tri-alkyl substitution products are obtained as primary products, one of the hydrogen atoms of each of the amido-groups being displaced. When, for example, rosaniline is heated with methyl chloride, it yields, in the first place, the chloride of *trimethyl*-rosaniline,



$$\mathrm{CH_3{\cdot}NH{\cdot}C_6H_4{\cdot}C}\left\langle\begin{array}{l}\mathrm{C_6H_4{\cdot}NH{\cdot}CH_3}\\ \mathrm{C_6H_3(CH_3){:}NH(CH_3)Cl.}\end{array}\right.$$

This compound is a reddish-violet dye; the corresponding *triethyl*-rosaniline chloride is the principal constituent of *Hofmann's violet*, *dahlia*, *primula*, &c. dyes, which have now been superseded by more brilliant violets.

By the continued action of methyl iodide on rosaniline, the iodide of *tetramethyl*-rosaniline is obtained. This substance is a magnificent, bluish-violet dye, but is now little used; it is a tertiary base, and, like dimethylaniline, it combines directly with methyl iodide, forming an additive compound of the composition, $C_{20}H_{16}N_3(CH_3)_4I,CH_3I + H_2O$, which, curiously enough, is green, and was formerly used under the name '*iodine green*.'

Starting, then, from rosaniline, which is a brilliant red dye, and substituting methyl-groups for hydrogen, the colour first becomes reddish-violet, and then bluish-violet, as the number of alkyl-groups increases. This change is more marked when ethyl-groups are introduced, and still more so when phenyl- or benzyl-groups are substituted for hydrogen, as in the latter case pure blue dyes are produced (see below); in fact, by varying the number and character of the substituting groups, almost any shade from red to blue can be obtained.

Lastly, it is interesting to note that when a violet dye, like tetramethylrosaniline, combines with an alkyl halogen compound, it is converted into a bright-green dye, which, however, is somewhat unstable, and, on warming, readily decomposes into the alkyl halogen compound and the original violet dye. A piece of paper, for example, which has been dyed with 'iodine green' becomes violet when warmed over a Bunsen burner, and methyl iodide is evolved.

The alkyl-derivatives of pararosaniline and of rosaniline are no longer prepared by heating the dyes with alkyl halogen compounds, but are obtained by more economical methods. The dyes of this class now actually manufactured, examples of which are described below, are, with few exceptions, derivatives of pararosaniline.

Methylviolet appears to consist principally of the chloride of *hexamethyl*-pararosaniline; it is usually manufactured by heating a mixture of dimethylaniline, potassium chlorate, cupric chloride (or sulphate), and sodium chloride, at 50–60°, for about eight hours;* the product is treated with hot water, the copper removed by passing hydrogen sulphide, the solution concentrated, and the dye precipitated by the addition of salt.

Methylviolet comes into the market in the form of hard lumps, which have a green metallic lustre; it is readily soluble in alcohol and hot water, forming beautiful violet solutions, which dye silk, wool, and cotton, under the same conditions as are employed in the case of malachite green (p. 522).

When rosaniline is treated with aniline at 100°, in the presence of some weak acid, such as acetic, benzoic, or stearic acid (which combines with the ammonia), phenyl-groups displace the hydrogen atoms of the amido-groups,

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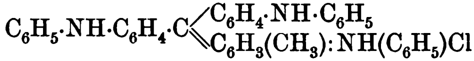
* The changes which take place during this remarkable process are doubtless very complex, and cannot be discussed here.

just as in the formation of diphenylamine from aniline and aniline hydrochloride (p. 379),

$$C_6H_5{\cdot}NH_2 + C_6H_5{\cdot}NH_2,HCl = (C_6H_5)_2NH + NH_3,HCl.$$

Here, as in the case of the alkyl-derivatives of rosaniline, the colour of the product depends on the number of phenyl-groups which have been introduced; the mono- and di-phenyl-derivatives are reddish-violet and bluish-violet respectively, whereas triphenylrosaniline is a pure blue dye, known as *aniline blue.*

Aniline blue,



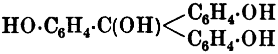
$$C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}C\begin{cases}C_6H_4{\cdot}NH{\cdot}C_6H_5\\C_6H_3(CH_3){:}NH(C_6H_5)Cl\end{cases}$$

(triphenylrosaniline chloride), is prepared by heating rosaniline with benzoic acid and an excess of aniline at 180° for about four hours, and until the mass dissolves in dilute acids, forming a pure blue solution. The product, which contains the aniline blue in the form of the colour-base, is then treated with hydrochloric acid, whereupon the chloride crystallises out in an almost pure condition.

Aniline blue is very sparingly soluble in water, and in dyeing with it, the operation has to be conducted in alcoholic solution. In order to get over this difficulty, the insoluble dye is treated with anhydrosulphuric acid, and thus converted into a mixture of sulphonic acids, the sodium salts of which are readily soluble, and come into the market under the names '*alkali blue,*' '*water blue,*' &c.

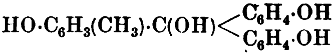
In dyeing silk and wool with these colouring matters, the material is first dipped into alkaline solutions of the salts, when a light-blue tint is obtained, and it is not until it has been immersed in dilute acid (to liberate the sulphonic acid) that the true blue colour is developed. Cotton is dyed in the same way, but must first be mordanted with tannin.

The tri-hydroxy-derivatives of triphenyl carbinol and of tolyl-diphenyl carbinol, which correspond with the tri-amido-compounds described above, are respectively represented by the following formulæ,



$$\mathrm{HO\cdot C_6H_4\cdot C(OH)}<\begin{matrix}\mathrm{C_6H_4\cdot OH}\\ \mathrm{C_6H_4\cdot OH}\end{matrix}$$

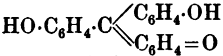
Trihydroxytriphenyl Carbinol.



$$\mathrm{HO\cdot C_6H_3(CH_3)\cdot C(OH)}<\begin{matrix}\mathrm{C_6H_4\cdot OH}\\ \mathrm{C_6H_4\cdot OH}\end{matrix}$$

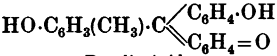
Trihydroxytolyldiphenyl Carbinol.

These compounds may be obtained from the corresponding triamido-derivatives (the colour-bases of pararosaniline and of rosaniline) with the aid of the diazo-reaction; in other words, the amido-compounds are treated with nitrous acid, and the solutions of the diazo-salts are then heated. The hydroxy-compounds thus produced are, however, unstable, and readily lose one molecule of water, yielding coloured compounds—*aurin* and *rosolic acid*—which correspond with the pararosaniline and rosaniline dyes in constitution,



$$\mathrm{HO\cdot C_6H_4\cdot C}\begin{matrix}\diagup\mathrm{C_6H_4\cdot OH}\\ \diagdown\!\!\diagdown\mathrm{C_6H_4{=}O}\end{matrix}$$

Aurin.



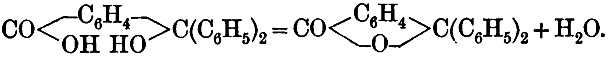
$$\mathrm{HO\cdot C_6H_3(CH_3)\cdot C}\begin{matrix}\diagup\mathrm{C_6H_4\cdot OH}\\ \diagdown\!\!\diagdown\mathrm{C_6H_4{=}O}\end{matrix}$$

Rosolic Acid.

These substances are of little use as dyes, owing to the difficulty of fixing them.

The Phthaleïns.

The phthaleïns, like malachite green and the rosanilines, are derivatives of triphenylmethane, inasmuch as they are substitution products of *phthalophenone*, a compound formed from *triphenylcarbinol-o-carboxylic acid*, by loss of one molecule of water,*



$$\mathrm{CO}<\begin{matrix}\mathrm{-C_6H_4-}\\ \mathrm{OH\ HO}\end{matrix}>\mathrm{C(C_6H_5)_2=CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{-O-}\end{matrix}>\mathrm{C(C_6H_5)_2+H_2O.}$$

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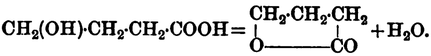
* Compounds produced in this way from one molecule of a hydroxy-acid, by loss of water, are called *lactones*. Many hydroxy-acids yield lactones, but, as a rule, only when the hydroxyl-group is in the γ- or δ-position (Part I. p. 166).

γ-Hydroxybutyric acid, for example, cannot be isolated, because when set free from its salts, by the addition of a mineral acid, it at once decomposes with formation of its lactone,

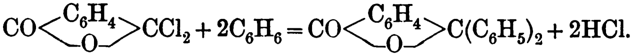


$$\mathrm{CH_2(OH)\cdot CH_2\cdot CH_2\cdot COOH}=\begin{matrix}\mathrm{CH_2\cdot CH_2\cdot CH_2}\\ \mathrm{|\qquad\quad |}\\ \mathrm{O\text{———}CO}\end{matrix}+\mathrm{H_2O.}$$

γ-Butyrolactone.

The fatty lactones are mostly neutral volatile liquids, but those belonging to the aromatic series are crystalline solids; all lactones dissolve in caustic alkalies, yielding salts of the hydroxy-acids from which they are derived.

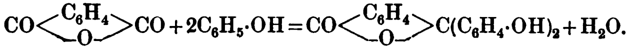
Phthalophenone is prepared by acting on a mixture of phthalyl chloride (p. 438) and benzene, with aluminium chloride,



$$CO<\begin{matrix}C_6H_4\\O\end{matrix}>CCl_2 + 2C_6H_6 = CO<\begin{matrix}C_6H_4\\O\end{matrix}>C(C_6H_5)_2 + 2HCl.$$

It crystallises in colourless needles, melts at 115°, and dissolves in alkalies, yielding salts of triphenylcarbinol-*o*-carboxylic acid. This acid, on reduction with zinc-dust in alkaline solution, is converted into *triphenylmethane-o-carboxylic acid*, $COOH\cdot C_6H_4\cdot CH(C_6H_5)_2$, from which, by distillation with lime, *triphenylmethane* is obtained—a proof that the phthaleïns are derivatives of this compound.

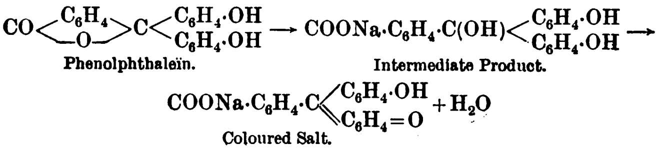
Phenolphthaleïn, or dihydroxyphthalophenone, $C_{20}H_{14}O_4$, is prepared by heating phthalic anhydride (3 parts) with phenol (4 parts) and powdered zinc chloride (5 parts), at 115–120° for eight hours; the product is washed with water, dissolved in soda, and the phenolphthaleïn precipitated from the filtered solution with acetic acid,



$$CO<\begin{matrix}C_6H_4\\O\end{matrix}>CO + 2C_6H_5\cdot OH = CO<\begin{matrix}C_6H_4\\O\end{matrix}>C(C_6H_4\cdot OH)_2 + H_2O.$$

Phenolphthaleïn separates from alcohol in small yellowish crystals, and melts at 250°; it dissolves in alkalies giving solutions which have a deep-pink colour, owing to the formation of coloured salts, but on the addition of acids the colour vanishes, hence the use of phenolphthaleïn as an indicator in alkalimetry; it is, however, of no value as a dye.

The conversion of feebly coloured phenolphthaleïn into an intensely coloured salt is probably due to its transformation into a derivative of quinone, just as in the case of the conversion of the colourless salt of tetramethyldiamidotriphenyl carbinol into the green dye (p. 521), and may be expressed as follows,



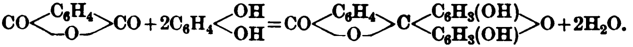
$$\underset{\text{Phenolphthaleïn.}}{CO<\begin{matrix}C_6H_4\\O\end{matrix}>C<\begin{matrix}C_6H_4\cdot OH\\C_6H_4\cdot OH\end{matrix}} \rightarrow \underset{\text{Intermediate Product.}}{COONa\cdot C_6H_4\cdot C(OH)<\begin{matrix}C_6H_4\cdot OH\\C_6H_4\cdot OH\end{matrix}} \rightarrow$$

$$\underset{\text{Coloured Salt.}}{COONa\cdot C_6H_4\cdot C\begin{matrix}\diagup C_6H_4\cdot OH\\ \diagdown C_6H_4=O\end{matrix}} + H_2O$$

Phenolphthaleïn. Intermediate Product.

Coloured Salt.

Fluoresceïn, $C_{20}H_{12}O_5$, is a very important dye-stuff, produced by heating together phthalic anhydride and resorcinol,



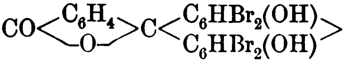
$$CO{<}\begin{matrix}C_6H_4\\ O\end{matrix}{>}CO + 2C_6H_4{<}\begin{matrix}OH\\ OH\end{matrix} = CO{<}\begin{matrix}C_6H_4\\ O\end{matrix}{>}C{<}\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}{>}O + 2H_2O.$$

Fluoresceïn.

In this Change, two hydrogen atoms of the two benzene rings unite with the oxygen atom of one of the >CO groups of the phthalic anhydride (as in the formation of phenolphthaleïn), a second molecule of water being eliminated from the hydroxyl-groups of the two resorcinol molecules.

Phthalic anhydride (1 mol.) and resorcinol (2 mols.) are heated together at 200° until the mass becomes quite solid; the dark product is then washed with hot water, dissolved in soda, the filtered alkaline solution acidified with sulphuric acid, and the fluoresceïn extracted with ether.

Fluoresceïn crystallises from alcohol in dark-red crusts; it is almost insoluble in water, but dissolves readily in alkalies, forming dark reddish-brown solutions, which, when diluted, show a most magnificent yellowish-green fluorescence (hence the name fluoresceïn). In the form of its sodium salt, $C_{20}H_{10}O_5Na_2$, fluoresceïn comes into the market as the dye '*uranin.*' Wool and silk are dyed yellow, and at the same time show a beautiful fluorescence, but the colours are faint, and soon fade; hence fluoresceïn has a very limited application alone, and is generally mixed with other dyes, in order to impart fluorescence. The great value of fluoresceïn lies in the fact that its derivatives are very important dyes.



Eosin, $CO{<}\begin{matrix}C_6H_4\\ O\end{matrix}{>}C{<}\begin{matrix}C_6HBr_2(OH)\\ C_6HBr_2(OH)\end{matrix}{>}O$ (tetrabromofluoresceïn), is formed when fluoresceïn is treated with bromine, four atoms of hydrogen in the resorcinol nuclei being displaced.

Fluoresceïn is treated with the calculated quantity of bromine in acetic acid solution, and the eosin which separates is collected, washed with a little acetic acid, and dissolved in dilute potash. The filtered solution is then acidified, and the eosin extracted with ether.

Eosin separates from alcohol in red crystals, and is almost insoluble in water, but dissolves readily in alkalies, forming deep-red solutions, which, on dilution, exhibit a beautiful green fluorescence, but not nearly to the same extent as solutions of fluoresceïn.

Eosin comes into the market in the form of its potassium salt, $C_{20}H_6Br_4O_5K_2$ (a brownish powder), and is much used for dyeing silk, wool, cotton, and especially paper, which fixes the dye without the aid of a mordant. Silk and wool are dyed with eosin directly in a bath acidified with a little acetic acid; but cotton must first be mordanted with tin, lead, or aluminium salts. The shades produced are a beautiful pink, and the materials also show a very beautiful fluorescence.

Tetriodofluoresceïn, $C_{20}H_8I_4O_5$, is also a valuable dye. Its sodium salt, $C_{20}H_6I_4O_5Na_2$, comes into the market under the name '*erythrosin.*'

Many other phthaleïns have been prepared by condensing phthalic acid and its derivatives with other phenols, and then treating the products with bromine or iodine.

Azo-dyes.

The azo-dyes contain the azo-group, $-N{:}N-$, to each of the nitrogen atoms of which a benzene or naphthalene nucleus is directly united. Azobenzene, $C_6H_5{\cdot}N{:}N{\cdot}C_6H_5$, the simplest of all azo-compounds, is not a dye, although it is intensely coloured (compare p. 514), and this is true also of other *neutral* azo-compounds; if, however, one or more hydrogen atoms in such compounds be displaced by amido-, hydroxyl-, or sulphonic-groups, the products, as, for example,

Amidoazobenzene,	$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2$,
Hydroxyazobenzene,	$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$,
Azobenzenesulphonic acid,	$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3H$,

are yellow or brown dyes.

Azo-dyes are usually prepared by one of two general methods—namely, by treating a *diazo-chloride* with an *amido-compound*,*

$$C_6H_5{\cdot}N_2Cl + C_6H_5{\cdot}N(CH_3)_2 = \underset{\text{Dimethylamidoazobenzene Hydrochloride.}}{C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2,HCl},$$

$$\underset{p\text{-Diazotoluene Chloride.}}{CH_3{\cdot}C_6H_4{\cdot}N_2Cl} + \underset{o\text{-Toluidine.}}{CH_3{\cdot}C_6H_4{\cdot}NH_2} = \underset{\text{Amidoazotoluene Hydrochloride.}}{CH_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(CH_3){\cdot}NH_2,HCl},$$

or by treating a *diazo-chloride* with a *phenol*,

$$C_6H_5{\cdot}N_2Cl + C_6H_5{\cdot}OH = \underset{\text{Hydroxyazobenzene.}}{C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH} + HCl,$$

$$C_6H_5{\cdot}N_2Cl + C_6H_4(OH)_2 = \underset{\text{Dihydroxyazobenzene.}}{C_6H_5{\cdot}N{:}N{\cdot}C_6H_3(OH)_2} + HCl.$$

In the first case the products—amidoazo-compounds—are *basic* dyes, whereas in the second case they are *acid* dyes.

Another method of some general application for the direct preparation of azo-dyes containing a sulphonic-group, consists in treating diazobenzenesulphonic acid, or its anhydride (p. 397), with an amido-compound or with a phenol,

$$SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}OH + C_6H_5{\cdot}NH_2 = \underset{\text{Amidoazobenzenesulphonic Acid.}}{SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2} + H_2O.$$

$$SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}OH + C_6H_5{\cdot}OH = \underset{\text{Hydroxyazobenzenesulphonic Acid.}}{SO_3H{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH} + H_2O.$$

As, however, the yield is generally a poor one, such dyes are usually prepared by sulphonating the amidoazo- or hydroxy-azo-compounds.

In all these reactions the diazo-group, $-N_2-$, displaces hydrogen of the benzene nucleus from the *p*-position to one of the amido- or hydroxyl-groups; substances such as *p*-toluidine, in which the *p*-position is occupied, either do not interact with diazo-chlorides or do so only with great difficulty.

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* In cases where a diazoamido-compound is first produced (p. 386), an excess of the amido-compound is employed and the mixture warmed until the intramolecular change into the amidoazo-compound is complete (p. 387).

The technical operations involved in the production of azo-colours are, as a rule, very simple. In combining diazo-compounds with phenols, for example, the amido-compound (1 mol.) is diazotised (p. 385), and the solution of the diazo-salt is then slowly run into the *alkaline* solution of the phenol, or its sulphonic acid, care being taken to keep the solution slightly alkaline, otherwise the liberated hydrochloric acid prevents combination taking place. After a short time the solution is mixed with salt, which causes the colouring matter to separate in flocculent masses; the product is then collected in filter-presses and dried, or sent into the market in the form of a paste.

The combination of diazo-compounds with amido-compounds is generally brought about by simply mixing the aqueous solution of the diazo-compound with that of the salt of the amido-compound (compare foot-note, p. 534), and then precipitating the colouring matter by the addition of common salt; in some cases, however, the reaction takes place only in alcoholic solution.

Acid azo-colours (that is, hydroxy- and sulphonic-derivatives) are taken up by animal fibres directly from an acid bath, and are principally employed in dyeing wool; they can be fixed on cotton with the aid of mordants (tin and aluminium salts being generally employed), but, as a rule, only with difficulty; nevertheless some acid dyes, notably those of the *congo-group* (p. 537), dye cotton directly without a mordant.

Basic azo-dyes are readily fixed on cotton which has been mordanted with tannin, and are very largely used in dyeing calico and other cotton goods.

At the present time a great many azo-colours are manufactured, but only a few of the more typical are mentioned here.

Aniline yellow, a salt of amidoazobenzene (p. 387), $C_6H_5 \cdot N{:}N \cdot C_6H_4 \cdot NH_2$, is no longer used in dyeing, because the colour is not fast, and is in many ways inferior to other readily obtainable yellow dyes.

Chrysoïdine (diamidoazobenzene), $C_6H_5 \cdot N{:}N \cdot C_6H_3(NH_2)_2$, is produced by mixing molecular proportions of diazobenzene chloride and *m*-phenylenediamine (p. 376) in aqueous solution. The hydrochloride crystallises in reddish needles, is moderately soluble in water, and dyes silk and wool directly, and cotton mordanted with tannin, an orange-yellow colour.

Bismarck brown, $NH_2 \cdot C_6H_4 \cdot N{:}N \cdot C_6H_3(NH_2)_2$ (triamidoazobenzene), is prepared by treating *m*-phenylenediamine hydrochloride with nitrous acid, one half of the base being converted into the diazo-compound, which then interacts with the other half, producing the dye,

$$NH_2 \cdot C_6H_4 \cdot N_2Cl + C_6H_4(NH_2)_2 = NH_2 \cdot C_6H_4 \cdot N{:}N \cdot C_6H_3(NH_2)_2,HCl.$$

The hydrochloride is a dark-brown powder, and is largely used in dyeing cotton (mordanted) and leather a dark brown.

Helianthin (dimethylamidoazobenzenesulphonic acid) is very easily prepared by mixing aqueous solutions of diazobenzenesulphonic acid and dimethylaniline hydrochloride,

$$SO_3H \cdot C_6H_4 \cdot N_2 \cdot OH + C_6H_5 \cdot N(CH_3)_2 = SO_3H \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4 \cdot N(CH_3)_2 + H_2O.$$

The sodium salt (methylorange) is a brilliant orange-yellow powder, and dissolves freely in hot water, forming a yellow solution, which is coloured red on the addition of acids; hence its use as an indicator. It is seldom employed as a dye, on account of its sensibility to traces of acid.

Resorcin yellow (tropæölin O) is prepared by combining diazobenzenesulphonic acid and resorcinol, and has the constitution $SO_3H \cdot C_6H_4 \cdot N{:}N \cdot C_6H_3(OH)_2$. Its sodium salt is a moderately brilliant orange-yellow dye, and is not readily acted on by acids; it is chiefly employed, mixed with other dyes of similar constitution, in the production of olive-greens, maroons, &c.

By using various benzene derivatives, and combining them as in the above examples, *yellow* and *brown* dyes of almost any desired shade can be obtained; in order, however, to produce a *red* azo-dye, a compound containing at least one naphthalene nucleus must be prepared. This can be readily done by combining a benzenediazo-compound with a naphthylamine, naphthol, naphthalenesulphonic acid, &c., just as described above. The dyes thus obtained give various shades of reddish-brown or scarlet, and are known collectively as 'Ponceaux' or 'Bordeaux.'

When, for example, diazoxylene chloride is combined with β-naphtholdisulphonic acid, a scarlet dye (scarlet R) of the composition $C_6H_3(CH_3)_2{\cdot}N{:}N{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$ is formed; another scarlet dye (Ponceau 3R) is produced by the combination of diazo-pseudocumene chloride with β-naphtholdisulphonic acid, and has the composition $C_6H_2(CH_3)_3{\cdot}N{:}N{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$.

Rocellin, $SO_3H{\cdot}C_{10}H_6{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH$, a compound produced by combining β-naphthol with the diazo-compound of naphthionic acid (p. 468), may be mentioned as an example of an azo-dye containing two naphthalene nuclei. It gives beautiful red shades, very similar to those obtained with the natural dye, cochineal, which rocellin and other allied azo-colours have, in fact, almost superseded.

Within recent years a great number of exceedingly valuable colouring matters have been prepared from benzidine, $NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$ (p. 391), and its derivatives.

Benzidine may be compared with two molecules of aniline, and when diazotised it yields the salt of a di-diazo- or *tetrazo-diphenyl*, $ClN_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2Cl$. This substance interacts with amido-compounds, phenols, and their sulphonic acids, just as does diazobenzene chloride (but with 2 mols.), producing a variety of most important colouring matters, known as the dyes of the *congo-group*.

Congo-red, a dye produced by the combination of tetrazodiphenyl chloride with naphthionic acid, is one of the most valuable compounds of this class. Its sodium salt,

$$SO_3Na{\cdot}(NH_2)C_{10}H_5 \vdots N{:}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N{:}N \vdots C_{10}H_5(NH_2){\cdot}SO_3Na,$$

is a scarlet powder, which on the addition of acids turns blue, owing to the liberation of the free sulphonic acid.

The congo-dyes possess the unusual property of combining with unmordanted cotton, producing brownish-red shades which are fast to soap. They are much used for dyeing cotton, but they become dull in time in any atmosphere which contains traces of acid fumes, as, for example, in the air of manufacturing towns, owing to the liberation of the blue sulphonic acids.

The **Benzopurpurins** are also exceedingly valuable dyes of the congo-group; they are produced by combining tetrazoditolyl salts * with the sulphonic acids of α- and β-naphthylamine, and are, therefore, very similar to congo-red in constitution. They dye unmordanted cotton splendid scarlet shades, and are used in very large quantities.

Various Colouring Matters.

Martius' yellow (dinitro-α-naphthol), $C_{10}H_5(NO_2)_2 \cdot OH$, is obtained by the action of nitric acid on α-naphtholmono- or di-sulphonic acid, the sulphonic group or groups being eliminated during nitration. The commercial dye is the sodium salt, $C_{10}H_5(NO_2)_2 \cdot ONa$; it is readily soluble in water, and dyes silk and wool directly an intense golden yellow.

When α-naphthol-trisulphonic acid is nitrated, two of the sulphonic groups are eliminated, and the resulting substance has the formula $C_{10}H_4(NO_2)_2(OH) \cdot SO_3H$; it is, in fact, the sulphonic acid of Martius' yellow. This valuable dye-stuff is called **naphthol yellow**, and comes into the market in the form of its potassium salt, $C_{10}H_4(NO_2)_2(OK) \cdot SO_3K$; it is very largely used, as the yellow shades are faster to light than those of Martius' yellow.

Methylene blue, $C_{16}H_{18}N_3SCl$, was first prepared by Caro,

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* *Tolidine*, $NH_2 \cdot (CH_3)C_6H_3 \cdot C_6H_3(CH_3) \cdot NH_2$, is produced from nitrotoluene by reactions similar to those by which benzidine is produced from nitrobenzene; when its salts are treated with nitrous acid they yield salts of tetrazoditolyl, just as benzidine gives salts of tetrazodiphenyl.

in 1876, by the oxidation of dimethyl-*p*-phenylenediamine (p. 379) with ferric chloride in presence of hydrogen sulphide.

Nitrosodimethylaniline (p. 378) is reduced in strongly acid solution with zinc-dust, or with hydrogen sulphide, and the solution of dimethyl-*p*-phenylenediamine thus obtained is treated with ferric chloride in presence of excess of hydrogen sulphide. The intensely blue solution thus obtained is mixed with salt and zinc chloride, which precipitate the colouring matter as a zinc double salt, in which form it comes into the market.

Methylene blue is readily soluble in water, and is a valuable cotton-blue, as it dyes cotton, mordanted with tannin, a beautiful blue, which is very fast to light and soap; it is not much used in dyeing silk or wool.

Indigo, $C_{16}H_{10}N_2O_2$, is a natural dye which has been used from the earliest times. It is contained in the leaves of the indigo-plant (*Indigofera tinctoria*) and in woad (*Isatis tinctoria*) in the form of the glucoside 'indican;' when the leaves are macerated with water, this glucoside undergoes fermentation, and indigo separates as a blue scum.

Indigo comes into the market in an impure condition in the form of dark-blue lumps, and, especially when rubbed, shows a remarkable copper-like lustre; it is insoluble in water and most other solvents, but dissolves readily in hot aniline, from which it crystallises on cooling; it sublimes, when heated, in the form of a purple vapour, and condenses as a dark-blue crystalline powder, which consists of pure 'indigotin' or indigo-blue, the principal and most valuable constituent of commercial indigo.

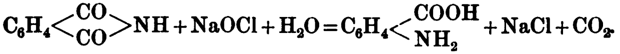
Reducing agents convert indigotin into its leuco-compound, *indigo-white*, which, in contact with air, is rapidly reconverted into indigo-blue, a property made use of in dyeing with this substance (p. 519); concentrated sulphuric acid dissolves indigotin with formation of *indigodisulphonic acid*, $C_{16}H_8N_2O_2(SO_3H)_2$, the sodium salt of which is used in dyeing under the name 'indigo carmine.'

The great value of indigotin (indigo-blue) as a dye naturally made it an attractive object for investigation, and as the result of laborious research on the part of many chemists, the constitution of indigo-blue was established about 1880, chiefly by the work of Baeyer and his pupils. During his investigations Baeyer succeeded in preparing indigo-blue artificially by various methods, two of which have already been described (pp. 421 and 446), but these and several other methods subsequently discovered were found to be unsuitable for the manufacture of the dye at a price which would enable it to compete with the natural product.

Recently, however, by the application of scientific knowledge and of untiring energy, processes have been worked out in Germany by which it seems possible to produce indigo-blue synthetically on the large scale and at a profit.

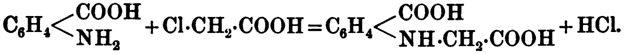
The most important of these methods is based on a discovery of Heumann, who found that indigo-blue could be obtained by heating phenylglycine (phenylamidoacetic acid) with alkalies in presence of air. The whole process may be summarised as follows: Naphthalene is oxidised to phthalic anhydride by heating it with sulphuric acid in presence of mercuric sulphate (p. 438). Phthalic anhydride is converted into phthalimide (p. 439) by heating it with ammonia under pressure.

Phthalimide is converted into anthranilic acid (*o*-amidobenzoic acid, p. 435) by treating it with an alkali hypochlorite, a method discovered by Hoogewerf, which is analogous to that used by Hofmann in converting amides into amines (Part I. p. 205),



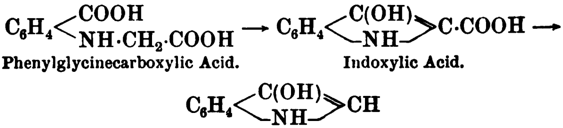
$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NH + NaOCl + H_2O = C_6H_4{<}\begin{matrix}COOH\\NH_2\end{matrix} + NaCl + CO_2.$$

Anthranilic acid is then treated with chloracetic acid to obtain phenylglycinecarboxylic acid,



$$C_6H_4{<}\begin{matrix}COOH\\NH_2\end{matrix} + Cl{\cdot}CH_2{\cdot}COOH = C_6H_4{<}\begin{matrix}COOH\\NH{\cdot}CH_2{\cdot}COOH\end{matrix} + HCl.$$

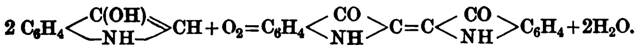
This compound, like phenylglycine itself, is converted into indigo-blue when it is fused with alkalies, the change taking place in several stages which may be indicated as follows:



Phenylglycinecarboxylic Acid. Indoxylic Acid.

Indoxyl.

$$C_6H_4{<}\begin{matrix}COOH\\NH{\cdot}CH_2{\cdot}COOH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}C(OH)\\NH\end{matrix}{>}C{\cdot}COOH \longrightarrow C_6H_4{<}\begin{matrix}C(OH)\\NH\end{matrix}{>}CH$$



$$2\,C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{NH}>CH+O_2=C_6H_4<\genfrac{}{}{0pt}{}{CO}{NH}>C=C<\genfrac{}{}{0pt}{}{CO}{NH}>C_6H_4+2H_2O.$$

Indoxyl. Indigo-blue.

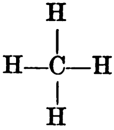
The last reaction—namely, the conversion of indoxyl into indigo-blue—is carried out by dissolving the fused mass in water and passing a stream of air through the alkaline solution.

CHAPTER XXXVI.

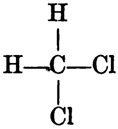
OPTICAL- AND STEREO-ISOMERISM.

The constant use of graphic formulæ in studying carbon compounds was strongly recommended in an early chapter, because, as was then pointed out, such formulæ, being based on the chemical behaviour of the substances which they represent, afford a fairly sure and complete summary of the chemical properties of those substances, whereas the ordinary molecular formulæ express little, and are besides more difficult to remember. The limited significance of graphic formulæ was also explained; the lines which are drawn between any two atoms simply express the conclusion that, as far as can be ascertained experimentally, these particular atoms are directly united, and they do not pretend to give the slightest indication of the nature of this union, or of the direction in which the force of affinity is exerted.

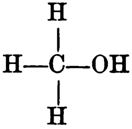
When, therefore, formulæ such as the following,



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -Cl \\ & | & \\ & Cl & \end{array}$$



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -OH \\ & | & \\ & H & \end{array}$$

are employed, it must not be supposed that they are intended to give any idea whatever of the actual form of the molecule, or to indicate that all the atoms in the molecule lie in one plane; such an assumption would be unsupported by facts, and is, moreover, shown to be incorrect by many considerations, some of which will be mentioned later.

Now, as the study of organic compounds advanced and more attention was paid to *constitution*, isomeric substances—the existence of which could not be explained with the aid of the ordinary graphic formulæ—were discovered; as an instance of this the classical example of tartaric acid may be considered.

Tartaric acid, $C_4H_6O_6$, obtained from grape-juice, is *optically active*—that is to say, its solutions have the property of rotating the plane of polarisation of polarised light. The mother liquors from which this tartaric acid is obtained contain an acid, originally called para-tartaric acid, but now known as *racemic acid,* which has the same molecular formula as tartaric acid, and is identical with it chemically; racemic acid, however, differs from tartaric acid in *physical* properties, and its solutions have *no action* on polarised light.

From these two acids, sodium ammonium salts having the composition $C_4H_4O_6NaNH_4 + 4H_2O$ were obtained; these salts, like the acids themselves, differed in their action on polarised light, the salt of tartaric acid being *dextrorotatory*, that of racemic acid being optically *inactive.*

At one time it was thought that this was the only difference between the two salts, but in 1848 Pasteur discovered the fact that the two salts also differed in crystalline structure; he found that *all* the perfect or well-grown crystals of the salt obtained from tartaric acid had certain small faces or facets (*a*, *b*) arranged in one particular manner, as shown in the crystal D (fig. 25), in which these particular faces are darkened; the crystals of the salt obtained from racemic acid, on the other hand, were of *two kinds,* the one being identical with those of the salt of tartaric acid, the other having the particular faces (*a*, *b*) arranged as shown in the crystal L (fig. 25).

The two kinds of crystals obtained from racemic acid were, in fact, found to be related to one another as an object, such as the hand, is related to its mirror-image; a left hand held before a mirror gives an image which is a right hand, and *vice versâ;* similarly, a D crystal (fig. 25) if held before a mirror gives an image identical with the L crystal viewed directly.

Having observed the existence of two kinds of crystals, Pasteur picked out a number of each from the mixture and placed them in two heaps; he then dissolved the two kinds separately in water and examined the solutions in the polarimeter. One solution was *dextrorotatory*—that is, rotated the plane of polarisation of polarised light to the right—the other was *levorotatory.*

This highly important discovery was carefully followed up by Pasteur, who next found that one of the sodium ammonium salts (the dextrorotatory one) gave an acid identical with ordinary tartaric acid in every respect, whereas the other salt—namely, the levorotatory one—gave an acid identical with ordinary tartaric acid in *chemical* properties, but which rotated the plane of polarisation of polarised light to the *left* to exactly the same extent as a solution of tartaric acid of the same concentration rotated it to the *right.* Further, by heating the cinchonine salt of tartaric acid, Pasteur obtained another form of tartaric acid (mesotartaric acid),*

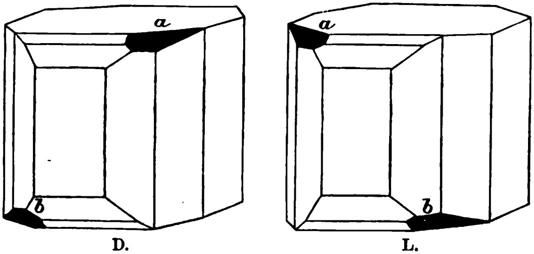


Fig. 25.

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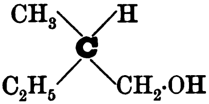
* It was subsequently found that this acid is most conveniently obtained by heating dextrotartaric acid with a little water at 165° (p. 251).

which, like racemic acid, is optically *inactive*, but from which only one kind of sodium ammonium salt was formed, this salt also being different from those previously obtained. *Four* isomeric tartaric acids thus came to be known, and judging by their chemical behaviour, they must all be represented by the constitutional formula COOH·CH(OH)·CH(OH)·COOH.

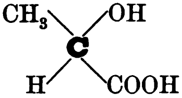
A simple explanation of this and of similar cases of isomerism is afforded by a theory advanced in 1874 by Le Bel and van't Hoff almost simultaneously and independently.

These chemists were led to conclude that optical activity depends on the constitution of the compound, and that a substance is optically active only when its molecule contains at least one carbon atom which is directly united with four *different* atoms or groups.

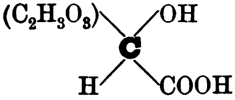
If the following graphic formulæ of various optically active compounds be examined, it will be seen that in every case there is (at least) one carbon atom in the molecule—namely, that printed in heavy type—which is thus directly united with four different atoms or groups; such a carbon atom is termed **asymmetric.**



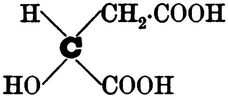
Active Amyl Alcohol.



Lactic Acid.



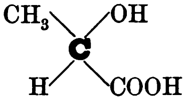
Tartaric Acid.



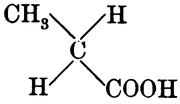
Malic Acid.

That this property of rotating the plane of polarisation of polarised light is due to the presence in the molecule of an asymmetric carbon atom is now practically proved by the fact that all optically active compounds of known constitution contain a carbon atom united in this way, and also by the fact that if by any means the asymmetric character of the carbon atom be destroyed, the power of rotating the plane of polarisation also disappears.

Sarcolactic acid (Part I. p. 233), for example, is optically active, but when reduced with hydrogen iodide it yields propionic acid, which is inactive, because it does not contain a carbon atom united with four different atoms or groups.

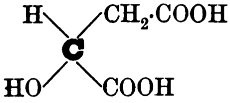


Active.

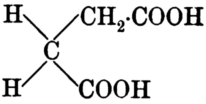


Inactive.

Malic acid, again, is optically active, but on reduction inactive succinic acid is formed,

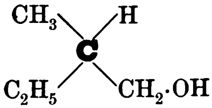


Active.

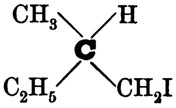


Inactive.

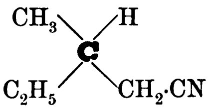
A still more instructive case is afforded by active amyl alcohol and the following derivatives,



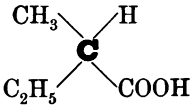
Amyl Alcohol.



Amyl Iodide.

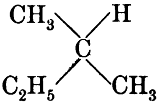


Amyl Cyanide.



Methylethylacetic Acid.

These substances, prepared from active amyl alcohol by the usual series of reactions, are themselves optically active, because they still contain an asymmetric carbon atom; if, however, the iodide be reduced to the hydrocarbon,



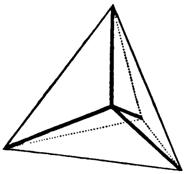
Dimethylethylmethane.

the asymmetric character of the carbon atom vanishes, and a substance is formed which is optically inactive.

The relation between the presence of an asymmetric carbon atom and the property of rotating the plane of polarisation of polarised light is thus supported by such a mass of evidence that it may now be regarded as established.

The next point in Le Bel and van't Hoff's theory concerns the *arrangement in space* of the four atoms or groups united to a tetravalent carbon atom.

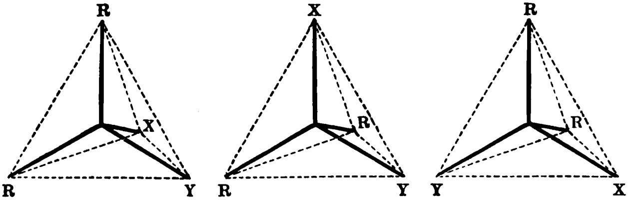
According to this theory, the existence of isomeric optically active compounds is explained by assuming that each of the several atoms or groups with which a carbon atom is united is situated at some point on one of four different lines, which are symmetrically arranged in the space around the carbon atom. In other words, it may be supposed that the carbon atom is situated in the centre of an imaginary regular tetrahedron, and that its four affinities (those forces by virtue of which it unites with four atoms or groups) act in the directions of straight lines drawn from the centre of the tetrahedron to the four corners, as represented by the dark lines in the following figure:



This view of the arrangement in space of the groups united to the carbon atom explains not only the existence of isomerides such as those referred to above, but also accounts satisfactorily for other facts observed in the study of carbon compounds; the application of Le Bel and van't Hoff's theory to such compounds generally may now be considered, and the following conclusions drawn therefrom.

(1) A compound of the type CR_3X (where R and X represent any atom or group), as, for example, CH_3Cl, $CHCl_3$, $CH_3 \cdot OH$, $CH_3 \cdot COOH$, &c., can only exist in *one* form, because whichever corner of the tetrahedron be occupied by X, the result is the same.

(2) A compound of the type CR_2XY (that is to say, one in which any two atoms or groups are identical), as, for example, CH_2ClBr, CH_2Cl_2, $CH(CH_3)_2 \cdot OH$, can only exist in *one* form; arrangements at the corners of the tetrahedron such as the following,



which may appear to be different on paper, are in reality identical.

Points such as these can only be clearly understood by actually handling models made to represent arrangements of this kind;* it will then be seen at once that, in whatever manner the positions of the different atoms R R X Y are varied, only one arrangement is possible, the apparent difference which exists on paper vanishing at once on rotating the models.

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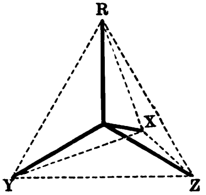
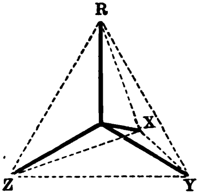
* In order to facilitate the study of stereochemistry, sets of models similar to those recommended by Friedländer have been specially prepared at the authors' request by Messrs Baird & Tatlock (14 Cross Street, Hatton Garden, London, E.C.), from whom they may be obtained at a cost of eighteenpence. Such sets contain sufficient models for the study of the isomerism of the tartaric acids, but larger sets suitable for the study of the sugars may also be obtained.

(3) Compounds of the type C, R, X, Y, Z—in which the carbon atom is united with four different atoms or groups—should exist in *two*, but only two, different forms, which may be represented by the following figures,





In working with the models this is very clearly seen, by first inserting the red, white, blue, and yellow balls into the two india-rubber carbon models, in such a way as to produce identical arrangements; by then interchanging any two of the balls in one of the models, a form will be obtained which cannot be made to coincide with the other; these two arrangements represent the two forms.

These two arrangements, moreover, are related to one another, in the same way as an *object* to its *mirror-image*—that is to say, if one be held before a mirror, the positions of X, Y, and Z in relation to R in the mirror-image will be found to be identical with those in the other viewed directly; for the sake of convenience, one of these arrangements may be distinguished by + or *d*, the other by − or *l*, the actual choice being immaterial.

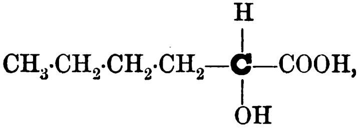
Returning to the case of some of the simplest optically active substances—namely, those containing *only one* asymmetric carbon atom, it is now known that they invariably exist in two optically active forms, one of which is dextrorotatory (*d* or +), the other levorotatory (*l* or −) to exactly the same extent. These two forms may be represented by the figures just given, and they are called *optical* (physical, or stereochemical) *isomerides.* The two optical isomerides have the same chemical properties and chemical constitution, and their molecules differ only as regards the arrangement in space. They have also the same melting-point and boiling-point, and are identical in other physical properties, except that, if solids, they always differ to a greater or less extent in crystalline form; the crystals of the one are, in fact, related to those of the other as an object to its mirror-image, just as in the case of the sodium ammonium salts already referred to. Such crystals are said to be *enantiomorphous* or *hemihedral.*

When any substance containing *one* asymmetric carbon atom is prepared synthetically, the product is found to be optically *inactive.* When, for example, lactic acid is produced from α-bromopropionic acid, or malic acid from bromosuccinic acid (Part I. pp. 231 and 245), the product in each case has no action on polarised light.

This is due to the fact that the product contains equal quantities of the *d* and *l* forms, and the action on polarised light of the one is exactly counterbalanced by that of the other. By simply dissolving together equal quantities of the *d* and *l* forms, and then evaporating the solution, an inactive product, identical with that produced synthetically, is obtained.

When, however, this inactive product is a solid, it is often found to differ very considerably from the active forms in physical properties; it may have a different melting-point (usually a higher one), different solubility, different density, and a different *crystalline form.* Such a crystallographic combination of the *d* and *l* forms is termed a *racemic* compound. Liquid racemic modifications do not exist, and sometimes the *d* and *l* forms of solids do not unite to form a racemic compound, but remain as a mere mixture; when, for example, a solution containing the sodium ammonium salts of both *d*- and *l*-tartaric acids is evaporated, the crystals are deposited separately, side by side, if the temperature of the solution is kept below 28° during crystallisation (p. 557). Such a mixture is termed *externally compensated.*

In compounds containing only *one* asymmetric carbon atom, it does not matter how many carbon atoms the molecule may contain, or what the nature of the other atoms may be, as long as only one of the carbon atoms is combined with four different atoms or groups, the compound exists only in the above three optically different forms—namely, *d*, *l*, and racemic or externally compensated; a substance of the constitution,

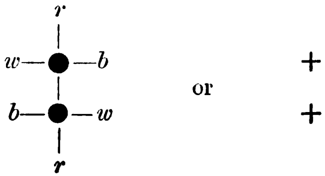


$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle OH}{\mathbf{C}}}{-}COOH,$$

for example, would not form a larger number of optical isomerides than a simple substance such as lactic acid.

When, however, a compound contains *two* asymmetric carbon atoms, a larger number of modifications may exist in accordance with the above theory, as will be seen at once by constructing models in the following manner:

I. Make two *identical* asymmetric carbon atoms, **C**, *r*, *b*, *w*, *y*,* each of which, for convenience, may be designated +; now remove *y* from both models, join the two open ends by means of the rod, and lay the model on the table, so that the two red balls point upwards. This is one possible modification, a plane figure of which may be obtained by pressing the red balls outwards on the table, when it will appear like this,



Modification I.

The removal of one of the balls, representing one of the atoms or groups, and the substitution for it of the more complex group (**C**, *r*, *b*, *w*), still leaves each carbon atom

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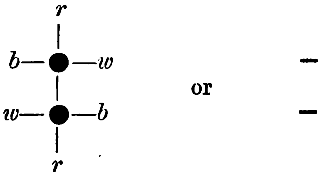
* The letters *r*, *b*, *w*, and *y* refer to the red, blue, white, and yellow balls in the sets of models.

asymmetric; in other words, each is now combined with the four different groups (*r*), (*b*), (*w*), and (C, *r*, *b*, *w*), instead of with (*r*), (*b*), (*w*), and (*y*).

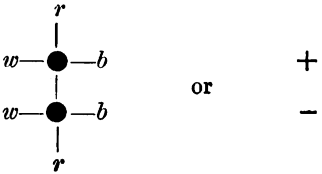
II. Repeat the above operations, starting, however, with two *identical* asymmetric carbon atoms, **C**, *r*, *b*, *y*, *w*, which are the mirror-images of those taken in I., and which may, therefore, be called −; the plane representation of this model will be,



Modification II.

This form is quite different from I., and the one cannot possibly be made to coincide with the other; if, for example, II. be turned over, although the positions of *b* and *w* will correspond with those in I., the two are not identical, because *r*, *r* will now point downwards in II., whereas they pointed upwards in I.; if, in fact, this model (II.) be held before a mirror, it will be seen that it is *not* identical with its mirror-image, but that its mirror-image *is* identical with I. viewed directly.

III. If now two *different* asymmetric carbon atoms, C, *r*, *b*, *w*, *y*, and C, *r*, *b*, *y*, *w*, or + and −, be joined in the same manner as before, another modification will be obtained, which is quite different from I. and II., and which may be represented thus,



Modification III.

No other forms different from these three can be constructed. It is evident, then, that a compound containing *two* asymmetric carbon atoms may form *three* distinct modifications. One of these (I.) will be dextrorotatory, because it contains two *identical* (+) asymmetric carbon atoms; the other (II.) will be levorotatory to exactly the same extent, because it contains two *identical* (−) asymmetric carbon atoms. The third form, on the other hand, will be optically inactive; the molecule which it represents contains two *different* asymmetric carbons atoms, one + and the other − but otherwise identical, and consequently the dextrorotatory action of the one is exactly counterbalanced by the levorotatory action of the other; in other words, the rotatory power of one *part* of this molecule is compensated or neutralised by that of the other part; such a compound is said to be inactive by *internal compensation.*

There is, however, a fourth modification which has not yet been considered in the present case; by dissolving equal quantities of the two active (*d* and *l*) forms, and then evaporating, an externally compensated or a *racemic* modification may be obtained, just as in the case of compounds containing one asymmetric carbon atom.

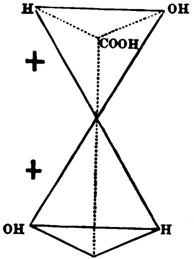
In order to decide which two of the above three forms represent the active (*d* and *l*) modifications of the substance, it is only necessary to determine which two models behave to each other as object to mirror-image. This will be found to be the case with the forms I. and II., which are therefore the active forms; on the other hand, the form III. coincides with its own mirror-image, and is therefore inactive.

The same conclusions are arrived at by disconnecting and then comparing the asymmetric carbon atoms, when it is easy to see that one of the models is composed of two *different* arrangements; this, therefore, is the form which is inactive by internal compensation.

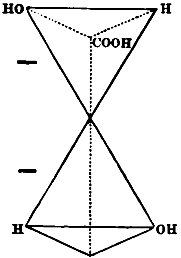
Optical-isomerism of the Tartaric Acids.

One of the best-known examples of optical-isomerism in substances containing two asymmetric carbon atoms is that of the tartaric acids investigated by Pasteur. Tartaric acid, $\mathrm{COOH\cdot\mathbf{C}H(OH)\cdot\mathbf{C}H(OH)\cdot COOH}$, contains two carbon atoms, each of which is united with four different atoms or groups—namely, $\{\mathrm{COOH}\}$, $\{\mathrm{H}\}$, $\{\mathrm{OH}\}$, and $\{\mathrm{CH(OH)\cdot COOH}\}$, and consequently, as just shown, there should be four physically isomeric forms of this acid.

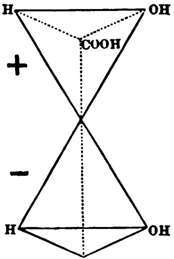
These four modifications—namely, dextrotartaric, levotartaric, mesotartaric, and racemic acid—are all known (Part I. p. 251), and the first three compounds may be represented with the aid of the tetrahedral models as follows,



d-Tartaric Acid.

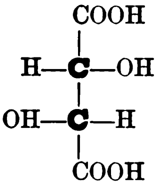


l-Tartaric Acid.



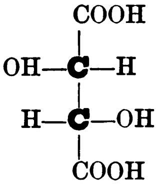
Mesotartaric Acid.

For ordinary purposes the *configurations* represented above may be more conveniently symbolised by using projections of these models, which correspond with those already employed (pp. 550, 551).



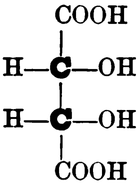
$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H{-}\mathbf{C}{-}OH}\\ |\\ \mathrm{OH{-}\mathbf{C}{-}H}\\ |\\ \mathrm{COOH}\end{array}$$

d-Tartaric Acid.



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{OH{-}\mathbf{C}{-}H}\\ |\\ \mathrm{H{-}\mathbf{C}{-}OH}\\ |\\ \mathrm{COOH}\end{array}$$

l-Tartaric Acid.



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H{-}\mathbf{C}{-}OH}\\ |\\ \mathrm{H{-}\mathbf{C}{-}OH}\\ |\\ \mathrm{COOH}\end{array}$$

Mesotartaric Acid.

Dextrotartaric acid and levotartaric acid are the two optically active forms. The one rotates the plane of polarisation to the right to exactly the same extent as the other to the left;

but in all other respects they are identical, except for the differences in crystalline form already mentioned. They possess the same melting-point, and the same solubility in a given solvent; their metallic salts have the same composition, and crystallise with the same number of molecules of water. Their esters boil at the same temperature; all their salts, like the acids themselves, are optically active to the same extent, but in opposite directions.

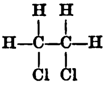
Mesotartaric acid, $C_4H_6O_6$, is the *simple* optically inactive form of tartaric acid; that is to say, it is inactive by internal compensation.

It differs from the two optically active forms in many respects, as, for example, in melting-point, solubility, and crystalline form. It might, in fact, be regarded as quite a different substance from an examination of its *physical* properties, and of those of its salts, although, in *chemical* properties, it is identical with the active forms. Mesotartaric acid *cannot be resolved into two optically active modifications*, because it is a simple substance.

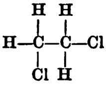
Racemic acid is simply a crystallographic union of equal quantities of dextro- and levo-tartaric acids, and is inactive by external compensation. It is obtained on evaporating a solution of equal quantities of the two active modifications, and it *can be again separated into these two forms* by certain methods given below. Racemic acid only exists in the solid state, but in this state it behaves as if it were a distinct substance, as far as *physical* properties are concerned.

It will be seen from the above examples that the existence of optical isomerides, and the number of such modifications, is in complete accordance with the theory of Le Bel and van't Hoff, and a great many other cases might be mentioned in which the agreement is also perfect.

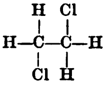
The view that the atoms or groups united to carbon are arranged in space of three dimensions is also strongly supported by considerations based on the phenomenon of structural isomerism, because an arrangement of the atoms or groups in one plane would render possible the existence of isomerides in cases where experience has shown that isomerism does not occur; in the case of the compound $C_2H_4Cl_2$, for example, two structural isomerides, namely, $CH_3{\cdot}CHCl_2$ and $CH_2Cl{\cdot}CH_2Cl$, are known, in accordance with theory; were all the atoms arranged in one plane, the following *five* isomeric compounds should be capable of existence,



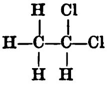
$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}{-}H}$$



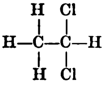
$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}Cl}$$



$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}{-}\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}{-}H}$$



$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}{-}Cl}$$



$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}{-}H}$$

As the number of asymmetric carbon atoms increases, the number of isomerides naturally becomes larger, so that a substance such as saccharic acid (Part I. p. 269),

$$COOH{\cdot}\mathbf{C}H(OH){\cdot}\mathbf{C}H(OH){\cdot}\mathbf{C}H(OH){\cdot}\mathbf{C}H(OH){\cdot}COOH,$$

which contains four asymmetric carbon atoms, is capable of existing in ten optically isomeric forms (which may be constructed with the aid of models); many other examples of optical isomerism occur among the polyhydric alcohols (Part I. p. 264) and the carbohydrates and their derivatives (Part I. p. 266).

As in the case of chemical isomerism, however, all the theoretically possible isomerides of a given substance have not always been actually obtained, owing to experimental difficulties; dimethylsuccinic acid,

$$COOH{\cdot}\mathbf{C}H(CH_3){\cdot}\mathbf{C}H(CH_3){\cdot}COOH,$$

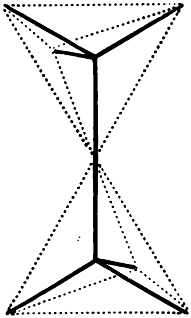
for example, like tartaric acid, should exist in four forms, but only two are known, both of which are optically inactive, the two active forms not having yet been isolated.

An examination of the models of substances containing two asymmetric carbon atoms—or, in fact, of those of any substance derived from the accompanying symbol (p. 556)—might lead to the supposition that they should exist in many modifications.

In the first place, the model could be so arranged that the directions of the affinities of the two carbon atoms would be as shown in the figure. If, then, one of the carbon atoms were slowly rotated about an axis, an infinite number of forms would be produced, all of which would be different, because they would represent different relative positions in space of the atoms constituting the molecule.

This difficulty, however, at once disappears on considering the matter a little more carefully.

In a compound represented by this symbol (atoms or groups being supposed attached to the corners of the tetrahedra), the atoms or groups united with one of the carbon atoms will exert attraction or repulsion on those united with the other; if, then, the carbon atoms be capable of *free rotation* about an axis, a certain position of equilibrium, which is the resultant of all the forces, will be attained.



This position may be disturbed by the application of heat, &c., but on removing the disturbing element the original form will be restored, so that, under given conditions, the compound only exists in one form, unless, of course, it contains asymmetric carbon atoms.

Resolution of externally compensated Modifications.

The externally compensated modification of tartaric acid and the corresponding forms of other optically active substances—namely, those which are inactive because they are composed of equal quantities of the *d* and *l* forms—may generally be resolved into their components by one or other of the following methods :

(1) By mere crystallisation of the substance itself or of one of its compounds with an optically *inactive* substance. This

method was first employed by Pasteur; in the case of racemic (tartaric) acid, it depends on the fact that if a solution of the sodium ammonium salt be allowed to crystallise at a temperature below 28°, enantiomorphous crystals (right- and left-handed, as shown in the fig., p. 543) are deposited. If, however, crystallisation take place at temperatures above 28°, only one kind of crystal is deposited—namely, crystals of sodium ammonium racemate, which do *not* exist in enantiomorphous forms, and which, indeed, belong to quite a different crystalline system. This method of separation is seldom applicable, because, as a rule, the two active components unite to form a racemic compound, or if deposited separately, their crystals are not sufficiently well defined to allow of their mechanical separation. Racemic acid itself cannot be resolved by this method.

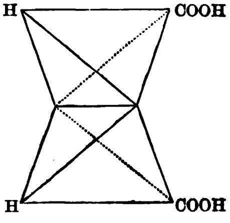
(2) A second method, also discovered by Pasteur, consists in fractionally crystallising the salt formed from an externally compensated acid or base with an optically *active* substance. This method depends on the fact that the two constituents, *d* and *l*, of the externally compensated compound form, with one and the same optically active substance, salts which *differ in solubility*, and which, therefore, can be separated by fractional crystallisation in the ordinary way. If, for example, racemic acid be combined with the optically active base cinchonine (p. 506) or strychnine (p. 506), the product may be resolved into the salts of the dextro- and levo-acids; in a similar manner the inactive modification of coniine (p. 501) may be resolved into its constituents by fractional crystallisation of the salt which it forms with *d*-tartaric acid.

(3) Another method of separation, quite different in principle from the foregoing, depends on the fact that if certain organisms, such as *penicillium glaucum*, be placed in a solution of an externally compensated modification, they feed on and, therefore, destroy one—usually the dextro—modification, the result being that, after a time, the solution contains the opposite isomeride.

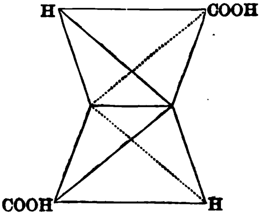
Stereo-isomerism of Unsaturated Compounds.

The occurrence of isomerism among certain unsaturated compounds was observed long ago, but for many years a satisfactory explanation of the existence of such isomerides could not be given. Fumaric acid and maleïc acid, for example, are both unsaturated compounds of the constitution COOH·CH:CH·COOH (Part I. pp. 246–247); their isomerism is not *structural*—that is to say, it is not due to the atoms being in a different state of combination—as is proved by their methods of formation and by their whole chemical behaviour; and yet the isomerides differ considerably in properties, both physical and chemical. Maleïc acid, for example, is readily converted into an anhydride, whereas fumaric acid does not give an anhydride of its own, but on distillation it gives water and maleïc anhydride.

This and similar cases of isomerism among unsaturated compounds were explained by van't Hoff and Wislicenus as follows: Unsaturated compounds contain (at least) two carbon atoms united together by two affinities of each. Representing the molecule of such a compound of the type $CR_2:CR_2$ with the aid of the tetrahedral models, it will be seen that if two corners of the one tetrahedron be joined to two corners of the other (to represent the double binding) the four groups, R, now lie in *one plane*. If, then, all the four groups, or any three of them, be identical, or if any two united with one and the same carbon atom be identical, only one arrangement is possible; if, however, the compound be of the type $CRX:CR_1X_1$—that is to say, the groups attached to both carbon atoms are different—then *two* isomerides, represented respectively by the following figures, are possible, and it makes no difference whether R and R_1, or X and X_1, are identical or different.

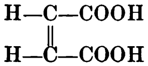


Maleïc Acid.



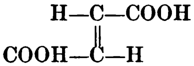
Fumaric Acid.

The existence of maleïc and fumaric acids is therefore explained, and as maleïc acid readily forms an anhydride, whereas fumaric acid does not, it may be represented by the first formula, in which the carboxyl-groups appear to be more suitably situated for anhydride formation than in the second. For ordinary purposes, the projections of such models are employed and the *configurations* of the two acids expressed in the following manner,



$$\begin{array}{c} \mathrm{H{-}C{-}COOH} \\ \| \\ \mathrm{H{-}C{-}COOH} \end{array}$$

Maleïc Acid.



$$\begin{array}{c} \mathrm{H{-}C{-}COOH} \\ \| \\ \mathrm{COOH{-}C{-}H} \end{array}$$

Fumaric Acid.

On reduction, maleïc and fumaric acids give one and the same product, namely, succinic acid, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, because as soon as the carbon atoms become singly bound they regain the property of free rotation, and by the mutual actions of the different atoms and groups *the* position of equilibrium is attained (compare p. 556).

Isomerism such as that of these two acids is generally called *stereo-isomerism.*

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[Where more than one reference is given, and one of them is in heavy type, the latter refers to the systematic description of the substance.]

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THE END.

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$C_8 H_{12} N_2$

1,4