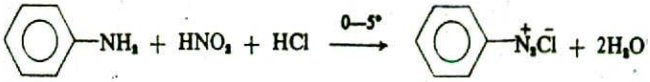
Aryldiazonium Salts

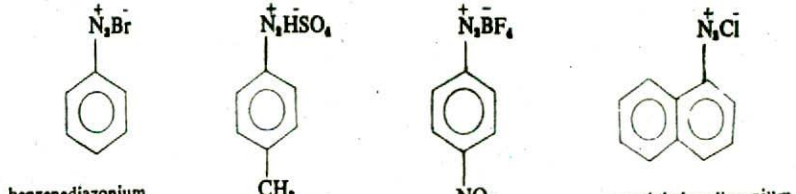
Aromatic amines when treated with nitrous acid in cold mineral acid solution, yield a very important class of compounds known as **Aryldiazonium Salts.** For example, aniline reacts with nitrous acid in hydrochloric acid solution at 0°—5°C to form a solution of benzenediazonium chloride.



aniline — benzenediazonium chloride

Such aryldiazonium salts were discovered by Johan Peter Griess in 1858, and the reaction producing them is referred to as **Diazotisation.**

Diazonium salts have the general formula $Ar—\overset{+}{N}_2\overset{-}{X}$, where **X** is any of a large number of anions, such as Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-, etc. They are named by adding *diazonium* to the name of the hydrocarbon followed by the name of the anion. Thus,



benzenediazonium bromide

p-toluenediazonium hydrogen sulphate

p-nitrobenzenediazopium fluoroborate

α-naphthalenediazonium chloride

The aryldiazonium salts have proved of enormous value in the synthesis of organic compounds and are comparable with Grignard reagents in versatility.

PHYISCAL PROPERTIES

(1) Aryldiazonium salts are colourless, crystalline solids which turn brown on exposur to air.

(2) Most of them are unstable and explode when warmed or subjected to shock, when dry.

(3) They are extremely soluble in water, sparingly soluble in ethanol and glacial acetic acid, and insoluble in ether.

(4) They form double salts with metallic salts like zinc chloride *e.g.*, $(ArN_2)_2^{2+}\ ZnCl_4^{2-}$, which are generally stable in solution.

(5) Their aqueous solutions are neutral and conduct electric current through them, showing their salt-like character, furnishing aryldiazonium ions.

$$\underset{\text{aryldiazonium chloride}}{Ar-\overset{+}{N_2}Cl} \longrightarrow \underset{\text{aryldiazonium ion}}{Ar-\overset{+}{N_2}} + \overset{-}{Cl}$$

STRUCTURE

We will elucidate the structure of aryldiazonium salts by taking the example of benzenediazonium chloride ($C_6H_5N_2Cl$). Of the three *p*-orbitals of the central N atom, one overlaps with sp^2 orbital of the carbon framework of benzene. The remaining two *p* orbitals overlap with their counterparts of the second N atom, to form two π bonds between the two nitrogen atoms. The nonbonded electron pair resides in the free lobe of the *p*-orbital of the second N atom. Hence orbital model of benzenediazonium chloride can be visualised as in Fig. 41·1.

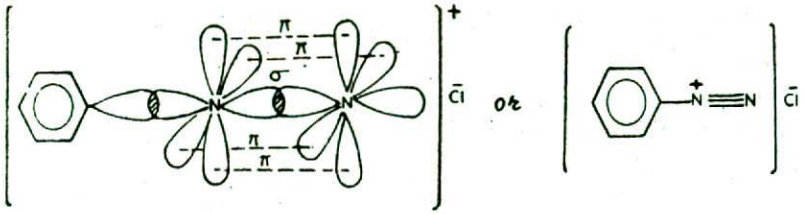


Fig. 41·1. Structure of Benzenediazonium chloride.

In true perspective, two N atoms of the diazonium group are bonded by *p-p* σ bond and a π bond. The third *p* orbital of each of the N atoms is aligned with the *p* orbitals of the six carbons of benzene ring. These available *p* arbitals of the two N atoms interact with those of the benzene sextet, and bring about the delocalisation of electrons. The delocalised electrons now encompass the six carbons of the ring as also the two N atoms of the diazonium group.

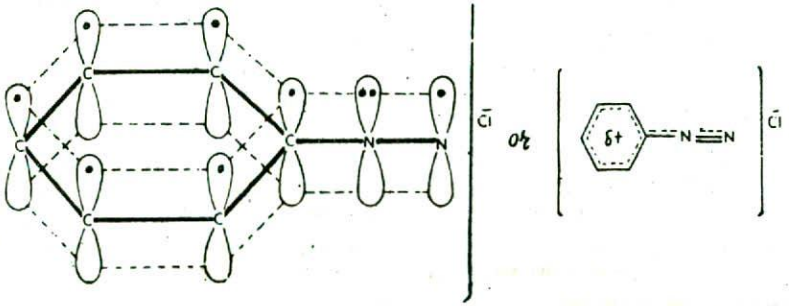
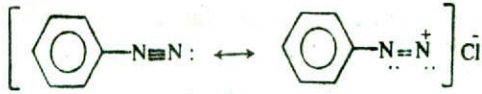


Fig. 41·2. Delocalisation of electrons in $C_6H_5\overset{+}{N_2}\overset{-}{Cl}$ structure.

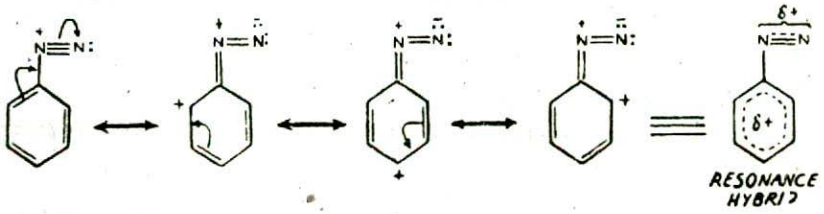
The C—N bond in the above structure gets some double bond character, and makes aryldiazonium salts more stable than the alkyldiazonium salts which lack benzenoid structure.

The electronic structure of benzenediazonium chloride is shown, where the $C_6H_5-\overset{+}{N_2}$ cation exhibits resonance.



Thus the positive charge of the cation is distributed over both the nitrogen atoms.

The relative stability of the diazonium cation is also ascribed to the fact that its structure is a resonance hybrid of the following canonical forms involving the participation of the benzene ring.



The hybrid structure shows that : (*a*) benzene ring is deactivated to the attack of electrophiles; (*b*) the C—N bond acquires some double bond character and becomes stronger. Alkyldiazonium salts cannot exhibit such resonance and hence C—N bond in them is weak. That is why they are unstable relative to their aromatic counterparts.

PREPARATION

Alkyldiazonium salts are prepared by cooling a solution of the aromatic 1° amine in excess of mineral acid (HCl or H_2SO_4) in an ice-bath. This is then added to an ice-cold solution of sodium nitrite with constant stirring. When the resulting solution gives test for presence of excess of nitrous acid (starch-iodide paper turned blue), the reaction is complete.

$$\underset{\text{1° amine}}{Ar{-}NH_2} + HCl \longrightarrow \underset{\substack{\text{arylammonium}\\ \text{chloride}}}{Ar{-}\overset{+}{N}H_3\overset{-}{Cl}}$$

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$Ar{-}\overset{+}{N}H_3\overset{-}{Cl} + HNO_2 \xrightarrow[\textit{aq solution}]{0-5^\circ} \underset{\substack{\text{aryldiazonium}\\ \text{chloride}}}{Ar{-}\overset{+}{N}_2\overset{-}{Cl}} + 2H_2O$$

The dry diazonium salts are unstable and explosive, and are seldom separated. For synthetic purposes, they are prepared in aqueous solution and used at once. However, in rare instances when the diazonium salt is required to be isolated in the pure state, an ethanolic solution of the amine is treated with the requisite mineral acid and amyl nitrite, and added to the cooled mixture. The salt either separates out immediately or is thrown out by the addition of ether.

Preparation of Benzenediazonium Chloride. Benzenediazonium chloride may be prepared by the addition of concentrated solution of 1 mole of sodium nitrite to 1 mole of aniline dissolved in 3 moles of hydrochloric acid at 0° – 5°C.



aniline — benzenediazonium chloride

PROCEDURE. One mole of aniline is dissolved in 3 moles of hydrochloric acid (1 mole to form salt with aniline, 1 mole to liberate nitrous acid, and 1 mole to keep the reaction mixture acidic) and cooled to 0°C in ice-bath. An aqueous solution of sodium nitrite, also cooled in ice-bath, is added to it at such a rate that the temperature does not rise above 5—10°C. The addition of sodium nitrite is stopped as soon as the reaction mixture just gives a blue colour with starch–potassium iodide paper. Excess of nitrous acid must be avoided as it interferes with subsequent reactions of the diazonium salt so produced in solution. If necessary, excess of nitrous acid may be destroyed by adding urea.

$$H_2N{-}CO{-}NH_2 + 2\,HONO \longrightarrow CO_2 + 2\,N_2 + 3\,H_2O$$

Since benzenediazonium chloride slowly decomposes even at ice-bath temperature, the resulting pale yellow solution is used immediately for various synthetic reactions.

CHEMICAL PROPERTIES

Aryldiazonium salts give two types of reactions :

(*a*) *those in which the* $-N_2X$ *is replaced by another univalent atom or group, with the liberation of* N_2 *gas.*

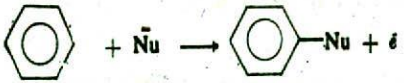
(*b*) *those in which the two N atoms are retained.*

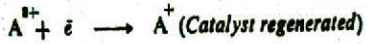
The first type of reactions again can be subdivided into two classes :

(*i*) When the diazonium group is replaced by a free radical mechanism in the presence of a catalyst (A^+),



benzene free radical

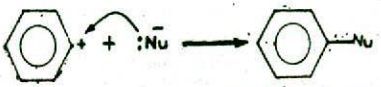




(*ii*) When N_2 is abstracted to form benzene cation which is then attacked by the nucleophile to give the corresponding substituted benzene,



BENZENE CATION

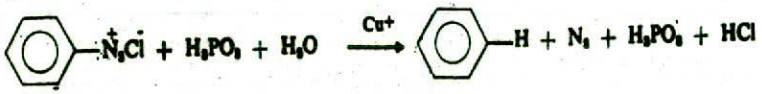


SUBSTITUTED BENZENE

A large number of benzene derivatives can be thus synthesised *via* diazonium salts. This will be illustrated by taking example of benzenediazonium chloride.

REPLACEMENT REACTIONS IN WHICH N_2 IS LIBERATED

(1) Replacement by Hydrogen. When an aryldiazonium salt is reduced by hypophosphorus acid (H_3PO_2) in the presence of cuprous chloride (Cu^+Cl^-), the product is the corresponding aromatic hydrocarbon.



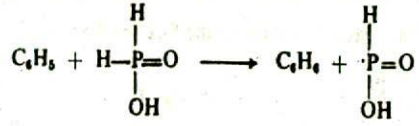
benzene

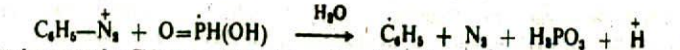
MECHANISM. The reaction proceeds by a chain mechanism.

Initiation Step :

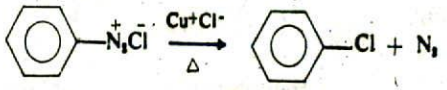


Propagation Step :

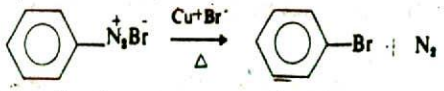




(2) **Replacement by Chlorine or Bromine.** The diazonium group can be replaced readily by any of the halogens, although different conditions may be required. For replacement by chlorine (—Cl) or bromine (—Br), the aqueous solution of the diazonium salt is heated with cuprous chloride (Cu^+Cl^-) or cuprous bromide (Cu^+Br^-).



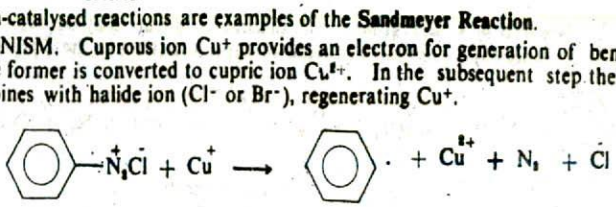
benzenediazonium chloride — chlorobenzene



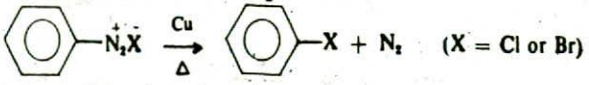
benzenediazonium bromide — bromobenzene

Such ceprous ion-catalysed reactions are examples of the **Sandmeyer Reaction**.

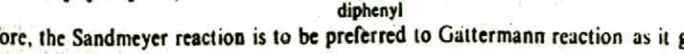
MECHANISM. Cuprous ion Cu^+ provides an electron for generation of benzene free radical, when the former is converted to cupric ion Cu^{2+}. In the subsequent step the benzene free radical combines with halide ion (Cl^- or Br^-), regenerating Cu^+.



A modification of the above reaction in which the cuprous salts are replaced by copper powder is named as the **Gattermann Reaction**.

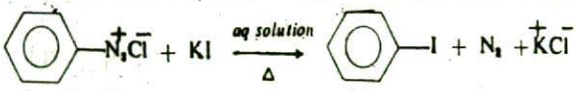


This reaction forms some diphenyl as a byproduct.



Therefore, the Sandmeyer reaction is to be preferred to Gattermann reaction as it gives better yield.

(*b*) **Replacement by Iodine.** The diazonium group may be replaced by iodine (—I) by simply heating an aqueous solution of the diazonium salt and potassium iodide.



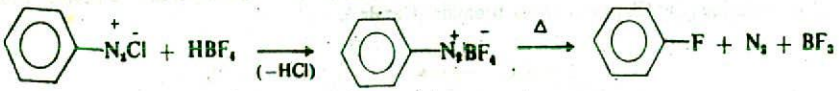
benzenediazonium chloride — iodobenzene

This is regarded as the best method for introducing iodine into the benzene ring.

MECHANISM. The reaction occurs by the S_N2 mechanism.



(3) **Replacement by Fluorine.** Aryl fluorides are conveniently prepared by adding the diazonium salt solution to fluoroboric acid, HBF_4. The fluoroborate precipitates, and is washed and dried When heated it decomposes into nitrogen, boron trifluoride and aryl fluoride (*Balz-Schiemann Reaction*).

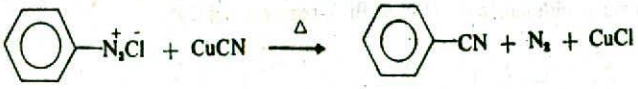


benzenediazonium fluoroborate — fluorobenzene

MECHANISM. Here one of the fluoride ions of BF_4^- acts as a nucleophile.

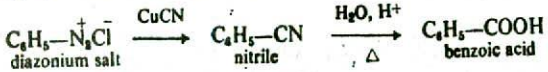


(4) **Replacement by Cyano group.** The diazonium group may be replaced by a cyano group (—CN) by using cuprous cyanide (instead of cuprous halide) in the *Sandmeyer Reaction*.



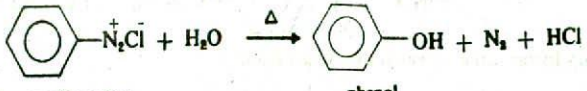
phenyl cyanide, benzonitrile

nce the nitrile can be hydrolysed to the acid, the reaction affords a method for replacing the azonium group by —COOH group as well.



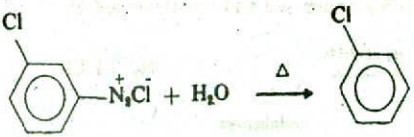
diazonium salt — nitrile — benzoic acid

(5) **Replacement by Hydroxyl group.** When an aqueous solution of aryldiazonium loride is heated, the diazonium group is replaced by —OH group. Thus a phenol results.



benzenediazonium chloride — phenol

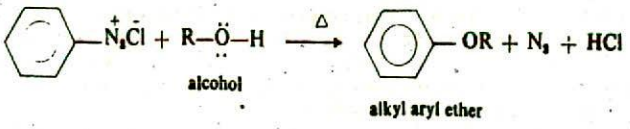
This reaction is usually conducted in an acid medium to prevent the coupling of phenol ith the unreacted diazonium salt. It is useful for the preparation of phenols which cannot synthesised by electrophilic chlorination of phenol, such as *m*-chlorophenol.



MECHANISM. In this reaction water ($H_2\ddot{O}$:) is the nucleophile.

$$C_6H_5\overset{+}{N}_2 \longrightarrow N_2 + C_6\overset{+}{H}_5 \xrightarrow{H_2\ddot{O}:} C_6H_5{-}OH_2 \xrightarrow{-H^+} \underset{\text{phenol}}{C_6H_5{-}OH}$$

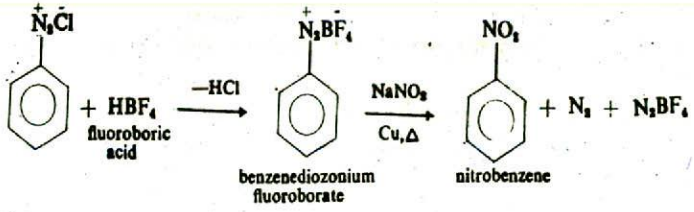
(6) **Replacement by Alkoxy group.** On heating an aqueous solution of aryldiazonium chloride in presence of an excess of an alcohol (R—OH), the diazonium group is replaced by the alkoxy group —OR. Thus alkyl aryl ether is formed.



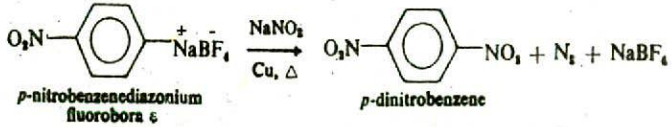
MECHANISM. Here ROH acts as the nucleophile.

$$C_6H_5\overset{+}{N}_2\bar{Cl} \longrightarrow \overset{+}{N}_2 + C_6\overset{+}{H}_5 \xrightarrow{R-\ddot{O}-H} C_6H_5{-}\overset{\cdot\cdot}{\underset{\underset{H}{|}}{O}}{-}R \xrightarrow{-H^+} C_6H_5{-}\ddot{O}{-}R$$

(7) **Replacement by Nitro group.** When diazonium fluoroborates are heated with aqueous sodium nitrite, the diazonium group is replaced by $-NO_2$ group.



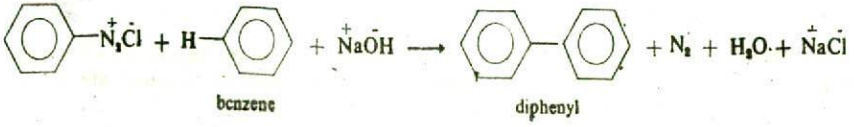
This reaction makes possible the synthesis of nitro compounds which cannot be prepared by direct nitration. For example,



(8) **Replacement by Arsono group.** The arsono group, $-AsO_3H_2$, may be introduced into the aromatic ring by heating benzenediazonium chloride solution with sodium arsenite in the presence of cupric salts. In this way the sodium salt of phenylarsonic acid, $C_6H_5AsO_3H_2$, is obtained. (*Bart Reaction*)

$$\underset{\text{benzenediazonium chloride}}{C_6H_5\overset{+}{N}_2\bar{Cl}} + Na_2AsO_3 \xrightarrow[(-N_2,-NaCl)]{CuSO_4} \underset{\text{sodium salt}}{C_6H_5AsO_3Na_2} \xrightarrow{2HCl} \underset{\text{phenylarsonic acid}}{C_6H_5AsO_3H_2} + 2NaCl$$

(9) **Replacement by Aryl group.** When an aryldiazonium chloride is treated with an aromatic hydrocarbon in the presence of sodium hydroxide, diaryl results.



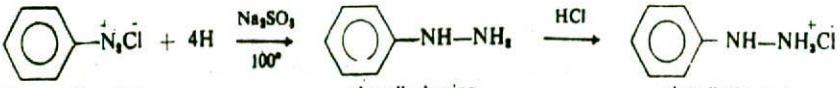
MECHANISM. The reaction is believed to occur by a free radical mechanism.

$$(i)\ C_6H_5\overset{+}{N}_2\bar{Cl} + \overset{+}{Na}\bar{O}H \longrightarrow C_6H_5{-}N{=}N{-}OH + \overset{+}{Na}\bar{Cl}$$
$$(ii)\ C_6H_5{-}N{=}N{-}OH \longrightarrow \cdot C_6H_5 + N_2 + \cdot OH$$
$$(iii)\ C_6H_6 + \cdot C_6H_5 \longrightarrow C_6H_5{-}C_6H_5 + H\cdot$$
$$(iv)\ H\cdot + \cdot OH \longrightarrow H_2O$$

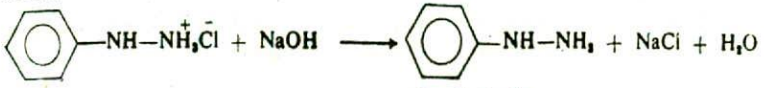
REACTIONS NOT INVOLVING LOSS OF NITROGEN

(1) **Reduction to Hydrazine.** Diazonium salts when reduced with sodium sulphite are reduced to give phenylhydrazine. The process is carried in three steps : (*i*) addition of diazonium salt solution to a warm solution of sodium sulphite heated to 100°C ; (*ii*) this is followed by acidification with HCl when phenylhydrazonium chloride is produced ; (*iii*) the resulting solution when treated with alkali yields phenylhydrazine.

$$Na_2SO_3 + 2H_2O \longrightarrow Na_2SO_4 + 4H$$

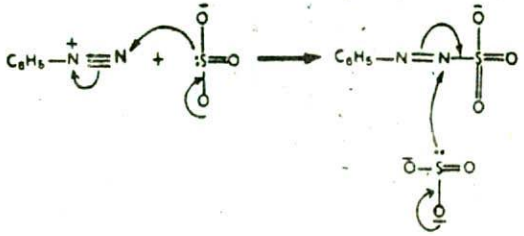


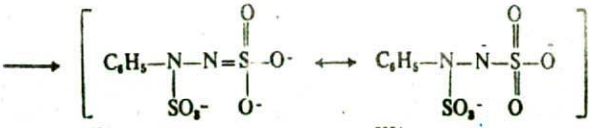
benzenediazonium chloride — phenylhydrazine — phenylhydrazonium chloride



phenylhydrazine

MECHANISM. The mechanism of the reduction with sodium sulphite may be illustrated as follows.





phenylhydrazine

(2) **Coupling Reactions.** Aryldiazonium salts react with aromatic rings of phenols and tertiary amines ($Ar{-}NR_2$), to form highly coloured azo compounds, in which the two nitrogen atoms are retained. Thus,

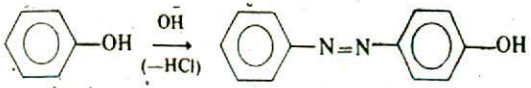
$$[Ar{-}\overset{+}{N} \equiv N : \longleftrightarrow Ar{-}\ddot{N}{=}\overset{+}{\ddot{N}}\,]\,\bar{Cl} + H{-}Ar' \longrightarrow Ar{-}N{=}N{-}Ar' + \overset{+}{H}\bar{Cl}$$

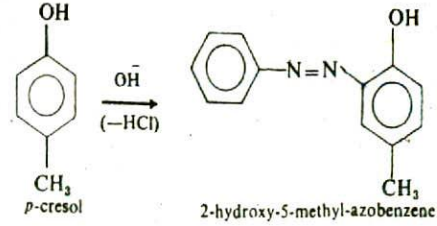
diazonium salt — phenol or 3° amine — azo compound

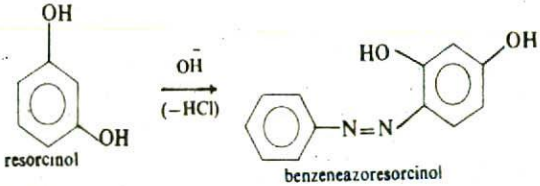
These reactions which bring about a union or 'coupling' of the diazonium cation with the phenol or 3° amine, are called **Coupling Reactions.** The diazonium cation usually attacks the aromatic ring of phenol or amine in para position because of steric hindrance in the ortho

position. But if the para position is already occupied, the coupling occurs in the ortho position. Phenol coupling generally takes place in weakly basic solutions (*p*H 7 to 8), while amines do so in weakly acidic solutions (*p*H 6 to 7).

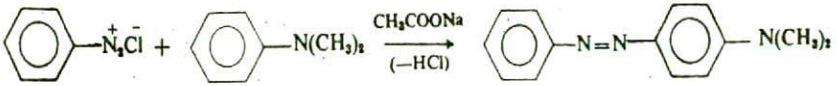
EXAMPLES OF PHENOLIC COUPLING :



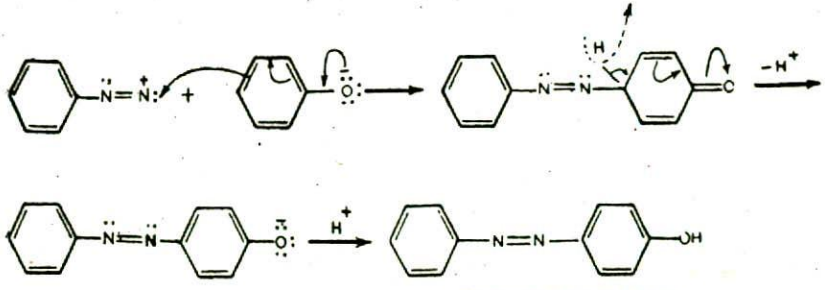




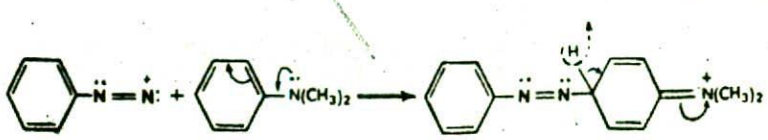
EXAMPLE OF AMINE COUPLING:



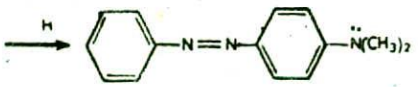
MECHANISM. The phenol coupling is an electrophilic substitution reaction. The diazonium cation having positive charge on the N atom is the electrophile. The coupling with phenols occurs *via* the phenoxide anion which is considerably more strongly activated to electrophiles than phenol itself. It is, therefore, necessary to carry out the reaction in alkaline solution.



AMINE COUPLING : The amine coupling is also a similar electrophilic substitution reaction. Here the diazonium cation adds to the tertiary amine in the para position and a proton is eliminated.

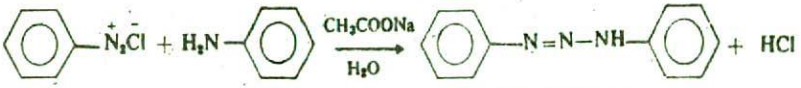


DIAZONIUM CATION DIMETHYLANILINE



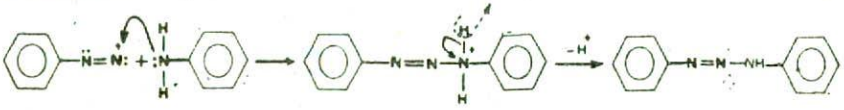
p-DIMETHYLAZOBENZENE

(3) **Reaction with 1° and 2° Amines.** With primary and secondary aromatic amines, the coupling reaction first forms diamino compounds (*N*-azo compounds). Thus benzenediazonium chloride reacts with aniline to yield diazoaminobenzene.



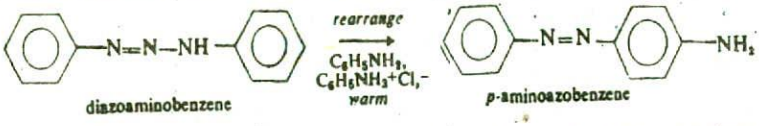
aniline diazoaminobenzene

MECHANISM :



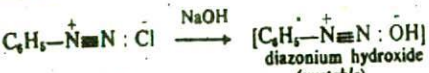
DIAZOAMINOBENZENE

When diazoaminobenzene is warmed with aniline and aniline hydrochloride, it rearranges to the aminoazo isomer, with substitution occurring in the para position.

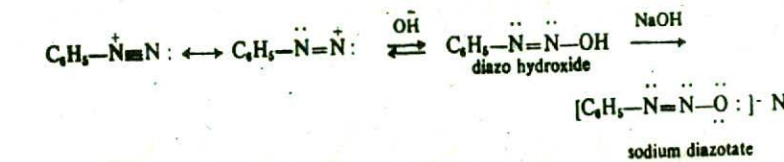


diazoaminobenzene *p*-aminoazobenzene

(4) **Reaction with Alkalis.** When an aryldiazonium salt is made alkaline, the diazonium hydroxide liberated rapidly rearranges to the diazo hydroxide. This reacts with alkali to form salts which are called **Diazotates.**



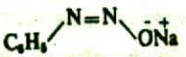
diazonium hydroxide (*unstable*)



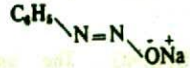
diazo hydroxide

sodium diazotate

The diazotates exist in two geometrical isomeric forms, the *syn-* (*cis-*) and *anti-* (*trans-*).



sodium *n*-diazotate (*syn* form)



sodium *iso*-diazotate (*anti* form)

Phenylhydrazine, $C_6H_5—NH—NH_2$

It is the most important substituted hydrazine.

Preparation. Phenylhydrazine may be prepared by the reduction of benzenediazonium chloride with stannous chloride and hydrochloric acid.

$$C_6H_5—\overset{+}{N}_2\overset{-}{Cl} + 4H \xrightarrow{SnCl_2/HCl} \underset{\text{phenylhydrazine hydrochloride}}{C_6H_5—NH—NH_2.HCl}$$

The phenylhydrazine is liberated from the resulting salt solution by adding an excess of NaOH solution.

$$C_6H_5—NH—NH_2.HCl + NaOH \longrightarrow \underset{\text{phenylhydrazine}}{C_6H_5—NH—NH_2} + NaCl + H_2O$$

The free base separates as a brown oil which is extracted with ether and dried over solid NaOH. Ether is removed by distillation and finally phenylhydrazine is purified under reduced pressure.

The reduction of benzenediazonium chloride is carried out industrially with sodium sulphite, when subsequent treatment with HCl and then NaOH yields phenylhydrazine.

$$\underset{\text{benzenediazonium chloride}}{C_6H_5—\overset{+}{N}_2\overset{-}{Cl}} + 4H \xrightarrow[100°]{Na_2SO_3} C_6H_5—NH—NH_2 \xrightarrow{HCl} C_6H_5—NH—NH_2HCl \xrightarrow{NaOH} \underset{\text{phenylhydrazine}}{C_6H_5—NH—NH_2}$$

Properties. Phenylhydrazine is a colourless oily liquid, bp 241°C. When freshly distilled, it has an unpleasant odour, suggestive of aniline, and quickly darkens on standing in air due to oxidation by air. It is very slightly soluble in water but dissolves readily in organic solvents. It is very poisonous and attacks skin. Its important reactions are listed below.

(1) *Basic Nature.* It is strongly basic in nature and forms well-defined salts *e.g.*,

$$C_6H_5—NH—NH_2 + HCl \longrightarrow \underset{\text{phenylhydrazonium chloride}}{C_6H_5—NH—\overset{+}{N}H_3\overset{-}{Cl}}$$

It is best kept as its salt, since these are relatively stable to atmospheric oxidation.

(2) *Reducing Nature.* It is a powerful reducing agent and reduces Fehling solution

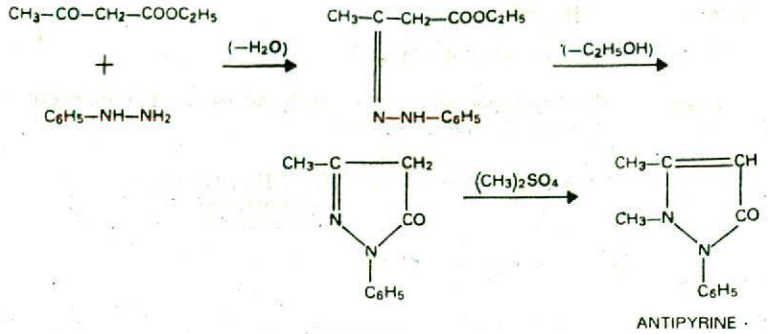
$$C_6H_5—NH—NH_2 + 2CuO \longrightarrow C_6H_6 + \underset{\text{red ppt}}{Cu_2O\downarrow} + N_2\uparrow + H_2O$$

(3) *Reduction to Aniline.* When reduced with a vigorous reducing agent *e.g.*, zinc and hydrochloric acid, phenylhydrazine yields aniline and ammonia.

$$C_6H_5—NH—NH_2 + 2H \xrightarrow{Zn/HCl} \underset{\text{aniline}}{C_6H_5—NH_2} + NH_3$$

(4) *Formation of Phenylhydrazones and Osazones.* It reacts with aldehydes and ketones to form phenylhydrazones. These derivatives are usually well-defined crystalline salts. With monosaccharides (glucose, fructose, mannose), it forms osazones. The formation of phenylhydrazones and osazones is used for characterisation of carbonyl compounds and simple sugars.

(5) *With Acetoacetic Ester.* When treated with acetoacetic ester followed by methylation, it gives antipyrene which is used in medicine as a febrifuge.



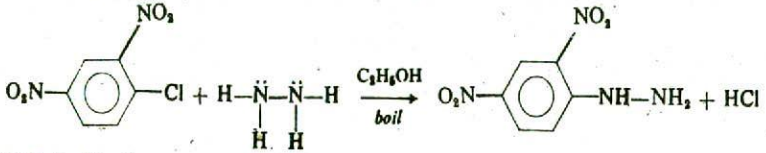
ANTIPYRINE

Uses. Phenylhydrazine is used: (1) as a mild oxidising agent ; (2) for making antipyrine and some important dyestuffs ; (3) as a reagent for the identification of aldehydes, ketones and sugars.

p-**Nitrophenylhydrazine,** $O_2N-C_6H_4-NH-NH_2$

It is prepared by reduction of the corresponding diazonium salt with sodium sulphite. It is used as a reagent in place of phenylhydrazine itself, since it ives derivatives with carbonyl compounds which crystallise readily..

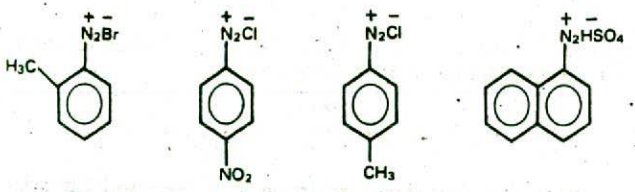
2,4-Dinitro- and *p*-bromophenylhydrazines are still better reagents for the identification of aldehydes and ketones. Of these 2,4-dinitrophenylhydrazine, which is most commonly used, may be prepared by the action of hydrazine and 2,4-dinitrochlorobenzene in boiling alcohol. Nucleophilic replacement of the chlorine atom takes place in this reaction.



2,4-dinitrochlorobenzene hydrazine

QUESTIONS

1. What are diazonium salts ? Write their general formula and assign names to the following structures.



2. Describe the general physical characteristics of aromatic diazonium salts. Why are they soluble in water and insoluble in nonpolar organic solvents ?

3. Discuss the orbital model of benzenediazonium chloride. How do you account for the stability of aryldiazonium salts as compared to their aliphatic counterparts.

4. State briefly the general methods of preparation of aryldiazonium salts, taking example of benzenediazonium chloride. Discuss the Cumene Process for the industrial production of this compound.

5. Discuss in detail the preparation of benzenediazonium chloride starting from aniline. Why is it not separated in solid state, and used as soon as produced in solution ?

6. Describe broadly the type of synthetic reactions shown by aromatic diazonium salts. Give the general mechanism of reactions in which $-N_2X$ is replaced by various nucleophiles.

7. Write a note on Sandmeyer Reaction. Give its mechanism.

8. How can you convert benzene into the following *via* the formation of diazonium salt ; (*i*) chlorobenzene ; (*ii*) fluorobenzene ; (*iii*) benzoic acid ; (*iv*) nitrobenzene ; (*v*) diphenyl ; and (*vi*) phenylhydrazine.

9. What do you understand by 'Coupling' of diazonium salts with phenols and amines. Mention two examples of the coupling reaction and discuss their mechanism.

10. Give the laboratory method of preparation, properties and uses of phenylhydrazine.

11. Describe the structure, preparation, and synthetic applications of benzenediazonium chloride.

(Bangalore BSc, 1993; Osmania BSc Hons, 1994 ; Bombay BSc, 1994)

12. Write a note on : Sandmeyer reaction. *(Madras BSc, 1994; Delhi BSc Hons, 1994)*

13. Write a note on : Coupling reactions. *(Pandicherry BSc, 1993)*

14. How will you synthesise : (*a*) *p*-Cresol (*p*-methylphenol) from toluene ; and (*b*) Iodobenzene from nitrobenzene.

(Panjab BSc, 1994)

Hint. (*a*) (*i*) HNO_3/H_2SO_4, (*ii*) Sn/HCl, (*iii*) $NaNO_2$/HCl/0-5°C, and (*iv*) H_2O/H^+; (*b*) (*i*) Sn/HCl. (*ii*) $NaNO_2$/HCl/0–5°C, and (*iii*) KI.

15. How will you synthesise :

(*a*) *p*-Toluidine from toluene ; and (*b*) Azobenzene from benzene. *(Gulbarga BSc, 1994)*

Hint. (*a*) (*i*) HNO_3/H_2SO_4, and (*ii*) Sn/HCl; (*b*) (*i*) HNO_3/H_2SO_4, (*ii*) Sn/HCl, (*iii*) $NaNO_2$/HCl/0-5°C, and (*iv*) C_6H_6

16. How will you synthesise :

(*a*) Biphenyl from aniline ; and (*b*) *m*-Dichlorobenzene from benzene. *(North Eastern Hill BSc Hons, 1994)*

Hint. (*a*) (*i*) $NaNO_2$/HCl/0-5°C, (*ii*) KI, and (*iii*) Na (Wurtz reaction); (*b*) (i) HNO_3/H_2SO_4/100°C, (*ii*) Sn/HCl, (*iii*) $NaNO_2$/HCl/0-5°C, and (*iv*) CuCl.

17. An amide (A), $C_{13}H_{11}NO$, was heated with aqueous sodium hydroxide. When cooled, the mixture consisted of two separate layers. The top oily layer contained compound (B), which was soluble in acid. The bottom layer on acidification gave a precipitate, (C). Treatment of (B) with cold nitrous acid produced a compound, (D), that formed a dye with phenol. Treatment of (C) with $SOCl_2$ followed by NH_3 produced (E) C_7H_7NO. When (E) was treated with alkaline NaOBr, compound (B) was formed. Write structures for (A) through (E) and give equations for all reactions.

Answer. (A) *is* *N*-phenylbenzamide; (B) *is* aniline; (C) *is* benzoic acid; (D) *is* benzenediazonium chloride; and (E) *is* benzamide.

Chapter 42

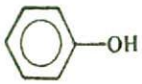
Phenols and Aromatic Alcohols

The hydroxy derivatives of aromatic hydrocarbons can be divided into two main classes :

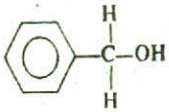
(*a*) *Phenols*, Ar—OH, in which the hydroxy group is directly attached to a carbon atom of the aromatic ring ; and

(*b*) *Aromatic alcohols*, Ar—CH_2—OH, in which the hydroxy group is attached to a carbon of a side-chain.

For illustration,



phenol
(OH directly attached to benzene ring)
A PHENOL



benzyl alcohol
(OH attached to benzene ring through a carbon of the side-chain)
AN AROMATIC ALCOHOL

While aromatic alcohols resemble closely with aliphatic alcohols, phenols differ from them considerably in the methods of preparation and in chemical behaviour. In fact, the two classes of compounds will be better studied separately.

PHENOLS

The class name 'phenol' is adopted from the name of the simplest member—the monohydroxybenzene (Gr. *phene* = benzene ; *ol* = OH). They are classified as *monohydric*, *dihydric*, and *trihydric* phenols according as they contain one, two or three hydroxy groups on the benzene ring.

Phenols, in general, occur in coal tar, wood tar and petroleum distillates. As a class they occupy an important position in the modern synthetic organic chemistry for the preparation of dyes, antioxidants, phenolic resins and certain pharmaceutical products. A number of commercial synthetic processes have been recently developed for the production of phenol to meet its increased requirements.

STRUCTURE

The orbital representation of phenols can be illustrated by taking example of 'the first member' of the class, C_6H_5OH. In fact, the orbital structure of phenol is similar to that of chlorobenzene which we have discussed earlier. It is made of an oxygen atom forming a σ bond with a hydrogen atom on one side and a carbon atom of the benzene ring. At the same time it has a *p* orbital with a nonbonded pair of electrons, which lies in a plane of the σ skeleton of the molecule.

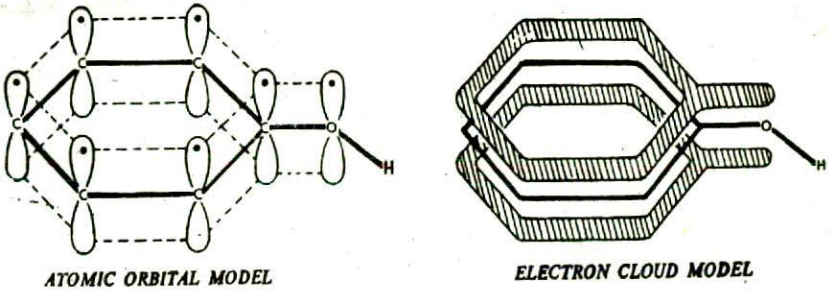
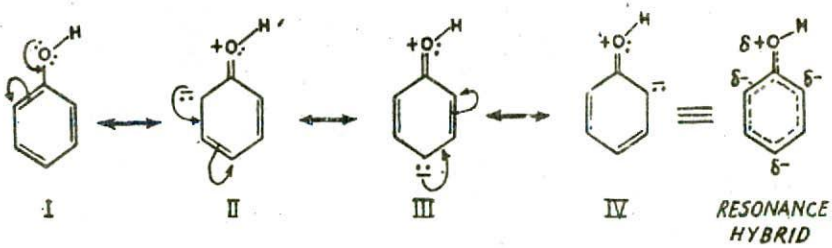


Fig. 42·1. Structure of phenol, C_6H_5OH.

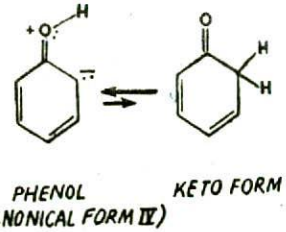
The *p* orbitals of the six carbons of the ring and the unused *p* orbital of the oxygen atom of OH group interact to form an extended delocalised orbital (Fig. 42·1). The extended π cloud now encompasses the oxygen atom in addition to the six carbons of the benzene ring. This delocalisation of the nonbonded electrons lends some double bond character to the C—O bond.

The electronic structure of phenol can be represented as a resonance hybrid of the following canonical forms.



This explains the activation of benzene ring as also the ortho-para directive influence of —OH group on the entering electrophiles.

Phenols could well be regarded as enols of special type. Thus it exists as a tautomeric mixture.



As shown by the actual bond energies of the two forms, the tautomeric mixture strongly favours the phenol, and only a very small amount of the keto form is present in the equilibrium mixture.

NOMENCLATURE

(1) Many phenols are known by distinctive trivial names. The hydroxy derivatives of toluene have been given the common name *Cresols*.

(2) Phenols are generally named as derivatives of the simplest member phenol. In doing so, the number 1 is assigned to the carbon bearing the OH group.

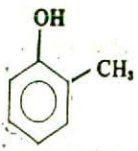
(3) When a phenolic moiety is included in a compound that is named by IUPAC system, the hydroxy group is specified as a substituent according to the order of precedence. In such a case a substituent (COOH or CHO) is assigned number 1.

The nomenclature of phenols including systematic and common names is illustrated by the following examples. The systematic names are followed by the common names.

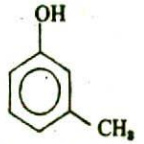
MONOHYDRIC PHENOLS :



phenol



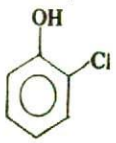
2-methylphenol,
1-hydroxy-2-methylbenzene,
o-cresol



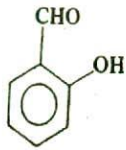
3-methylphenol,
1-hydroxy-3-methylbenzene,
m-cresol



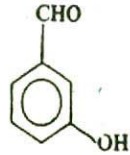
4-methylphenol,
1-hydroxy-4-methyl-
benzene,
p-cresol



2-chlorophenol,
2-chloro-1-hydroxy-
benzene

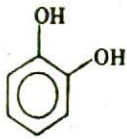


2-hydroxybenzaldehyde,
o-hydroxybenzaldehyde

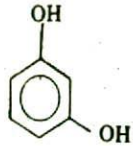


3-hydroxybenzoic acid,
m-hydroxybenzoic acid

DIHYDRIC PHENOLS :



1,2-dihydrozybenzene,
catechol

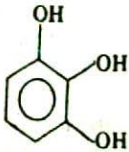


1,3-dihydroxybenzene,
resorcinol

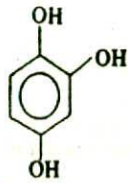


1,4-dihydroxybenzene,
hydroquinone

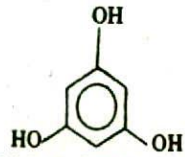
TRIHYDRIC PHENOLS :



1,2,3-trihydroxybenzene,
pyrogallol



1,2,4-trihydroxybenzene,
hydroxyquinone



1,3,5-trihydroxybenzene,
phloroglucinol

The prefixes *ortho*, *meta* and *para* are also often used in place of numbers 2, 3 and 4 while naming monohydric substituted phenols or hydroxytoluenes.

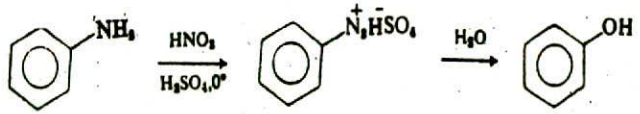
METHODS OF PREPARATION

The following general methods of synthesis of phenols are used for their laboratory preparation.

(1) **Hydrolysis of Diazonium Salts.** Phenols can be obtained by heating aqueous solutions of diazonium salts.

$$\underset{\substack{\text{aryldiazonium}\\ \text{hydrogen sulphate}}}{Ar{-}N_2HSO_4} + H_2O \xrightarrow{\Delta} \underset{\text{phenol}}{Ar{-}OH} + N_2 + H_2SO_4$$

Diazonium chlorides are not used as they lead to the formation of byproducts (*e.g.*, ArCl). For example, phenol is obtained from aniline as follows.



aniline — diazonium hydrogen sulphate — phenol

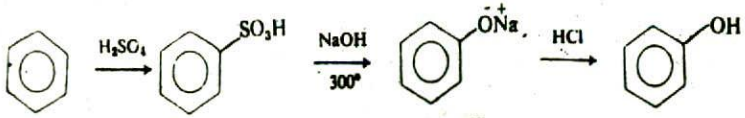
It is a valuable method for making phenols from aryl amines produced by nitration and reduction of arenes.

(2) **Alkali fusion of Sodium arenesulphonate.** Simple phenols are prepared conveniently by fusing sodium arenesulphonates with sodium hydroxide at about 300°C. A mixture of sodium phenoxide and sodium sulphite is produced from which phenol may be liberated by acidification.

$$\underset{\text{sod arenesulphonate}}{Ar{-}SO_3\overset{+}{N}a} + 2NaOH \longrightarrow \underset{\text{sod phenoxide}}{Ar{-}O\overset{+}{N}a} + Na_2SO_3 + H_2O$$

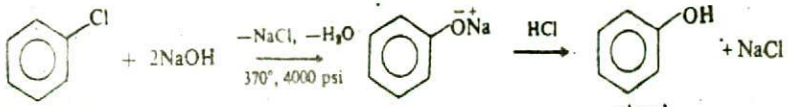
$$Ar{-}O\overset{+}{N}a + HCl \longrightarrow \underset{\text{phenol}}{Ar{-}OH} + NaCl$$

For example, phenol is synthesised from benzene as follows.



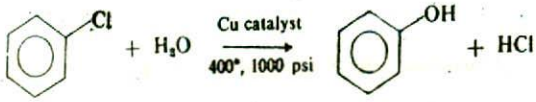
benzene — benzenesulphonic acid — sod phenoxide — phenol

(3) **Hydrolysis of Aryl halides.** Aryl halides yield phenol when hydrolysed with aqueous sodium hydroxide. For example, chlorobenzene is hydrolysed to phenol at high temperature and pressure by NaOH (*Dow's Process*).

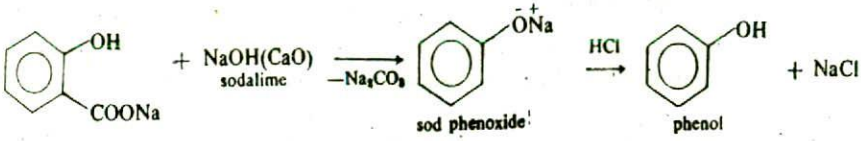


chlorobenzene — phenol

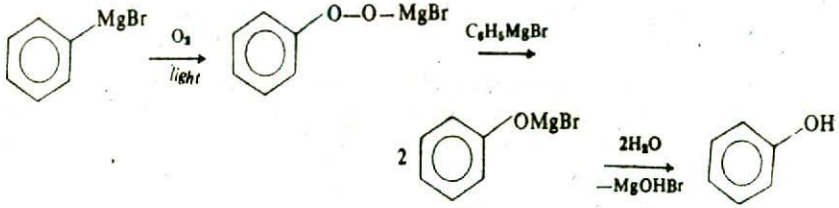
The above hydrolysis can also be effected by water in the presence of copper as catalyst.



(4) **Decarboxylation of Phenolic acids.** When phenolic acids are distilled with sodalime, they decarboxylate to form sodium phenoxide. This on acid hydrolysis gives phenol. Thus,



(5) **Oxidation of Grignard Reagent followed by hydrolysis.** An aryl Grignard reagent on treatment with oxygen in the presence of light, and subsequent hydrolysis of the product with mineral acid yields phenol in fair yield.



COMMERCIAL PREPARATION

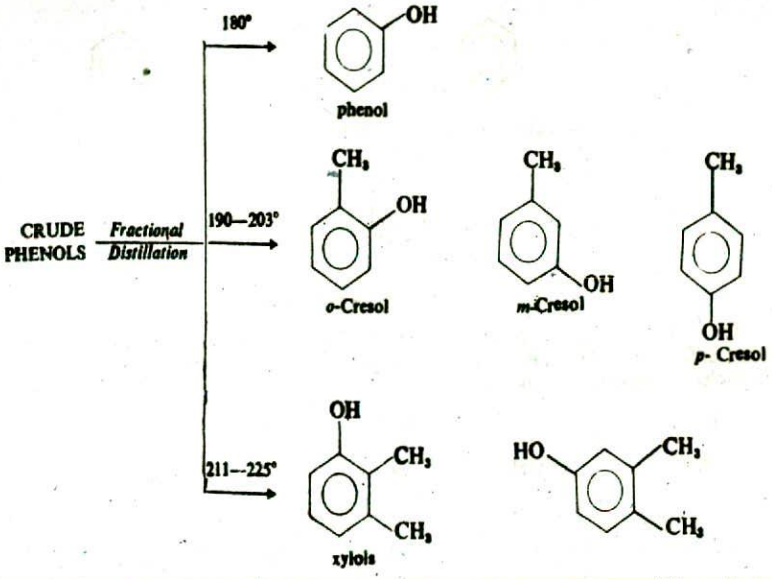
A certain amount of phenols are still obtained from coal-tar but most of them (over 90 %) are now produced industrially by synthetic methods. Besides the syntheses described before, special synthetic processes for preparing certain of these members from petroleum sources have been developed recently.

(1) **From Coal Tar.** Middle oil and Heavy oil fractions, which contain phenols and naphthalene, are subjected to excessive cooling. Napthalene crystals thus separated are removed by filter press. The remaining oil is treated with aqueous NaOH when phenols dissolve as phenoxides. Carbon dioxide is then blown through the solution to liberate phenols.

$$\underset{\text{phenols}}{Ar{-}OH} + NaOH \longrightarrow \underset{\text{sod phenoxide}}{Ar{-}\overset{-}{O}\overset{+}{Na}} + H_2O$$

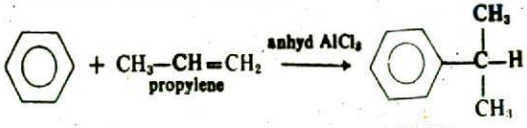
$$2\,Ar{-}\overset{-}{O}\overset{+}{Na} + CO_2 + H_2O \longrightarrow \underset{\text{phenol}}{2\,Ar{-}OH} + Na_2CO_3$$

The aqueous layer containing Na_2CO_3 is drawn off, leaving crude phenols behind. This is fractionated to recover the individual phenols.

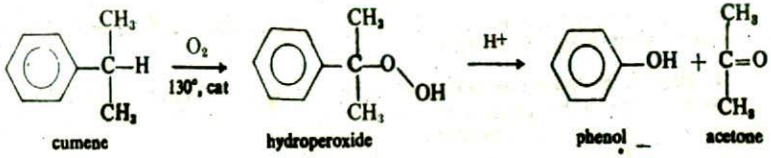


(2) **From Cumene derived from Petroleum.** The most recent commercial synthesis of phenol involves two steps :

(*a*) Preparation of isopropylbenzene or *cumene* from propylene and benzene, both derived from petroleum, by Friedel-Crafts Reaction.



(*b*) Cumene is then oxidised by oxygen at 130°C in the presence of a metal catalyst (or initiator) which yields cumene hydroperoxide. Treatment of the hydroperoxide with dilute sulphuric acid induces a molecular rearrangement, leading to phenol and acetone.



This method is assuming great importance as it provides two very useful commercial chemicals, phenol and acetone.

PHYSICAL PROPERTIES

(1) The simplest phenols are liquids or low-melting solids. They are colourless when pure but as usually seen they are red coloured owing to the presence of oxidation products.

(2) **Melting and Boiling Points.** Phenols have the same capabilities for hydrogen bond formation as aliphatic alcohols.

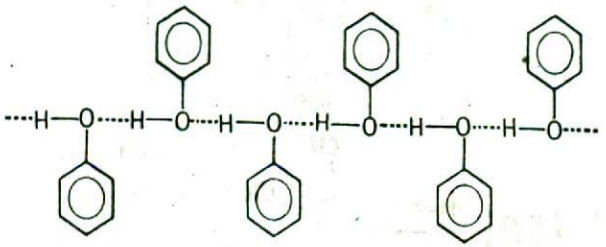
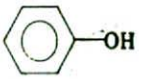
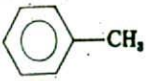


Fig. 42·2. Association among phenol molecules due to hydrogen bonding.

The capacity of intermolecular hydrogen bonding and high dipole moment are reflected in marked differences in their melting and boiling points compared to aryl hydrocarbons of compa able molecular weights. Thus,

	mol wt	*mp*	*bp*
Phenol, 	94	41°C	182°C
Toluene, 	92	−95°C	111°C

(3) **Solubility.** Phenols are generally water-soluble as they form hydrogen bonds with ater much in the same fashion as do aliphatic alcohols.

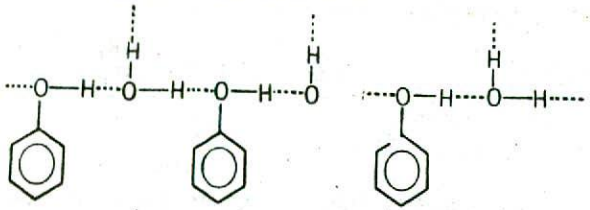
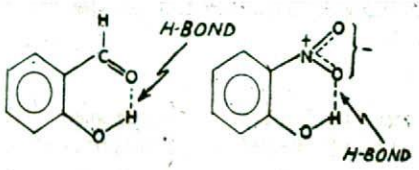


Fig. 42·3. Solubility of phenols in water is due to hydrogen bonding with water molecules.

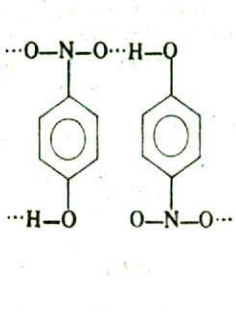
It is interesting to note that phenol, similar in molecular weight to hexanol, is much more soluble in water (9·3 g/100 ml H_2O).

(4) Effect of substituents on boiling points and solubility. When an aldehyde or a nitro group is present in the ortho position to the phenolic OH group, intramolecular hydrogen bonding occurs giving rise to a six-membered cyclic structure.

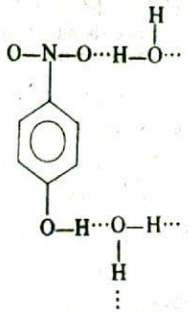


SALICYLALDEHYDE O-NITROPHENOL

Therefore, here the phenolic OH group is no longer available for intermolecular hydrogen bonding. Hence salicylaldehyde and nitrophenol exhibit lower boiling point and solubility compared to their meta and para isomers which are capable of forming intermolecular hydrogen bonding as also with water molecules.



Intermolecular hydrogen bonding in *p*-nitrophenol



Hydrogen bonding between *p*-nitrophenol and water molecules

(5) **Toxic Character.** Phenols are highly toxic and kill all types of cells. On account of their toxic effect on micro-organisms, phenols have antiseptic properties.

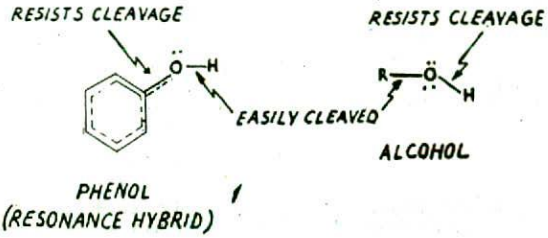
Table. Physical Properties of some Phenols

Name	*mp* °C	*bp* °C	*Solubility* g/100 H_2O at 25°C	*Acidity Constant* $K_a \times 10^{-10}$
Phenol	41	182	9·3	1·1
o-Cresol	31	191	2·5	0·63
m-Cresol	11	201	2·6	0·98
p-Cresol	35	202	2·3	0·67
Catechol	104	246	45	1
Hydroquinone	173	286	8	2
Resorcinol	110	281	123	3
Salicylaldehyde	—7	196·5	—	—
o-Chlorophenol	9	173	2·8	77
m-Chlorophenol	33	214	2·6	16
p-Chlorophenol	43	220	2·7	6·3
o-Nitrophenol	45	217	0·2	600
m-Nitrophenol	96	—	1·4	50
p-Nitrophenol	114	—	1·7	690
2,4,6-Trinitrophenol	122	—	1·4	very large

CHEMICAL PROPERTIES

Phenols and alcohols both are made of a carbon frame-work carrying a hydroxy group, but they differ significantly in their chemical reactions. This is attributed to the structural difference between the two classes of compounds.

As already discussed, a nonbonded electron pair of oxygen atom of the phenolic OH nteracts with the π system of the benzene ring and is delocalised. The delocalised electrons iow belong to all the six carbons of the ring as also to the oxygen atom. This delocalisation if nonbonded electrons caused by resonance is represented by the hybrid structure of phenol given below. As a result of delocalisation of electrons as shown in Fig. 42·1, the C—O bond acquires some double bond character and becomes stronger than O—H σ bond. Also, the increased electron density in the benzene ring activates it, and gives electrophilic substitution reactions.



In alcohols, no resonance is obviously possible and the nonbonded pairs of electrons remain localised on the oxygen atom. The C—O linkage thus retains its σ bond character and is weak as compared to that in phenols.

Thus, while alcohols give reactions in which OH group is replaced by other substituents (C—O cleavage), phenols do not do so normally. On the other hand, phenols are dissociated at the O—H bond and behave as weak acids, forming salts with alkalis. Alcohols do not form salts with alkalis.

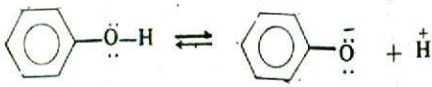
Now we proceed to discuss the general reactions of phenols (Ar—OH) under two main heads :

(*a*) *those involving the phenolic OH group* ; *and*

(*b*) *those involving the aromatic ring.*

A. REACTIONS INVOLVING —OH GROUP

(1) **Acid Character; Salt Formation.** The acidity of a compound is defined as its proton releasing ability in the presence of water : (Lewis base). Phenols behave as weak acids because they ionise when dissolved in water, to form phenoxide anions. Thus,

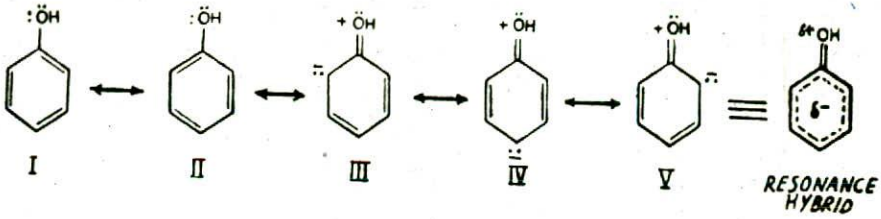


phenol phenoxide anionum

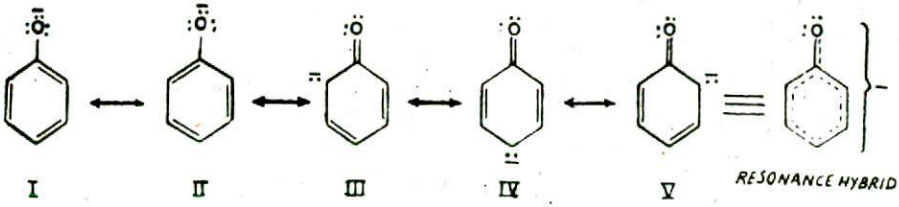
Phenols are markedly more acidic than alcohols, although less so than carboxylic acids. This is evident from the values of K_a given in the table.

Table: *K_a values at 25°C*	
Ethanol	$\sim 10^{-18}$
Phenol	$1{\cdot}3 \times 10^{-10}$
Acetic acid	$1{\cdot}8 \times 10^{-5}$

The ease with which a phenol releases a proton, is explained by the difference in the resonance stabilisation of the phenol and its phenoxide anion. As we know, phenol is a resonance hybrid of five forms.



The phenoxide anion also occurs in five resonance forms :

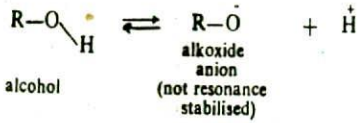


It may be noted that both phenol and phenoxide anion have two Kekule forms. In addition, they have three other charged forms each with the negative charge on the *ortho* and *para* position. In phenol these charged forms (III to V) contribute much less to the hybrid than do Kekule forms (I and II). This is so because charge separation costs energy and high-energy forms cannot stabilise the hybrid much. The resonance forms of the phenoxide ion in which the charge is in the ring, however, acquire no charge separation. The charge is only delocalised. Hence these forms (III to V) stabilise the phenoxide anion very much. Thus relatively the resonance hybrid of phenoxide anion is much more stable than the resonance hybrid of phenol itself.



Since phenoxide anion hybrid is more stable than the phenol hybrid, the equilibrium is displaced to the right, releasing H^+ ions. This explains why phenols can behave as acids.

Alcohols, on the other hand, are 'neutral' in the sense that their acidity ($K_a = \sim 10^{-18}$) is no more than that of water ($K_a = 10^{-14}$). This is understandable because the formation of alkoxide anion is not favoured as it is not resonance stabilised.



Considering from another view point, ionisation of both phenol and alcohol requires energy. But the ionisation of phenol would require smaller energy (ΔE_1) owing to resonance stabilisation of phenoxide anion, than the ionisation of alcohol (ΔE_1) as the alkoxy anion is not resonance stabilised. This is why the ionisation of phenol is favoured greatly as compared to that of phenols. Or that, phenol is much more acidic than alcohols.

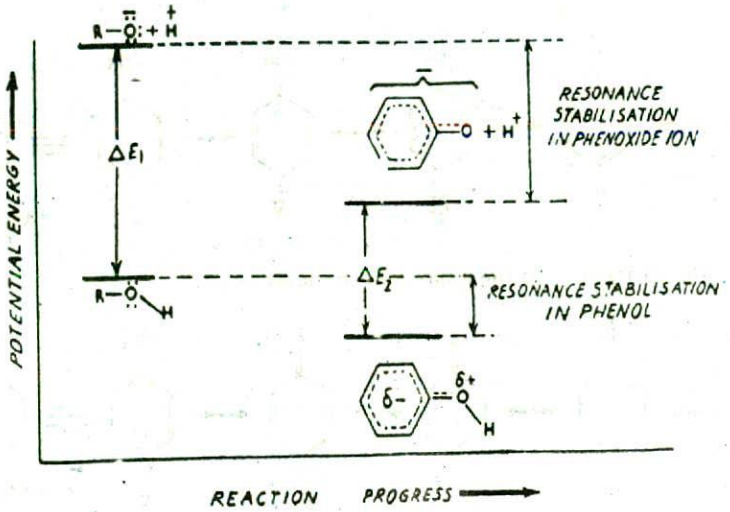


Fig. 42·4. Ionization energy of phenol is less than that of alcohol ($\Delta E_2 > \Delta E_1$) due to resonance stabilisation in phenol and phenoxide, favouring the former reaction.

Effect of Substituents on the Acidity of Phenols. We have already discussed that the acidity of a phenol is determined by the stability of the phenoxide anion it produces. An electron releasing substituent 'A' (say CH_3) pumps electrons into the benzene system and intensifies the negative charge of the phenoxide anion. This makes the anion less stable, thereby decreasing the acidity of phenol. On the other hand, an electron withdrawing substituent 'B' (X, NO_2, CHO, COOH), withdraws electrons from the ring system which results in the dispersal of the negative charge of the phenoxide anion. This stabilises the phenoxide anion and, therefore, the acidity of phenol is increased. The two situations are illustrated below.

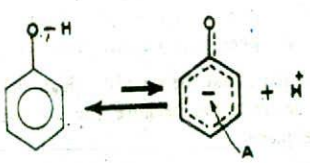


Fig. 42·5. 'A' pumps electrons into the ring, strengthens the negative charge on phenoxide anion and destabilises it, decreasing acidity of phenol.

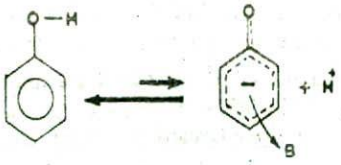
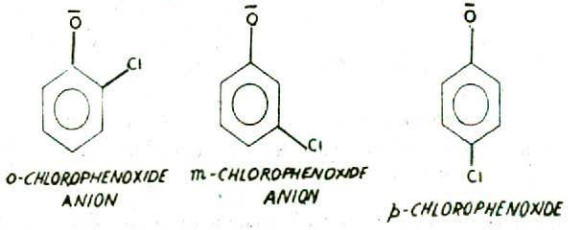


Fig. 42·6. 'B' withdraws electrons from the ring, thereby decreasing the negative charge of phenoxide anion and stabilising it, which enhances the acidity of phenol.

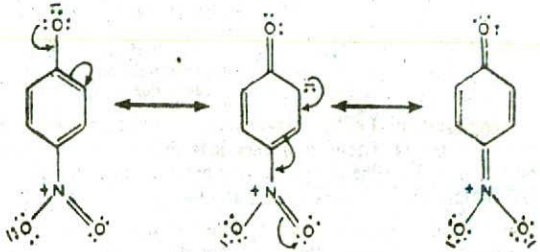
This explains why methylbenzenes are less acidic than phenol, while chlorophenols are more acidic than phenol.

The intensification of the negative charge on the isomeric chlorophenoxide anions will depend on the distance of the electron pumping group from the $-O^-$ group.

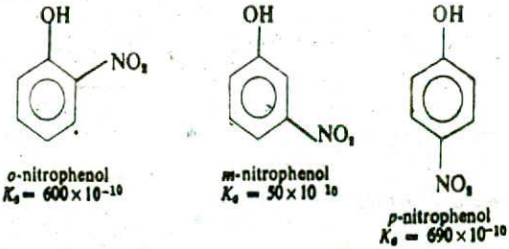


That is why the values of K_a for the isomeric chlorophenols follow the order: K_a *ortho* > K_a *meta* > K_a *para*.

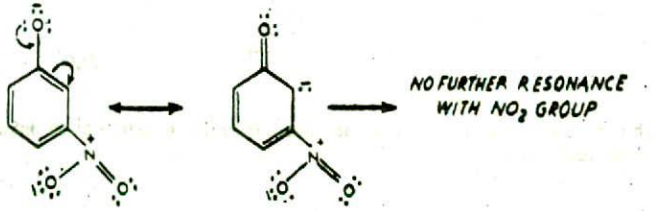
A substituent such as the $-NO_2$ group, when present at ortho or para to the $-OH$ group, withdraws electrons from the benzene ring system by inductive and resonance effects. This stabilises the phenoxide anion by dispersal of the negative charge as shown below in case of *p*-nitrophenol.



Therefore, nitrophenols are much more acidic than phenol.



The marked lower acidity in case of meta isomer is explained by the fact that *m*-nitrophenoxide anion is stabilised by inductive effect only and no resonance effect operates with $-NO_2$ group (absence of conjugate system).



The cumulative effect of three $-NO_2$ groups in 2,4,6-trinitrophenol (picric acid) makes it as strongly acidic as mineral acids.

Salt Formation. Phenols dissolve in aqueous NaOH or KOH (but not Na_2CO_3) to form soluble sodium salts known as phenoxides.



phenol sod phenoxide

Phenol can be regenerated by acidification of the resulting solution either by a mineral acid or by blowing carbon dioxide through it (phenol is a weaker acid than carbonic acid). This sequence of reactions may be used for the separation of phenols from mixtures of organic substances. The nonreactivity of phenols with sodium carbonate may be made use for the separation of mixtures of phenols and carboxylic acids. Like alcohols, phenols also react with alkali metals, Grignard reagents and lithium aluminium hydride, to form the respective alkoxides.

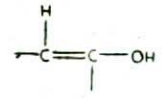
$$C_6H_5OH + Na \longrightarrow \underset{\text{sod phenoxide}}{C_6H_5ONa} + \tfrac{1}{2}H_2$$

$$C_6H_5OH + CH_3MgI \longrightarrow \underset{\substack{\text{magnesium}\\ \text{phenoxy iodide}}}{C_6H_5OMgI} + CH_4$$

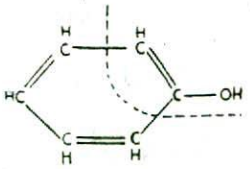
$$4C_6H_5OH + LiAlH_4 \longrightarrow \underset{\substack{\text{lithium aluminium}\\ \text{phenoxide}}}{LiAl(OC_6H_5)_4} + 4H_2$$

(2) **Coloured Complexes with $FeCl_3$.** Phenols form coloured iron complexes when treated with neutral ferric chloride solution. These complexes have characteristic colours and this reaction is often used as a test for phenols. Phenol gives *violet* colouration ; resorcinol, *violet* ; catechol, *green* ; pyrogallol, *red* ; phloroglucinol, *dark violet* ; and so on.

The formation of the iron complexes is attributed to the existence of keto-enol tautomerism in phenols as already mentioned. Since a phenol is mostly in the enol form, it forms coloured complexes with ferric chloride — a character associated with compounds containing enolic structure.

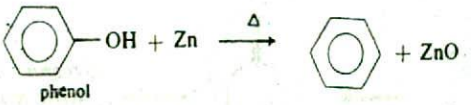


ENOLIC STRUCTURE



PHENOL CONTAINING ENOLIC STRUCTURE

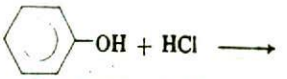
(3) **Replacement of OH by H.** When a phenol is distilled with zinc dust, the —OH function is replaced by a hydrogen atom. Zinc removes the oxygen of the phenolic group as zinc oxide, to yield the parent hydrocarbon.



phenol

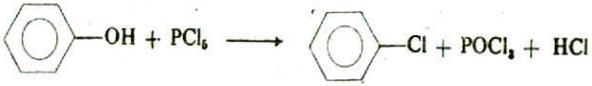
This reaction is useful in getting the first clue to the structure of an unknown complex phenolic compound.

(4) **Replacement of OH by Halogens.** Unlike alcohols, phenolic OH cannot be replaced by halogen by reaction with hydrogen halides.



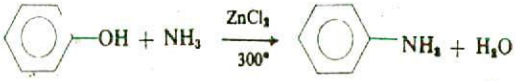
(*Cf.* $C_2H_5OH + HCl \longrightarrow C_2H_5Cl + H_2O$)

However, PCl_5 or PBr_5 reacts with phenols to form aryl halides.



The yield is very poor owing to the main reaction of phenol with PCl_5 to form esters of phosphoric acid *e.g.*, $(C_6H_5)_3PO_4$. Phosphorus trichloride reacts with phenol to form only the ester of phosphorus acid, $(C_6H_5)_3PO_3$, and no aryl chloride is obtained.

(5) **Replacement of OH by NH_2 function.** The replacement of phenolic OH by amino function can be brought about by heating a phenol with ammonia in presence of zinc chloride



phenol aniline

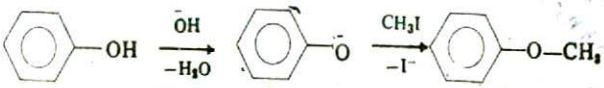
Polyhydric phenols undergo the reaction even more readily.

(6) **Ether Formation.** Phenols form ethers easily by reaction of sodium phenoxide with alkyl halides (*Williamson Synthesis*). The phenoxide ion is nucleophilic and will displace the halogen from an alkyl halide, giving a mixed alkyl aryl ether.



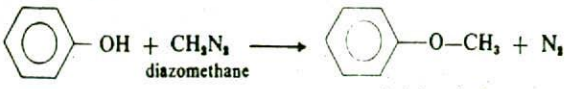
sod phenoxide alkyl aryl ether

Sodium phenoxide is obtained easily by dissolving phenol in aqueous NaOH solution, *e.g.*,

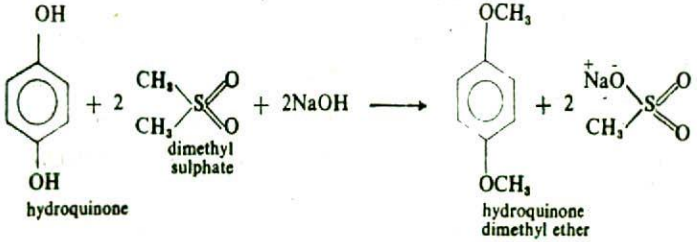


phenol phenoxide anion (*nucleophile*) anisole, methyl phenyl ether

Unlike alcohols, phenols can also be alkylated by reagents such as diazomethane and dimethyl sulphate in alkali solution.

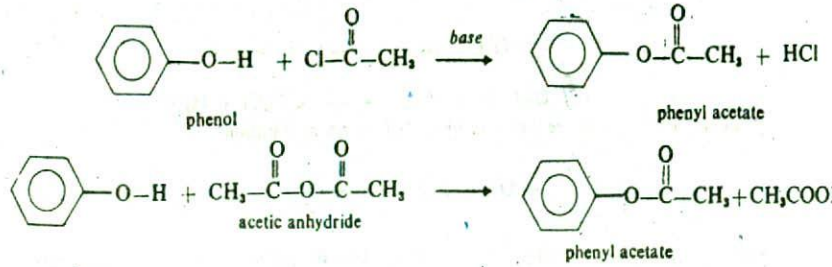


diazomethane methyl phenyl ether



hydroquinone dimethyl sulphate hydroquinone dimethyl ether

(7) **Esterification.** Phenols react with acyl halides or anhydrides to form esters, in presence of a base (NaOH or pyridine).



Unlike alcohols, phenols are not directly esterified by reaction with a carboxylic acid in presence of mineral acid catalyst. This is attributed to a lesser nucleophilic oxygen of the phenol compared to that of alcohol (*See reactions of carboxylic acids*).

B. REACTIONS INVOLVING THE BENZENE RING

(1) **Direct Electrophilic Substitution.** As previously discussed, the delocalisation of a nonbonding electron pair of OH function into the benzene ring system activates it to electrophilic (E) attack. Further the points of attack are the ortho and para position to OH, since a negative charge is placed here due to resonance. This is illustrated by the resonance hybrid structure shown below.

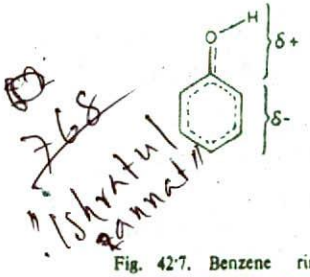


Fig. 42·7. Benzene ring in phenol activated by increase of overall electron density by delocalisation of nonbonding electron pair.

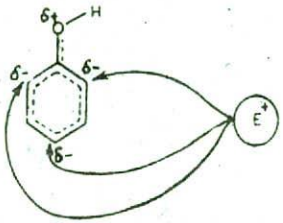
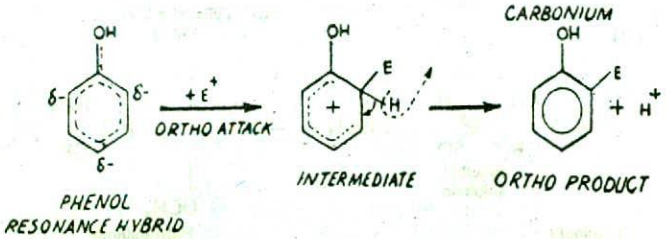
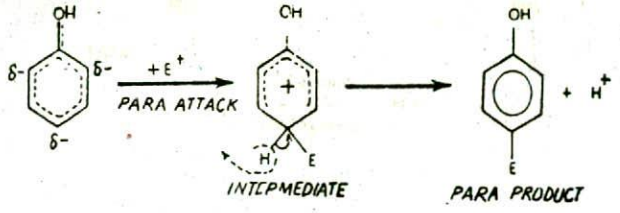


Fig. 42·8. Electrophile (E^+) attacks at ortho and para positions which being electron rich bear a negative charge (δ^-)

Thus phenols readily undergo electrophilic reactions and the OH function directs them to ortho and para positions.

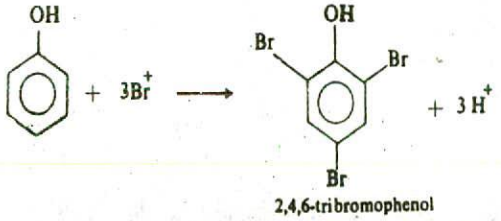




(*i*) HALOGENATION. The —OH group on the benzene ring is a very powerful activator and special precautions are necessary to check polysubstitution in the ring.

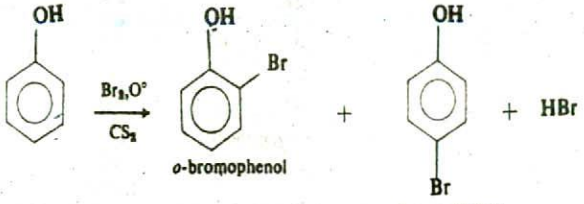
Phenol when treated with excess of aqueous bromine solution yields 2,4,6-tribromophenol straightway.

$$Br_2 + Br_2 \rightleftharpoons Br^+ + Br_2^-$$



2,4,6-tribromophenol

However, bromination may be limited to monobromination stage by using calculated amount (1 mole) of bromine dissolved in less polar solvent such as CS_2 or $CHCl_3$. Thus,

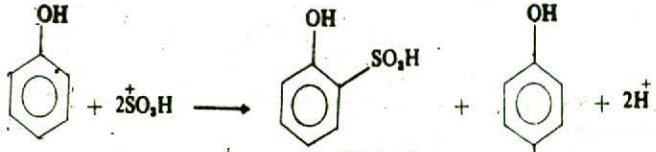


o-bromophenol

p-bromophenol

(*ii*) SULPHONATION. Phenols are readily sulphonated with conc. H_2SO_4. Here $\overset{+}{S}O_3H$ is the electrophile.

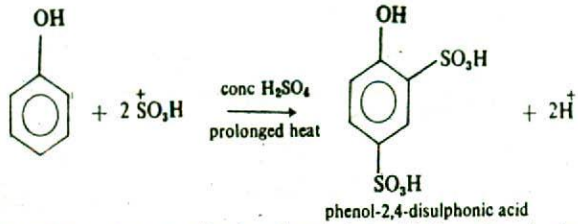
$$H_2SO_4 + H_2SO_4 \rightleftharpoons \overset{+}{S}O_3H + HSO_4^- + H_2O$$



o-phenolsulphonic acid

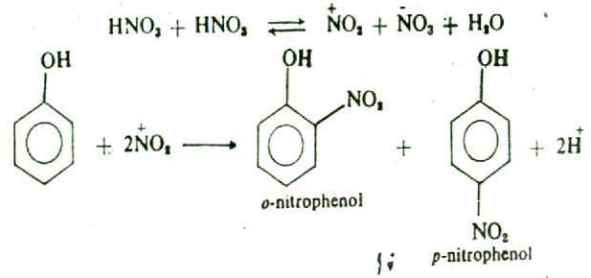
p-phenolsulphonic acid

If sulphonation is carried at room temperature, ortho isomer is the chief product, while at 100°C the para isomer. On prolonged heating with concentrated sulphuric acid, another —SO_3H group is introduced in meta position to the previous one.

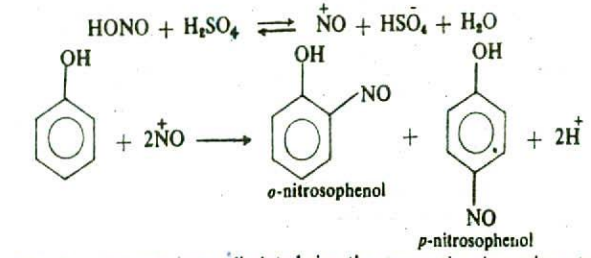


phenol-2,4-disulphonic acid

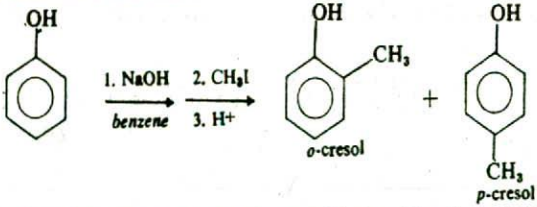
(*iii*) NITRATION. Benzene ring in phenols being highly activated, phenols undergo nitration with dilute nitric acid. $\overset{+}{N}O_2$ (nitronium ion) is the electrophile.



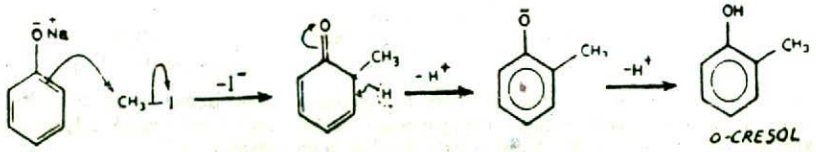
(*iv*) NITROSATION. Here the electrophile is nitrosonium ion, $\overset{+}{N}O$.



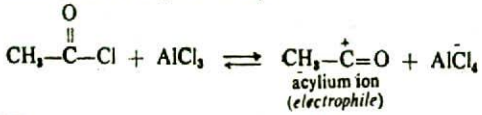
(2) Alkylation. Phenols are alkylated in the aromatic ring when treated with alkyl halides, alkali solution, and acidified.

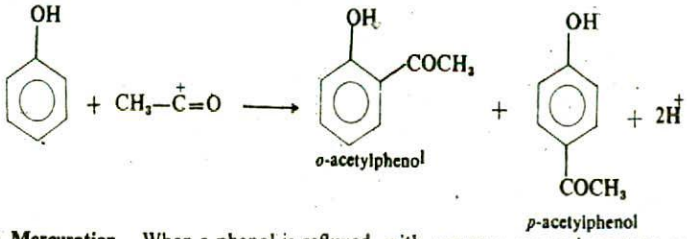


MECHANISM. NaOH solution reacts with phenol to give sod phenoxide which reacts with methyl iodide.

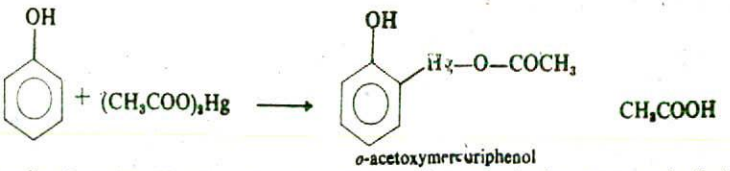


(3) **Acylation.** Phenols react with aryl chlorides in the presence of $AlCl_3$ to form ortho and para acylphenols (*Friedel-Craft Reaction*).

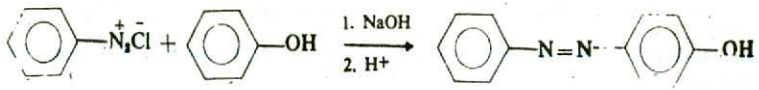




(4) **Mercuration.** When a phenol is refluxed with aqueous mercuric acetate, *o*-acetoxymercuriphenol is obtained.



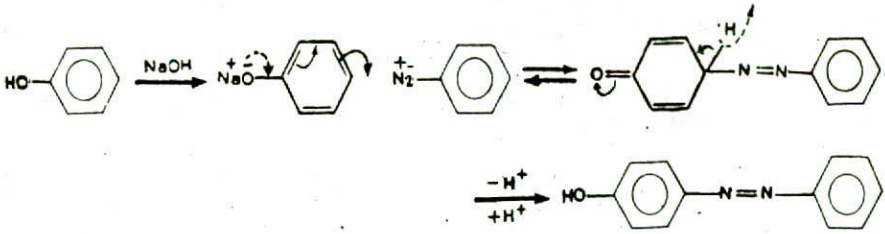
(5) **Coupling Reaction.** Phenol reacts with aryldiazonium salts in the presence of alkali to form azo compounds. Thus :



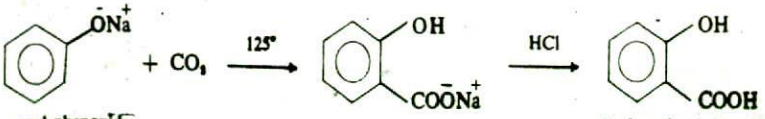
phenyldiazonium chloride — phenol — *p*-hydroxyazobenzene (*dye*)

This reaction is referred to as *Coupling Reaction* and is used extensively for the synthesis of dyes.

MECHANISM. It is a typical example of electrophilic substitution on an aromatic ring activated by —OH group in the para position.

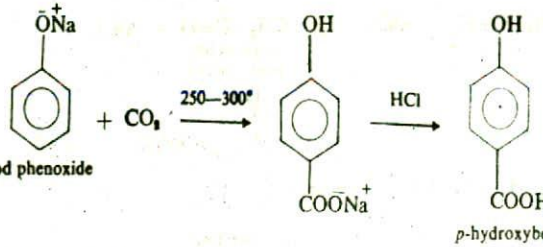


(6) **Kolbe's Reaction.** On passing carbon dioxide over sodium phenoxide at 125°, COOH is directly introduced into the aromatic ring in ortho position to OH. Thus :



sod phenoxide — *o*-hydroxybenzoic acid (salicylic acid)

If the carbonation of sodium phenoxide is carried at 250—300°C, *p*-carboxylation product is obtained.

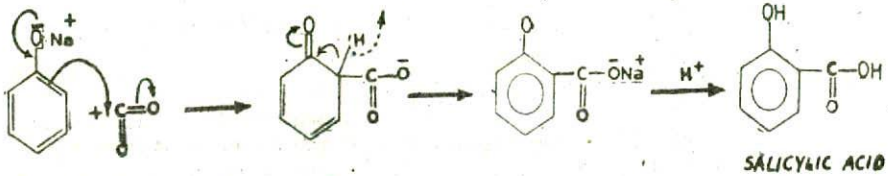


sod phenoxide

p-hydroxybenzoic acid

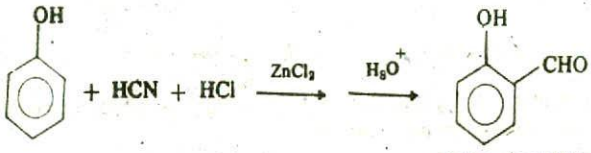
This reaction involving the carbonation of phenols to give phenolic acids is named as *Kalbe's Reaction*.

MECHANISM. Carbon dioxide ($\overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$) acts as a weak electrophile and brings about electrophilic substitution by usual mechanism.



SALICYLIC ACID

(7) **Gattermann Reaction ; Formylation.** When a phenol is treated with a mixture of hydrogen cyanide, hydrogen chloride and zinc chloride catalyst, an aldehyde (or formyl, —CH=O) group is introduced in the ortho position to OH. Thus, phenol yields *o*-hydroxybenzaldehyde.



o-hydroxybenzaldehyde

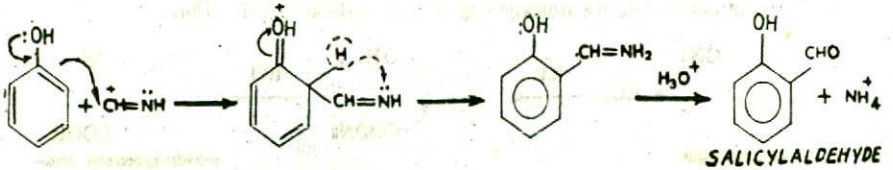
This reation known as *Gattermann Reaction* is a general one and is used for formylation of aromatic rings to which an electron withdrawing group (—OH , —OCH_3, etc) is attached.

MECHANISM. The electrophile $\overset{+}{H}C=NH$ is derived from formiminochloride, and the electrophilic substitution takes place by the usual mechanism.



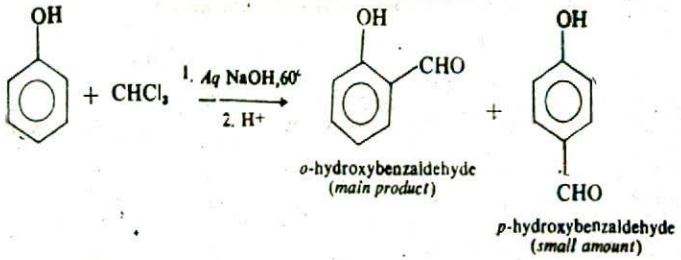
formiminochloride





SALICYLALDEHYDE

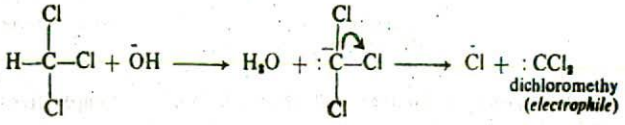
(8) **Reimer-Tiemann Reaction.** The treatment of a phenol with chloform ($CHCl_3$) and aqueous NaOH at 60°C, followed by acidification, introduces a —CHO group in the aromatic ring mainly in the ortho position to OH group. For example,



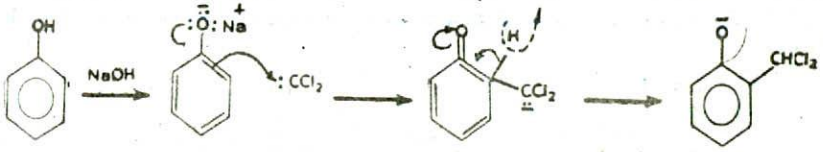
This reaction known as *Reimer-Tiemann Reaction* is employed for preparing phenolic aldehydes.

MECHANISM. The reaction is believed to proceed by the following steps :

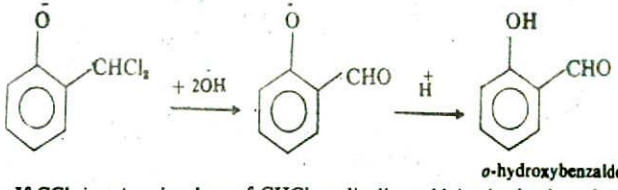
(*i*) Formation of dichloromethylene (dichlorocarbene) from chloroform



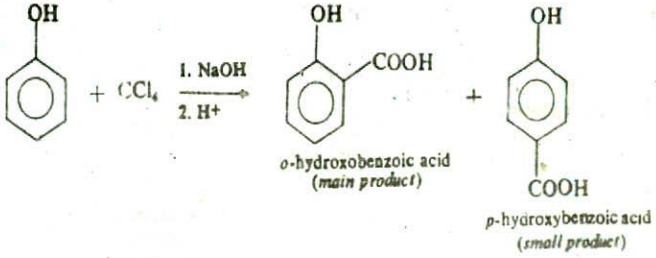
(*ii*) Electrophilic substitution in the phenol ring



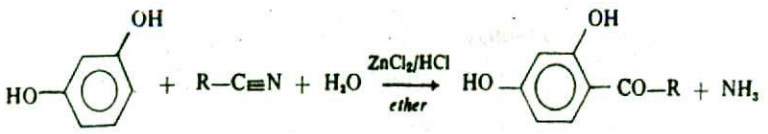
(*iii*) Hydrolysis and acidification



If CCl_4 is taken in place of $CHCl_3$, salicylic acid is obtained, ortho derivative being the main product.

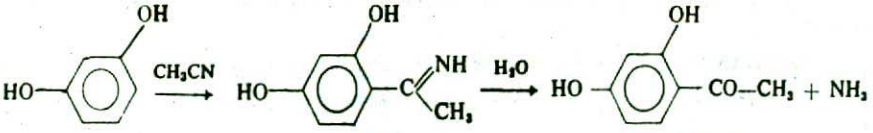


(9) **Houben-Hoesch Reaction.** Highly reactive polyhydric phenols in which OH groups are *meta* to one another, may be acylated when treated with alkyl cyanides in the presence of zinc chloride and hydrogen chloride. The product is a phenolic ketone.



resorcinol phenolic ketone

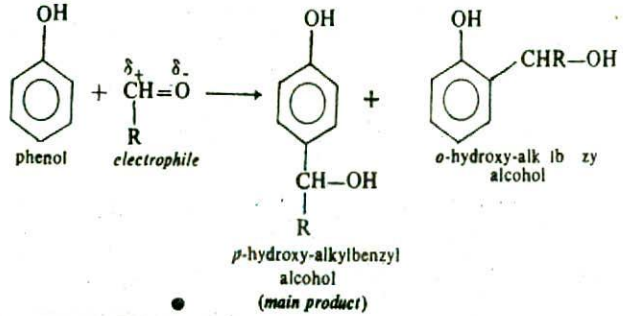
For example,



ketimine (*intermediate*) resacetophenone

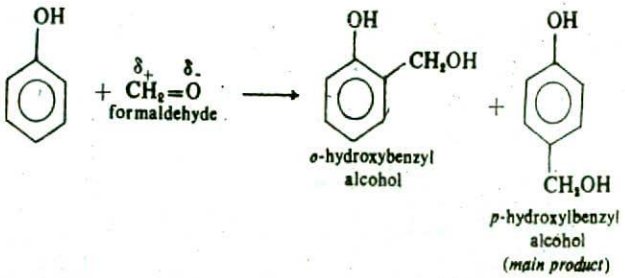
This reaction given by Houben and Hoesch in 1927, is named after them. Phenol does not respond to Hauben-Hoesch Reaction.

(10) **Condensation with Aldehydes.** Phenols undergo condensation with aldehydes by electrophilic substitution in ortho and para positions in presence of acids or alkalis as catalyst.



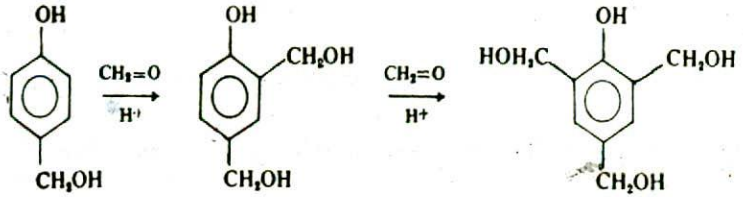
phenol *electrophile* *p*-hydroxy-alkylbenzyl alcohol (*main product*) *o*-hydroxy-alk lb zy alcohol

Formaldehyde undergoes such condensation to give *o*- and *p*-hydroxybenzyl alcohols.



o-hydroxybenzyl alcohol *p*-hydroxylbenzyl alcohol (*main product*)

This reaction is known as **Lederer-Manasse Reaction**. If the reaction mixture contains excess of formaldehyde disubstitution and trisubstitution occurs. Thus,



p-hydroxybenzyl alcohol — 2,4-dihydroxymethyl-phenol — 2,4,6-trihydroxymethyl-phenol

Intermolecular condensation of these hydroxymethylphenols leads to the formation of a high molecular weight and highly cross-linked polymer, known as formaldehyde resin or **Bakelite.**

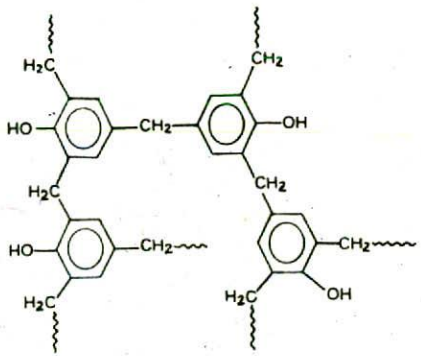
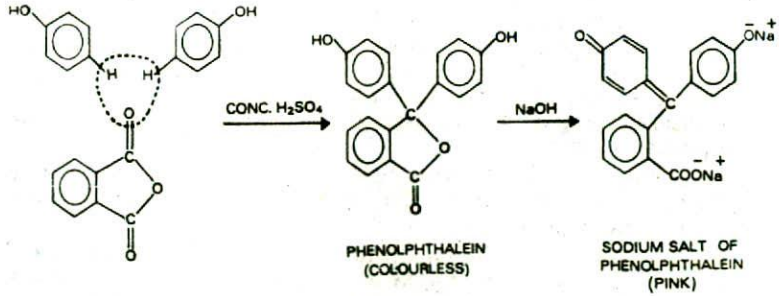


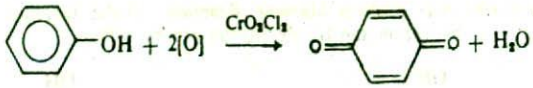
Fig. 42·9. Phenol-formaldehyde resin (*Bakelite*).

(11) **Condensation with Phthalic anhydride.** Many phenols undergo condensation with phthalic anhydride to give useful products. Thus phenol when heated with H_2SO_4 gives phenolphthalein, a colourless compound which produces beautiful pink colour with alkali solutions due to formation of coloured sodium salt.



Phenolphthalein is a popular indicator for acid-alkali titrations.

(12) **Oxidation.** Phenol is easily oxidised without disruption of its carbon skeleton to form *p*-benzoquinone.



phenol p-benzoquinone

Similarly hydroquinone on oxidation with silver salts yields *p*-benzoquinone.



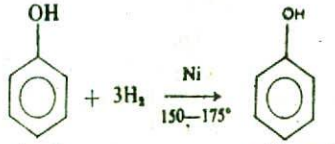
hydroquinone p-benzoquinone

This reaction leads to the use of hydroquinone as a photographic developer.

The ready oxidation of phenols is explained by the fact that the presence of —OH group on the ring, furnishes electrons to the ring which is thus rendered susceptible to oxidation, especially in alkaline medium.

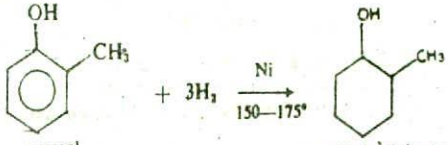
With a drastic oxidising agent such as alkaline $KMnO_4$, the aromatic ring of phenol cleaves to form tartaric acid, oxalic acid and carbon dioxide.

(13) **Reduction.** The —OH group is stable, and the catalytic reduction of phenol yields cyclohexanol.



phenol cyclohexanol

Substituted phenols would similarly form substituted cyclohexanols.



o-cresol *o*-methylcyclohexanol

IDENTIFICATION OF PHENOLS

(1) **Solubility Test.** If the substance is more soluble in NaOH solution than in water, but insoluble in sodium bicarbonate, it is probably a phenol.

(2) **Ferric Chloride Test.** To the aqueous or ethanolic solution of the substance, add a few drops of neutral $FeCl_3$ solution. The appearance of an intense colour—*red*, *green* or *black* —confirms the presence of a phenol.

(3) **Bromine Water Test.** Bromine water is added to aqueous solution of the substance until the yellow colour of bromine persists. The formation of a precipitate (*substitution product*) confirms the presence of a phenol.

(4) **Libermann's Test.** The substance is warmed with a little concentrated sulphuric acid and sodium nitrate. The dark-coloured product so obtained is treated with dilute NaOH solution. The production of intense blue or green colour confirms the presence of a phenol.

(5) **Spectral Analysis.** While alcohols are almost transparent in the ultraviolet spectrum, phenols have moderately strong absorption, arising from the benzene ring. Thus phenol has a band at 210 nm (ϵ 6200).

The infrared absorption region of phenolic hydroxy group (O—H stretch) is the same as that for alcohols (3600 cm^{-1}). In addition a C—O stretching absorption is also characteristic of hydroxy containing compounds. In phenols it occurs near 1200 cm^{-1} and in alcohols at 1100 ± 50 cm^{-1}. The benzene nucleus is identified by its own absorption spectrum. However there are complications due to intermolecular hydrogen bonding, or intramolecular hydrogen bonding in various ortho derivatives.

MONOHYDRIC MEMBERS

PHENOL, CARBOLIC ACID, *Hydroxybenzene*

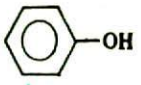
It was discovered by Runge in 1834 in coal-tar. He named it *carbolic acid* (*carb*=coal; *oleum*=oil). It is also present in *wood-tar*.

Phenol may be prepared by any of the general methods. As already described, it is still obtained commercially from coal-tar *Middle oil* and *Heavy oil* fractions. But over 90 per cent of phenol is now prepared by synthetic methods of which the most important and recent one is from *cumene* derived from petroleum.

Properties. (*Physical*). Phenol is a colourless crystalline solid, mp 41°C, bp 182°C, having characteristic odour. It turns pink when exposed to air and light. It is sparingly soluble in water but dissolves readily in ethanol and other organic solvents. It is a violent poison when taken orally, and produces painful blisters in contact with skin. Phenol is rarely used as an antiseptic because of its extreme toxic character.

(*Chemical*). The reactions of phenol have been discussed in detail under the general properties of this class of compounds. However, a resume of these reactions, which are in fact the reactions of the hydroxy group and the phenyl group will be given here by way of recapitulation.

REACTIONS OF –OH GROUP:



phenol

$$+ \overset{+}{Na}\overset{-}{OH} \xrightarrow{water} \underset{\text{sod phenoxide}}{C_6H_5-\overset{-}{O}\overset{+}{Na}} + H_2O$$

$$+ FeCl_3 \longrightarrow \textit{Coloured complex; violet colouration}$$

$$+ Zn \xrightarrow{\Delta} \underset{\text{benzene}}{C_6H_6}$$

$$+ PCl_5 \longrightarrow \underset{\text{chlorobenzene}}{C_6H_5-Cl} + POCl_3 + HCl$$

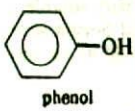
$$+ NH_3 \xrightarrow[\Delta]{ZnCl_2} \underset{\text{aniline}}{C_6H_5-NH_2} + H_2O$$

$$+ NaOH \longrightarrow \underset{\substack{\text{sodium}\\\text{phenoxide}}}{C_6H_5\overset{-}{O}\overset{+}{Na}} \xrightarrow{CH_3I} \underset{\text{anisole}}{C_6H_5-O-CH_3}$$

$$+ CH_2N_2 \longrightarrow \underset{\text{anisole}}{C_6H_5-O-CH_3} + N_2$$

$$+ CH_3COCl \longrightarrow \underset{\text{phenyl acetate}}{C_6H_5-O-CO-CH_3} + HCl$$

REACTIONS INVOLVING BENZENE RING :



phenol

+ *aq* $3Br_2$ ⟶ 2,4,6-tribromophenol + 3HBr (*Bromination*)

+ conc H_2SO_4 ⟶ phenol-2,4-disulphonic acid (*Sulphonation*)

+ dil HNO_3 ⟶ *o*-nitrophenol + *p*-nitropheno (*Nitration*)

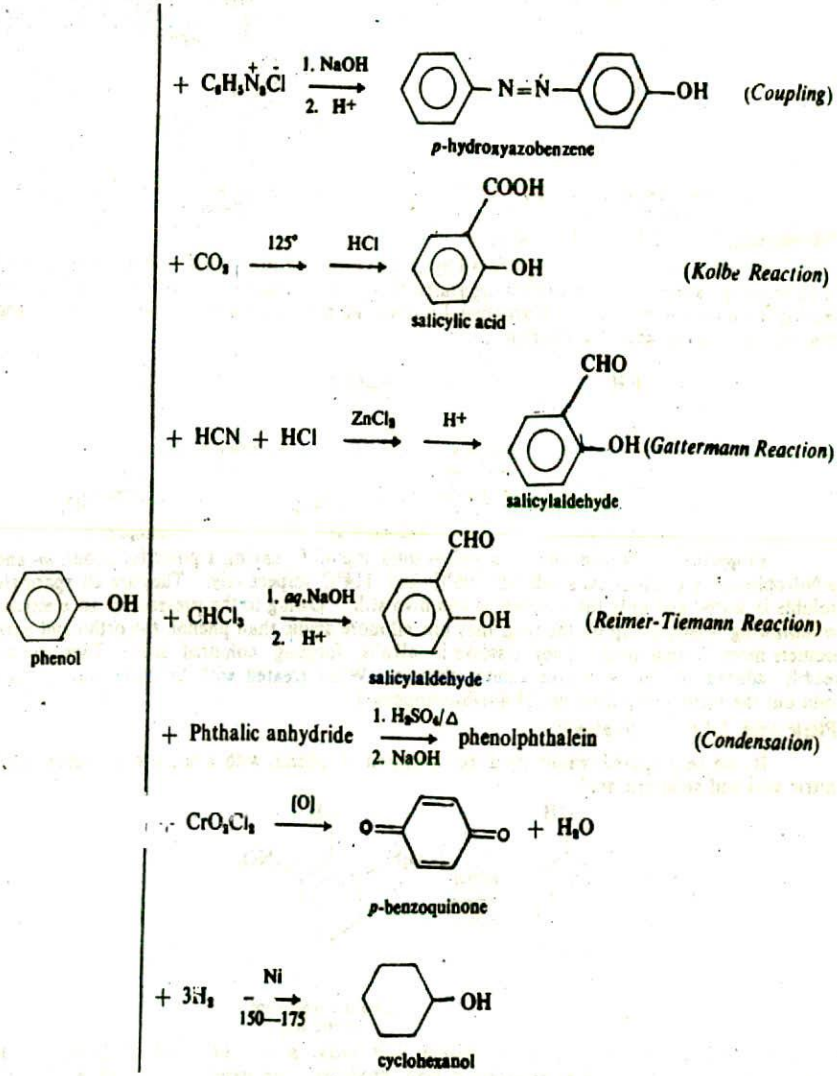
+ HONO $\xrightarrow{H_2SO_4}$ *o*-nitrosophenol + *p*-nitrosophenol (*Nitrosation*)

+ NaCH $\xrightarrow{CH_3I}$ *o*-cresol + *p*-cresol (*Methylation*)

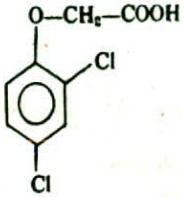
+ CH_3COCl ⟶ *o*-acetylphenol + *p*-acetylphenol (*Acetylation*)

+ $(CH_3COO)_2Hg$ ⟶ *o*-acetoxymercuriphenol + CH_3COOH (*Mercuration*)

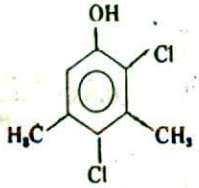
+ $CH_2=O$ ⟶ *p*-hydroxybenzyl alcohol $\xrightarrow[(excess)]{CH_2=O}$ *BAKELITE*



Uses. Phenol has a number of commercial uses : (1) in the manufacture of phenol-formaldehyde plastics *e.g.*, Bakelite; (2) for the production of cyclohexanol, required for the production of *Nylon*; (3) as a starting material for the manufacture of pharmaceutical product such as salicylic acid, salol, aspirin etc; (4) for making picric acid; for phenolphthalein and certain other dyes; (5) for preparing 2,4-dichlorophenoxyacetic acid (*a weed killer*), and 2,4-dichloro-3,5-dimethylphenol (*a powerful antiseptic*, "Dettol").



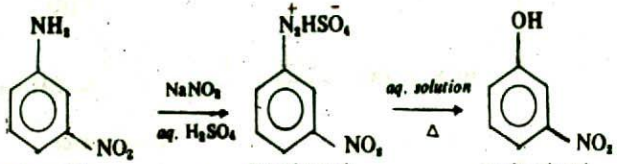
2,4-dichlorophenoxyacetic acid
(*weed killer*)



2,4-dichloro -3,5-dimethylphenol
(*Dettol*)

Nitrophenols, $O_2N—C_6H_4—OH$ (*o*, *m*, *p*)

o- and *p*-Nitrophenols are prepared by direct nitration of phenol with dilute nitric acid at room temperature. The mixture is separated by steam distillation, the *o*-isomer passing over leaving the *p*-isomer behind. *m*-Nitrophenol is obtained by diazotisation of *m*-nitroaniline and heating the resulting aqueous solution.

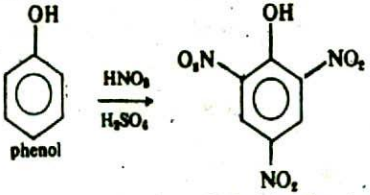


m-nitroaniline diazonium salt *m*-nitrophenol

Properties. *o*-Nitrophenol is a yellow solid, mp 45°C, having a powerful odour. *m*- and *p*-Nitrophenols are colourless solids, mp 96°C and 114°C respectively. They are all sparingly soluble in water, and only the *o*-isomer is steam-volatile. Owing to the presence of an electron withdrawing $—NO_2$ group on the ring, they are all more acidic than phenol, the ortho and para isomers more so than meta. They dissolve in alkalis, forming coloured salts. They are all readily reduced to the respective amino phenols. When treated with bromine water, they split out the nitro group forming 2,4,6-tribromophenol.

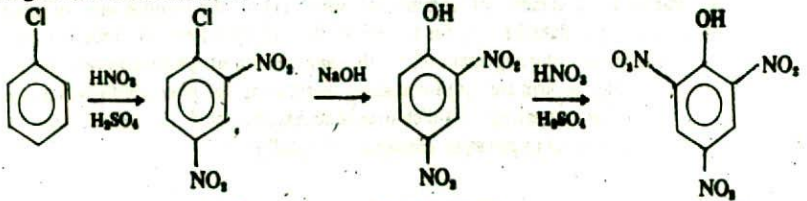
Picric Acid, 2,4,6-*Trinitrophenol*

It can be prepared readily by direct nitration of phenol with a mixture of concentrated nitric acid and sulphuric acid.



phenol 2,4,6-trinitrophenol
(picric acid)

Since phenol is largely destroyed by oxidation with nitric acid, the yield of picric acid is poor. For this reason this high explosive is now produced commercially through a synthesis that begins with chlorobenzene.



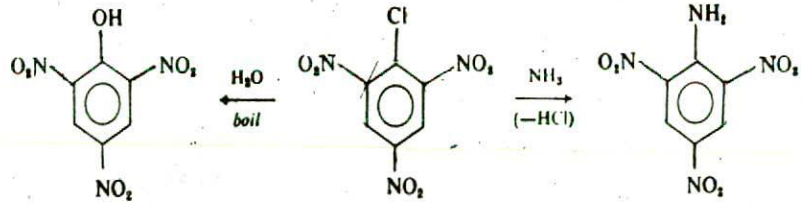
2,4-dinitrochlorobenzene 2,4-dinitrophenol picric acid
(2,4,6-trinitrophenol)

Two $-NO_2$ groups in 2,4-dinitrophenol are deactivating and thus their presence sufficiently counteracts activation due to —OH group. Hence the oxidation of the ring is avoided in the last stages of nitration.

Properties. Picric acid is a yellow crystalline solid, mp 122°C, having a bitter taste (hence its name, Gr. *pikros* = bitter). It is sparingly soluble in cold water giving intensely yellow solutions. It dissolves readily in ethanol and benzene. It is poisonous.

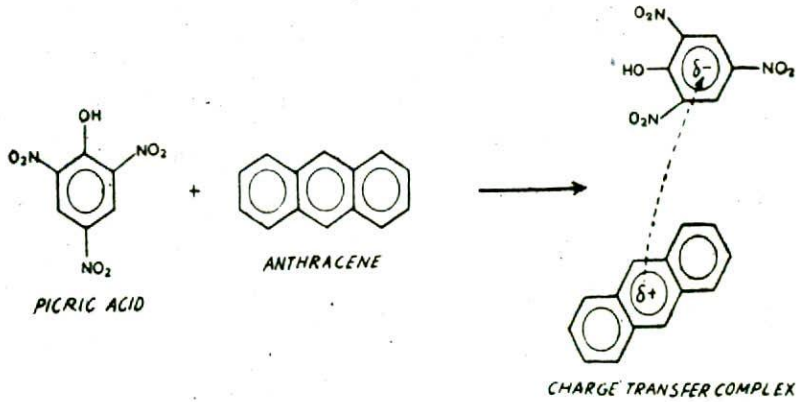
(1) The electron-withdrawing effect of the three $-NO_2$ groups greatly increases the acidity of phenolic —OH group, making the compound nearly as acidic as mineral acids. For this reason it goes under the name of picric acid. Thus it reacts with alkalis and decomposes carbonates to form salts.

(2) When treated with PCl_5, it readily gives *picryl chloride*. On boiling with water picryl chloride forms picric acid, and when shaken with ammonia, *picramide*. These reactions are made possible because the Cl atom is activated by presence of three $-NO_2$ groups.



picric acid picryl chloride picramide

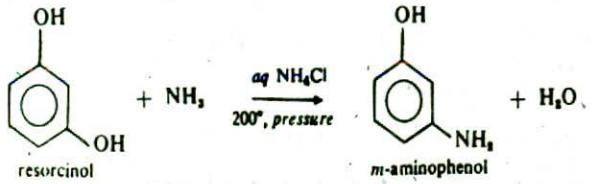
(3) It forms molecular complexes with aromatic hydrocarbons. These are well-defined crystalline compounds (*picrates*) and are used for the isolation and identification of aromatic hydrocarbons. For example, picric acid produces red, crystalline, high-melting compound with anthracene. The bond between the reactants, is formed by interaction between the electron-poor ring of picric acid (Lewis acid) and the electron-rich ring of anthracene (Lewis base). The compounds of this type are often referred to as 'Charge-transfer Complexes'.



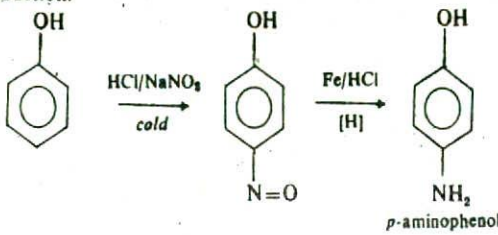
PICRIC ACID CHARGE TRANSFER COMPLEX

Uses. Picric acid is used : (1) for making explosives (*Lyddite* and *Melinite*) ; (2) as a reagent for the identification of aromatic hydrocarbons, amines etc; (3) as a direct yellow dye for silk and wool; (4) Butesin picrate, picrate of *n*-butyl-*p*-aminobenzoate is a useful surface anaesthetic for the treatment of burns

Aminophenols. They may be prepared by the reduction of the corresponding nitrophenols with metal and acid (Sn or Fe/HCl). *m*-Aminophenol is obtained commercially by reaction of resorcinol with ammonia and aqueous ammonium chloride under pressure at 200°C.

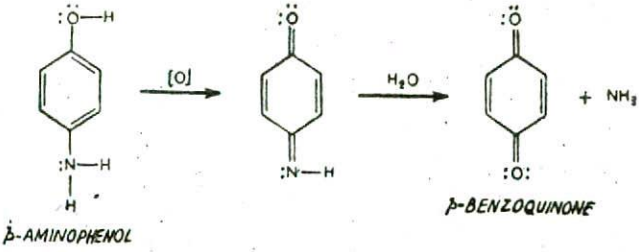


p-Aminophenol is prepared commercially by the electrolytic reduction of nitrobenzene in sulphuric acid solution. The nitrobenzene is reduced to *N*-hydroxyaniline, C_6H_5—NH—OH, which rearranges to yield phenol. It is also obtained from phenol by nitrosation, followed by reduction.



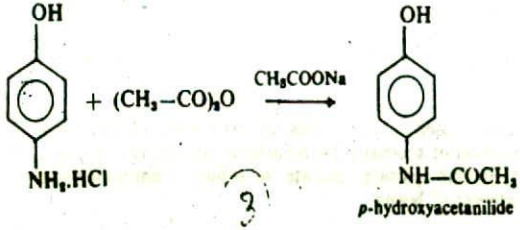
Properties. All the three aminophenols are colourless solids, melting points are *o*-137°, *m*-123°, *p*-186°C. The *o*- and *p*-aminophenols are less acidic than phenol, and do not form phenoxides with alkalis. On the other hand, they form salts with strong acids *e.g.*, hydrochlorides.

The *o*- and *p*- aminophenols are very readily oxidised to *o*- and *p*-benzoquinones respectively.

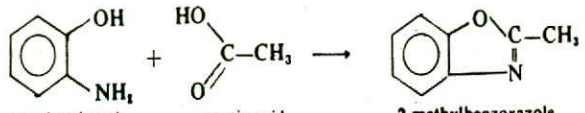


Therefore, they act as reducing agents, and are used as photographic developers.

The amino group is more readily acetylated than the phenolic hydroxy group. Thus, acetylation with acetic anhydride leads to *N*-acetylation.



o-Aminophenol reacts with acetic acid to form 2-methylbenzoxazole



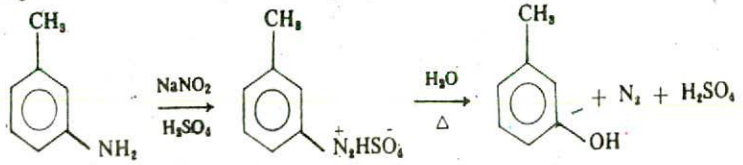
o-aminophenol acetic acid 2-methylbenzoxazole

p-Aminophenol is an important photographic developer. This is also used as a dye intermediate. *m*-Aminophenol is also an intermediate in dyestuff manufacture.

CRESOLS, *Hydroxytoluenes*, $CH_3—C_6H_4—OH$

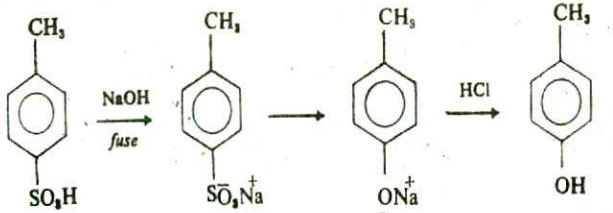
The mixture of *o*-, *m*- and *p*-cresols is called 'Creosote' as these form major constituent of *Creosote Oil*—a coal, wood or petroleum tar fraction. The mixture is separated into individual cresols by using a sophisticated fractionating column.

Preparation. (1) Each of the isomeric cresols may be synthesised by diazotisation of the corresponding toluidine and warming the resulting aqueous solution. For example,



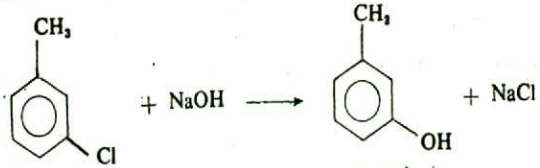
m-toluidine diazonium salt *m*-cresol

(2) Cresols may also be obtained by fusion of the corresponding toluenesulphonic acid with NaOH.



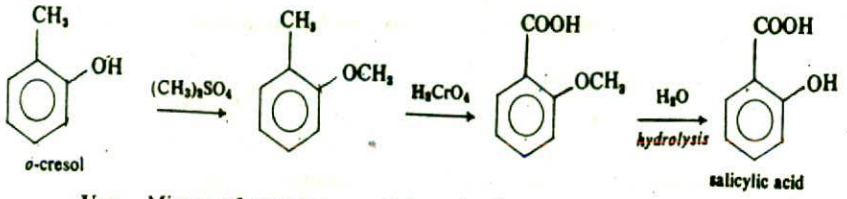
p-toluenesulphonic acid *p*-cresol

(3) When either *o*- or *m*-chlorotoluene is heated with aqueous NaOH at 300—320°C under pressure, *m*-cresol is produced.



m-chlorotoluene *m*-cresol

Properties. Cresols are colourless liquids having phenolic odour. Their boiling points are *o*- 191°, *m*- 201°, *p*- 202°C. They are less toxic than phenol but have a greater germicidal value. They produce violet colouration with ferric chloride and give most of the reactions of phenols. In addition, cresols are readily oxidised with chromic acid to give corresponding carboxylic acids if the —OH group is blocked by alkylation or acylation.



o-cresol

salicylic acid

Uses. Mixture of cresols (*creosote*) is used : (1) as preservative for timber, railway sleepers etc., (2) for making liquid disinfectant *lysol*, a solution of cresol in soapy water; (3) for manufacture of synthetic resins, plasticisers, dyes and explosives.

THYMOL AND CARVACROL

These are two isomeric higher homologues of phenol which are extensively used in perfumery and as antiseptics.



Thymol
(2-hydroxy-4-isopropyltoluene)

Carvacrol
(3-hydroxy-4-isopropyltoluene)

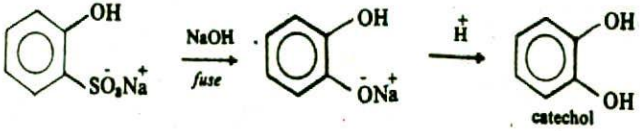
Thymol occurs in the essential oil, *oil of thyme*, and is prepard by heating *m*-cresol and isopropanol with sulphuric acid. Carvacrol is obtained by heating camphor with iodine.

DIHYDRIC MEMBERS

CATECHOL, *o-Dihydroxybenzene*

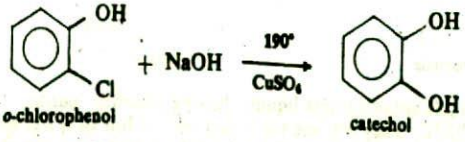
Catechol occurs in Indian catechu (obtained from Acacia Catechu tree) and hence its name.

Preparation. (1) By alkaline fusion of *o*-phenolsulphonic acid.



catechol

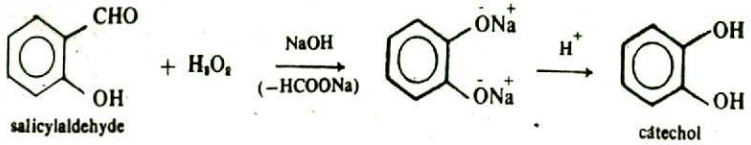
(2) By heating *o*-chlorophenol or *o*-dichlorobenzene with aqueous NaOH in presence of traces of $CuSO_4$ at 190°C.



o-chlorophenol

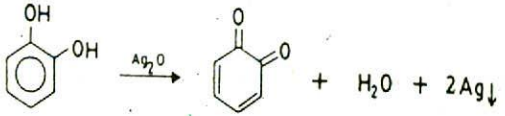
catechol

(3) By the action of alkaline hydrogen peroxide on salicylaldehyde. (*Laboratory method*)



salicylaldehyde — catechol

Properties. Catechol is a white crystalline solid, mp 104°C. It is readily soluble in water, ethanol and ether. It gives green colouration with ferric chloride. Its aqueous solutions darken due to oxidation. It reduces cold $AgNO_3$ and warm Fehling's solution. On oxidation with silver oxide in ether solution, it is oxidised to 1,2-benzoquinone, hence its use as a photographic developer.

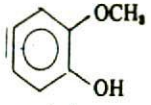


o-BENZOQUINONE
(1, 2 - benzoquinone)

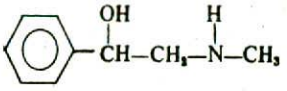
It condenses with phthalic anhydride in the presence of sulphonic acid to form alizarin.

Uses. Catechol is used : (1) as a photographic developer ; (2) for manufacture of *alizarin* ; (3) as antioxidant in gasoline.

Guaicol and Adrenalin. These are the two valuable derivatives of catechol.



guaicol
(*mp* 32°)

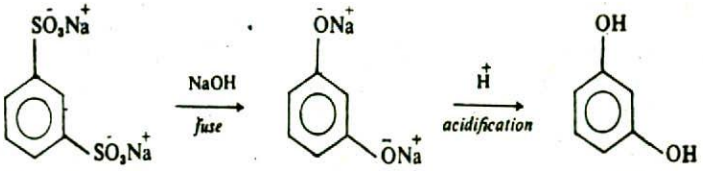


adrenalin
(*hormone secreted by adrenal gland*)

RESORCINOL, *m-Dihydroxybenzene*

It gets its name from the fact that it was originally obtained by the fusion of certain resins with alkalis.

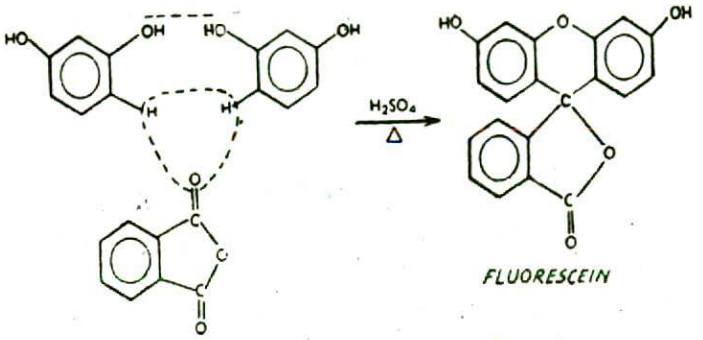
Preparation. Resorcinol is prepared by fusion of sodium *m*-benzenedisulphonate with sodium hydroxide and subsequent acidification.



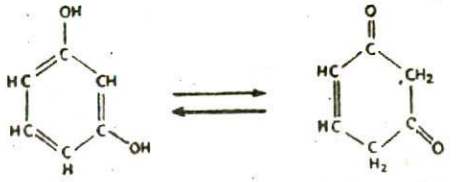
sod *m*-benzenedisulphonate — resorcinol

Properties. Resorcinol forms white needle-like crystals, mp 110°C. It turns grey in air due to oxidation. It is highly soluble in water, ethanol and ether. It gives a deep violet colouration with $FeCl_3$ and forms a precipitate of 2, 4, 6-tribromoresorcinol with bromine water. On nitration resorcinol forms 2,4,6-trinitroresorcinol known as *styphnic acid* whose salts are used to identify certain compounds.

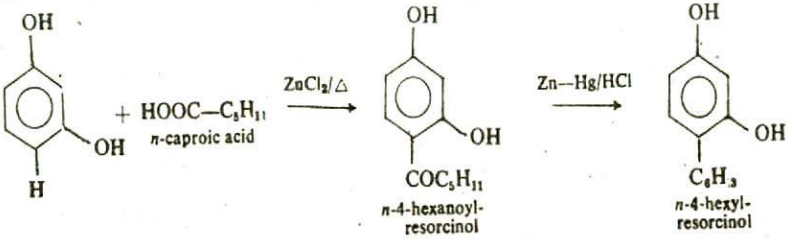
It couples with diazonium salts to form azo dyes and condenses with phthalic anhydride to form fluorescein which shows intense green fluorescence when alkalised.



Resorcinol exhibits keto-enol tautomerism which is shown by the fact that it forms a dioxime and bisulphite compound.



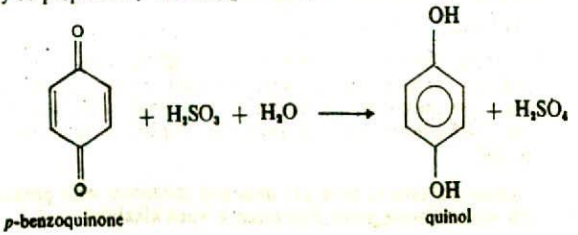
When heated with *n*-caproic acid and zinc chloride, it forms *n*-4-hexanoylresorcinol which on Clemmensen reduction yields *n*-4-hexylresorcinol, a powerful antiseptic.



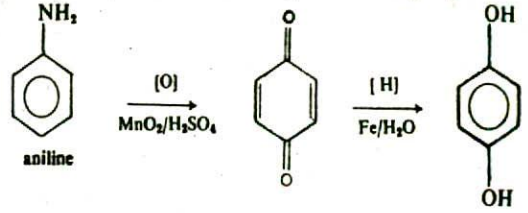
Uses. Resorcinol is used : (1) as antiseptic in ointments for eczema; (2) for manufacturing a number of dyes such as azo dyes, fluorescein, eosin, etc., (3) for preparing *n*-4-hexylresorcinol, a powerful antiseptic for curing hookworm and urinary disorders; and (4) for preparing certain aldehyde resins needed for bonding plywood.

QUINOL, HYDROQUINONE, *p-Dihydroxybenzene*

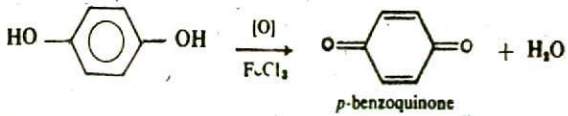
It may be prepared by reducing *p*-benzoquinone with sulphurous acid.



Commercially it is made from aniline by the following steps.

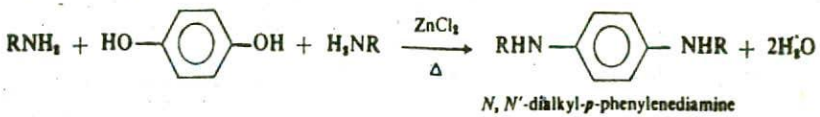


Properties. Quinol is a white crystalline solid, mp 173°C. It is highly soluble in water, ethanol and ether. Its aqueous solutions turn brown in air due to oxidation. Quinol is a powerful reducing agent and thus even a mild oxidising agent like ferric chloride converts it into *p*-benzoquinone (a green solid).



Quinol exhibits tautomerism like resorcinol, and forms dioxime with NH_2OH and a bisulphite addition compound with $NaHSO_3$.

Ammonolysis of hydroquinone with a primary amine in presence of zinc chloride gives *N, N'*-dialkyl-*p*-phenylenediamine. It is an important antioxidant for preserving gasoline and rubber products.

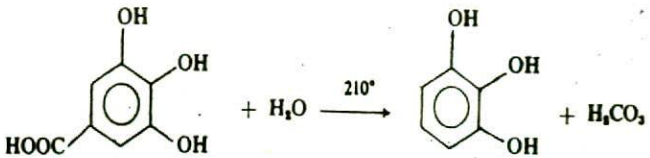


Uses. Quinol is used (1) as a photographic developer; (2) as an antioxidant or inhibitor in autoxidation and polymerisation reactions; (3) as antiseptic solution in the treatment of *conjuctivitus*.

TRIHYDRIC MEMBERS

PYROGALLOL, *1,2,3-Trihydroxybenzene*

Preparation. It is obtained by heating aqueous solution of gallic acid at 210°C under pressure.

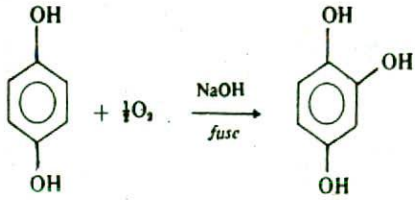


Properties. Pyrogallol is a white crystalline solid, mp 133°C. It is soluble in water, ethanol and ether. Its aqueous solutions produce red colouration with $FeCl_3$. Alkaline solution of pyrogallol absorbs oxygen rapidly from air and turns brown. This property is used in *gas analysis* for the absorption of oxygen. Of all the phenols, it is the most powerful reducing agent. It reduces $AgNO_3$ and Fehling's solution in cold. It can also reduce salts of silver, gold, platinum and mercury to the respective metals.

Uses. Pyrogallol is used : (1) as an excellent photographic developer; (2) for preparing antiseptic ointments for skin; (3) as a hair dye; and (4) for absorbing oxygen in gas analysis.

HYDROXYQUINOL. *1,2,4-Trihydroxybenzene*

It is prepared by alkaline fusion of quinol in air.

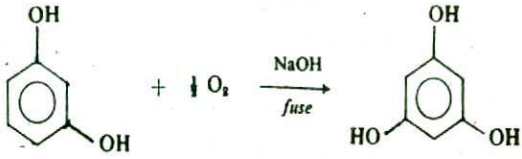


quinol hydroxyquinol

Hydroxyquinol is a white crystalline solid, mp 140°C. Like other isomers it is very soluble in water. Its aqueous solutions give a greenish-brown colouration with $FeCl_3$.

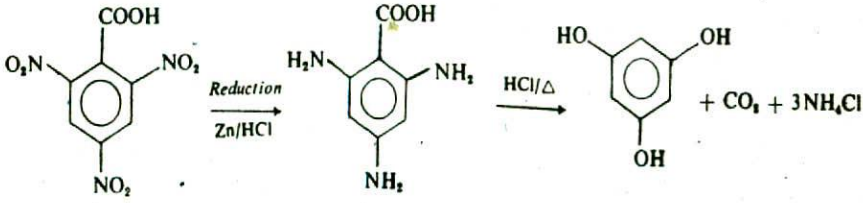
PHLOROGLUCINOL, *1,3,5-Trihydroxybenzene*

It is prepared by fusing resorcinol with NaOH in air.



resorcinol 1,3,5-trihydroxybenzene

In the laboratory it is obtained conveniently by the following sequence of reactions.

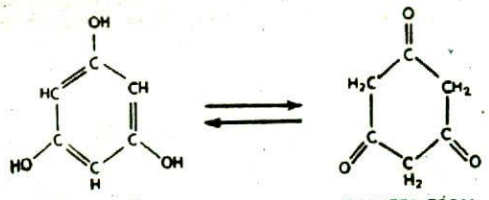


2,4,6-trinitrobenzoic acid 2,4,6-triaminobenzoic acid phloroglucinol

In the last step, 2,4,6-triaminobenzoic acid decarboxylates and the $-NH_2$ groups are replaced by —OH groups.

Properties Phloroglucinol is a white crystalline solid, mp 218°C. It is fairly soluble in water. Its aqueous solutions taste sweet and give bluish violet colouration with $FeCl_3$. Its alkaline solutions rapidly darken on exposure to air due to oxidation.

Phloroglucinol behaves as a trihydric phenol, forming tripotassium derivative, triethers, and triesters. Also, it gives a trioxime as if it were a triketocyclohexane. Thus phloroglucinol exhibits tautomerism.



TRIENOLIC FORM TRIKETO FORM

Phloroglucinol is used for detecting carbohydrates, producing a red coloration with them in presence of sulphuric acid.

AROMATIC ALCOHOLS

Aromatic alcohols contain the —OH group in the side-chain. They may well be regarded as aryl-substituted aliphatic alcohols. Aromatic alcohols may also be classified as 1°, 2°, or 3° alcohols. They resemble aliphatic alcohols both in the methods of preparation and properties.

BENZYL ALCOHOL, *Phenylcarbinol*, $C_6H_5—CH_2OH$

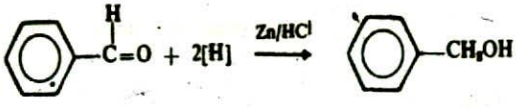
It is the simplest member of the class and is isomeric with cresols. It occurs in Peru and Tolu balsams as free alcohol and as esters (acetate and benzoate) *oil of jasmine* and other essential oils.

Preparation. (1) By hydrolysis of benzyl chloride with aqueous sodium hydroxide. (*Commercial*)



benzyl chloride benzyl alcohol

(2) By reducing benzaldehyde with zinc and HCl.



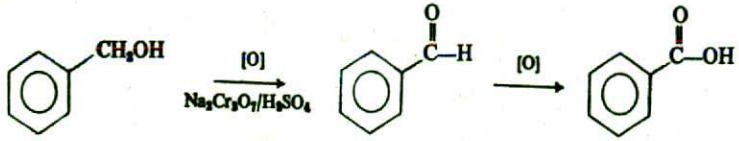
benzaldehyde benzyl alcohol

(3) By treatment with concentrated NaOH solution. (*Cannizzaro Reaction*)

Benzyl alcohol may also be produced from benzaldehyde and formaldehyde by crossed Cannizzaro Reaction.

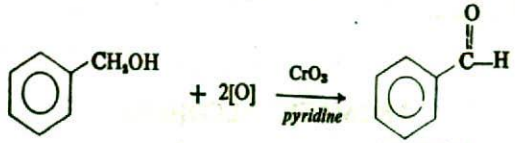
Properties. Benzyl alcohol is a colourless liquid bp 206°C, having a faint pleasant odour. It is slightly soluble in water, but readily soluble in most organic solvents.

Chemically it behaves like aliphatic primary alcohols and also gives substitution reactions in the aromatic ring. It is oxidised in two stages, it first forms benzaldehyde and finally benzoic acid.



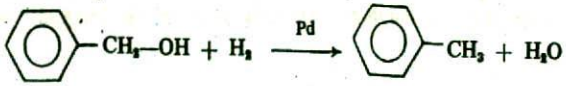
benzyl alcohol benzaldehyde benzoic acid

The oxidation can be stopped at the benzaldehyde stage by oxidation of benzaldehyde with chromium trioxide in pyridine solution.



benzaldehyde

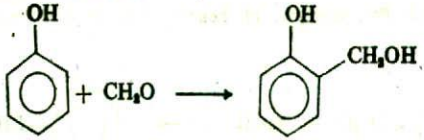
Benzyl alcohol may be reduced with hydrogen in the presence of palladium as catalyst.



benzyl alcohol toluene

Uses. Benzyl alcohol and its esters are largely used in the perfumery industry. Being a local anaesthetic and antiseptic, it is used in making ointments for relieving itching. Benzyl benzoate is a remedy for *asthma* and *whooping cough.*

o-Hydroxybenzyl alcohol, *Salicyl alcohol, Saligenin. It occurs as* glucoside, *Salicin.* It is prepared by the *Lederer-Manasse Reaction.*



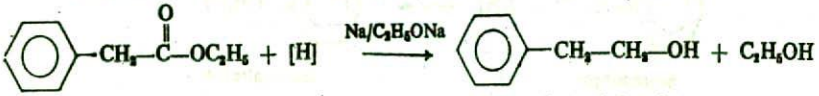
salicyl alcohol

It is a crystalline solid, mp 87°C, and is used in medicine as antipyretic.

β-PHENYLETHYL ALCOHOL, *Phenylethanol,* $C_6H_5—CH_2—CH_2—OH$

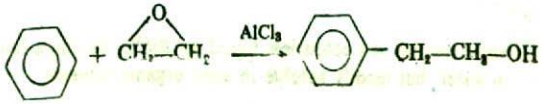
It occurs in the oil of roses. The synthetic product and its esters are now used in perfumery.

Preparation. (1) By reducing ethyl phenylacetate with sodium and absolute ethanol.



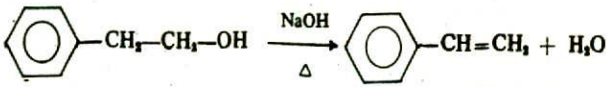
ethyl phenylacetate β-phenylethyl alcohol

(2) By reaction between ethylene oxide and benzene in the presence of aluminium chloride.



Properties. β-Phenylethyl alcohol is a colourless liquid, bp 221°C, having a strong rose-like odour. It is only slightly soluble in water but freely miscible with ethanol and ether.

When heated with alkali, it forms styrene (vinyl benzene).



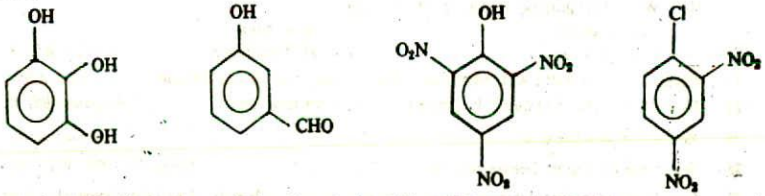
styrene

QUESTIONS

1. What are phenols and how do they differ structurally from aromatic alcohols. Give an example of each class of such compounds.

2. Discuss the structure of phenol, drawing the picture of its orbital model. Give the various canonical forms of phenol and write down the approximate structure of the resonance hybrid.

3. How are phenols named? Write the systematic and common names of any of the following structures.



4. Give five important methods of introducing OH group in an aromatic ring.

5. Describe the following methods of preparation of phenol : (*a*) Hydrolysis of Aryl halide ; (*b*) Decarboxylation of phenolic acids; (*c*) Alkali fusion of sodium arenesulphonate; (*d*) Hydrolysis of diazonium salts.

6. How is phenol obtained from coal tar? Give a modern synthetic method for the preparation of phenol from a petroleum source.

7. (*a*) How do you explain high melting and boiling points of phenol? (*b*) How is it that phenol is very much more soluble than hexanol which has a comparable molecular weight? (*c*) Salicylaldehyde and nitrophenol exhibit lower solubility relative to their meta and para isomers. Why?

8. Phenols are acidic in character, while alcohols are almost neutral. Explain in detail.

How is it that for isomeric chlorophenols, K_a is in the order Ortho > Meta > Para ?

9. 'Nitrophenols are more acidic than phenol' : Comment. Why the meta isomer has significantly low acidity ?

10. Discuss the reactions of phenols due to the OH group. Compare and contrast these reactions with those of aliphatic alcohols.

11. Discuss five important reactions of phenols involving the aromatic ring. Give general mechanism of an electrophilic substitution reaction of benzene ring of phenol.

12. State the following reactions with reference to phenol and give mechanism in each case.

(*i*) Kolbe's Reaction; (*ii*) Gattermann Reaction ; (*iii*) Reimer Tiemann Reaction ; and (*iv*) Lederer Manasse Reaction.

13. Write the methods of preparation and properties of picric acid and benzyl alcohol.

14. Explain: (*a*) A nitro substituent group increases the acidity of Phenol but a methyl group decreases it. (*Mysore BSc II, 1980*)

(*b*) Phenol is more acidic than ethyl alcohol.

15. (*i*) Write the various canonical forms for the phenoxide ion.

(*ii*) With benzene as the starting material, how would you prepare resorcinol ?

(*Kerala BSc III, 1980*)

16. (*a*) How does sodium phenoxide react with:

(*i*) CH_3CH_2Cl (*ii*) CH_3COCl.

(*b*) Explain : Phenol is acidic in nature. (*Panjab BSc Chem Engg, 1980*)

17. Describe the preparation of Benzyl alcohol. Give the action of the following on benzyl alcohol:
(*i*) Nitric acid (*ii*) Sodium
(*iii*) Acetyl chloride (*iv*) Phosphorus pentachloride. (*Kashmir BSc, 1980*)

18. How will you convert phenol into:
(*i*) Salicylic acid (*ii*) Phenolphthalein
(*iii*) Ethoxybenzene.
Give mechanism where necessary. (*Himachal BSc III, 1981*)

19 How is pehnol obtained from coal-tar ? Compare the properties of phenol with the properties of alcohol (*Jabalpur BSc III, 1981*)

20. (*a*) Why is phenol acidic while alcohols are not ?
(*b*) How are the following obtained from phenol ?
(*i*) Salicylaldehyde (*ii*) p-hydroxyacetophenone.
Discuss the mechanism involved in each case. (*Venkateswara BSc II, 1981*)

21 Describe the preparation of phenol from
(*i*) lumene (*ii*) aniline. (*Osmania BSc III, 1981*)

22. (*a*) Give four important properties of phenol to show how it differs from alcohol.
(*b*) Write the graphic formulae of any three:
(*i*) Catechol (*ii*) Resorcinol
(*iii*) Picric acid (*iv*) Hydroquinone. (*Saugar BSc II, 1981*)

23. Phenol can be nitrated with nitric acid alone. Explain this giving mechanism. (*Poona BSc, 1981*)

24. How can Catechol and quinol be prepared ? What are their uses ? (*Bangalore BSc II. 1981*)

25. How is picric acid prepared ? (*Jadavpur BSc, 1994*)

26. Write a note on : Reimer-Tiemann reaction. (*Kanpur BSc, 1994; Shivaji BSc, 1994*)

27. Describe the mechanism of Reimer-Tiemann reaction. (*Delhi BSc Hons, 1994; Osmania BSc Hons, 1994*)

28. Write a note on : Fries rearrangement. (*Kalyani BSc Hons, 1993*)

29. Explain : Phenol is more acidic than ethanol. (*Mysore BSc, 1994*)

30. Explain : Phenol is a weaker acid than *p*-nitrophenol. (*North Bengal BSc Hons, 1994*)

31. What is the effect of substituents on the acidity of phenol ? (*Madurai BSc, 1994*)

32. How will you synthesise *m*-nitrophenol from benzene ? (*Dibrugarh BSc, 1993*)

Hint. Use the following steps : (*i*) $HNO_3/H_2SO_4/60°C$, (*ii*) Conc. H_2SO_4, (*iii*) NaOH/ room temperature, (*iv*) NaOH/fuse, and (*v*) H_2O/H^+.

33. How will you synthesise 1-phenylethanol from benzene ?

Hint. Use the following steps : (*i*) $Br_2/FeBr_3$, (*ii*) Mg/ether, (*iii*) CH_3CHO, and (*iv*) H_2O/H^+

34. How will you distinguish between phenol and benzyl alcohol ? (*Pandicherry BSc, 1994*)

Hint. When a solution of phenol in water is treated with Br_2 in H_2O, a pale yellow precipitate of 2,4,6-tribromophenol is formed. Benzyl alcohol does not give this reaction. Also, phenol is soluble in aqueous NaOH solution. Benzyl alcohol is insoluble.

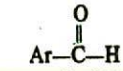
35. Compound (A), C_7H_8O, is a solid that is slightly soluble in aqueous sodium hydroxide. When (A) is treated with bromine water, the solid (B), $C_7H_6Br_2O$, is formed. Write possible structures for (A) and (B).

Answer. (A) is *p*-cresol ; and (B) is 2,5-dibromo-4-methylphenol.

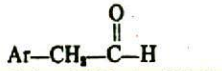
Aromatic Aldehydes and Ketones

I. ALDEHYDES

Aromatic aldehydes are of two types : (*a*) those in which the aldehyde group (CHO) is directly attached to a carbon of the aromatic ring ; and (*b*) those in which the aldehyde group is attached to a carbon of the side-chain. Aldehydes of type (*a*) are called aromatic aldehydes, while those of type (*b*) are best regarded as aryl-substituted aliphatic aldehydes.



aromatic aldehyde
(*CHO attached to aromatic ring*)

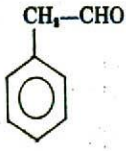


aryl-substituted aliphatic aldehyde
(*CHO attached to side-chain*)

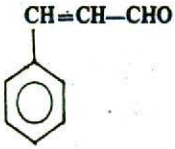
Benzaldehyde is a typical aromatic aldehyde, while phenylacetaldehyde and cinnamic aldehyde are to be designated as aryl-substituted aliphatic aldehydes.



benzaldehyde



phenylacetaldehyde



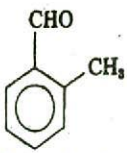
cinnamic aldehyde

NOMENCLATURE

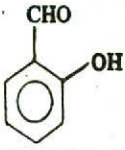
(1) The **IUPAC Name** of an aromatic aldehyde is derived by dropping the ending *-ene* of the name of the parent hydrocarbon and appending the suffix *-al*. Thus,



benzal



2-methylbenzal

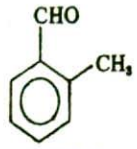


2-hydroxybenzal

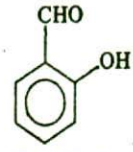
(2) They are generally called by their **Common Names** which are derived from the names of the corresponding carboxylic acid by replacing the *-ic* or *-oic acid* by *-aldehyde*. Thus the name benzaldehyde is derived from benzoic acid, *o*-tolualdehyde is derived from *o*-toluic acid, and salicylaldehyde from salicylic acid.



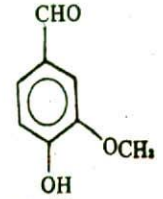
benzaldehyde
(benzal)



o-tolualdehyde
(2-methylbenzal)



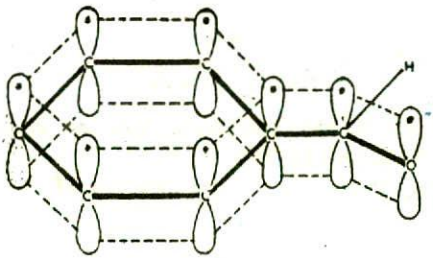
salicylaldehyde
(2-hydroxybenzal)



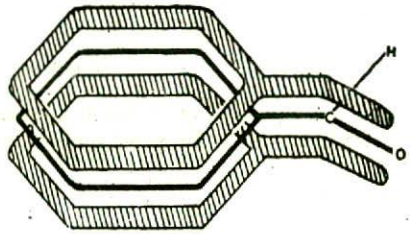
vanillin
(4-hydroxy-3-methoxy-
benzaldehyde)

STRUCTURE

The molecular structure of aromatic aldehydes will be illustrated by taking the case of benzaldehyde. It is similar to the structure of nitrobenzene which we have already discussed. The *p* orbitals involved in the π bond of the carbon-oxygen double bond are aligned with the corresponding *p* orbitals of the benzene ring and, therefore, interact with them. The extended molecular orbital so formed encompasses the carbonyl carbon and oxygen atoms as also the ring carbons of benzene.



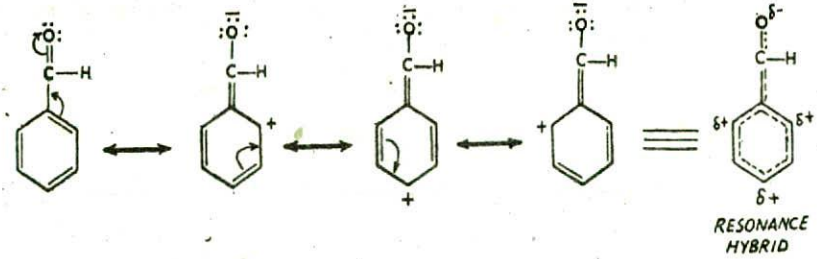
ATOMIC ORBITAL MODEL



ELCTRON CLOUD MODEL

Fig. 43·1. Molecular structure of Benzaldehyde.

Electronic structure of benzaldehyde is the resonance hybrid of the followiug four canonical forms.

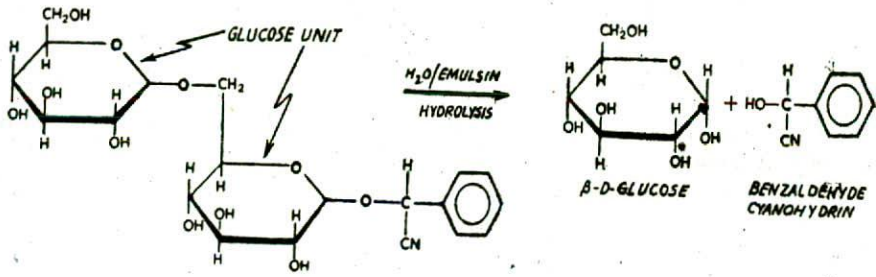


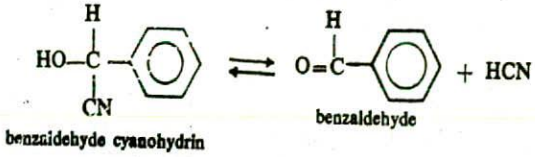
RESONANCE HYBRID

BENZALDEHYDE, *Benzal*, $C_6H_5—\overset{H}{\underset{|}{C}}=O$

Benzaldehyde is a typical and the simplest aromatic aldehyde and will be used for illustrating the preparation and properties of this class of compounds.

Benzaldehyde is found in nature as the glycoside **amygdalin** in bitter almonds which on hydrolysis with dilute acids or the enzyme *emulsin* produces free benzaldehyde, β-D-glucose and hydrogen cyanide. This is why in pharmacy it is known as *'Oil of bitter almonds'*



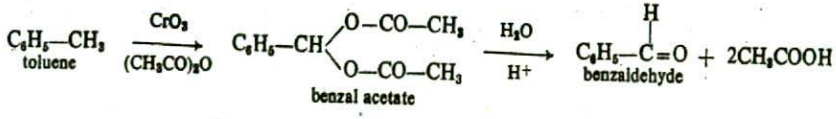


Amygdalin is poisonous because it hydrolyses to give HCN. Benzaldehyde cyanohydrin as such is found in the reactor glands of *millipedes*. When attacked, the millipede ejects its benzaldehyde cyanohydrin past an enzyme which breaks it into benzaldehyde plus HCN on the way out.

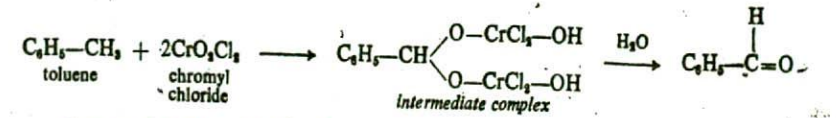
Methods of Preparation

Benzaldehyde may be prepared by the following methods which are applicable to aromatic aldehydes in general.

(1) Oxidation of Toluene. Benzaldehyde may be conveniently prepared by oxidising toluene with chrominum trioxide in acetic anhydride, and hydrolysis of the benzal acetate so produced with HCl or H_2SO_4.



Another procedure (*Etard Reaction*) uses chromyl chloride as the oxidising agent. The intermediate complex thus formed is hydrolysed to give benzaldehyde in good yield.



Commercially the oxidation of toluene is done with air diluted with nitrogen (to prevent complete oxidation) at 500°C in the presence of V_2O_5 as a catalyst.

(2) **Oxidation of Benzyl chloride.** Benzaldehyde is produced by the oxidation of benzyl chloride by boiling with aqueous copper or lead nitrate.

$$\underset{\text{benzyl chloride}}{C_6H_5-CH_2Cl} + \underset{\text{(from hydrolysis of Pb-nitrate)}}{HNO_3} \xrightarrow{Pb(NO_3)_2,\ boil} \underset{\text{benzaldehyde}}{C_6H_5-\overset{H}{\overset{|}{C}}=O} + HNO_2 + HCl$$

This is a convenient method for preparing benzaldehyde in the laboratory and industry. Benzyl chloride is made cheaply by chlorination of toluene.

(3) **Hydrolysis of Benzal chloride.** Benzaldehyde is manufactured by the hydrolysis of benzal chloride.

$$\underset{\text{benzal chloride}}{C_6H_5-CH\begin{matrix}Cl\\Cl\end{matrix}} + H_2O \longrightarrow C_6H_5-\overset{H}{\overset{|}{C}}=O + 2HCl$$

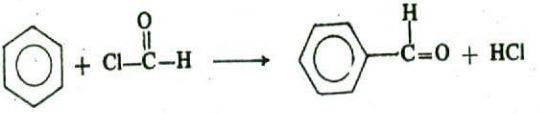
Benzal chloride is obtained by chlorinating toluene until the gain in weight corresponds to the substitution of two chlorine atoms per molecule.

$$C_6H_5-CH_3 + 2Cl_2 \xrightarrow{h\nu} \underset{\text{benzal chloride}}{C_6H_5-CHCl_2} + 2HCl$$

(4) **Gattermann-Kotch Reaction.** When an equimolecular mixture of carbon monoxide and hydrogen chloride is bubbled through a solution of benzene in ether containing anhydrous aluminium chloride, benzaldehyde is produced.

Carbon monoxide and hydrogen chloride behave as formyl chloride (H—CO—Cl), which enters into Friedel-Crafts type reaction with benzene.

$$CO + HCl \longrightarrow \underset{\text{formyl chloride}}{H-\overset{O}{\overset{\|}{C}}-Cl}$$



benzene benzaldehyde

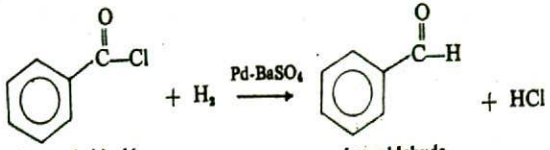
(5) **Gattermann Aldehyde Reaction.** Benzene is treated with a mixture of hydrogen cyanide and hydrogen chloride in the presence of anhydrous aluminium chloride. An addition product (formimino chloride) first formed enters into Friedel-Crafts type reaction with benzene to give the imine which is decomposed with water to produce benzaldehyde.

$$HCl + HCN \longrightarrow \underset{\substack{\text{formimino}\\\text{chloride}}}{HN=\overset{H}{\overset{|}{C}}-Cl}$$

$$C_6H_6 + Cl-\overset{H}{\overset{|}{C}}=NH \xrightarrow{AlCl_3} \underset{\text{imine}}{C_6H_5-\overset{H}{\overset{|}{C}}=NH} \xrightarrow{H_2O} \underset{\text{benzaldehyde}}{C_6H_5-\overset{H}{\overset{|}{C}}=O} + NH_3$$

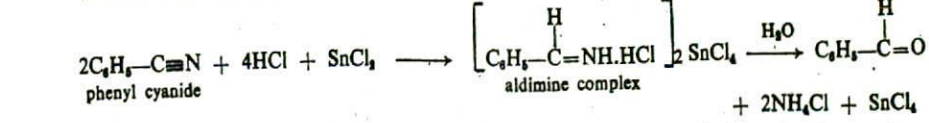
This method is particularly used to introduce CHO group in phenols with convenience.

(6) **Rosenmund Reaction.** Benzaldehyde may be produced by the reduction of benzoyl chloride with palladium-barium sulphate catalyst.



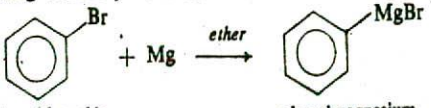
benzoyl chloride — benzaldehyde

(7) **Stephen's Reaction.** Phenyl cyanide on reduction with stannous chloride and hydrochloric acid forms an aldimine complex. This on subsequent hydrolysis yields benzaldehyde.

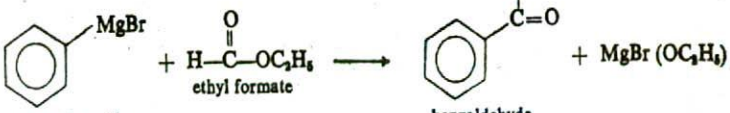


phenyl cyanide — aldimine complex

(8) **Grignard Reaction.** Benzaldehyde may be obtained by producing phenylmagnesium bromide and then reacting with ethyl formate.



phenyl bromide — phenylmagnesium bromide



phenylmagnesium bromide — ethyl formate — benzaldehyde

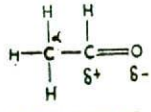
Benzaldehyde can also be made by the oxidation of benzyl alcohol and by heating a mixture of calcium benzoate and calcium formate. But these methods are not actually used for aromatic aldehydes.

Physical Properties

Benzaldehyde is a colourless, highly refractive oily liquid, bp 179°C. It has a pleasant almond-like odour. It is only slightly soluble in water but dissolves readily in organic solvents like ethanol, diethyl ether, etc. It is steam-volatile. Like all other aromatic aldehydes, it gives a band near 2800 cm^{-1} in the infrared spectrum which is not shown by the ketones.

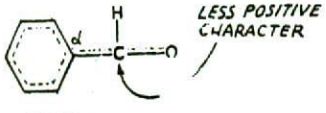
Chemical Properties

Benzaldehyde having the aldehyde group (CHO) attached to the aryl ring undergoes most of the general reactions of the aliphatic aldehydes in which α-hydrogen atom is not involved. However, conjugation of the carbonyl carbon with the aryl ring reduces the electrophilic reactivity of the carbonyl-carbon atom due to delocalisation of π electrons. Hence in general aromatic aldehydes react less readily at the CHO group than their aliphatic counterparts.



ACETALDEHYDE

(α-H present; carbonyl carbon has positive character)



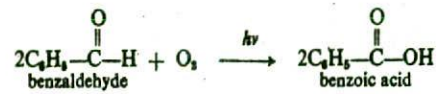
BENZALDEHYDE

(no α-H ; carbonyl carbon has much less pronounced positive character)

Also, the absence of α-hydrogen atom in benzaldehyde makes it possible to employ stronger basic or acidic catalysts in condensation reactions. Thus it undergoes a number of condensations which are not possible with aliphatic aldehydes.

A. REACTIONS OF CHO GROUP SIMILAR TO ALIPHATIC ALDEHYDES

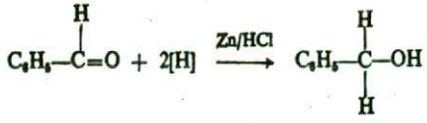
(1) **Oxidation.** Benzaldehyde is not oxidised as readily as aliphatic aldehydes by solution of oxidising agents. While it reduces ammoniacal silver nitrate forming a mirror, it does not reduce Fehling's solution. Nevertheless, benzaldehyde undergoes oxidation by atmospheric oxygen at ordinary temperature. This process known as autoxidation is catalysed by light.



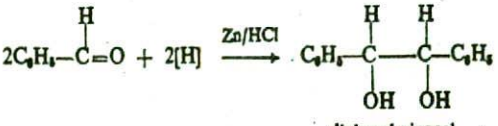
benzaldehyde benzoic acid

The autoxidation which possibly proceeds by free radical mechanism is very slow in the case of simple aliphatic aldehydes.

(2) **Reduction.** When benzaldehyde is reduced with zinc and hydrochloric acid, or with sodium amalgam and water or alcohol, benzyl alcohol is produced along with pinacol.



benzyl alcohol

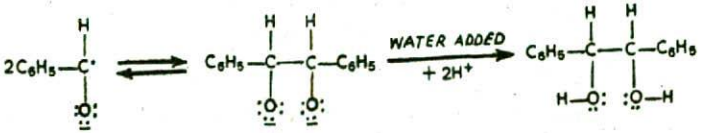


diphenyl pinacol

When sodium in ether is used as the reducing agent, higher yield of the pinacol is obtained.

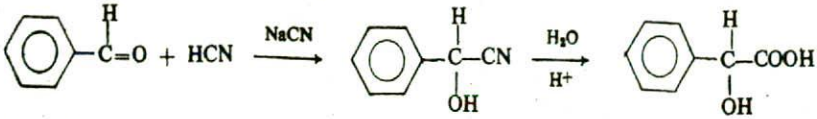
MECHANISM.





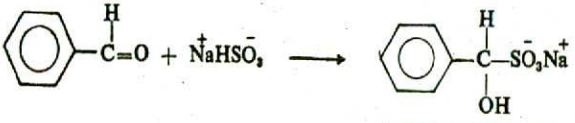
This condensation reaction which is given by aliphatic aldehydes as well, although not so readily, is known as the pinacol condensation.

(3) **Addition of Hydrogen Cyanide.** When hydrogen cyanide is added to benzaldehyde in presence of alkali cyanide (NaCN) the cyanohydrin, (mandelonitrile) is produced. This on hydrolysis with concentrated hydrochloric acid gives racemic mandelic acid.



benzaldehyde mandelonitrile mandelic acid

(4) **Addition of Sodium bisulphite.** Benzaldehyde adds sodium bisulphite to form the bisulphite compound.

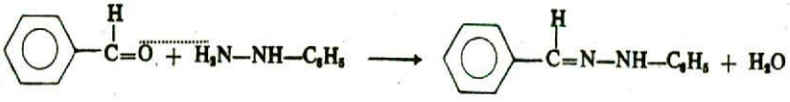


benzaldehyde sodium bisulphite

(5) **Condensation with Hydroxylamine and Phenylhydrazone.** Benzaldehyde condenses with hydroxylamine(NH_2OH) and phenylhydrazine ($C_6H_5NHNH_2$), to form benzaldoxime and the phenylhydrazone respectively.



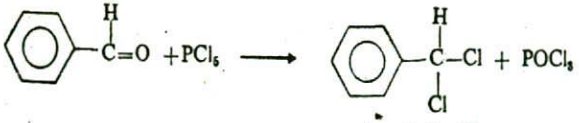
benzaldehyde benzaldoxime



phenylhydrazone

Similarly, benzaldehyde reacts with hydrazine and semicarbazide to give the hydrzaone and semicarbazone respectively.

(6) **Reaction with PCl_5.** Benzaldehyde reacts with phosphorus pentachloride to form the *gem*-dihalide.

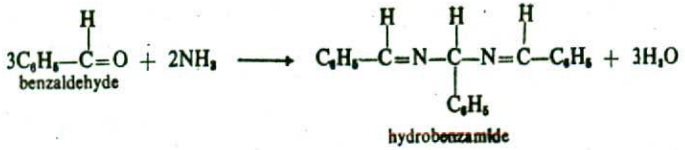


benzal chloride

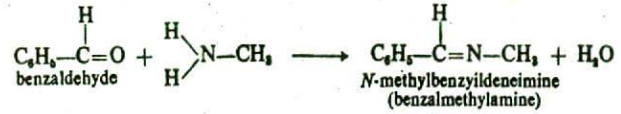
(7) **Reaction with Schiff's Reagent.** It restores the pink colour of Schiff's reagent.

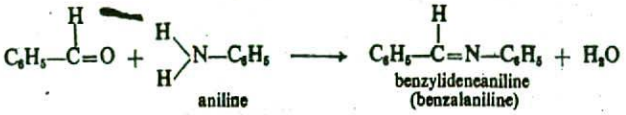
B. REACTIONS OF CHO GROUP GIVEN PARTICULARLY BY AROMATIC ALDEHYDES.

(1) **Reaction with Ammonia.** With ammonia, benzaldehyde does not form a simple aldehyde-ammonia, but a more complex condensation product called *hydrobenzamide*

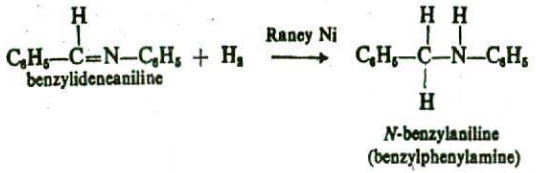


(2) **Reaction with Amines.** Benzaldehyde reacts with primary aliphatic or aromatic amines to form derivatives known as *Schiff's bases.*



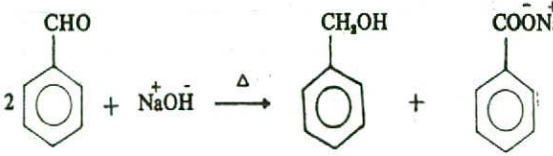


The products from aromatic amines are also called *anils.* Schiff's bases in general can be reduced easily by hydrogen and Raney nickel to yield secondary amines. Thus,



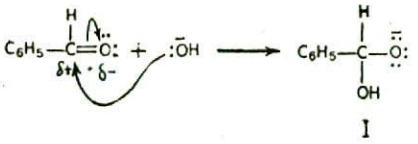
Aliphatic aldehydes do not react with amines to form compounds similar to Schiff's bases.

(3) **Intermolecular Oxidation and Reduction ; Cannizzaro Reaction.** Benzaldehyde does not contain an α hydrogen atom and hence cannot undergo aldol condensation. When heated with a concentrated sodium or potassium hydroxide solution, it undergoes an intermolecular oxidation-reduction reaction. One molecule of it is reduced to benzyl alcohol at the expense of another molecule which is oxidised to benzoic acid. Thus benzaldehyde on treatment with concentrated sodium hydroxide solution yields, in effect, benzyl alcohol and sodium benzoate.



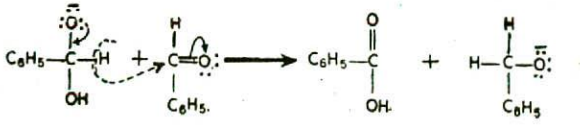
The above reaction involving the mutual oxidation-reduction of two molecules of benzaldehyde is called the *Cannizzaro Reaction.*

MECHANISM. (*i*) Attack of the nucleophile $\bar{O}H$ at the carbonyl group to from the adduct I.



I

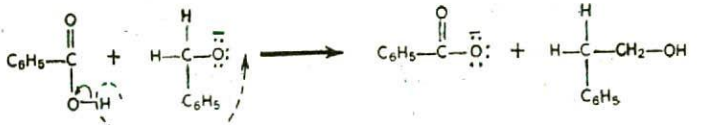
(*ii*) The adduct then transfers a hydride ion ($:\bar{H}$) to the carbonyl carbon of another molecule of benzaldehyde, to form benzoic acid (II) and alkoxide ion (III).



I II III

BENZOIC ACID ALKOXIDE ION

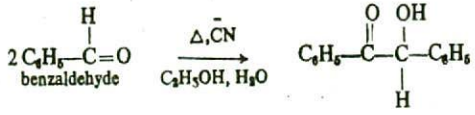
(*iii*) Proton transfer from II to III yields benzoate anion and benzyl alcohol.



II

BENZOATE ANION BENZYL ALCOHOL

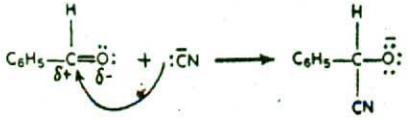
(4) **Benzoin Condensation.** When benzaldehyde is heated with aqueous-ethanolic NaCN or KCN, it dimerizes to form an α-hydroxy ketone called *benzoin*. This reaction involving self-condensation of an aromatic aldehyde in the presense of $\bar{C}N$ anion as catalyst, is referred to as *benzoin condensation.*



benzaldehyde

benzoin
(α-hydroxy ketone)

MECHANISM. (*i*) Nucleophilic addition of a cyanide anion to the carbonyl carbon.



(*ii*) The CN group acidifies the former aldehyde H atom which migrates to the former carbonyl group.



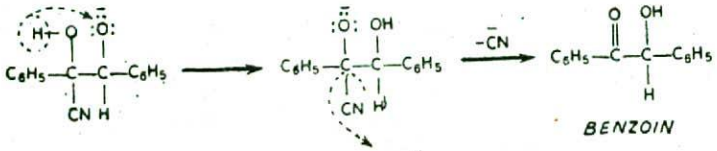
RESONANCE STABILISED CARBANION

(*iii*) The resonance-stabilised carbanion adds to the carbonyl carbon of another molecule of benzaldehyde.



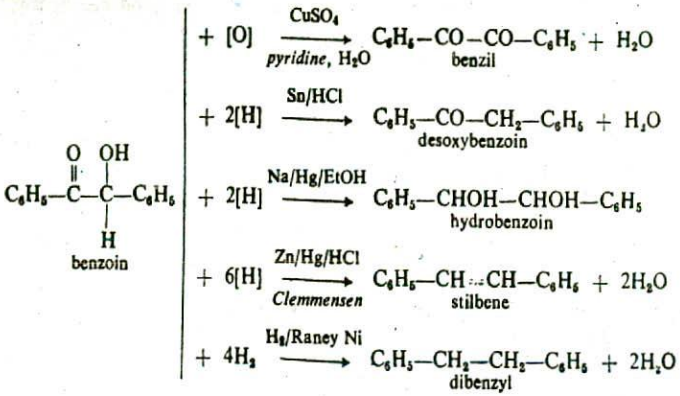
INTERMEDIATE

(*iv*) The migration of the proton of OH to the oxygen accompanied by abstraction of cyanide anion, forms benzoin.

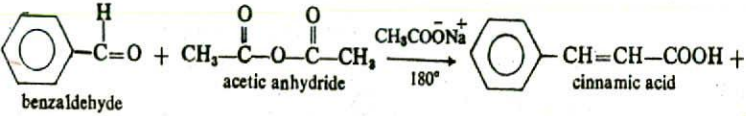


BENZOIN

Benzoin can be readily oxidised to a diketone, benzil, and reduced to a number of substances such as desoxybenzoin, hydrobenzoin, stilbene and dibenzyl.

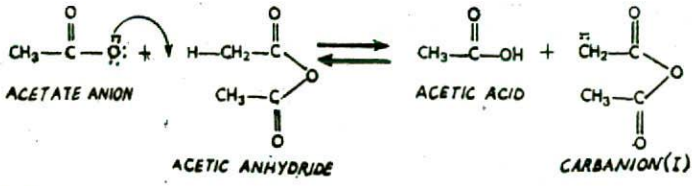


(5) **Perkin Reaction or Perkin Condensation.** When an aromatic aldehyde is heated with the anhydride of an aliphatic acid in the presence of the sodium salt of the same acid (catalyst). α, β-unsaturated acid results. Thus benzaldehyde on heating with acetic anhydride and sodium acetate for several hours at 180°C, yields cinnamic acid.

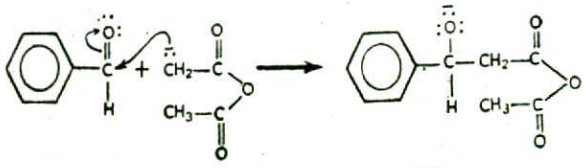


This condensation reaction between an aromatic aldehyde and aliphatic anhydride is named as *Perkin Reaction* (W.H. Perkin, 1868), or *Perkin Condensation*. It is a useful synthetic method for the synthesis of α, β-unsaturated acids (β-aryl acrylic acids).

MECHANISM : (*i*) In Perkin's Reaction the CH_3COO^- anion furnished by sodium acetate acts as a basic catalyst and helps in the abstraction of an α-hydrogen from the aliphatic anhydride to form carbanion (I).

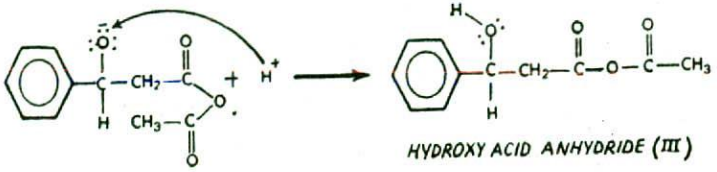


(*ii*) Carbanion I adds to the carbonyl of aromatic aldehyde to form intermediate II.



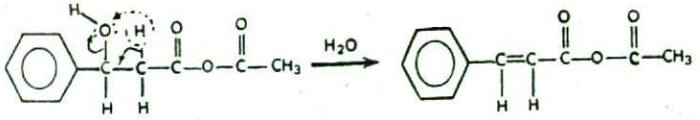
(II)

(*iii*) Protonation of the intermediate II at the anionic oxygen produces hydroxy acid anhydride III.



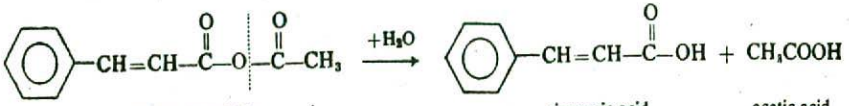
HYDROXY ACID ANHYDRIDE (III)

(*iv*) Internal proton transfer leads to elimination of a water molecule to form α, β-unsaturated mixed anhydride (IV).



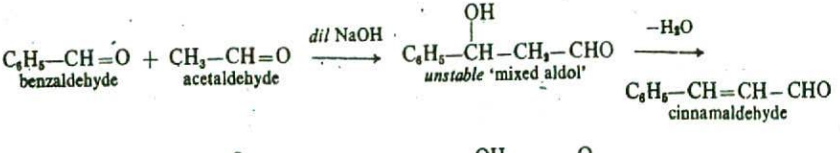
UNSATURATED MIXED ANHYDRIDE(IV)

(*v*) Hydrolysis of the unsaturated mixed anhydride (IV) finally yields cinnamic acid.

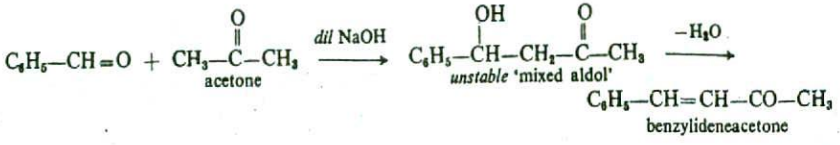


mixed anhydride — cinnamic acid — acetic acid

(6) **Claisen-Schmidt Condensation.** Benzaldehyde condenses with aliphatic aldehyde or methyl ketones in the presence of dilute alkali at room temperature to form unsaturated aldehydes or ketones. This type of 'mixed aldol condensation' is known as the *Claisen-Schmidt Condensation.*



benzaldehyde — acetaldehyde — *unstable* 'mixed aldol' — cinnamaldehyde

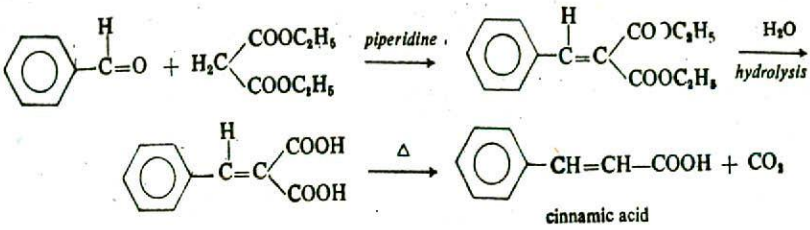


acetone — *unstable* 'mixed aldol' — benzylideneacetone

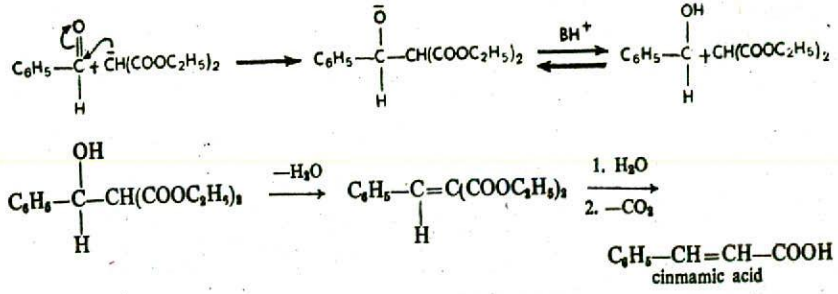
This reaction proceeds well because benzaldehyde, having no α hydrogen, cannot undergo self-condensation. The mechanism of the Claisen-Schmidt Condensation is similar to that of aldol condensation.

(7) **Knoevenagel Condensation.** Benzaldehyde undergoes condensation with substances containing active methylene groups such as diethylmalonate, ethylacetoacetate, ethyl

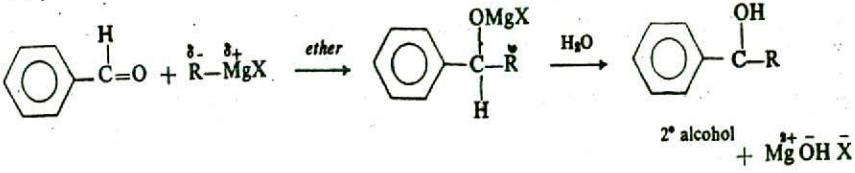
cyanoacetate etc., in the presence of an organic base (piperidine, pyridine) to form α, β-unsaturated esters which upon hydrolysis and heating give the respective α, β-unsatuared acids. Thus,



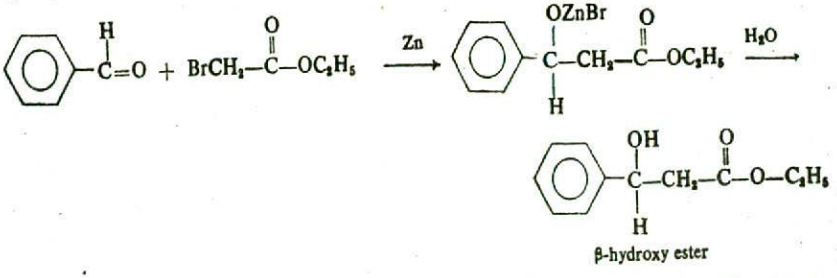
MECHANISM. (*i*) Proton abstraction by base (*B*); (*ii*) nueleophilic addition at the carbonyl carbon ; (*iii*) elimination of water; (*iv*) hydrolysis and decarboxylation.



(8) **Action with Grignard Reagents.** Benzaldehyde reacts with Grignard reagents to form a product which hydrolyses to give a secondary alcohol.

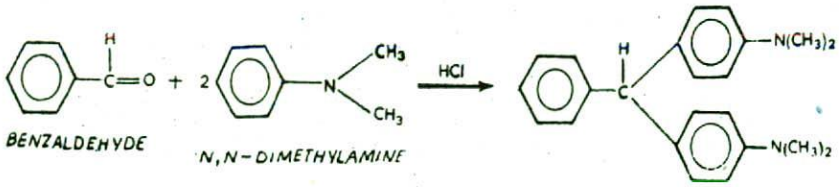


(9) **Reformatsky Reaction.** It reacts with α-halogenated esters in the presence of zinc to give β-hydroxy esters.



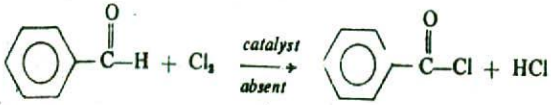
The β-hydroxy ester may be hydrolysed to give the β-hydroxy acid which is readily dehydrated to form the unsaturated acid.

(10) **Condensation with Tertiary Aromatic amines.** Benzaldehyde condenses with tertiary aromatic amines such as *N, N*-dimethylaniline, in the presence of strong acids (HCl or H_2SO_4) to form derivatives of triphenylmethane. Thus,



The above product is readily oxidised by means of lead dioxide and hydrochloric acid to give the dyestuff *Malachite Green.*

(11) **Action with Chlorine to form Benzoyl chloride.** Because benzaldehyde has no α-hydrogen atoms, it behaves differently with chlorine from the simple aliphatic aldehydes. The aldehyde group attached directly to the benzene ring is deactivating and hence chlorine does not substitute in the ring in the absence of a catalyst. Instead, the chlorine substitutes in the aldehyde group and benzoyl chloride is formed.



benzaldehyde benzoyl chloride

C. REACTIONS OF THE BENZENE RING

The CHO group withdraws electrons from the benzene ring of benzaldehyde by inductive effect and resonance. This causes a drain of electrons from the benzene ring and renders it positive and hence deactivated to electrophilic reagents. Although the benzene ring is deactivated, attack by electrophiles will still take place under difficult conditions.

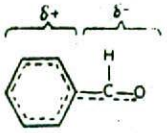
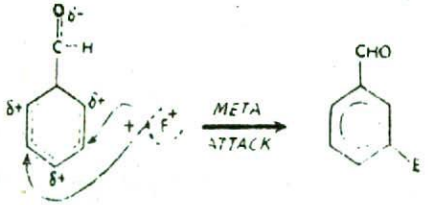


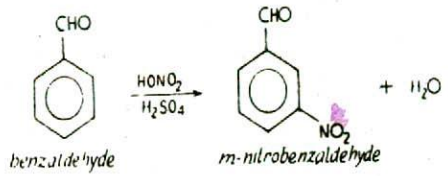
Fig. Electrons are withdrawn from the benzene ring of benzaldehyde, by inductive effect of CHO and resonance. The overall effect is that the benzene ring becomes positively charged and hence resistant to attack by electrophiles.

An electrophile (E^+) seeking to attack the most negative positions will avoid the ortho and para positions, and hence will attack the meta position which does not have a positive charge.



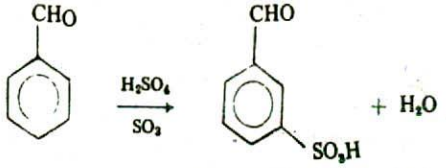
Electrophilic Substitution Reactions. Benzaldehyde undergoes nitration, sulphonation and halogenation in the aryl ring, the substitution taking place in the meta position to the CHO group.

(*i*) Nitration with a mixture of nitric acid and sulphuric acid.



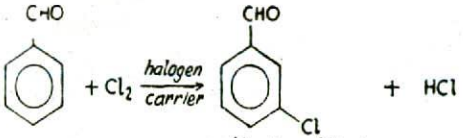
benzaldehyde *m-nitrobenzaldehyde*

(*ii*) Sulphonation with fuming sulphuric acid.



m-benzaldehydesulphonic acid

(*iii*) Halogenation with chlorine or bromine in the presence of halogen carrier.



m-chlorobenzaldehyde

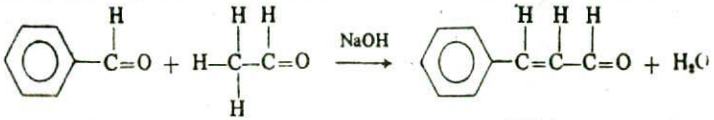
Uses of Benzaldehyde

Benzaldehyde is used : (*i*) in formulating perfumes and as a flavouring agent; (2) in the manufacture of dyes (malachite green) ; (3) as a starting material for the synthesis of several other organic compounds *e.g.*, cinnamaldehyde, cinnamic acid, benzoyl chloride etc.

SOME IMPORTANT AROMATIC ALDEHYDES

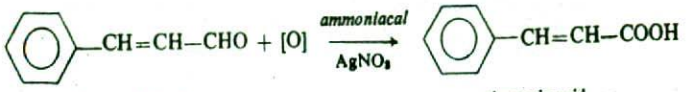
CINNAMALDEHYDE, *3-Phenylpropenal*, $C_6H_5—CH=CH—CHO$

It is the pleasant smelling constituent of *cinnamon oil* and can be isolated from it through the formation of its bisulphite compound. It is prepared synthetically by the action of dilute sodium hydroxide upon a mixture of benzaldehyde and acetaldehyde (*Claisen Condensation*).



benzaldehyde acetaldehyde cinnamaldehyde

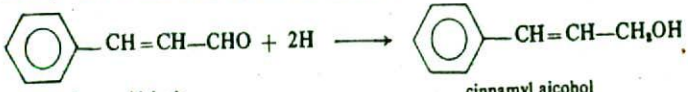
Properties. Cinnamaldehyde is a colourless oil, bp 252°C. (1) On mild oxidation with air or ammoniacal silver nitrate, it is converted into cinnamic acid.



cinnamaldehyde cinnamic acid

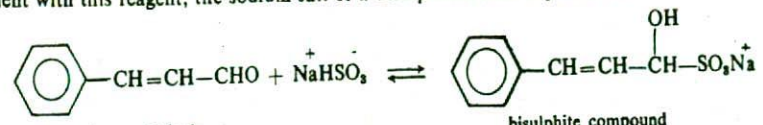
With a vigorous oxidising agent like potassium permanganate, the molecule is split out at the double bond, forming benzoic acid.

(2) Cinnamaldehyde is reduced with aluminium isopropoxide or aluminium hydride to yield cinnamyl alcohol and adds bromine at the double bond to form the dibromide.

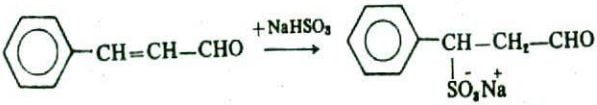


cinnamaldehyde cinnamyl alcohol

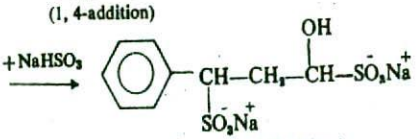
(3) It forms the normal bisulphite compound with $NaHSO_3$. However, on prolonged treatment with this reagent, the sodium salt of a disulphonic acid is produced.



cinnamaldehyde bisulphite compound



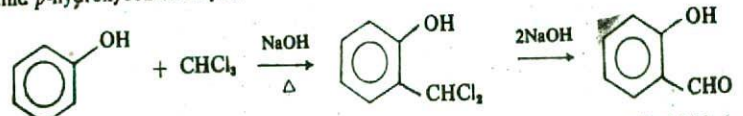
(1, 4-addition)



sodium salt of disulphonic acid

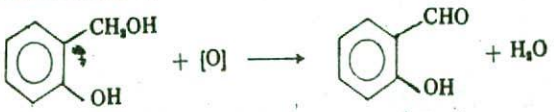
SALICYLALDEHYDE, *o-Hydroxybenzaldehyde*

It occurs in *Oil of Spirea*. (1) It may be made from phenol with the help of Reimer-Tiemann Reaction. An alkaline solution of phenol is refluxed with chloroform at 60°C, acidified with sulphuric acid, and then steam-distilled. *o*-Hydroxybenzaldehyde distils over, leaving behind *p*-hydroxybenzaldehyde.



phenol salicylaldehyde (steam-volatile)

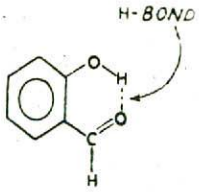
(2) It is manufactured by the oxidation of *o*-hydroxybenzyl alcohol.



o-hydroxybeazyl alcohol salicyladehyde

Properties. Salicylaldehyde is a colourless oil, bp 196°, having a pleasant smell. It gives the reactions of both aldehydes and phenols. Its aqueous solution gives a violet coloration with ferric chloride. It may be oxidised to salicylic acid or reduced to *o*-hydroxybenzyl alcohol.

Salicylaldehyde is high boiling compared to *m*- and *p*-isomers which is attributed to hydrogen bonding.

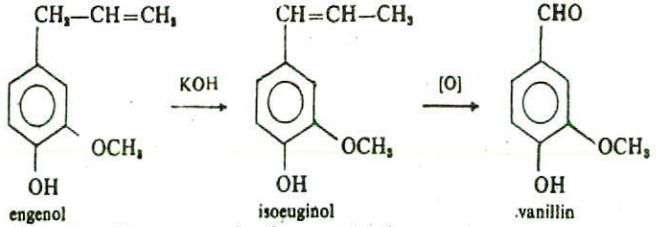


Salicylaldehyde is used for the preparation of coumarin by Perkin's reaction.

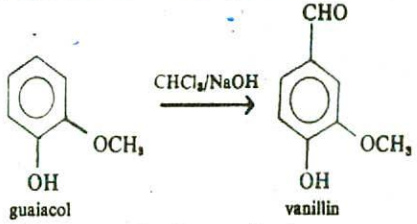
VANILLIN, *p*-Pydroxy-*m*-*methoxybenzaldehyde*

It is the sweet-smelling principle of *vanilla bean* and is extracted from it by means of ethanol. It is obtained industrially :

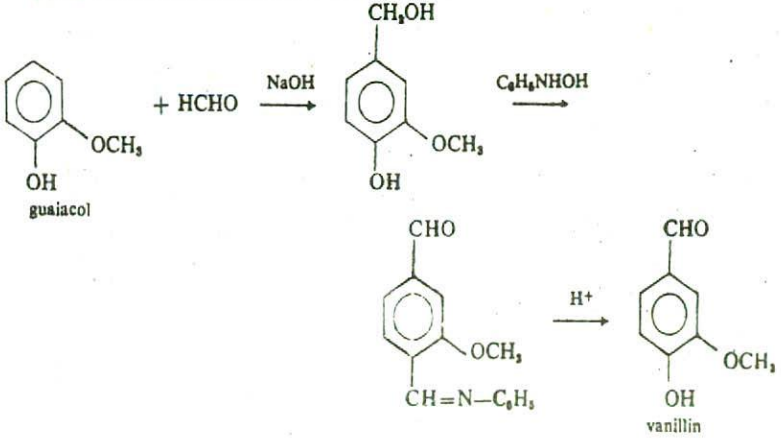
(1) By oxidation of *isoeuginol* with nitrobenzene.



(2) By Reimer-Tiemann reaction from *guaiacol*.



(3) By Lederer-Manasse reaction from guaiacol.



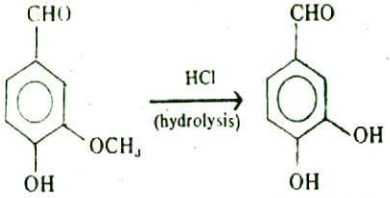
(4) Much of our present-day supply of vanillin is obtained by the hydrolysis of lignin, which is a by-product of paper industry.

Properties. Vanillin is a white crystalline solid, mp 81°C. It gives blue coloration with ferric chloride solution. On hydrolysis by heating with hydrochloric acid, it forms protocatechualdehyde. Oxidation with silver oxide in aqueous sodium hydroxide converts vanillin into vanillic acid.

2½ per cent ethanolic solution of vanillin is much used for flavouring confectionery.

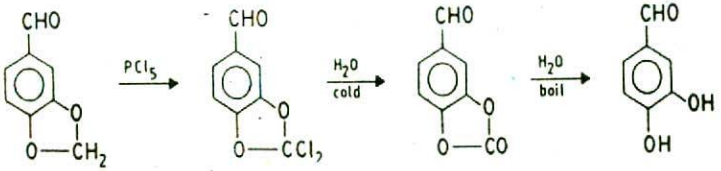
PROTOCATECHUALDEHYDE, *3, 4-Dihydroxybenzaldehyde*

(1) It may be prepared by heating vanillin with hydrochloric acid.



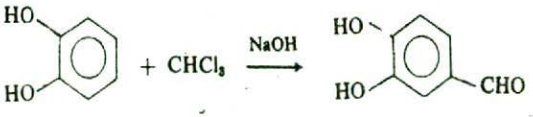
vanillin protocatechualdehyde

(2) By adding phosphorus pentachloride to piperonal, then treating the product with cold water, and finally boiling the solution.



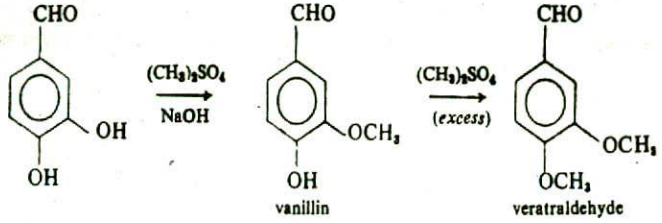
PIPERONAL PROTOCATECHU-ALDEHYDE

(3) By synthesis from catechol by Reimer-Tiemann reaction.



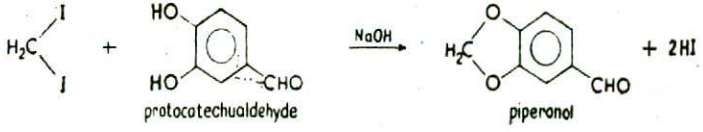
catechol protocatechualdehyde

Properties. Protocatechualdehyde is a crystalline solid, mp 153°C. It produces green coloration with ferric chloride and reduces ammoniacal silver nitrate solution. On oxidation it gives protocatechuic acid. When treated with dimethyl sulphate it gives vanillin and veratraldehyde.

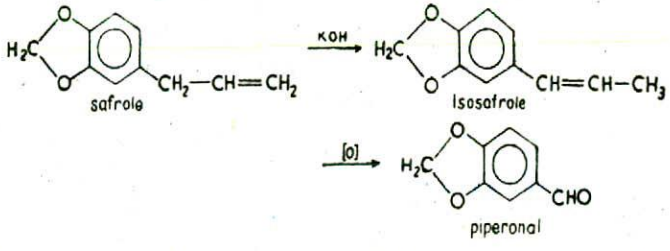


PIPERONAL, 3, 4-Methylenedioxybenzaldehyde

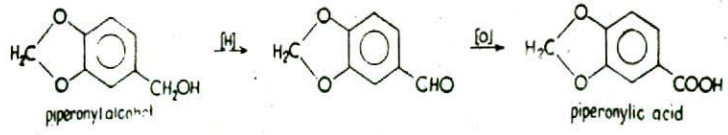
It is the methylene ether of protocatechualdehyde. It was so named as it is produced by oxidation of piperic acid (from alkaloid piperine). It may be synthesised by treating protocatechualdehyde with methylene di-iodide (CH_2I_2) and alkali.



It is made industrially from *safrole* by the same steps as for vanillin from eugenol



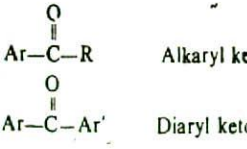
Properties. Piperonal is a white solid, mp 137°C. It has the smell of helitrope; hence its name *heliotropin*. It can be oxidised to piperonylic acid and reduced to piperonyl alcohol.



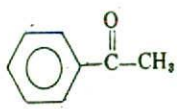
When heated with dilute hydrochloric acid, piperonal is decomposed to form protocatechuic aldehyde together with formaldehyde or methanol. Piperonal has a pleasant odour and is used in perfumery.

II. KETONES

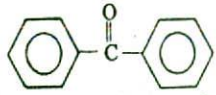
Ketones in which one or both the hydrocarbon groups attached to the carbonyl (—CO—) are aryl, are referred to as **Aromatic Ketones**. Thus these could be designated as *alkaryl* or *diaryl ketones*.



Ketones containing the carbonyl group attached to a benzene ring are named **Phenones.** The individual name of such a ketone is derived by adding *-phenone* or *-ophenone* to the stem formed by removing *-ic* from the name of the corresponding acid (RCOOH or Ar'COOH).



acetophenone
(methyl phenyl ketone)



benzophenone
(diphenyl ketone)

The common names of aromatic ketones are obtained as usual by naming the alkyl or aryl groups attached to the carbonyl group, followed by the word *ketone*. These are given in the brackets above.

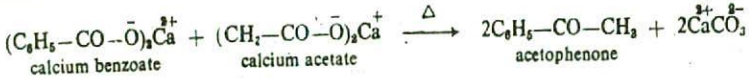
Although aromatic ketones may be prepared by any of the methods used for aliphatic ketones, they are generally prepared by means of Friedel-Crafts reaction between an aromatic hydrocarbon and acyl chloride or acid anhydride.

The reactivity of the carbonyl group in aromatic ketones is not greatly affected by the aryl groups attached to it In consequence, they undergo the same general reactions as aliphatic ketones. However, they decline to form the bisulphite compound, and in addition give the usual substitution reactions in the aromatic ring.

ACETOPHENONE, *Methyl phenyl ketone, Acetylbenzene*

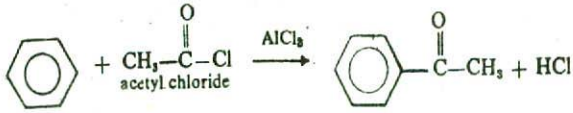
It is the best known alkaryl ketone.

Preparation. (1) It may be prepared by distilling a mixture of calcium benzoate and calcium acetate.



calcium benzoate + calcium acetate → acetophenone + $2Ca^{3+}CO_3^{2-}$

(2) It is obtained conveniently in the laboratory by Friedel-Crafts reaction from benzene and acetyl chloride.



acetyl chloride; acetophenone

(3) It is produced industrially by the catalytic oxidation of ethylbenzene with air at 126° C under pressure in the presence of manganese acetate

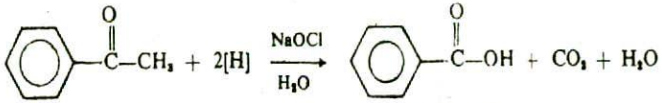


ethylbenzene; acetophenone

Properties (*Physical*). Acetophenone is a colourless, crystalline solid, mp 20°C, bp 202°C, having a smell of hay. It is sparingly soluble in water but dissolves readily in ethanol and diethyl ether. It is steam-volatile. When administered orally, it produces a natural type of sleep.

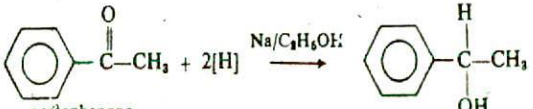
(*Chemical*). Acetophenone gives all the reactions of aliphatic ketones, except that it does not form a bisulphite compound, probably owing to steric hindrance offered by the phenyl group.

(1) On oxidation with NaOCl in water, or with potassium permanganate, or nitric acid, it is converted to benzoic acid.



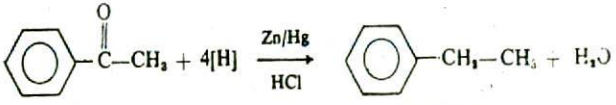
acetophenone benzoic acid

(2) On reduction with sodium and ethanol, it form methylphenylcarbinol.



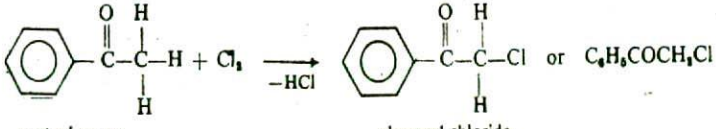
acetophenone methylphenyl carbinol (2° alcohol)

On reduction with amalgamated zinc and hydrochloric acid, it forms ethylbenzene.



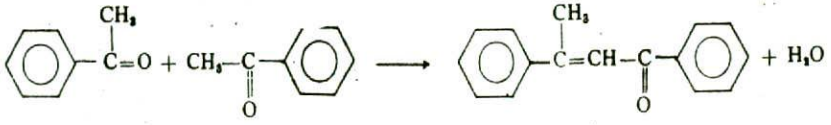
ethylbenzene

(3) On chlorination it readily forms *phenacyl chloride* which is a relatively harmless but powerful lachrymator and is used by police as '*mob gas*'.



acetophenone phenacyl chloride

(4) In the presence of aluminium *tert*-butoxide, acetophenone condenses with itself to give dypnone.



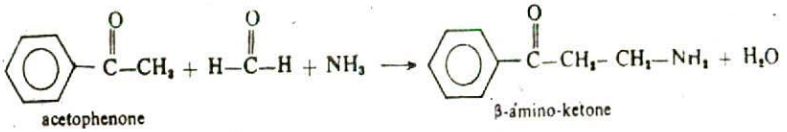
acetophenone (2 moles) dypnone

(5) When acetophenone is heated with equimolecular quantities of sulphur and an anhydrous amine, a thioamide is the product. This on hydrolysis with acid or alkali yields aryl-substituted aliphatic acid. The total reaction (**Willgerodt Reaction**) is used for the synthesis of such acids.

$$\underset{\text{acetophenone}}{C_6H_5-CO-CH_3} + S + H_2NR \longrightarrow \underset{\text{a thioamide}}{C_6H_5-CH_2-\overset{\overset{S}{\|}}{C}-NR_2} \xrightarrow{H_2O/H^+} C_6H_5-CH_2-COOH + H_2S + HNR_2$$

phenylacetic acid

(6) Aryl alkyl ketones containing a hydrogen atom in the α position to the carbonyl group *e.g.*, acetophenone reacts with formaldehyde and ammonia (or a primary or secondary amine) to form β-amino-ketone. The product is often referred to as *Mannich Base* and the reaction is called **Mannich Reaction**.



acetophenone β-amino-ketone

The further reaction of the product with excess of ammonia takes place in a similar fashion.

Uses. Acetophenone has been used in perfumery; and as hypnotic under the name 'hypnone' but it has now been replaced by more effective drugs.

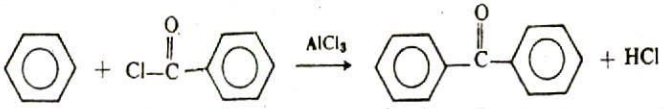
BENZOPHENONE, *Diphenyl ketone*, $C_6H_5-CO-C_6H_5$

It it a diaryl ketone with two benzene rings bonded to carbony. group.

Preparation. (1) By distilling calcium benzoate.

$$\underset{\text{calcium benzoate}}{(C_6H_5-CO-\bar{O})_2\overset{2+}{Ca}} \xrightarrow{\Delta} \underset{\text{benzophenone}}{C_6H_5-CO-C_6H_5} + \overset{3+}{Ca}\overset{2-}{CO_3}$$

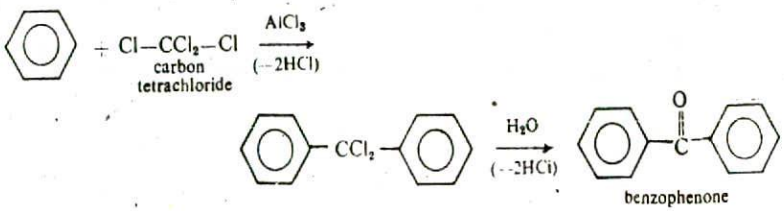
(2) By Friedel-Crafts reaction between benzene and benzoyl chloride.



benzophenone

Carbonyl chloride may be used in place of benzoyl chloride.

(3) It is often prepared by Friedel-Crafts reaction between benzene and carbon tetrachloride followed by hydrolysis of the geminal dichloride.

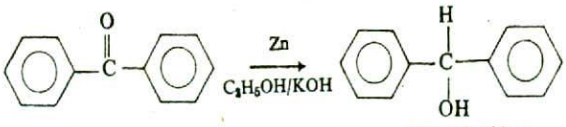


carbon tetrachloride

benzophenone

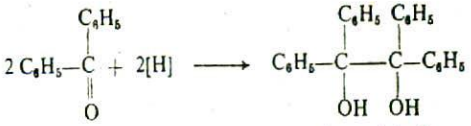
Properties. Benzophenone exists in two crystalline forms : a stable rhombic form, mp 49°C, and the other unstable monoclinic form, mp 26°C. It has an agreeable odour and is used in perfumery.

(1) *Reduction.* (*i*) When reduced with zinc and ethanolic potassium hydroxide, it gives diphenylcarbinol or benzhydrol (mp 68°C).



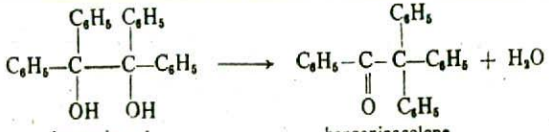
diphenylcarbinol
(benzhydrol)

(*ii*) When reduced with zinc and acetic acid, it yields benzopinacol.



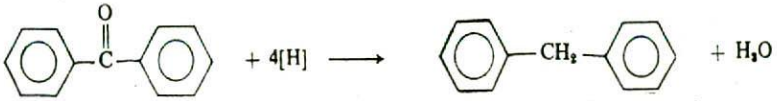
benzopinacol

Benzopinacol is also obtained by the reduction of benzophenone with a mixture of magnesium and magnesium iodide. Benzopinacol undergoes the pinacol-pinacolone rearrangement when heated in acetic acid and in the presence of iodine as catalyst.



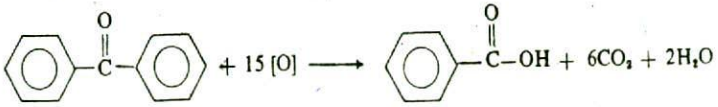
benzopinacol benzopinacolone

(*iii*) On reduction with hydrogen iodide, or with a mixture of lithium aluminium hydride and aluminium chloride, benzophenone produces diphenylmethane.



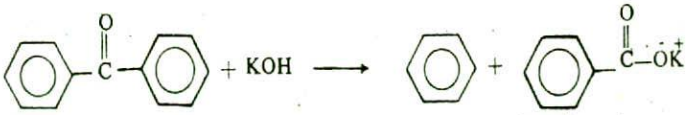
diphenylmethane

(2) *Oxidation.* On oxidation it yields benzoic acid, one benzene ring is completely oxidised.



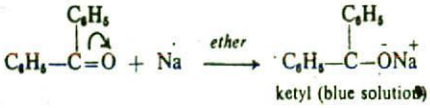
benzoic acid

(3) On fusion with potassium hydroxide, its molecule is split out to form benzene and potassium benzoate.

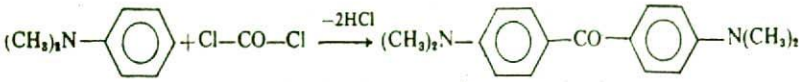


pot. benzoate

(4) Sodium dissolves in benzophenone in ether without the evolution of hydrogen to form a blue solution containing sodium salt of a free radical, **Metal ketyl**.



Michler's Ketone. It is an important derivative of benzophenone. It is prepared by treating dimethylaniline with carbonyl chloride in the presence of zinc chloride.

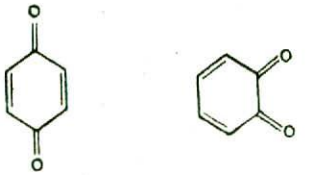


dimethylaniline carbonyl cloride Michler's ketone

Michler's ketone is used to prepare certain triphenylmethane dyes.

QUINONES

Quinones are cyclic α, β-unsaturated diketones. In these compounds the double bonds and the keto groups are conjugated. Truly speaking they are not aromatic derivatives, but they are readily prepared from, and converted into aromatic derivatives. The quinones derived from benzene are called **Benzoquinones**. In benzoquinones, the two keto groups usually exhibit the *para* configuration, although *ortho* quinones are known.



p-BENZOQUINONE, 1,4-BENZOQUINONE

o-BENZOQUINONE, 1, 2-BENZOQUINONE

A similar formula for the *m*-quinones cannot be constructed and it is not known to exist.

The name quinone is used both as a common name for *p*-benzoquinone and as a generic term for all compounds having an *ortho* or *para* quinonoid type of structure.

In quinones the low energy molecular orbitals of the original benzene ring have been replaced by other orbitals which extend over the carbon atoms of the ring and the two carbon-oxygen atoms. The structures of quinones are, therefore, stabilised by this delocalisation of the electrons.

Of the two benzoquinones, *p*-benzoquinone is by far the more important.

p-BENZOQUINONE, *p*-QUINONE

Being the most important member of the class, it is frequently referred to as simply *quinone*. In the classical structure of *p*-benzoquinone, each of the carbonyl double bonds is seen to be conjugated with both carbon-carbon double bonds. The structure is known as crossed conjugated system.

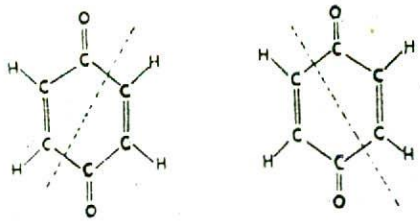
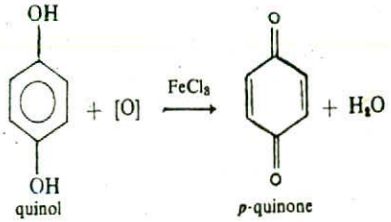
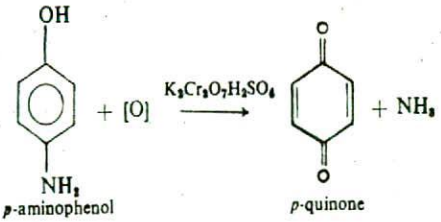


Fig. Crossed conjugation in *p*-benzoquinone.

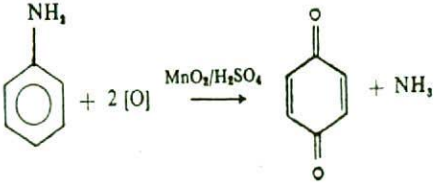
Preparation. (1) Quinone may be prepared by the oxidation of quinol with ferric chloride, manganese dioxide and sulphuric acid, or with acid dichromate.



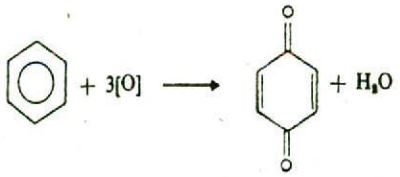
(2) It may be obtained by the oxidation of *p*-aminophenol with dichromate and sulphuric acid.



(3) It is prepared industrially by the oxidation of aniline with manganese dioxide and sulphuric acid or other oxidants.

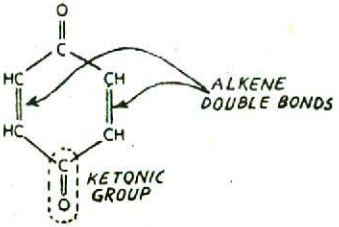


(4) It is also produced on a technical scale by the electrolytic oxidation of benzene in the presence of sulphuric acid.

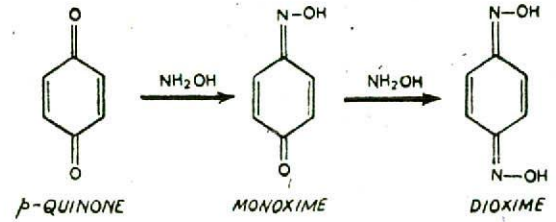


Properties. (*Physical*). *p*-Benzoquinone forms deep-yellow needle-like crystals, mp 116°C. It has a sharp pungent odour and causes sneezing. It is only slightly soluble in water but dissolves readily in ethanol, ether and chloroform. It sublimes when heated and is steam-volatile.

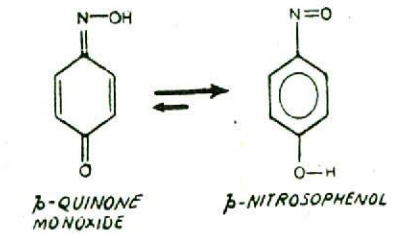
(*Chemical*). As expected from its structure, *p*-benzoquinone behaves as an α, β-unsaturated ketone. Thus it gives the reactions of alkenes as well as simple ketones. At any rate, quinone is not aromatic since it lacks the conjugate structure characteristic of aromatic compounds.



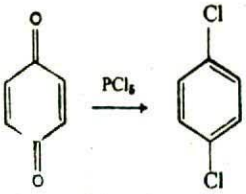
(1) *Reaction with Hydroxylamine.* Like simple ketones, *p*-quinone reacts with hydroxylamine to form a monoxime and dioxime, according to the proportions taken.



The monoxime is tautomeric with *p*-nitrosophenol.

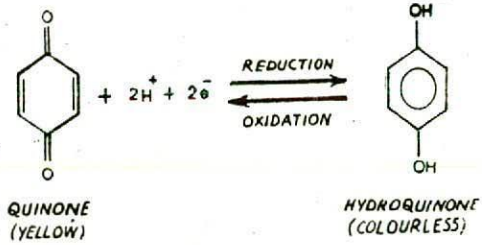


(2) *Reaction with PCl_5.* *p*-Quinone reacts with phosphorus pentachloride to form *p*-dichlorobenzene.



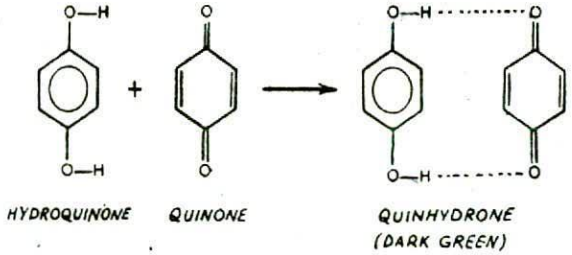
This reaction also illustrates the tendency of the quinonoid structure to pass to the more stable benzenoid structure. The net result of the reaction is that the carbonyl oxygen atoms are replaced by only one atom of chlorine, and not by two as is the case with normal ketones.

(3) *Reduction.* Quinone is reduced by sulphur dioxide, or $NaHSO_3$, or by Zn and HCl to form hydroquinone.



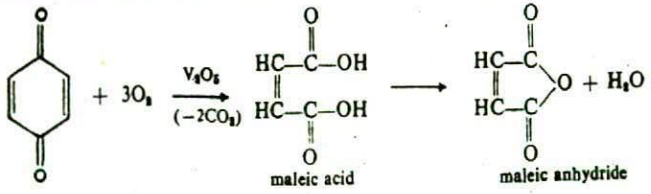
Since hydroquinone can easily be oxidised to quinone, these two compounds form an oxidation-reduction pair that may be used as indicator in redox reactions. While the quinone is yellow, hydroquinone is colourless.

When ethanolic solutions of quinone and hydroquinone are mixed, dark green crystals of *quinhydrone* are produced. Quinhydrone is a molecular complex composed of equimolecular amounts of quinone and hydroquinone.

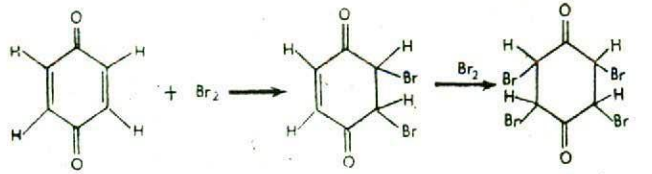


Quinhydrone is stable in the solid state but dissociates into its components in solution. It has an important practical use in the measurement of hydrogen ion concentration by the potentiometric method (quinhydrone electrode).

(4) *Oxidation.* When quinone is oxidised with air over vanadium pentoxide as catalyst, it yields maleic acid and then maleic anhydride. The reaction proceeds by ring fission.

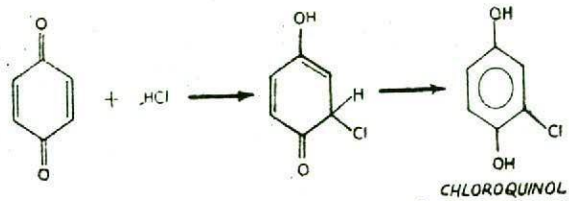


(5) *Addition of Bromine.* The carbon-carbon double bonds in p-quinone are olefinic in character. It undergoes addition reactions with reagents capable of adding to double bonds. Thus bromine will add to quinone in a 1, 2-addition to give the dibromide or the tetrabromide.



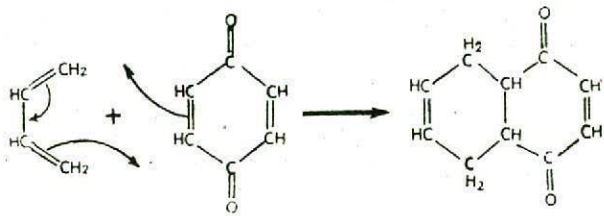
QUINONE QUINONE DIBROMIDE QUINONE TETRABROMIDE

(6) *Addition of HCl.* When hydrogen chloride gas is passed into a chloroform solution of *p*-quinone, 1, 4-addition takes place to form chlorohydroquinone.



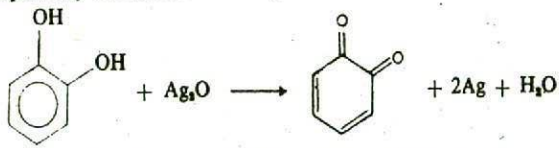
CHLOROQUINOL, CHLOROHYDROQUINONE

(7) *Addition of Dienes.* Dienes add across the carbon-carbon double bond of the quinone to yield cyclic compounds. (*Diels-Alder Diene Synthesis*).



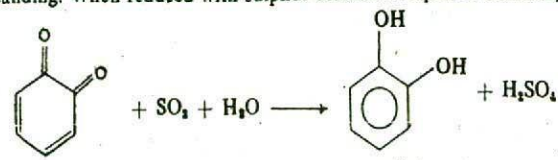
o-BENZOQUINONE, o-QUINONE

It is prepared by the oxidation of catechol with silver oxide in ether.



Anhydrous sodium sulphate is added to absorb the water produced in the reaction.

Properties. *o*-Quinone forms light-red crystals, mp 60-70° C with decomposition. It has no odour and is not volatile with steam. It is exceedingly unstable and decomposes spontaneously on standing. When reduced with sulphur dioxide in aqueous solution, it gives catechol.

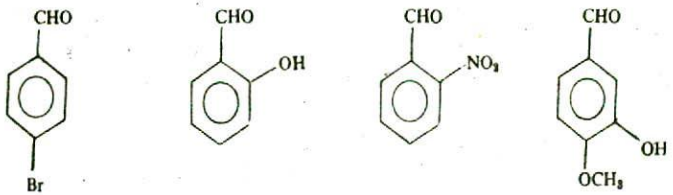


O-QUINONE catechol

QUESTIONS

1. How do you differentiate between aromatic aldehydes and aryl-substituted aliphatic aldehydes. Give one example of each type.

2. Assign IUPAC names to the following aromatic aldeydes.



3. Draw the molecular structure of benzaldehyde. In what way the presence of benzene ring modifies its behaviour compared to aliphatic aldehydes.

4. Discuss the methods of preparation of benzaldehyde as a representative of the aromatic aldehydes.

5 Bring out the differences in the chemical behaviour of aliphatic and aromatic aldehydes, taking examples of acetaldehyde and benzaldehyde.

6. Write notes on the following reactions, giving their mechanisms, as applied to benzaldehyde.
   (*a*) Cannizzaro reaction ; (*b*) Benzoin Condensation ; (*c*) Perkin Condensation ;
   (*d*) Knoevenagel Condensation ; (*e*) Reformatsky Reaction.

7. Write the methods of preparation, reaction and uses of
   (*i*) Cinnamaldehyde ; (*ii*) Salicylaldehyde ; (*iii*) Vanillin ; (*iv*) Protocatechualdehyde ;
   (*v*) Piperonal.

8. How do you define the terms *Aromatic Ketones* and *Phenones*. Write their general structural formulas.

9. How is Acetophenone obtained by synthesis on a large scale ? Give its reactions, making a special reaction of 'Willgerodt Reaction' and 'Mannich Reaction'.

10. Discuss the Friedel-Craft synthesis of benzophenone. What happens when it is subjected to oxidation and reduction.

11. What are Quinones ? Discuss in detail the preparation and reactions of *p*-Quinone

12. How is benzaldehyde converted into Cinnamic acid ? *(Mysore BSc II, 1980)*

13. How do you obtain benzoin from benzaldehyde ? Indicate the mechanism involved in the formation of benzoin from benzaldehyde. *(Andhra BSc II, 1980)*

14. Give an example of a Crossed Cannizzaro reaction, with benzaldehyde as one of the reactants. With benzophenone as the starting material, how would you prepare (*i*) Benzanilide and (*ii*) Diphenylmethane. *(Kerala BSc III, 1980)*

15. How do the following reagents react separately with acetaldehyde and benzaldehyde (any five):—
   (*i*) Hydrogen Cyanide (*ii*) Na/Hg and water (*iii*) Ammonia
   (*iv*) Caustic soda (*v*) Fehling solution
   (*iv*) Phosphorus pentachloride. *(Nagpur BSc II, 1981)*

16. How is acetophenone synthesised by Friedel-Crafts method ? Discuss the mechanism involved in it. How can you convert acetophenone into benzoic acid; methyl phenyl carbinol; ethylbenzene. *(Rajasthan BSc III, 1981)*

17. Give any two methods of preparing benzaldehyde from toluene. *(Gulbarga BSc II, 1981)*

18. What is Benzoin Condensation ? Explain it with mechanism. *(Poona BSc III, 1981)*

19. A compound $C_8H_{10}O$ reacts with $NaHSO_3$ to a white ppt. What structures it might have ? *(Osmania BSc III, 1981)*

20. (*a*) How is pure benzaldehyde prepared in lab ?
   (*b*) Explain the action of the following on benzaldehyde:
      (*i*) Sodium bisulphite
      (*ii*) Phenylhydrazine

(*iii*) Phosphorus pentachloride

(*iv*) Tollen's reagent

(*c*) How will you distinguish between acetaldehyde and benzaldehyde. (*Nagpur BSc II, 1982*)

21. Give three reactions to show that benzaldehyde and acetaldehyde react similarly and give four reactions to show that they react differently. (*Saugar BSc III, 1982*)

22. Write methods of preparation of benzaldehyde. (*Delhi BSc II, 1982*)

23. What reagent would best serve as the basis for a simple chemical test to distinguish between benzaldehyde and acetophenone ? (*Kerala BSc III, 1982*)

24. Give two methods of preparation and two reactions of benzaldehyde. (*Kerala BSc, 1992*)

25. Describe a method of preparation of salicylaldehyde. Give an example of Cannizzaro reaction. (*Kerala BSc, 1994*)

26. Write a note on : Perkin reaction. (*Madras BSc, 1994; Delhi BSc Hons, 1994*)

27. Write a note on : Cannizzaro reaction. (*Delhi BSc, 1993*)

28. Write a note on: Benzoin condensation. (*Madurai BSc, 1994*)

29. Discuss the mechanism of Perkin reaction. (*Bombay BSc, 1993; Anna BSc, 1994; Baroda BSc, 1994*)

30. Discuss the mechanism of Cannizzaro reaction. (*Marathwada BSc, 1993*)

31. Discuss the mechanism of Benzoin condensation. (*Karnataka BSc, 1994*)

32. How will you synthesise benzene from benzaldehyde ? (*Agra BSc, 1993*)

Hint. Use the following steps : (*i*) $KMnO_4$/heat, (*ii*) NaOH, and (*iii*) NaOH/CaO/heat.

33. Outline the methods of preparation, chemical properties, and uses of acetophenone. (*South Gujarat BSc, 1994*)

34. Give preparation and properties of aromatic aldehydes. (*Manipur BSc, 1994*)

35. Describe the laboratory preparation of benzaldehyde from benzyl chloride. From benzaldehyde how will you prepare the following ?

(*a*) Cinnamic acid; and (*b*) Benzaldoxime. (*Jadavpur BSc, 1994*)

36. How will you distinguish between benzaldehyde and acetophenone ? (*Madurai BSc, 1994*)

37. What happens when benzaldehyde is treated with acetic anhydride and sodium acetate at 180°C ? (*Delhi BSc, 1994*)

38. An unknown compound of molecular formula C_8H_8O gives the following results :

Tollens' test : *Negative*

2, 4-Dinitrophenylhydrazine : *Positive*

Iodoform : *Positive*

Suggest a possible structure of the compound.

Answer. $CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5$ (Acetophenone)

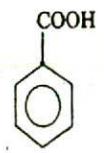
39. Compound (A), C_8H_9Cl, is hydrolysed by dilute acid to form (B), $C_8H_{10}Cl$. Compound (B) can be oxidised under mild reaction conditions to (C), C_8H_8O. Compound (C) gives positive iodoform test. Deduce and write structural formulas of compounds (A), (B) and (C).

Answer. (A) *is* 1-chloro-1-phenylethane; (B) *is* 1-phenylethanol; and (C) *is* acetophenone.

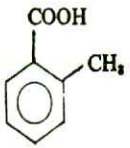
Aromatic Carboxylic Acids and Their Derivatives

Aromatic acids contain one or more carboxyl groups (COOH) attached directly to the aromatic nucleus. The acids in which the COOH group is attached to the side-chain may be regarded as aryl-substituted aliphatic acids. However, there are no characteristic differences in the behaviour of the nuclear and side-chain acids and the term 'aromatic acids' is rather loosely extended to include both classes of compounds.

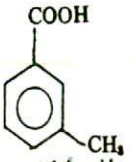
These are called by their common names or after the name of the parent hydrocarbon (IUPAC). Thus :



benzoic acid, benzenecarboxylic acid



o-toluic acid, *o*-methylbenzoic acid, 2-methylbenzenecarboxylic acid



m-toluic acid, *m*-methylbenzoic acid, 2-methylbenzenecarboxylic acid



p-toluic acid, *p*-methylbenzoic acid, 2-methylbenzenecarboxylic acid

STRUCTURE

Let us take the example of benzoic acid to illustrate the structure of this class of compounds. The structure of benzoic acid is very similar to the structure of nitrobenzene. Here the carbon of the carbonyl group is close enough to the benzene carbon so that the π electrons of the carbon-oxygen double bond interact with the π electrons of the benzene ring. The *p* orbitals of the C=O bond of the carboxyl group are aligned and they interact with the orresponding *p*-orbitals of the ring carbons to give an extended delocalised orbital.

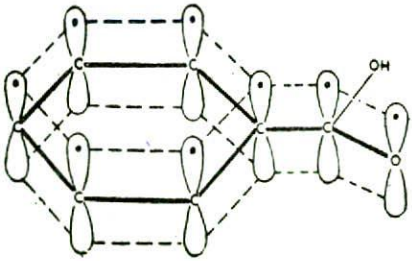


Fig. 44·1. Orbital structure of benzoic acid

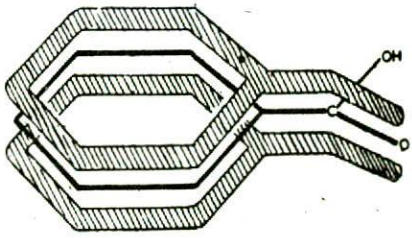
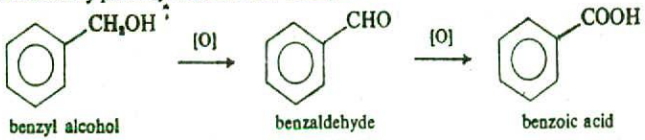


Fig. 44·2. Electron Cloud representation of benzoic acid

METHODS OF PREPARATION

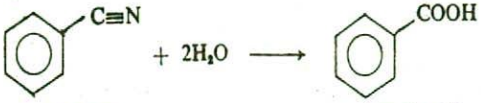
Aromatic acids can be prepared by the same general methods which are available for aliphatic acids. In addition they may be obtained by oxidation of aromatic hydrocarbons having a side-chain. It will suffice to list below the reactions by means of which aromatic acids can be prepared.

(1) *Oxidation of primary alcohols and aldehydes* :



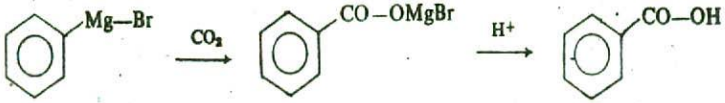
benzyl alcohol — benzaldehyde — benzoic acid

(2) Hydrolysis of Nitriles :



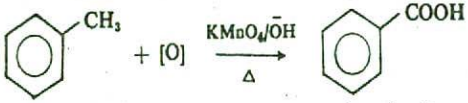
phenyl nitrile — benzoic acid

(3) *Carbonation of Grignard Reagents* :



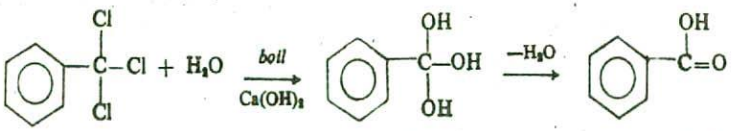
phenylmagnesium bromide — *intermediate* — benzoic acid

(4) *Oxidation of carbon side-chains* :



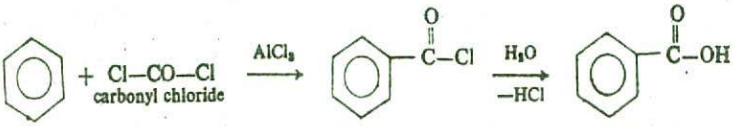
toluene — benzoic acid

(5) *Hydrolysis of trichloromethyl group on benzene nucleus* :



benzotrichloride — (*unstable*) — *benzoic acid*

(6) *Friedel-Crafts Reaction* :



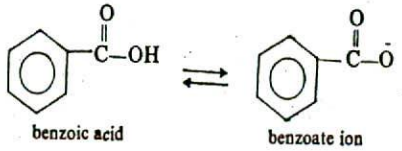
benzene — benzoyl chloride — benzoic acid

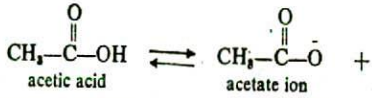
Properties (*Physical*). Aromatic acids are white crystalline solids, having higher melting points than aliphatic acids. They are slightly soluble in cold water but fairly so in hot water and organic solvents.

The infrared absorption region of the C=O group in aromatic acids is 1700 – 1680 $cm^{-1}(s)$. This is a lower frequency than for saturated aliphatic acids, and so can be distinguished from the latter.

(*Chemical*). For the most part the reactions of aromatic carboxylic acids are identical with those of aliphatic acids, the more important differences being in degree rather than in kind.

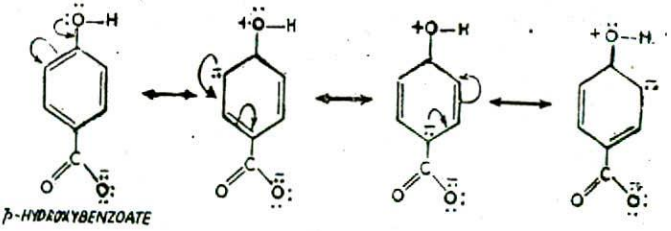
(1) **Acidity**. Aromatic carboxylic acids with unsubstituted benzene ring are slightly stronger acids than the aliphatic acids. Thus benzoic acid is somewhat stronger acid than acetic acid.

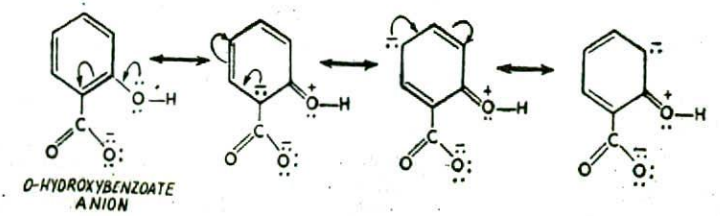




The effect of substituent groups in the ring on the acidity of benzoic acid (*i.e.*, on ionisation of —COOH) depends not only on the nature of the group but also its position with respect to the position of the COOH group.

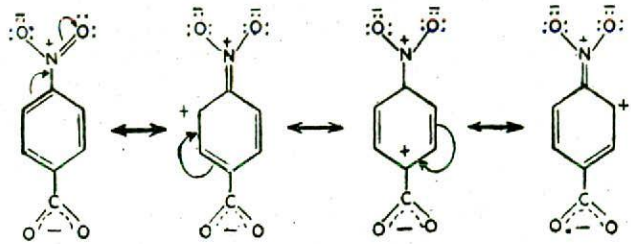
The acidity of aromatic carboxylic acids, in fact, is determined by the *inductive effect* as also the *resonance effect*. Electron-releasing substituents and ortho-para directors increase the electron-density in the ortho and para positions. Thus with OH group in the ortho or para position; the benzene ring is unable to delocalize the negative charge of the carboxylate anion (COO^-).





With long distances between the electron-releasing OH group, and carboxyl group, the inductive effect is important. However, with the decreasing distance, the inductive effect dominates over the resonance effect. That is why *o*-hydroxybenzoic acid is stronger ($Ka=100\times10^{-5}$) and *p*-hydroxybenzoic acid weaker ($Ka=2{\cdot}9\times10^{-5}$) than benzoic acid ($Ka=6{\cdot}3\times10^{-5}$).

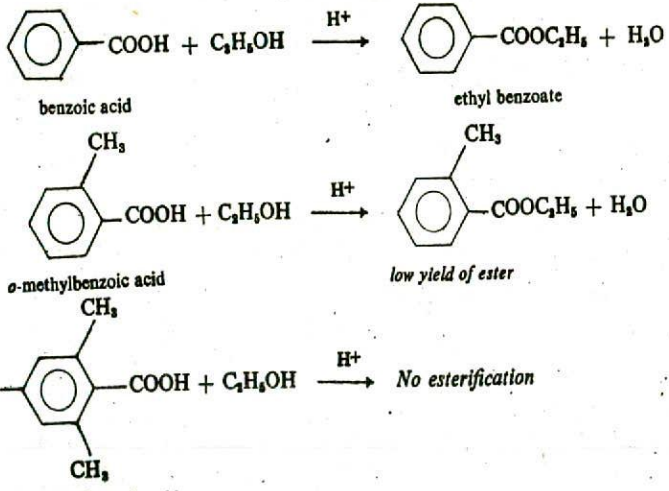
Electron-withdrawing substituents and meta directors like NO_2 group, on the other hand, decrease electron density ortho and para to them. Thus the negative charge of the carboxylate anion is delocalized and hence it is stabilised.



p-nitrobenzoate anion

That is why *p*-nitrobenzoic acid ($Ka = 40 \times 10^{-5}$) is stronger than benzoic acid ($Ka = 6{\cdot}3 \times 10^{-5}$). However, *p*-nitrobenzoic acid is weaker than *o*-nitrobenzoic acid ($Ka = 620 \times 10^{-5}$), where the strong inductive effect of the NO_2 group close to COO^- anion causes additional strong delocalization of the negative charge.

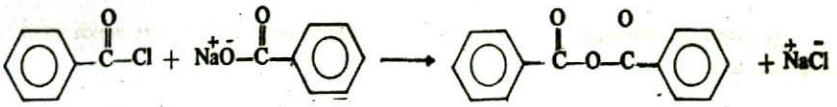
(2) **Esterification.** Aromatic acids having no substituent in the ortho position to COOH group, are readily converted into esters by direct reaction with alcohols in the presence of mineral acids (HCl or H_2SO_4) as catalyst. If, however, the ortho substituent is present, the rate of esterification is considerably reduced. When both ortho positions are occupied, esterification does not occur at all.



2, 4, 6-trimethylbenzoic acid

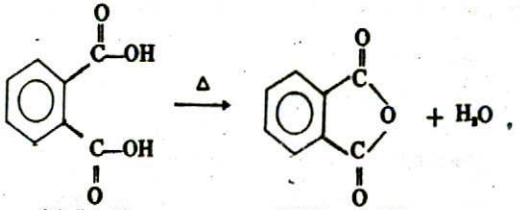
However, the esters of ortho-substituted benzoic acids can be prepared by the action of silver salts with alkyl halides. But once they are formed, they cannot be hydrolysed easily. These 'ortho effects' are observed regardless of the nature of substituents and are apparently due to *steric hindrance.* Groups larger than hydrogen so effectively occupy the space around the carbon of the COOH group that the intermediate *transition complex* necessary for the reaction to proceed cannot be formed.

(3) **Anhydride Formation.** The reaction of an aromatic acid chloride with sodium salt of the acid yields the anhydride.



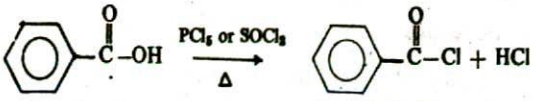
benzoyl chloride sod. benzoate benzoic anhydride

An aromatic dicarboxylic acid in which the two COOH groups are close together, give anhydride simply on heating. Thus, *o*-phthalic acid when heated forms *o*-phthalic anhydride, while *p*-phthalic acid is not decomposed.



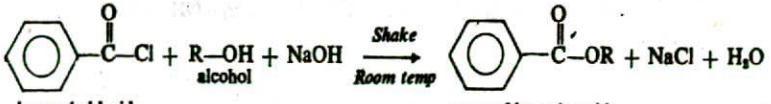
o-phthalic acid phthalic anhydride

(4) **Acid Halide Formation.** Aromatic acids, like the aliphatic acids, are converted to the corresponding acid halides by heating with phosphorus pentachloride or with thionyl chloride.

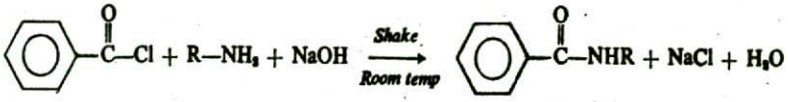


benzoic acid benzoyl chloride

The aromatic acid chlorides (aroyl chlorides), are insoluble in water and react with it very slowly. Hence alcohols, phenols and amines can be acylated in aqueous solution. When the acylation reaction is carried in the presence of alkali (NaOH), it is catalysed and the HCl formed in the reaction mixture is removed. This is called **Schotten-Baumann Reaction.** Thus,



benzoyl chloride ester of benzoic acid

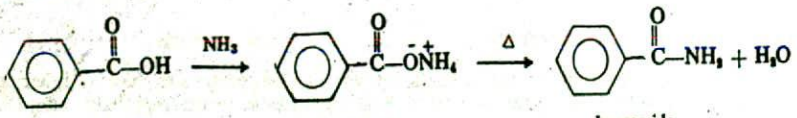


N-substituted benzamide

This is a good method of preparing benzoyl derivatives of alcohols or phenols, and of primary or secondary amines. It consists of shaking together at room temperature benzoyl chloride, dilute NaOH solution, and alcohol, phenol or amine.

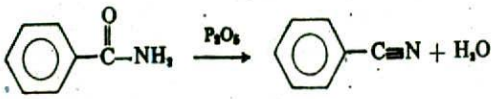
An improvement on the original Schotten-Baumann method is the use of pyridine in place of aqueous NaOH. The pyridine functions both as a solvent and a base for the removal of HCl produced in the reaction. Pyridine itself being a tertiary base does not react with benzoyl chloride. The use of NaOH on the other hand can convert the latter into sodium benzoate, thus lowering the yield of the product.

(5) **Acid Amide Formation.** Aromatic acids form ammonium carboxylates which upon heating yield acid amides.



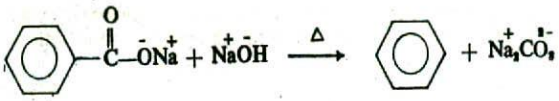
benzoic acid amm benzoate benzamide

In the presence of phosphorus pentoxide, amides further dehydrate to form nitriles.



benzamide benzonitrile

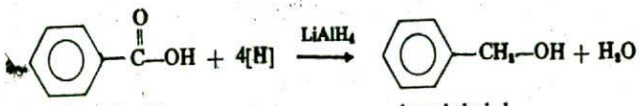
(6) **Decarboxylation.** Aromatic acids are readily decarboxylated by heating their salts with sodalime.



sod benzoate benzene

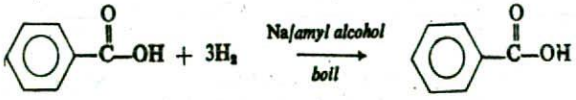
As compared to similar decarboxylation of aliphatic acids, the reaction here is much cleaner as less byproducts are produced.

(7) **Reduction.** Aromatic acids on reduction with lithium aluminium hydride give benzyl alcohols in 80 to 99 per cent yield.



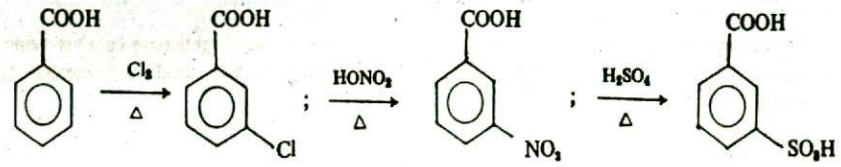
benzoic acid benzyl alcohol

Ordinary reducing agents, like hydrogen and metal catalyst or sodium and alcohol, fail to reduce the carboxyl group and rather bring about the reduction of the aromatic ring. Thus benzoic acid when reduced with sodium and boiling amyl alcohol is converted to cyclohexane carboxylic acid.



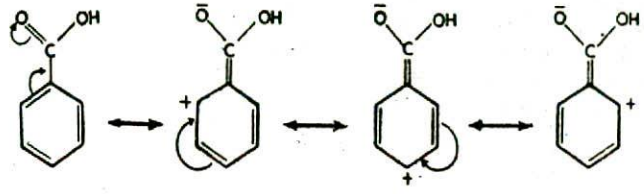
benzoic ocid cyclohexanecarboxylic acid

(8) **Electrophilic Substitution in Benzene ring.** Aromatic acids undergo electrophilic substitution reactions in the benzene ring. The COOH group is meta director and the substitution takes place less readily than in the parent hydrocarbon ring. For example, benzoic acid undergoes halogenation, nitration and sulphonation giving *m*-chlorobenzoic acid, *m*-nitrobe and *m*-benzenesulphonic acid.



benzoic acid — *m*-chlorobenzoic acid — *m*-nitrobenzoic acid — *m*-benzenesulphonic acid

The *m*-directive influence of COOH group operates through inductive and resonance effects.



The overall result is a *pi* electron drain from the benzene ring which is rendered electron-deficient. This means that the benzene ring has become deactivated towards attack by electrophilic reagents. Although the benzene ring is deactivated, the electrophilic attack will still take place, but less readily. Owing to resonance effect the carbon atoms 2, 4, and 6 become positively charged with respect to carbon atoms 3 and 5. Thus the electrophilic reagents will attack at carbon atoms 3 and 5.

BENZOIC ACID, *Benzenecarboxylic acid*, C_6H_5COOH

It is the simplest and the most familiar aromatic acid. It was first obtained by Scheele (1775) from gum benzoin (whence its name), a natural resin got from trees in Java and Sumatra. It occurs as benzyl ester in Peru and Tolu balsams and as benzoyl glycine in the urine of horses and oxen.

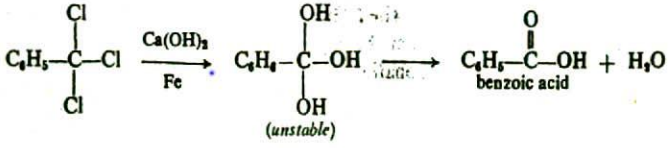
Preparation. Benzoic acid may be obtained by any of the general methods. Commercially it is prepared :

(1) By oxidation of toluene with air and Co-Mn acetates as catalyst.

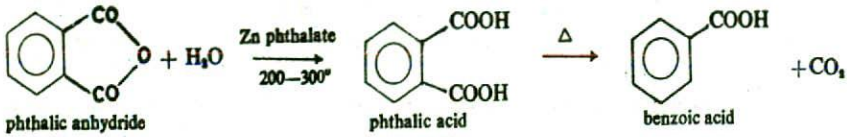
$$\underset{\text{toluene}}{2C_6H_5{-}CH_3} + 3O_2 \xrightarrow{170^\circ} \underset{\text{benzoic acid}}{2C_6H_5{-}COOH} + 2H_2O$$

(2) By chlorinating toluene to benzotrichloride and hydrolysing the latter by boiling with aqueous calcium hydroxide in the presence of iron powder as catalyst.

$$C_6H_5{-}CH_3 \xrightarrow[boil]{Cl_2} \underset{\text{benzotrichloride}}{C_6H_5{-}CCl_3}$$



(3) By passing phthalic anhydride and steam over a metal phthalate catalyst (zinc, chromium or nickel phthalate) at 200—300°C. The resulting phthalic acid is converted to benzoic acid by decarboxylation.



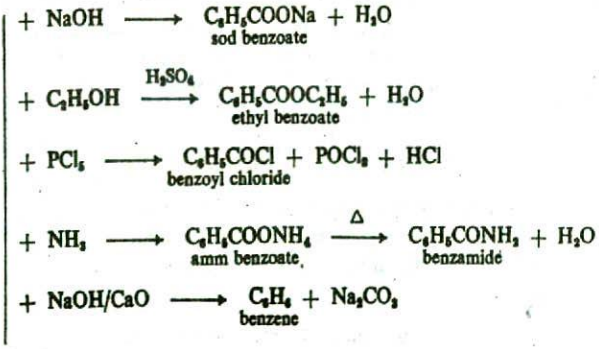
phthalic anhydride — phthalic acid — benzoic acid

Properties (*Physical*). Benzoic acid is a white solid, mp 122°C, crystallising from water in pearly flakes. It is sparingly soluble in cold water but dissolves readily in hot water, ether, ethanol and benzene. It is steam-volatile and may be sublimed. Its vapours have a peculiarly pungent odour which causes coughing and sneezing. Benzoic acid is a slightly stronger acid than acetic acid ($Ka = 6{\cdot}3 \times 10^{-5}$; $1{\cdot}75 \times 10^{-5}$).

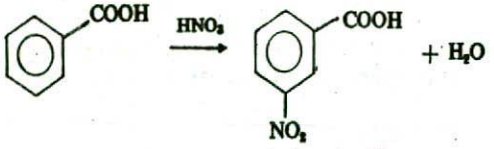
(*Chemical*). The reactions of benzoic acid are those of the carboxyl group and the benzene ring.

(*a*) *Reactions of COOH*:

C_6H_5COOH (Benzoic acid)



(2) *Reactions of* C_6H_5. The benzene ring of benzoic acid gives the usual electrophilic substitution reactions. The COOH group is meta director and substitution, therefore, takes place less readily than with benzene. Thus :



m-nitrobenzoic acid

Similarly with sulphuric acid it gives *m*-sulphonic acid and with chlorine *m*-chlorobenzoic acid.

Uses. Benzoic acid is used : (1) in medicine as urinary antiseptic and in vapour form for disinfecting bronchial tubes; (2) in the dye industry for making aniline blue; and (3) as a preservative. Sodium benzoate being less toxic, is used for preserving food products such as *tomato ketchup* and fruit juices.

BENZOYL CHLORIDE, *Benzenecarbonyl chloride,* $C_6H_5-CO-Cl$.

It is a typical aromatic acid chloride and occupies the same position in the aromatic series that acetyl chloride occupies among aliphatic compounds.

Preparation. (1) It is prepared most conveniently in the laboratory by distilling benzoic acid with phosphorus pentachloride or with thionyl chloride ($SOCl_2$).

$$\underset{\text{benzoic acid}}{C_6H_5-CO-OH} + PCl_5 \xrightarrow{\textit{distil}} \underset{\text{benzoyl chloride}}{C_6H_5-CO-Cl} + POCl_3 + HCl$$

$$C_6H_5-CO-OH + \underset{\text{thionyl chloride}}{Cl-SO-Cl} \xrightarrow{\Delta} C_6H_5-CO-Cl + SO_2 + HCl$$

(2) Benzoyl chloride is also obtained by the action of carbonyl chloride ($COCl_2$) on benzene in the presence of anhydrous aluminium chloride. (*Friedel-Crafts Reaction*)

$$C_6H_6 + \underset{\text{phosgene}}{Cl-CO-Cl} \xrightarrow{AlCl_3} C_6H_5-CO-Cl + HCl$$

(3) It is made commercially by chlorination of boiling benzaldehyde.

$$\underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{O}{\|}}{C}-H} + Cl_2 \xrightarrow{\textit{boil}} \underset{\text{benzoyl chloride}}{C_6H_5-\overset{\overset{O}{\|}}{C}-Cl} + HCl$$

Properties. Benzoyl chloride is a colourless liquid, bp 198°C, fuming in moist air. It has a pungent odour and its vapours cause profuse watering of eyes and nose. It is practically insoluble in water.

Benzoyl chloride gives all the reactions of acetyl chloride but at a slower rate.

(1) *Hydrolysis.* It is slowly hydrolysed by hot water to form benzoic acid.

$$\underset{\text{benzoyl chloride}}{C_6H_5-CO-Cl} + H-O-H \xrightarrow{\Delta} \underset{\text{benzoic acid}}{C_6H_5-CO-OH} + HCl$$

(2) *Alcoholysis.* It reacts with alcohols (and phenols) to form esters.

$$C_6H_5-CO-Cl + \underset{\text{ethyl alcohol}}{HO-C_2H_5} \longrightarrow \underset{\text{ethyl benzoate}}{C_6H_5-CO-OC_2H_5} + HCl$$

(3) *Ammonolysis.* It reacts with aqueous ammonia and amines to form benzamide and N-substituted-benzamides.

$$C_6H_5-CO-Cl + aqNH_3 \longrightarrow \underset{\text{benzamide}}{C_6H_5-CO-NH_2} + HCl$$

$$C_6H_5-CO-Cl + RNH_2 \longrightarrow \underset{\text{N-alkylbenzamide}}{C_6H_5-CO-NH-R} + HCl$$

(4) *Reaction with Sodium benzoate.* It reacts with sodium benzoate to yield anhydride.

$$C_6H_5-CO-Cl + \underset{\text{sod benzoate}}{\overset{+\ -}{Na}O-CO-C_6H_5} \longrightarrow \underset{\text{benzoic anhydride}}{C_6H_5-CO-O-CO-C_6H_5} + \overset{+\ -}{Na}Cl$$

(5) *Friedel-Crafts Reaction.* It reacts with benzene in the presence of $AlCl_3$ catalyst to give benzophenone.

$$C_6H_5-CO-Cl + C_6H_6 \xrightarrow{AlCl_3} \underset{\text{benzophenone}}{C_6H_5-CO-C_6H_5} + HCl$$

Uses. Benzoyl chloride is used : (1) in tear gases to disperse mobs; and (2) for introducing benzoyl group (C_6H_5CO-) in hydroxy and amino compounds (*Schotten-B umann Reaction*).

BENZAMIDE, $C_6H_5-CO-NH_2$

It is the amide of benzoic acid, $C_6H_5-CO-OH$. It may be prepared :

(1) By the action of concentrated aqueous ammonia or ammonium carbonate.

$$\underset{\text{benzoyl chloride}}{C_6H_5-CO-Cl} + 2NH_3 \longrightarrow \underset{\text{benzamide}}{C_6H_5-CO-NH_2} + NH_4Cl$$

(2) By Friedel-Crafts reaction between benzene and carbamyl chloride.

$$\underset{\text{benzene}}{C_6H_5-H} + \underset{\text{carbamyl chloride}}{Cl-CO-NH_2} \longrightarrow C_6H_5-CO-NH_2 + HCl$$

Properties. Benzamide is a white crystalline solid, mp 130°C. It is insoluble in cold water but dissolves in hot. It undergoes most of the general reactions of aliphatic acid amides. It is readily hydrolysed to benzoic acid and ammonia, on boiling with dilute mineral acid or alkali. It forms benzonitrile on heating with P_2O_5.

$$\underset{\text{benzamide}}{C_6H_5-CO-NH_2} + \underset{\text{water}}{HO-H} \xrightarrow{\bar{O}H} \underset{\text{benzoic acid}}{C_6H_5-CO-OH} + NH_3$$

$$C_6H_5-CO-NH_2 \xrightarrow[\Delta]{P_2O_5} \underset{\text{benzonitrile}}{C_6H_5-C\equiv N} + H_2O$$

The negative benzoyl group (C_6H_5-CO-) confers acidic properties to the hydrogen atom bonded to the nitrogen atom. Thus benzamide dissolves in alkali (NaOH) to form salts, *e.g.*, $C_6H_5-CO-NHNa$. With mercury oxide, it gives mercurybenzamide, $(C_6H_5-CO-NH)_2Hg$.

BENZOIC ANHYDRIDE, $C_6H_5-CO-O-CO-C_6H_5$

It may be prepared by heating benzoyl chloride with sodium benzoate.

$$\underset{\text{sod benzoate}}{C_6H_5-CO-\bar{O}\overset{+}{N}a} + \underset{\text{benzoyl chloride}}{Cl-CO-C_6H_5} \xrightarrow{\Delta} \underset{\text{benzoic anhydride}}{C_6H_5-CO-O-CO-C_6H_5} + \overset{+}{N}a\bar{C}l$$

A better method is to boil a mixture of benzoic acid and acetic anhydride.

$$\underset{\text{benzoic acid}}{2C_6H_5-CO-OH} + \underset{\text{acetic anhydride}}{(CH_3-CO)_2O} \xrightarrow{boil} \underset{\text{benzoic anhydride}}{(C_6H_5-CO)_2O} + 2CH_3COOH$$

Properties. Benzoic anhydride is a white crystalline solid, mp 42°C. Its reactions are similar to those of acetic anhydride, but it is much less reactive. It is only slowly decomposed by water to regenerate benzoic acid.

$$\underset{\text{benzoic anhydride}}{C_6H_5-CO-O-CO-C_6H_5} + H-O-H \longrightarrow \underset{\text{benzoic acid}}{2C_6H_5-CO-OH}$$

It may be used for benzoylation, but benzoyl chloride is more convenient for the purpose.

BENZOYL PEROXIDE, $C_6H_5-CO-O-O-CO-C_6H_5$

It is prepared by adding sodium peroxide to stirred mixture of benzoyl chloride, ice and water.

$$2C_6H_5-CO-Cl + Na_2O_2 \longrightarrow \underset{\text{benzoyl peroxide}}{C_6H_5-CO-O-O-CO-C_6H_5} + 2NaCl$$

Benzoyl peroxide is a relatively stable colourless solid, mp 108°C. It acts as an oxidising and disinfecting agent. Hence it is a harmless bleaching agent and is often used for bleaching edible oils and fats, and for wheat flour.

PHENYL CYANIDE, *Benzonitrile*, $C_6H_5-C\equiv N$

It can be prepared by heating benzamide with phosphorus pentoxide.

$$\underset{\text{benzamide}}{C_6H_5-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[\Delta]{P_2O_5} \underset{\text{phenyl nitrile}}{C_6H_5-C\equiv N} + H_2O$$

It may also be obtained by fusing sodium benzenesulphonate with sodium cyanide, or by Sandmeyer reaction by treating benzenediazonium chloride with potassium cyanide.

Benzonitrile is a colourless oil, bp 191°C, having smell of bitter almonds. It forms benzoic acid on hydrolysis, and benzylamine on reduction.

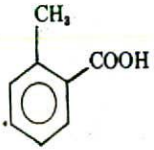
$$\underset{\text{benzonitrile}}{C_6H_5-C\equiv N} \xrightarrow{+H_2O} \underset{\text{benzamide}}{C_6H_5-CO-NH_2} \xrightarrow{H_2O} \underset{\text{benzoic acid}}{C_6H_5-CO-OH} + NH_3$$

$$C_6H_5-C\equiv N + 4[H] \longrightarrow \underset{\text{benzylamine}}{C_6H_5-CH_2-NH_2}$$

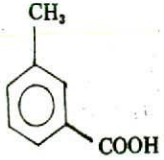
SUBSTITUTED BENZOIC ACIDS

TOLUIC ACIDS, *Methylbenzoic acids*, $C_6H_4(CH_3)COOH$

o-, *m*- and *p*-toluenecarboxylic acids are given the common name Toluic acids.



o-toluic acid,
2-methylbenzoic acid



m-toluic acid,
3-methylbenzoic acid

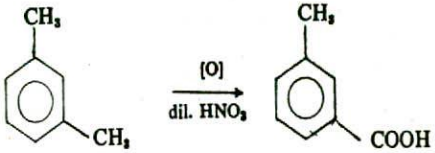


p-toluic acid
4-methylbenzoic acid

These are isomeric with phenylacetic acid.

Preparation. The toluic acids may be prepared :

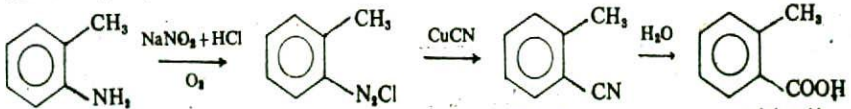
(1) By oxidation of one of the methyl groups of the corresponding xylene by dilute nitric acid or permanganate. Thus :



m-xylene

m-toluic acid

(2) From corresponding toluidines *via* the diazonium salt which is converted to nitrile and then hydrolysed. Thus :



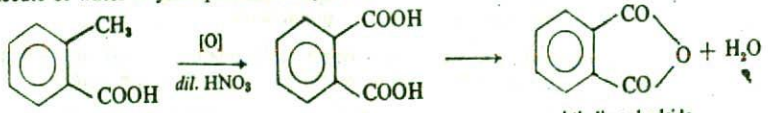
o-toluidine,
o-methylaniline

diazonium salt

nitrile

o-toluic acid

Properties. The toluic acids are white solids, mps : *ortho* 104°; *meta* 111° ; *para* 178°. Since the methyl groups are almost unreactive, toluic acids behave very similar to benzoic acid. However, on oxidation with dil HNO_3 or alkaline $KMnO_4$ they give the respective benzene-dicarboxylic acids. Unlike *m*- and *p*-phthalic acids, *o*-phthalic acid on heating eliminates a molecule of water to yield phthalic anhydride.

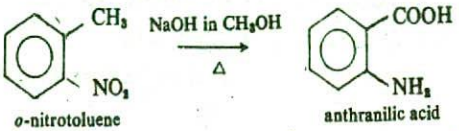


o-toluic acid *o*-phthalic acid phthalic anhydride

ANTHRANILIC ACID, *o-Aminobenzoic acid*

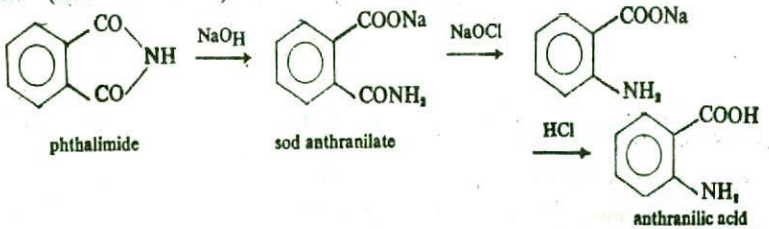
Of the three aminobenzoic acids, ortho derivative is the most important. It occurs as methyl ether in jasmine. Methyl anthranilate contributes to the odour and flavour of grapes.

Preparation. Anthranilic acid may be prepared by reducing *o*-nitrobenzoic acid, or by boiling alkaline solution of *o*-nitrotoluene in methanol (internal oxidation).



o-nitrotoluene anthranilic acid

Technically, it is made from phthalimide by action with aqueous alkali and sodium hypochlorite. (Hofmann Reaction)



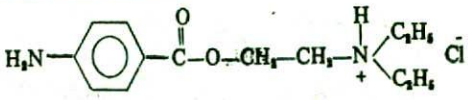
phthalimide sod anthranilate anthranilic acid

Properties. Anthranilic acid is a white solid, mp 145°C. It is readily soluble in water and ethanol; and has sweet taste. It gives all the reactions of aromatic amine and carboxylic acid. On heating it is decarboxylated to form aniline.

Uses. At one time large quantities of anthranilic acid were used for the synthesis of indigo. It is still used for the synthesis of thioindigo and other dyes. Methyl anthranilate is a constituent of natural aroma of jasmine and orange blossoms, and of grapes; hence its use in perfumery.

p-AMINOBENZOIC ACID (*PABA*)

It is prepared by the reduction of *p*-nitrobenzoic acid. It is a solid substance, mp 186°C. It is one of the substances present in the *Vitamin B complex*. It is used for the preparation of certain local anaesthetics as *novocaine*.



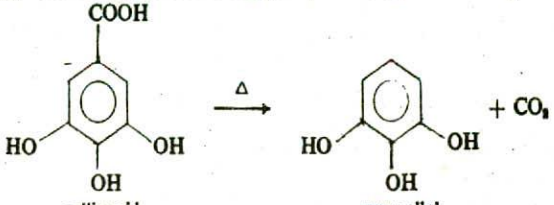
(β-diethylaminoethyl ester hydrochloride)

Novocaine is much used in dentistry.

GALLIC ACID, *3, 4, 5-Trihydroxybenzoic acid,* $C_6H_2(OH)_3COOH$

It occurs widely in galls, tea, oak bark, *kikar* bark etc., in the free state and as a unit of *tannin* (gallic acid esters of glucose) molecule. It is best prepared by the hydrolysis of tannin with dilute acid and extracting the gallic acid with ether.

Properties. Gallic acid forms white needles, mp 222°C. It is readily soluble in hot water, ethanol and ether. On heating at its melting point, it undergoes decarboxylation to pyrogallol.



gallic acid pyrogallol

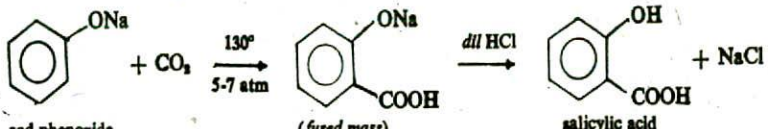
Gallic acid, like pyrogallol, is a reducing agent and has been used as a photographic developer. Its alkaline solutions readily absorb oxygen from the air and turn brown. Gallic acid forms colourless, water-soluble ferrous salts, which oxidise in air to blue black insoluble ferric salts. This property is utilised in making 'permanent' blue-black inks because the ferric salt so formed is more permanent to light and air than the dye used to make the ink initially visible.

Blue-black Inks. The blue-black writing inks consist chiefly of an aqueous solution of gallic acid, ferrous sulphate and a little blue dye. Some gum (protective agent), a little sulphuric acid (to retard oxidation of ferrous sulphate), and a trace of phenol (preservative) is also added. When the ink flows from the pen on the paper, the sulphuric acid is neutralised by alumina of the paper. The ferrous sulphate is then rapidly oxidised to ferric sulphate and this forms a deep black precipitate with gallic acid. Hence, the ink writes blue but becomes intensely black on drying.

SALICYLIC ACID, *o-Hydryxybenzoic acid*

Of the hydroxy acids, the *ortho isomer* salicylic acid, is by far the most important. It takes its name from *salicin*, the glucoside of the corresponding alcohol, from which it was first obtained (Piria, 1838) by hydrolysis and oxidation. It occurs as the methyl ester in many essential oils.

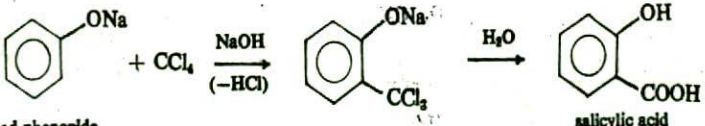
Preparation. (1) Salicylic acid is prepared commercially by heating sodium phenoxide (C_6H_5ONa) with carbon dioxide at 130°C and under pressure of 5-7 atmospheres in an autoclave (*Kolbe-Schmitt Reaction*).



sod phenoxide (*fused mass*) salicylic acid

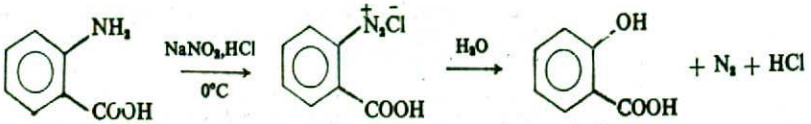
The fused mass from the autoclave is dissolved in water and the solution acidified to liberate free salicylic acid.

(2) It may also be made by heating phenol with carbon tetrachloride in alkali solution. (*Reimer Tiemann Reaction*)



sod phenoxide salicylic acid

(3) It may also be obtained by the action of sodium nitrite and dilute HCl on anthranilic acid *via* the diazonium salt.



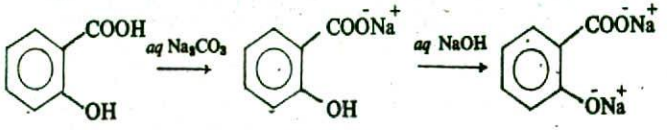
anthranilic acid — diazonium salt — salicylic acid

Salicylic acid may also be obtained by oxidation of *o*-cresol with potassium hydroxide and lead peroxide, or by fusion of the sodium salt of *o*-sulphobenzoic acid with sodium hydroxide.

Properties (*Physical*). Salicylic acid is a colourless, crystalline solid, mp 159°C. It is difficultly soluble in cold water but dissolves readily in hot water, ethanol and ether. It sublimes below its melting point and is steam-volatile. It is a stronger acid than benzoic acid. Salicylic acid is somewhat poisonous and has powerful antiseptic action.

(*Chemical*). It behaves both as a phenol as well as a carboxylic acid.

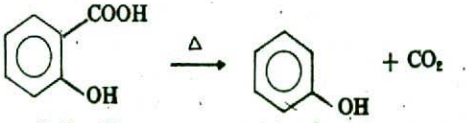
(1) It reacts with aqueous sodium carbonate or sodium bicarbonate to form sodium salicylate. With excess of sodium hydroxide it forms a di-sodium salt.



salicylic acid — sod salicytale

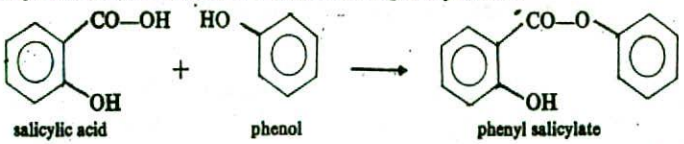
Like other aromatic acids it reacts with alcohols to form esters.

(2) When heated slowly, or with sodalime it undergoes decarboxylation.



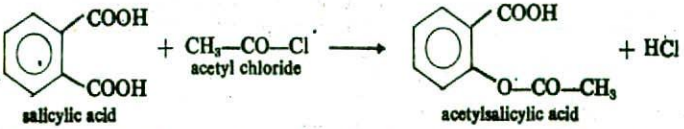
salicylic acid — phenol

(3) When heated at 208°C, in a closed vessel it gives phenyl salicylate. The phenol first produced by decarboxylation reacts with the remaining salicylic acid.



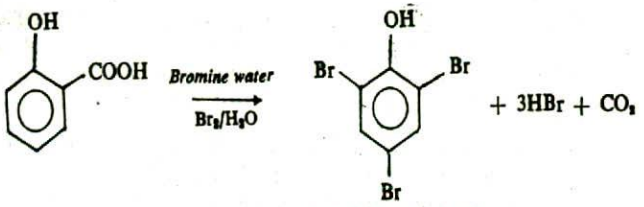
salicylic acid — phenol — phenyl salicylate

(4) Like most phenols, it gives violet coloration with $FeCl_3$, couples with diazonium salts, and forms acetyl derivatives at the OH group.

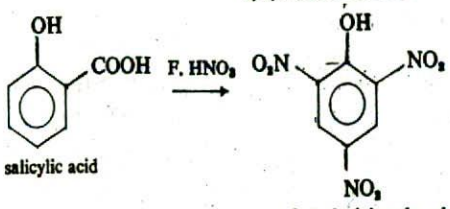


salicylic acid — acetylsalicylic acid

(5) Because the OH group is strongly activating, salicylic acid readily undergoes substitution in the benzene ring by electrophilic reagents. During these reactions, the COOH group is replaced by the entering group. For example,



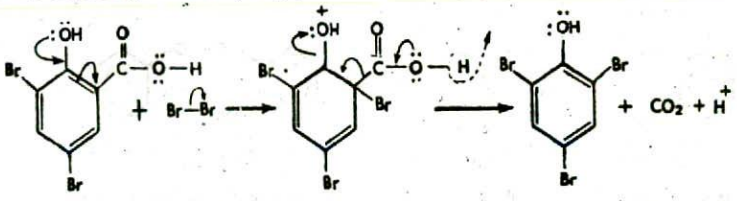
2, 4, 6-tribromophenol



salicylic acid

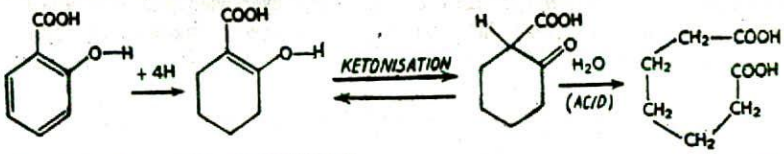
2, 4, 6-trinitrophenol
(picric acid)

MECHANISM. The mechanism of this reaction of elimination of the COOH group is similar to that of replacent of hydrogen of the aromatic ring.



2,4,6-TRIBROMOPHENOL

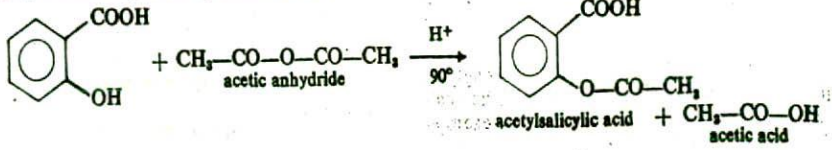
(6) When reduced with sodium and boiling isopentanol, salicylic acid ring is hydrogenated and cleaved to from pimelic acid



SALICYLIC ACID TETRAHEDROSALICYLIC ACID PIMELIC ACID

Uses. Salicylic acid is used : (1) as antiseptic and disinfectant; (2) for making dyes; (3) for preparing aspirin, salol, methyl salicylate ; and (4) as medicine, when it is administered as sodium salicylate in rheumatic conditions.

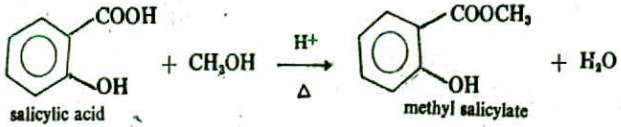
Acetylsalicylic acid, Aspirin. It is prepared by heating salicylic acid with acetic anhydride at 90°C in the presence of a small quantity of sulphuric acid. The acetylation of OH group occurs to give acetylsalicylic acid.



salicylic acid

Salicylic acid is a white solid, mp 134°C. It is still the world's largest selling analgesic. The annual production in US in 1964 was 28 million pounds, which comes to 204 5-grain tablets for every member of the entire population. 'Aspirin' is a mild analgesic, relieving certain types of pains such as headaches, toothache, and colds. It has also an antipyretic action.

Methyl Salicylate. It is the methyl ester of salicylic acid and occurs naturally in *oil of wintergreen, oil of sweet birch* and in other essential oils. It is prepared by esterifying salicylic acid with methyl alcohol in the presence of sulphuric acid.



salicylic acid methyl salicylate

Methyl salicylate is a colourless, pleasant smelling liquid, bp 224°C. It is used as a flavouring agent. It has a stimulating action on the skin and is, therefore, used in hair tonics, and in liniments for treating aches, sprains and bruises.

Phenyl Salicylate, Salol. It is prepared by heating salicylic acid in closed vessel at 200° C. This is possibly produced by the interaction of the phenol, formed by decarboxylation, with the undecomposed salicylic acid.

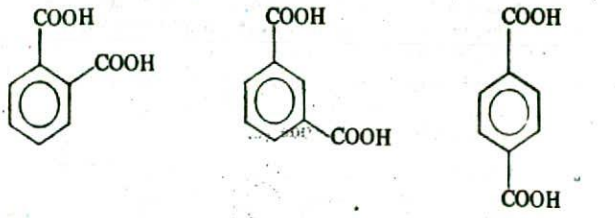


Salicylic acid Phenol Phenyl salicylate

It is a white solid, mp 43°C. It passes through the acidic medium of the stomach unchanged and is hydrolysed to salicylic acid in the alkaline medium of the intestines. It is used in medicine as internal antiseptic under the name *salol.* It is much used as enteric coating for medicinals that otherwise would be destroyed by the acidic secretions of the stomach. When the pill reaches the alkaline intestines, the salol coating gets hydrolysed, and the medicinal is liberated. Salol absorbs ultraviolet light, and its main use now is a sun-screening agent and stabiliser of plastics

BENZENEDICARBOXYLIC ACIDS

The *ortho, meta* and *para*-benzenedicarboxylic acids have the trivial names *phthalic, isophthalic,* and *terephthalic* acids respectively.



phthalic acid, benzene-1, 2-dicarboxylic acid

isophthalic acid benzene-1, 3-dicarboxylic acid

terephthalic acid benzene-1, 4-dicarboxylic acid

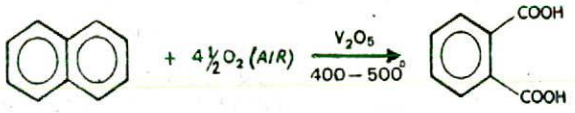
Benzenedicarboxylic acids can be prepared by the oxidation of the corresponding dialkylbenzenes (xylenes). They are white crystalline solids having relatively high melting points : phthalic acid 231° C; isophthalic acid 348° C; terephthalic acid 300° C. They give all the usual reactions of aromatic dicarboxylic acid, forming acid and normal derivatives. Phthalic acid is distinguished from the meta and para isomers as it forms an inner anhydride due to the close proximity of the two COOH groups on the benzene ring.

Of the t ree isomeric benzenedicarboxylic acids, phthalic acid (*ortho*) is the most important.

PHTHALIC ACID, *Benzene-1,2-dicarboxylic acid,* $C_6H_4(COOH)_2$

It was discovered by Laurent (1836) as an oxidation product of naphthalene. It is produced by the oxidation of any benzene derivative having only two carbon-chains bonded directly to benzene ring in ortho positions.

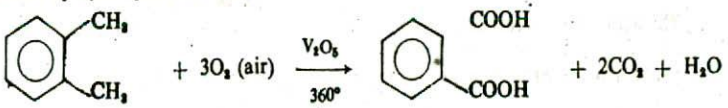
Preparation. (1) Phthalic acid is manufactured by passing a mixture of naphthalene vapour and air, over vanadium pentoxide as catalyst at 400-500°C.



NAPHTHALENE PHTHALIC ACID

In fact, the product obtained by the high-temperature oxidation of naphthalene is phthalic anhydride which is subsequently hydrolysed to yield the acid.

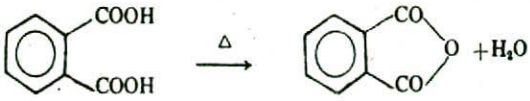
(2) In a newer method, introduced in USA, phthalic acid is produced on large scale by the catalytic oxidation of *o*-xylene derived from petroleum. As in the method (1) it is the phthalic anhydride which results from the dehydration at high temperature. This is converted to phthalic acid by hydrolysis with HCl.



Properties. Phthalic acid is a white crystalline solid which melts at about 231° C on rapid heating. It is slightly soluble in cold water but dissolves fairly rapidly in hot.

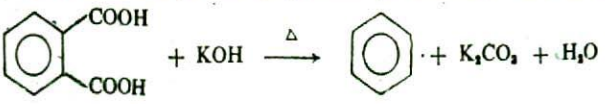
Phthalic acid gives most of the typical reactions of a dicarboxylic acid.

(1) It decomposes to yield its anhydride when heated at the melting point.



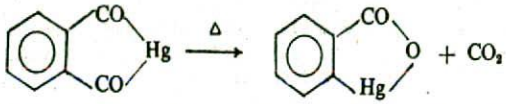
phthalic acid phthalic anhydride

(2) When heated with potassium hydroxide (or sodalime), it decarboxylates to benzene.

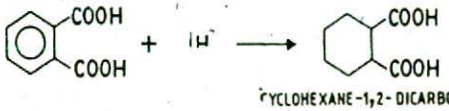


phthalic acid benzene

(3) Phthalic acid may be mercurated by fusing it with mercuric acetate, or by heating its mercury salt.



(4) When it is treated with sodium amalgam and sodium carbonate solution, the benzene ring can readily be reduced to give cyclohexane -1,2-dicarboxylic acid.

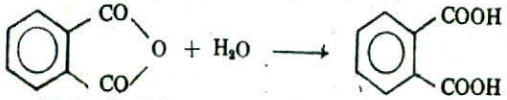


CYCLOHEXANE-1,2-DICARBOXYLIC ACID

The chief use of phthalic acid is the formation of its anhydride which is of great technical value. Benzoic acid is now manufactured by debarboxylation of phthalic acid.

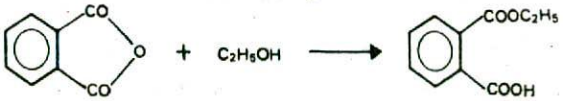
Phthalic Anhydride, $C_6H_4(CO)_2O$. It is made commercially by the catalytic high temperature oxidation of either naphthalene or *o*-xylene as described before. It is a white crystalline solid, mp 131° C. It gives all the normal reactions of acetic anhydride, though less readily.

(1) Phthalic anhydride reacts slowly with water to give phthalic acid On treatment with aqueous alkali or acid, the hydrolysis takes place quickly.



phthalic anhydride phthalic acid

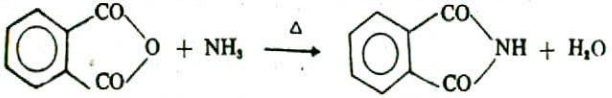
(2) When heated with alcohols, it gives acid esters.



Ethyl hydrogen phthalate

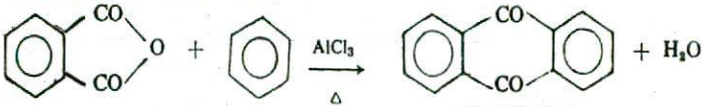
The acid esters may be converted to the normal diesters by the usual method of heating with excess of alcohol and sulphuric acid.

(3) When heated with aqueous ammonia, it gives phthalimide.



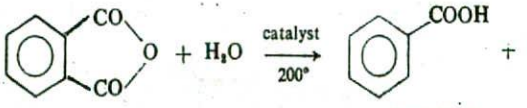
phthalimide

(4) On heating with benzene in presence of annydrous aluminium chloride, it yields anthraquinone. (*Friedel Crafts Reaction*)



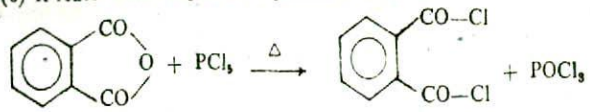
anthraquinone

(5) It is decarboxylated to benzoic acid in the presence of steam and a catalyst which consists of sodium dichromate containing small amounts of nickel and calcium oxides. (*Commercial*)



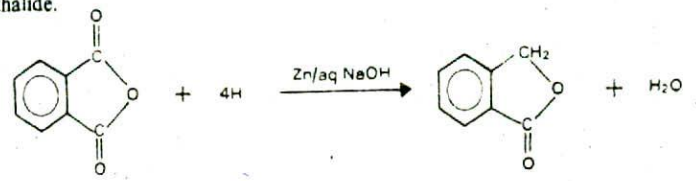
benzoic acid

(6) It reacts with PCl_5 to form phthaloyl chloride.



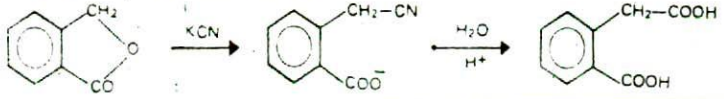
phthaloyl chloride

(7) When treated with zinc dust and aqueous NaOH, phthalic anhydride is reduced to give phthalide.



Phthalide

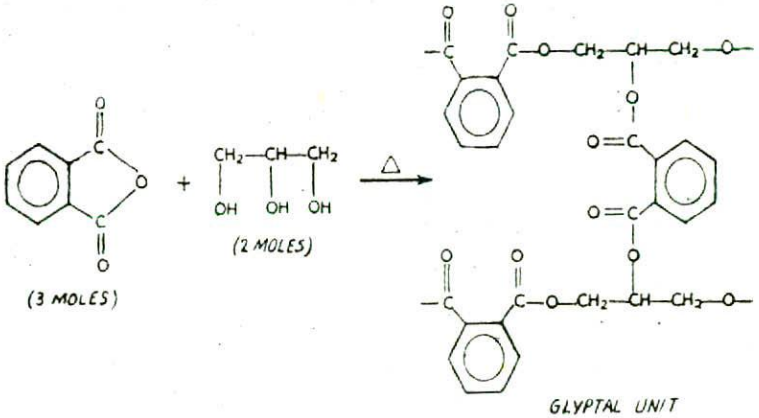
Phthalide is a γ-lactone. Upon treatment with KCN and hydrolysing the product with dil H_2SO_4, *homophthalic acid* is formed.



Phthalide Homophthalic acid

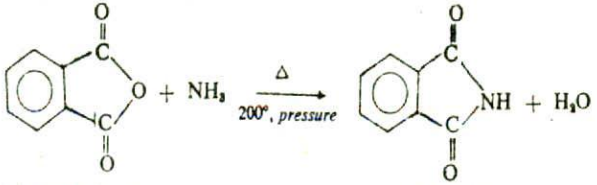
(8) It condenses to form phenolphthalein and fluorescein, when heated respectively with phenol and resorcinol, after adding a little sulphuric acid.

(9) Phthalic anhydride reacts with glycerol on heating to give polyesters which give resins known as *glyptals*. These are used as paints and varnishes. On application the glyptals form cross-linked giant molecules which offer a tough protective coating.



Uses. Phthalic anhydride is used for the industrial production of : (1) a number of dyestuffs (fluorescein) ; (2) *esters* needed as plasticisers for synthetic resins (dibutyl phthalate); dimethyl phthalate (DMP) as a mosquito and other insect repellent; diethyl phthalate as perfume; (3) chemicals such as phthalimide, anthraquinone, phenolphthalein etc ; and (4) synthetic resins (*glyptals*).

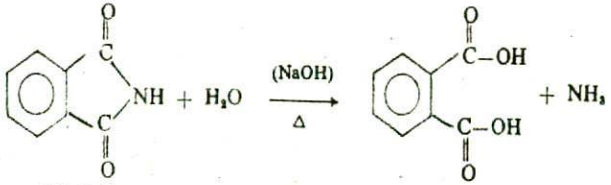
Phthalimide, $C_6H_4(CO)_2NH$. It is prepared by heating phthalic anhydride with ammonia gas under pressure at about 200°C.



phthalic anhydride phthalimide

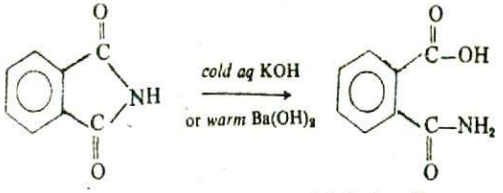
Phthalimide is a white, crystalline solid, mp 238° C. It is insoluble in water.

(1) *Hydrolysis.* It is readily hydrolysed by hot aqueous sodium hydroxide (or KOH) to give phthalic acid and ammonia.



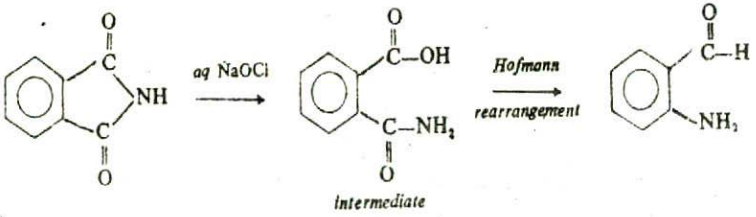
phthalimide phthalic acid

When allowed to stand in cold aqueous, or when warmed with barium hydroxide solution, only one C—N bond is broken and phthalamic acid is obtained.



phthalimide phthalamic acid (half amide phthalic acid)

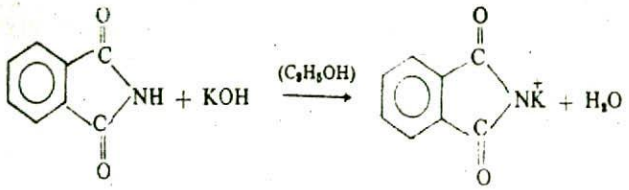
(2) *Conversion to Anthranilic acid.* When phthalimide is treated with cold aqueous sodium hypochlorite (NaOCl), it is converted to anthranilic acid.



Intermediate

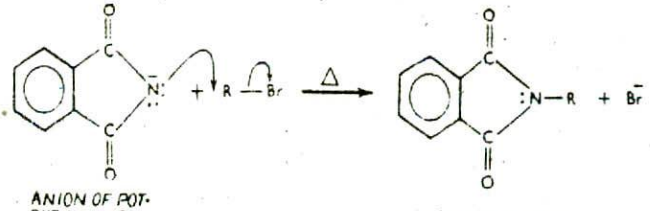
This is how anthranilic acid is produced as an intermediate in the manufacture of *indigotin* dye.

(3) *Weakly Acidic Character. Formation of Amines and Amino Acid.* Since the imino group is attached to two electron-withdrawing carbonyl groups, it is weakly acidic. Thus phthalimide reacts with ethanolic potassium hydroxide to form a salt, called potassium phthalimide.

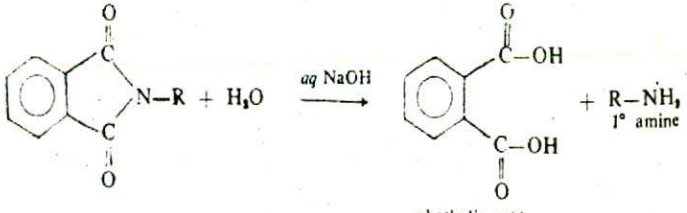


phthalimide pot phthalimide

(*a*) Potassium phthalimide when heated with an alkyl halide forms *N*-alkylphthalimide which on hydrolysis with aqueous alkali or conc. hydrochloric acid, yields phthalic acid and a primary amine. *Gabriel's Synthesis*

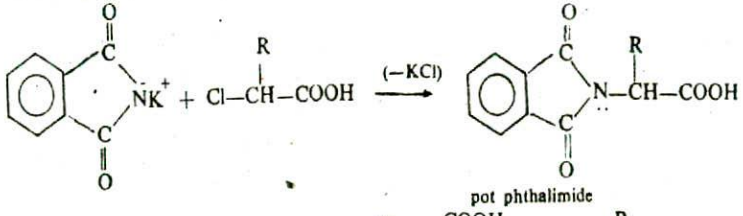


ANION OF POT-PHTHALIMIDE N-ALKYLPHTHALIMIDE



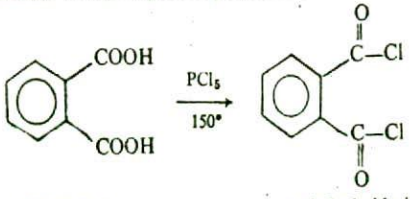
phathalic acid

(*b*) When potassium phthalimide is heated with α-chloro or α-bromo acid in place of alkyl halide, the hydrolysis of the product yields an α-amino acid.



Uses. Phthalimide is used in the synthesis of primary amines, α-amino acids and indigotin.

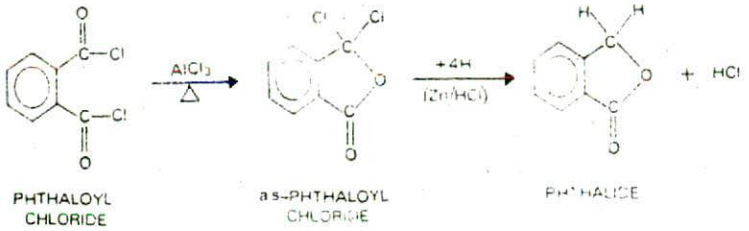
Phthaloyl Chloride, *Phthalyl chloride*, $C_6H_4(COCl)_2$. It is prepared by heating phthalic anhydride or phthalic acid with phosphorus pentachloride at 15°C.



phthalic acid phthaloyl chloride

It may also be obtained by heating phthalic acid with thionyl chloride ($SOCl_2$) at 220°C

Phthaloyl chloride is a colourless oily liquid, mp 15-16° C. On heating with aluminium chloride for some time at 95° C, it is converted into *as*-phthaloyl chloride, mp 89° C.



PHTHALOYL CHLORIDE — *as*-PHTHALOYL CHLORIDE — PHTHALIDE

When reduced with zinc and hydrochloric acid, *as*-phthaloyl chloride is reduced to phthalide.

ACIDS WITH COOH GROUP IN THE SIDE-CHAIN

A number of acids in which the COOH group is in the side-chain are of theoretical or practical importance

PHENYLACETIC ACID. *2-Phenylethanoic acid,* $C_6H_5-CH_2-COOH$

It is a typical acid with the COOH group attached to the side-chain. It is isomeric with toluic acids.

Preparation. (1) Phenylacetic acid is prepared easily by boiling benzyl chloride with ethanolic potassium cyanide, and hydrolysing the resulting nitrile by boiling with dilute sulphuric acid.

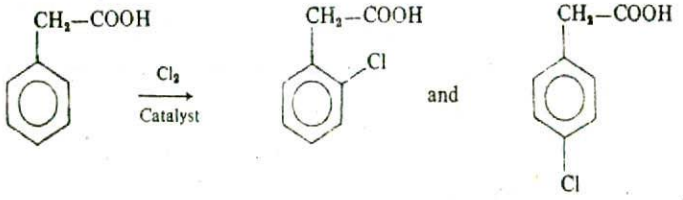
$$\underset{\text{benzyl chloride}}{C_6H_5-CH_2-Cl} \xrightarrow{KCN} \underset{\text{benzyl nitrile}}{C_6H_5-CH_2-CN} \xrightarrow[(H_2SO_4)]{H_2O} \underset{\text{phenylacetic acid}}{C_6H_5-CH_2-COOH}$$

(2) It may also be prepared by reducing mandelonitrile with hydriodic acid and red phosphorus.

$$\underset{\text{mandelonitrile}}{C_6H_5-\underset{OH}{\underset{|}{CH}}-CN} \xrightarrow{HI/P} C_6H_5-CH_2-CN \xrightarrow{H_2O} C_6H_5-CH_2-COOH$$

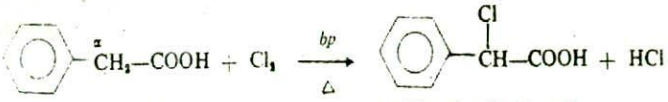
Properties. Phenylacetic acid is a white crystalline solid, mp 77° C, having unpleasant odour. It is a stronger acid than acetic acid.

(1) *Chlorination.* It is reactive in the side-chain as well as in the benzene ring. Thus on treatment with chlorine at room temperature in the presence of a catalyst, substitution takes place in the ring to form *o*- and *p*-chlorophenylacetic acids.



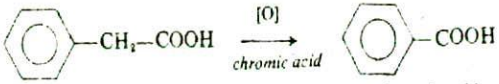
phenylacetic acid — *o*-chlorophenylacetic acid — *p*-chlorophenylacetic acid

On the other hand, when chlorine is passed into phenylacetic acid at its boiling point in the absence of a catalyst, it gives α-chlorophenylacetic acid



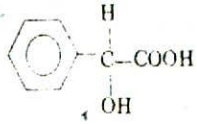
phenylacetic acid — α-chlorophenylacetic acid

(2) Upon oxidation with chromic acid, it is converted into benzoic acid.



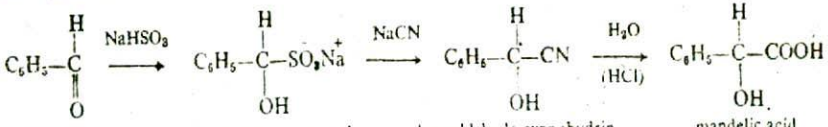
benzoic acid

MANDELIC ACID, *Phenylglycollic acid,*



Benzaldehyde occurs naturally as the glucoside, *amygadalin*, in bitter almonds from which source it may be obtained by hydrolysis and subsequent oxidation gives mandelic acid.

Preparation. Mandelic acid may be prepared by the hydrolysis of benzaldehyde cyanohydrin (mandelonitrile) which in turn is obtained by treating the bisulphite compound of benzaldehyde with concentrated solution of sodium cyanide.



benzaldehyde — bisulphite compound — benzaldehyde cyanohydrin — mandelic acid

Properties. Mandelic acid is a white crystalline solid, moderately soluble in water. Its molecule has an asymmetric carbon (attached to H, OH, COOH, C_6H_5), and hence the acid exhibits optical isomerism. Mandelic acid obtained by hydrolysis of amygdlain is the L-form, mp 133° C. DL-Mandelic acids melts at 118° C.

Mandelic acid behaves as a hydroxy acid. When reduced with hot hydriodic acid, it gives phenylacetic acid. Upon vigorous oxidation it is converted to benzoic acid. Mandelic acid is used as internal antiseptic.

CINNAMIC ACID, *trans-β-phenylacrylic acid*

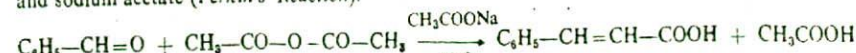
Owing to the presence of a double bond in the molecule, β-phenylacrylic acid, $C_6H_5-CH=CH-COOH$, exists in two geometrical forms.



trans-β-phenylacrylic acid (cinnamic acid) — *cis*-β-phenylacrylic acid (allocinnamic acid)

The *trans*-form is named as cinnamic acid, while the *cis*-form is called allocinnamic acid. Cinnamic acid is the stable form and occurs naturally, both free and as esters, in the oil of cinnamon, in balsams and resins.

Preparation. (1) It may be prepared by heating benzaldehyde with acetic anhydride and sodium acetate (*Perkin's Reaction*).



benzaldehyde — acetic anhydride — cinnamic acid

(2) It is also produced by the condensation of benzaldehyde with ethyl acetate in the presence of sodium ethoxide. (*Claisen Condensation*)

$$C_6H_5-CH=O + CH_3-COOC_2H_5 \xrightarrow{C_2H_5ONa} C_6H_5-CH=CH-COOC_2H_5$$

benzaldehyde — ethyl acetate — ethyl cinnamate

$$C_6H_5-CH=CH-COOC_2H_5 \xrightarrow[(H^+)]{H_2O} C_6H_5-CH=CH-COOH$$

cinnamic acid

(3) It is made commercially by the oxidation of benzalacetone with alkaline sodium hypochlorite. (*Cf.* haloform of acetone)

$$C_6H_5-CH=CH-CO-CH_3 \xrightarrow{NaOCl} C_6H_5-CH=CH-COOH$$

Benzalacetone — cinnamic acid

Properties Cinnamic acid is a white solid, mp 133° C, having a persistent sharp odour. It is very sparingly soluble in water. It gives the reactions of an α, β-unsaturated acid and the phenyl group.

(1) When reduced with sodium amalgam and water, it gives β-phenylpropionic acid.

$$C_6H_5-CH=CH-COOH + 2[H] \xrightarrow{Na\text{-}Hg/H_2O} C_6H_5-CH_2-CH_2-COOH$$

cinnamic acid — β-phenylpropionic

With lithium aluminium hydride both the double bond and the carbonyl group are reduced, yielding 3-phenylpropanol.

$$C_6H_5-CH=CH-COOH + 6[H] \xrightarrow{LiAlH_4} C_6H_5-CH_2-CH_2-CH_2OH$$

cinnamic acid — 3-phenylpropanol

(2) On oxidation with cold potassium permanganate, the double bond cleaves to form benzaldehyde, while vigorous oxidation yields benzoic acid.

$$C_6H_5-CH=CH-COOH \xrightarrow[KMnO_4]{[O]} C_6H_5-CH=O \xrightarrow[vigorous]{[O]} C_6H_5-COOH$$

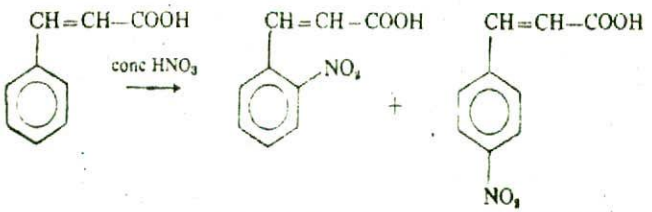
cinnamic acid — benzaldehyde — benzoic acid

(3) At the COOH group, cinnamic acid reacts with alkalis to form salts, and with alcohols to form esters. On heating with sodalime, it decarboxylates to styrene (phenylethylene)

$$C_6H_5-CH=CH-COOH \xrightarrow[\Delta]{\text{sodalime}} C_6H_5-CH=CH_2 + CO_2$$

styrene

(4) Nitration with concentrated nitric acid yields a mixture of *o*- and *p*-nitrocinnamic acids.

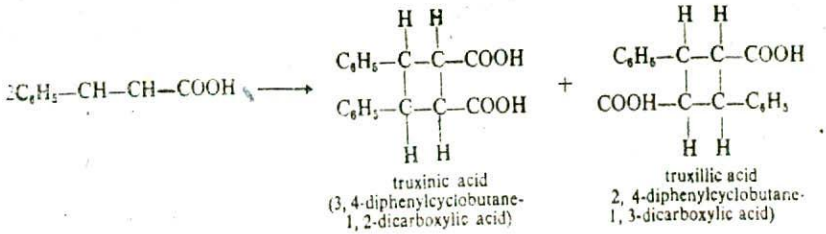


o-nitrocinnamic acid — *p*-nitrocinnamic acid

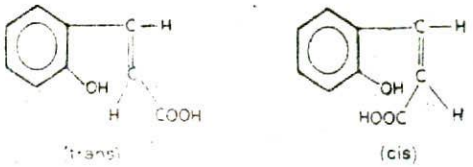
(5) When exposed to sunlight, cinnamic acid dimerises to two isomeric cyclobutane derivatives—*truxinic acid* and *truxillic acid*.

$$C_6H_5-CH=CH-COOH \xrightarrow{h\nu} C_6H_5-\dot{C}H-\dot{C}H-COOH$$

diradical

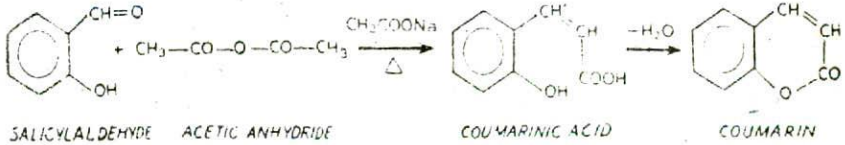


Coumarin. β-(Hydroxyphenyl)-acrylic acid also exists in two geometrically isomeric forms.



Coumarinic acid, as soon as it is produced, forms an internal cyclic ester or δ-lactone, known as Coumarin.

Coumarin is the odoriferous principle of woodruff, newly mown hay, and tonka beans. It is synthesised readily by Perkin's reaction from salicylaldehyde, acetic anhydride, and sodium acetate.



Coumarin is a white crystalline solid, mp 67°C, having flavour somewhat resembling that of vanillin. When warmed with sodium hydroxide, the ester ring opens up to form the sodium salt of coumarinic acid.

The use of coumarin as flavouring agent has been discontinued because of its toxicity. It is used for inhibiting the germination of seeds.

QUESTIONS

1. How do you define the term 'aromatic acid'? Name the three aromatic acids derived from toluene according to the common as also the IUPAC System.

2. Give the orbital structure of benzoic acid. In what way it is similar to the structure of nitrobenzene.

3. Discuss the general methods of preparation of aromatic monocarboxylic acids, taking example of benzoic acid.

4. "Aromatic carboxylic acids are slightly stronger acids than the aliphatic acids." Comment and elaborate.

5. Describe the general reactions of aromatic carboxylic acids with special reference to the following:

   (*a*) esterfication; (*b*) Schotten-Baumann reaction; (*c*) acid halide formation, (*d*) acid amide formation; and (*e*) reduction.

6. List the preparation, properties and uses of benzoic acid.

7. Write notes on : Benzoyl chloride, Benzamide, Benzoic anhydride, Benzonitrile and Benzoyl peroxide.

8. How are ortho, meta and para toluic acids obtained ? What happens when they are oxidised with dilute nitric acid and the product is heated.

9. Give the preparation, properties and uses of :

(*a*) anthranilic acid ; (*b*) *p*-aminobenzoic acid ; and (*c*) Gallic acid.

10. How can salicylic acid be prepared from phenol and from anthranilic acid ? What happens when :

(*i*) salicylic acid is heated with sodalime ;

(*ii*) it is heated at 200°C ;

(*iii*) it is treated with bromine water ;

(*iv*) it is heated with acetic anhydride.

11. Name two important derivatives of salicylic acid and discuss their reactions and uses.

12. Which of the three benzene dicarboxylic acids is important and why ?

13. How is phthalic anhydride obtained on a large scale ? Write equations for its reaction with benzene in the presence of $AlCl_3$, ammonia, PCl_5, and on decarboxylation.

14. Give a brief account of the formation, reactions and uses of : phthalimide, phthaloyl chloride and phenylacetic acid.

15. Write the structural formula of Mandelic acid and discuss its chemical behaviour.

16. How is Cinnamic acid prepared by Perkin's reaction ? State four of its reactions by means of equations.

17. What is Coumarin ? How can it be produced ? What happens when it is warmed with sodium hydroxide solution and state its uses.

18. How would you prepare benzoic acid from C_6H_6, salicylic acid from phenol and phthalic acid from naphthalene ? *(Punjabi BSc III, 1980)*

19. Show chemical reactions how benzene could be converted into Cinnamic acid and salicylic acid. *(Banaras BSc II, 1980)*

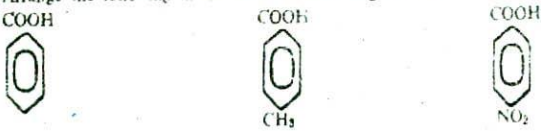
20. Show the steps involved in the conversion of o-Xylene into Phthalic anhydride. Indicate how would you prepare phenylacetic acid from benzyl chloride *(Kerala BSc III, 1980)*

21. How is phthalic acid prepared ? How would you convert it into

(*a*) Anthranilic acid (*b*) Benzoic acid

(*c*) Fluorescein. *(Gurhwal BSc II, 1980)*

22. Arrange the following in the order of increasing acidity.



(Madras BSc III, 1980)

23. (*a*) Describe two common methods for the preparation of benzoic acid and two of its uses.

(*b*) Describe one method each for the preparation of Benzoyl chloride, Benzene, Benzamide and Benzonitrile from Benzoic acid.

(*c*) What products will be formed on nitration and chlorination of benzoic acid, give reason. *(Meerut BSc III, 1980)*

24. How is phenylacetic acid prepared from benzoic acid ? *(Osmania BSc III, 1981)*

25. (*a*) How can a —COOH group be introduced in the benzene ring ?

(*b*) How is salicylic acid prepared from phenol ?

(*c*) How does salicylic acid react with:—

(*i*) Acetyl chloride (*ii*) bromine and fuming nitric acid

(Udaipur BSc II, 1981)

26. Cinnamic acid is obtained from a mixture of benzaldehyde, acetic anhydride and sodium acetate. Write the mechanism of the reaction *(Bangalore BSc II, 1981)*

27. (*a*) Describe a method for the preparation of Salicylic acid.
(*b*) How are the following prepared from it.
(*i*) 2,4,6-tribromophenol
(*ii*) 2,4,6-trinitrophenol
(*iii*) Salol
(*iv*) Chlorobenzoyl chloride ? *(Saugar BSc III, 1981)*

28. Give reactions in the form of equations of two methods of preparing Benzoic acid. How is benzoic acid converted into:
(*a*) Ethyl benzoate (*b*) Benzoyl chloride (*c*) Benzamide
(Maharishi Dayanand BSc, 1982)

29 (*a*) Which is more acidic, benzoic acid or p-chlorobenzoic acid ? Why ?
(*b*) How would you obtain benzoic acid and benzyl alcohol in one step from benzaldehyde ? Name the reaction. *(Kerala BSc III, 1982)*

30. How is phthalic acid manufactured ? How will you prepare the following from it
(*i*) Phthalic anhydride (*ii*) Phthalimide (*iii*) Benzene
(*iii*) Phenolphthalein (*iv*) Diethyl phthalate. *(Indore BSc II, 1982)*

31 Describe the preparation and properties of Anthralic acid and Phthalic acid. *(Jammu BSc III, 1982)*

32. Give the preparation, properties, and uses of phthalic anhydride. How will you convert phthalic acid into anthranilic acid ? *(Osmania BSc Hons, 1993)*

33. How is cinnamic acid prepared ? Discuss its properties. Compare the acid strength of benzoic acid and *p*-nitrobenzoic acid *(Gulbarga BSc, 1993)*

34. Give the preparation and properties of salicylic acid *(Madras BSc, 1993, Indore BSc, 1994)*

35. How will you synthesise benzoic acid from benzene ? *(Saugar BSc, 1993, Nagpur BSc, 1994)*

36. How will you synthesise aspirin from phenol ? *(Lucknow BSc, 1994, Delhi BSc1994)*

37. How will you synthesise *p*-toluic acid from benzene ?

Hint. Use the following steps (*i*) $CH_3Cl/AlCl_3$, (*ii*) $Br_2/FeBr_3$, (*iii*) Mg/ether (*iv*) CO_2, and (*v*) H_3O^+

38. How will you distinguish between benzoic acid and salicylic acid ? *(North Eastern Hill BSc, 1994)*

Hint. Salicylic acid reacts with bromine water to give a white precipitate of 2,4,6-tribromophenol. Benzoic acid does not give this test. Also, salicylic acid gives violet colour with $FeCl_3$ solution. Benzoic acid does not give this test.

39. An organic compound (A), C_7H_9N, when subjected to diazotisation followed by Sandmeyer reaction gave compound (B), C_7H_7Br. (B) reacts with magnesium to form (C), C_7H_7MgBr. (C) reacts with formaldehyde to give (D), $C_8H_{10}O$. Compound (D) undergoes oxidation to give a dicarboxylic acid (E), $C_8H_6O_3$, which easily forms an anhydride. Deduce the structural formulas of (A), (B), (C) and (D). Write equations for the reactions involved.

Answer. (A) is *o*-Toluidine, (B) is *o*-Bromotoluene, (C) is *o*-Methylphenylmagnesium bromide, (D) is *o*-Methylbenzyl alcohol, and (E) is Phthalic acid.

Colour, Dyes, and Pigments

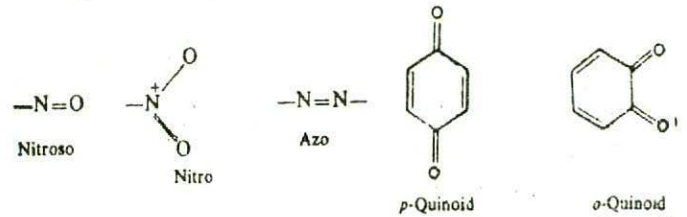
The dyeing of cloth and the fermentation of sugar to produce alcohol are the two specialized areas of organic chemistry that date back to antiquity. Fabrics dyed with indigo and maddar have been found in the tombs of predynastic Egypt. These, and a few matters extracted from insects and tropical woods formed the only sources of dyes until the middle of the last centuary.

The first synthetic dye was made in 1856 by William E. Perkin, which he named *mauveine*. He obtained this dye by oxidation of impure aniline. A few years later, the structures of natural dyes, indigo and alizarin, were determined, and these compounds were prepared by synthesis. However, the major development in chemistry of synthetic dyes was the discovery of diazotization and azo coupling. Since 1856, tens of thousands of dyes have been synthesized. Well over a thousand are commercially available now.

A. COLOUR AND CONSTITUTION

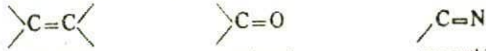
Witt's Theory of Colour

It was noticed by Otto N. Witt in 1876 that colour in organic compounds is associated with the presence of certain groups in the molecule. He designated a group that produces colour as a **Chromophore** (Gr. *chroma*, colour+*phoros*, to bear), and a molecule containing such a group as **Chromogen**. The most effective chromophores are :



The presence of any one of these groups in a molecule is usually sufficient to produce colour. Thus nitrobenzene is pale-green, azobenzene is orange-red, *p*-quinones are yellow, and *o*-quinones are orange or red.

Certain other unsaturated groups produce colour only when several of them are present in a molecule and when these are conjugated. They are :



Thus, although acetone ($CH_3—\overset{O}{\overset{\|}{C}}—CH_3$) is colourless, biacetyl ($CH_3—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—CH_3$) is yellow, and

acetylacetone ($CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$) in which the two carbonyl groups are not conjugated is colourless.

Witt also noticed that certain groups, while not producing colour themselves, are able to intensify the colour when present in a molecule together with a chromophore. These he called **Auxochromes** (Gk. *auxein*, to increase - *chroma*, colour). The most effective auxochromes are —OH, NH_2, —NHR, and $—NR_2$. Thus the nitrophenols and nitroanilines are more intensely coloured than nitrobenzene and are deep yellow to orange.

Modern Theory of Colour

Witt's classification of groups as chromophores and auxochromes is useful. However, for a better understanding of relationship of colour and constitution, we must consider the nature of light and its interaction with matter. The sensation of colour is produced when light having a wavelength within the *visible region* of electromagnetic spectrum strikes the retina of eye. As shown in Fig. 45·1, the visible region of the spectrum extends from 4,000 to 7,500 Å in wavelength (1 Å = 10^{-8} cm). The corresponding colours are those of the spectrum extending from violet (shorter wavelengths, 4000 to 4300 Å) to red (longer wavelengths, 6,300 to 7,500 Å). Beyond the red end of the visible spectrum lies the infrared (7500 to 2,000,000 Å) and beyond the violet end lies the ultraviolet (150 to 4000 Å). The energy of the visible light increases as we go from red to the violet end. Ultraviolet light has more energy than visible light; infrared has less.

Colour and Absorption of Light. When light passes through matter or is reflected from it, some of the light may be absorbed. The energy of light is transformed into energy of motion

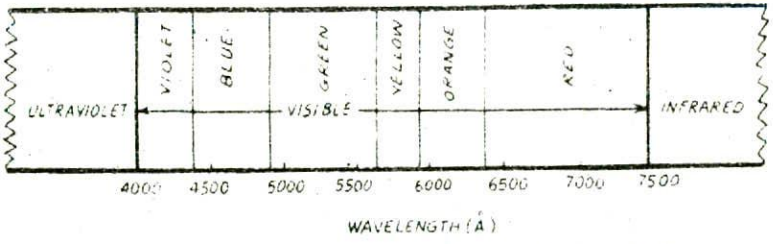


Fig. 45·1. Spectrum illustrating how colour depends on absorption of light

of molecules, or electrons in the molecules may be promoted to higher energy levels. The energy is eventually transformed into heat. This implies, when matter absorbs light energy, its temperature is raised. In rare cases, a part of light may be emitted as light of a longer wavelength, and this gives rise to phenomenon of *flourescence*. The most important source of colour in organic compounds is by absorption of light without subsequent emission.

If the light is absorbed from the infrared or ultraviolet regions, no colour will be seen; but if light is absorbed from the visible region, that substance will appear to be coloured. If substance absorbs all visible light except that corresponding to yellow, for instance, it will transmit or reflect only yellow and will be seen as yellow. More commonly, however, light of only one colour is absorbed, in which case the substance appears to have the complementary colour, as determined by the use of the colour wheel of Munsell (1915) (Fig. 45·2). Thus, if the light is absorbed from the violet region of the spectrum, the substance will be seen as yellow. If light is absorbed from the red region, the substance will appear green.

Colour and Conjugated Systems. When ultraviolet or visible light is absorbed by a molecule, an electron is excited, that is, it is promoted to an orbital of higher energy. The molecule is said to be in the excited state. The energy required to promote an electron varies with

the environment of the electron. The more stable the bond, the more difficult it is to promote an electron in that bond to the excited state. A higher energy is required. Sigma (σ)-bond electrons are tightly held. Extremely high energy (of short wavelengths) is neceassary to promote

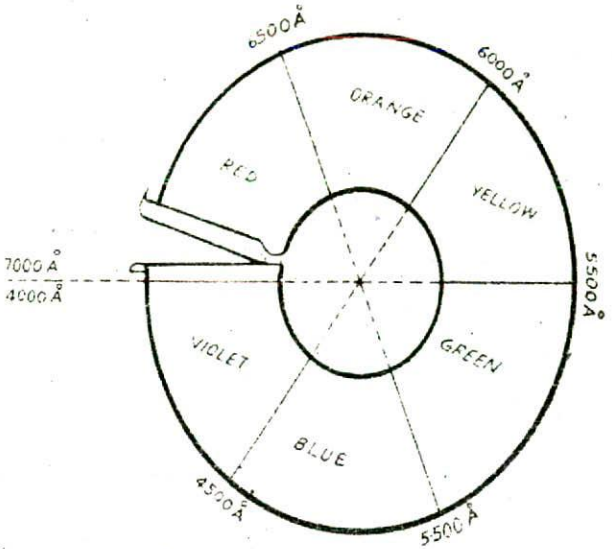


Fig 45·2. Colour Wheel of Munsell.

electrons. The energy required to promote σ-electrons is frequently high enough to break the σ-bond and form free radicals.

Pi(π)-bond electrons are less tightly held and require less energy to be promoted. Electrons in conjugated systems require even less energy. Conjugation and aromaticity help stabilize the excited state by sharing and delocalizing the higher energy of the excited electron.

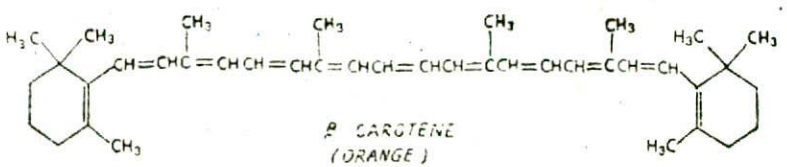
Organic compounds containing π-bonds absorb light in the ultraviolet region of the spectrum, while those containing only σ-bonds do not absorb light in this region. Conjugated π-bonds require less energy for electron promotion than isolated π-bonds and absorb ultraviolet light at a longer wavelength. As conjugation increases, the wavelength of light absorbed increases. When wavelengths are long enough to be in the visible region, we observe colour. This is illustrated by the following examples.

Ethylene absorbs light of wavelength far into the ultraviolet part of the spectrum, at 1800 Å. Butadiene, with two conjugated double bonds, absorbs at 2170 Å, a wavelength closer to the visible region than that absorbed by ethylene. Hexatriene, with three conjugated double bonds, absorbs still closer to the visible region, at 2580 Å. All three compounds are colourless. However, as the number of conjugated double bonds increases, the position of absorption falls nearer the visible region, and with enough conjugation the molecules are coloured. For example, β-carotene contains eleven conjugated double bonds and is responsible for the colour of carrots. It absorbs at 4510 Å. Although the light absorbed is blue, carrots are, of course, orange.

$CH_2=CH_2$ — ethylene — *COLOURLESS*

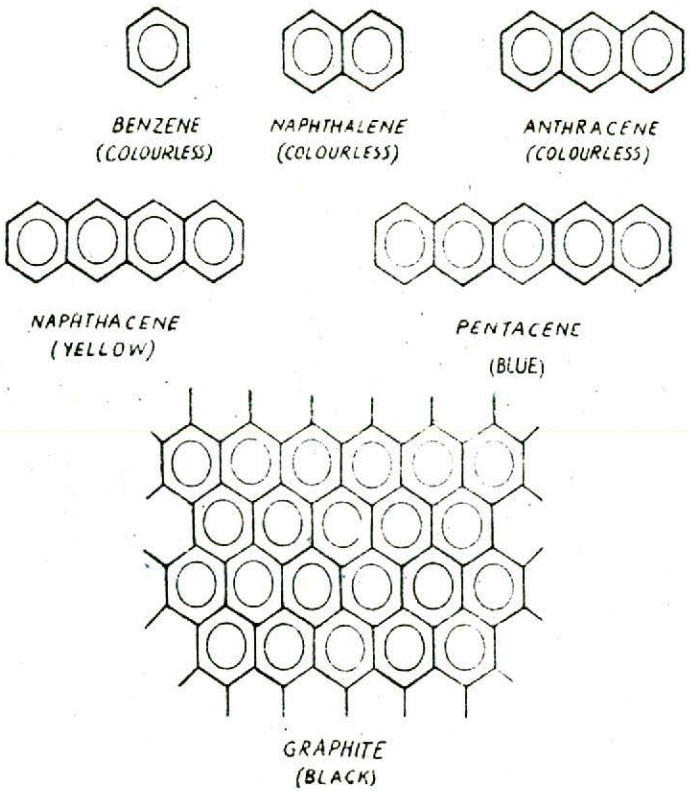
$CH_2=CH-CH=CH_2$ — 1, 3-butadiene — *COLOURLESS*

$CH_2=CH-CH=CH-CH=CH_2$ — 1,3,5-hexatriene — *COLOURLESS*



β CAROTENE
(ORANGE)

Benzene absorbs light at 2550 Å and is, therefore, colourless, as are naphthalene and anthracene. As the number of fused rings increases, the position of absorption approaches the visible region. Thus naphthacene, with four linearly fused rings, is yellow (absorbs blue light). Pentacene, with five fused rings, is blue (absorbs orange light). Graphite is a sheet of benzene rings fused in all directions ; it is black, absorbing all colours almost completely.



Carbon-carbon double bonds and benzene rings are not the only groups which produce colour in organic compounds. Other groups which contain easily excitable π-electrons also form important light absorbing (colour producing) units. Thus it is significant to note that all chromophores (Witt's Theory) have multiple bonds, that is, they are π-bonded systems. Intensification of colour by auxochromes is due to the formation of an extended, conjugated system (through delocalization) with the chromophore.

B. DYES

All coloured compounds are not dyes. Dyes are those coloured compounds that can be firmly fixed to the fabrics by chemical or physical bonding. To be of commercial significance, a dye must show fastness to light, washing, heat (sublimation) and bleaching.

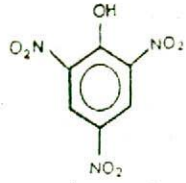
Nomenclature of Dyes. No systematic nomenclature of dyes is available. Manufacturers often assign trade names to dyes which they make, and hence the same dye may be sold under a variety of names. For example, the names rosaniline, magenta, and fuchsine all apply to the same rose-red dye. To avoid confusion, the Society of Dyers and Colourists (England), and the American Association of Textile Chemists and Colorists have collectively compiled a *Colour Index* in which each dye is assigned its individual colour number (*C.I. No*).

CLASSIFICATION OF DYES

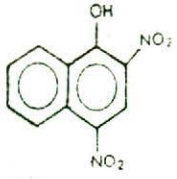
Dyes may be classified in two ways. The organic chemist classifies them according to a common parent structure (*Chemical Classification*). The dyer who is only interested in fixing the dye to the fibre, classifies them according to the method of application.

(A) CLASSIFICATION ACCORDING TO CHEMICAL STRUCTURE

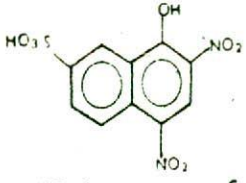
(1) **Nitro Dyes.** Nitro dyes are polynitro derivatives of phenols containing at least one nitro group *ortho* or *para* to the hydroxyl group. They are of relatively little importance industrially, because the colours are not very fast. Examples of this class are picric acid (2,4,6-trinitrophenol), Maritus yellow (2, 4-dinitro-1-naphthol), and Naphthol yellow *S* (2,4-dinitro-1-naphthol-7-sulphonic acid).



PICRIC ACID



MARITUS YELLOW

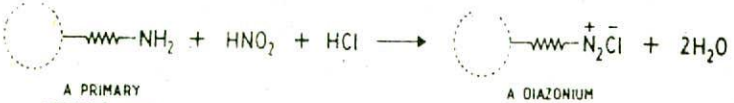


NAPHTHOL YELLOW S

Naphthol yellow *S* can be used to dye wool, and is one of the colours permitted in foods.

(2) **Azo Dyes.** The azo dyes represent the largest and the most important group of dyes. They are characterised by the presence of one or more azo groups (—N=N—), which form bridges between two or more aromatic rings. Preparation of azo dyes involves the following two steps.

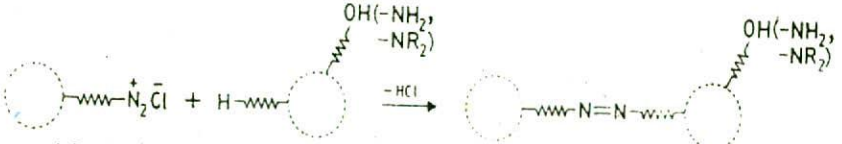
Step 1. Conversion of primary aromatic amines into diazonium compounds by treatment with sodium nitrite in excess hydrochloric acid (*Diazotisation*).



A PRIMARY AROMATIC AMINE

A DIAZONIUM COMPOUND

Step 2. Coupling of diazonium compounds with phenols, naphthols, or other aromatic amines. Coupling with phenols and naphthols is carried out in basic solution; coupling with amines is carried in acidic solution.



A DIAZONIUM COMPOUND

A PHENOL, NAPHTHOL or AN AMINE

A DYE

The above reactions are carried out at low temperatures (0 – 5°) because diazonium compounds are usually unstable. In the resulting dyes an aromatic system joined to the azo group is the *chromophore*, and the hydroxyl group or amino group is an *auxochrome*.

To simplify the description of azo dyes, only the coupling step will be shown. It will be assumed that the diazonium compound was obtained by diazotisation of the corresponding amine.

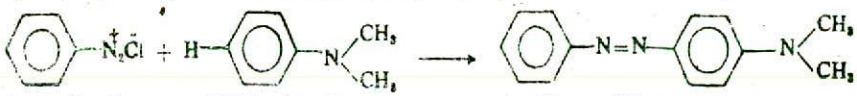
(*a*) **Aniline Yellow**, *Solvent Yellow 1*. It is *p*-aminoazobenzene. Aniline yellow is the simplest azo dye and is obtained by coupling benzenediazonium chloride with aniline in acidic medium.



BENZENEDIAZONIUM CHLORIDE — ANILINE YELLOW (*p*-aminoazobenzene)

Aniline yellow is used as a dye for oils and lacquers, and is also an intermediate for other dyes.

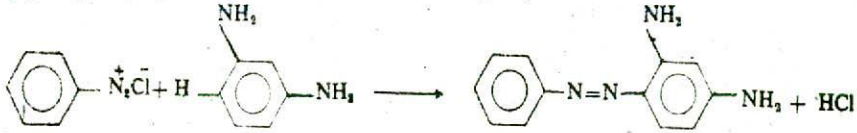
(*b*) **Butter Yellow**. It is *p*-*N*,*N*-dimethylaminoazobenzene. Butter yellow is obtained by coupling benzenediazonium chloride with *N*,*N*-dimethylaniline.



benzenediazonium cloride — *N*,*N*-dimethylaniline — Butter Yellow (*p*-*N*,*N*-dimethylaminoazobenzene)

Butter yellow has been used for colouring butter, margarine and oils.

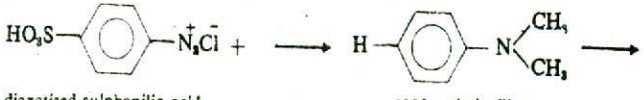
(*c*) **Chrysoidine**, *Basic Orange 2*. It is 2,4-diaminoazobenzene. Chrysoidine is prepared by coupling benzenediazonium chloride with *m*-phenylenediamine.



benzenediazonium chloride — *m*-phenylediamine — Chrysoidine (2,4-diaminoazobenzene)

Chrysoidine is an orange-red dye. It is used for dyeing paper, leather, and jute.

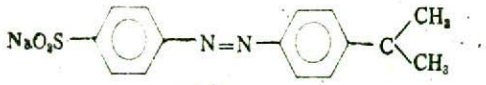
(*d*) **Methyl Orange**. It is prepared by treatment of *helianthine* with sodium hydroxide, whereas helianthine is obtained by coupling diazotised sulphanilic acid with *N*,*N*-dimethylaniline.



diazotised sulphanilic acid — *N*,*N*-methylaniline

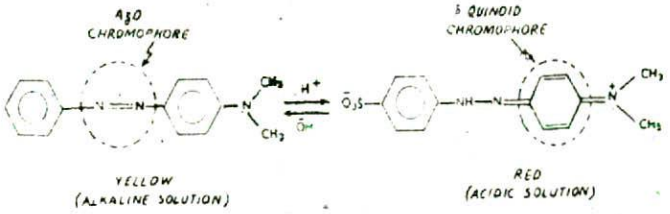


Helianthine

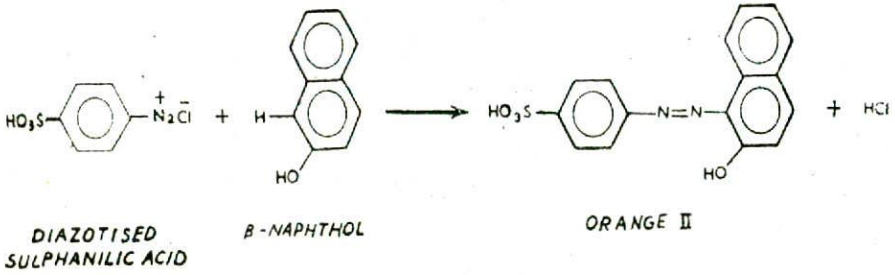


Methyl Orange

Methyl orange is not a satisfactory dye for textiles because it is sensitive to acids. It is used as an indicator in acid-base titrations. It is yellow in basic solutions (above *p*H 4·4), while red in acidic solutions (below *p*H 3·1). This change in the colour is attributed to change in the structure of its ion. Under alkaline conditions the ion contains the *azo* chromophore, while under acidic conditions it contains *p-quinoid* chromophore.

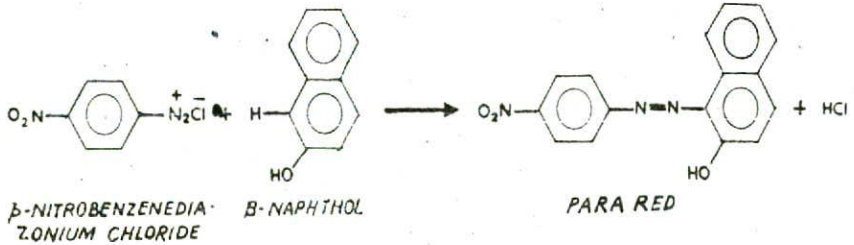


(*e*) **Orange II.** It is obtained by coupling diazotised sulphanilic acid with β-naphthol in basic medium.

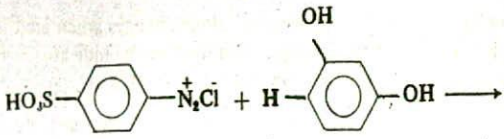


Orange II is used to dye wool, silk, nylon, paper and leather.

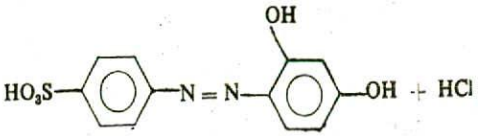
(*f*) **Para Red.** It is prepared by coupling *p*-nitrobenzenediazonium chloride with β-naphthol.



(*g*) **Resorcin Yellow.** It is made by coupling diazotised sulphanilic acid with resorcinol.



diazolised sulphanilic acid — resorcinol

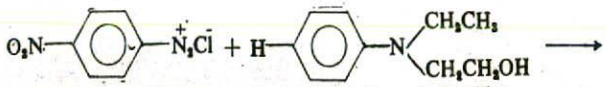


Resorcin Yellow

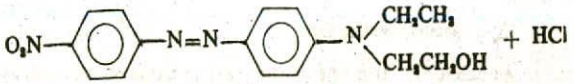
Resorcin yellow is used for dyeing silk.

(*h*) **Disperse Red 1.** It is obtained by coupling *p*-nitrobenzenediazonium chloride with *N*-ethyl-*N*-(β-hydroxyethyl)aniline in acidic medium.

Disperse red 1 is used for dyeing nylon, polyesters, cellulose acetates, and plastics.

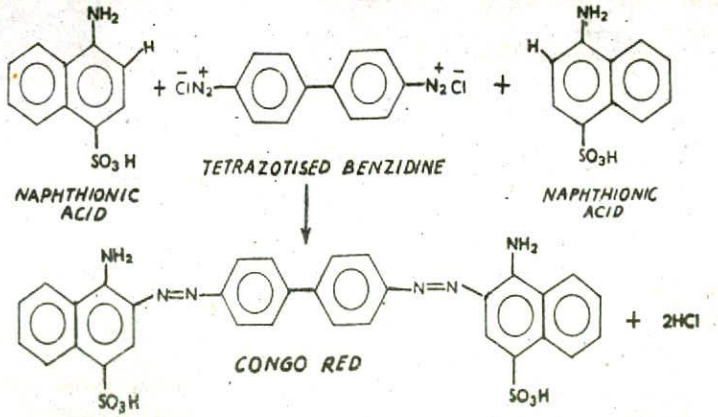


p-nitrobenzenediazonium chloride — *N*-ethyl-*N*-(β-hydroxyethyl) aniline



Disperse Red 1

(*i*) **Congo Red.** It is a diazo dye, that is, it contains two azo groups. Congo red is made by coupling tetrazotised benzidine with two molecules of naphthionic acid.

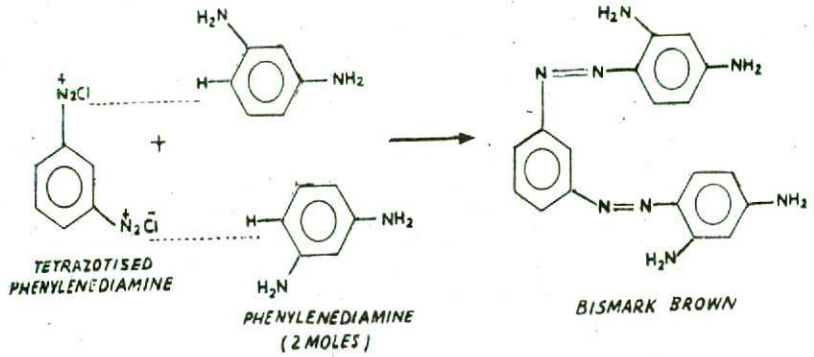


NAPHTHIONIC ACID — TETRAZOTISED BENZIDINE — NAPHTHIONIC ACID

CONGO RED

Congo red is not a good dye for textiles because the colour changes when acid is added. It was once an important stuff for dyeing paper. Congo red is used as an indicator. It is blue in acidic solutions (below *p*H 3) and red in solutions above *p*H 3.

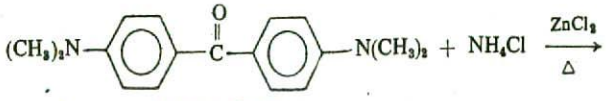
(*j*) **Bismark Brown**. It is also a diazo dye. Bismark brown is obtained by coupling tetrazotised *m*-phenylenediamine with two molecules of *m*-phenylenediamine.

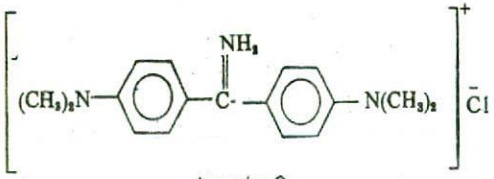


Bismark brown is used for dyeing leather, wool, and cotton.

(3) **Diphenylmethane Dyes** :

Auramine O. It is one of the most valuable of the diphenylmethane dyes. It is obtained by heating Michler's ketone with ammonium chloride and zinc chloride at 160°C.

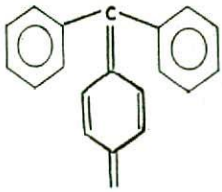




Auramine O is used to dye wool, silk, nylon, rayon and paper.

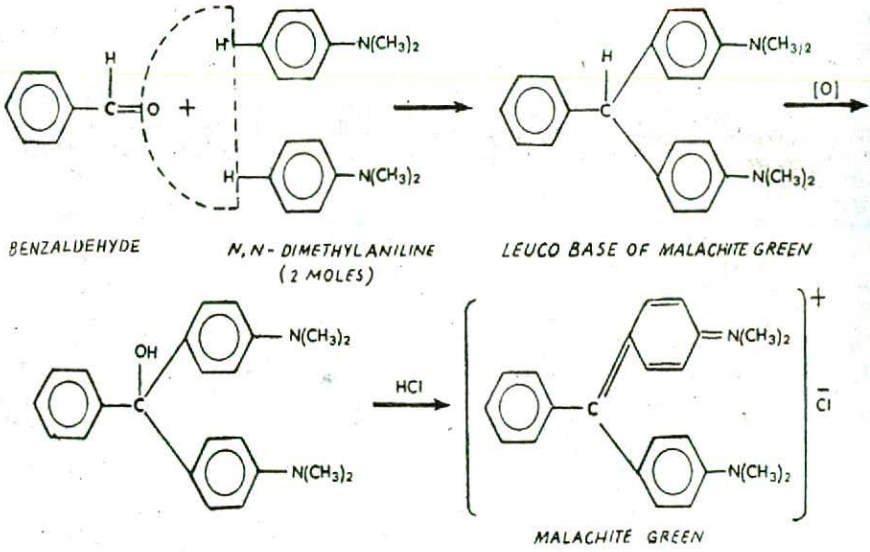
(4) **Triphenylmethane Dyes**

Triphenylmethane dyes can be identified by common structural feature shown below. Notice that the central carbon atom is joined to two benzene rings and to a *p*-quinoid group.



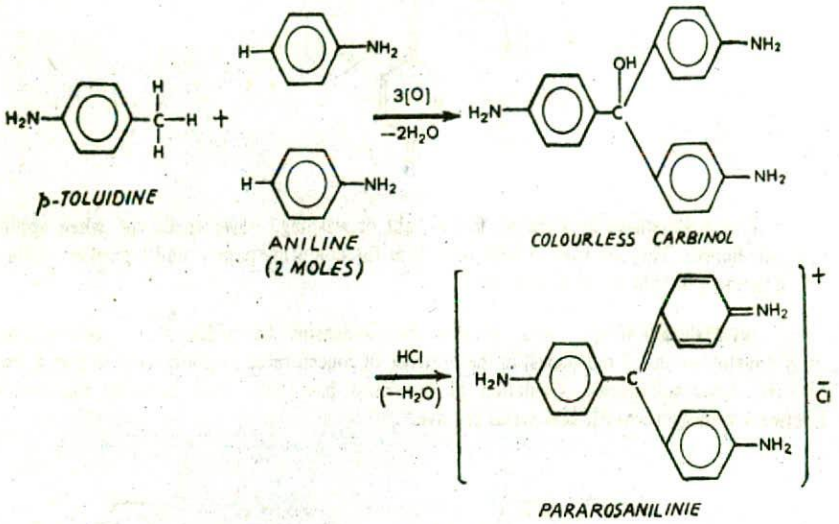
Triphenylmethane dyes are not fast to light or washing, however, except when applied to acrylic fibres. They are used in large quantities for colouring paper, and typewriter ribbons where fastness to light is not so important.

(*a*) **Malachite Green.** It is obtained by condensing benzaldehyde (1 molecule) with *N*, *N*-dimethylaniline (2 molecules) in the presence of concentrated sulphuric acid to give a leuco base (Gr. *leuco*, colourless). Oxidation of the leuco base with lead peroxide followed by treatment with hydrochloric acid yields the dye.



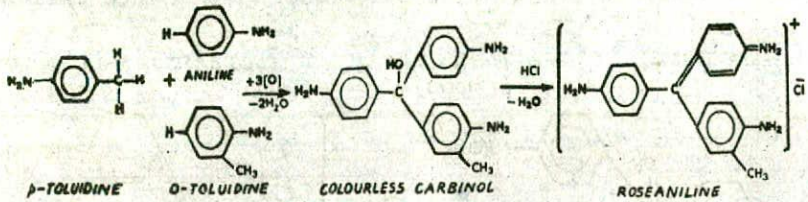
Malachite green takes its name from the fact that it has a deep blue-green colour resembling that of *malachite* (Copper ore). It is used as a dye for acrylic fibres, leather, paper, and lacquers.

(*b*) **Pararosaniline.** It is the simplest triphenylmethane dye Pararosaniline is obtained by condensing *p*-toluidine (1 molecule) with aniline (2 molecules) in the presence of nitrobenzene to give a colourless carbinol. Nitrobenzene serves both as a solvent and an oxidising agent. Treatment of the carbinol with hydrochloric acid yields the dye.



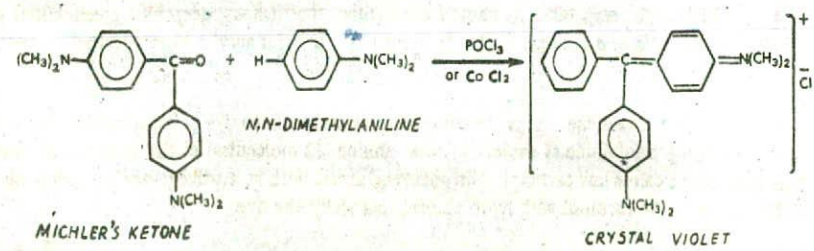
Pararosaniline has been used to dye cotton, wool and silk.

(*c*) **Rosaniline**, *Fuchsine, Magenta.* It is closely related to pararosaniline. Rosaniline is prepared by condensing one molecule each of aniline, *p*-toluidine, and *o*-toluidine in nitrobenzene to give a carbinol. Treatment of the carbinol with hydrochloric acid yields the dye.



Rosaniline has a greenish metallic lustre. It dissolves in water to give a deep-red colour. Rosaniline is used for dyeing cotton, silk and wool. Addition of sulphur dioxide to the dye solution produces the colourless *Schiff's reagent*, which is used to test the presence of aldehydes.

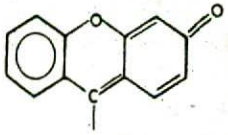
(*d*) **Crystal Violet.** It is obtained by condensing Michler's ketone with *N,N*-dimethylaniline in the presence of phosphorous oxychloride ($POCl_3$) or phosgene ($COCl_2$). If phosgene is used, then crystal violet can be prepared directly by heating phosgene and *N,N*-dimethylaniline, since these two react to give Michler's ketone.



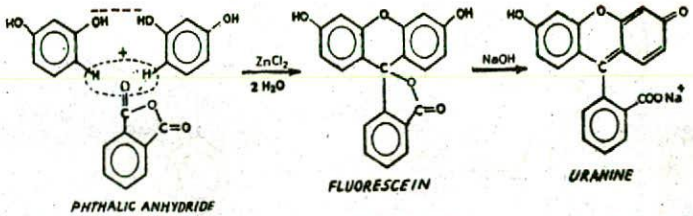
Crystal violet has a greenish-brown metallic lustre. It dissolves in water to give a deep-blue colour. Crystal violet is used in the manufacture of inks, stamping pads, and typewriter ribbons. It is also used as an indicator for the determination of hydrogen-ion concentration of solutions.

(5) **Xanthene Dyes.**

Xanthene dyes can be identified by a common structural feature shown below. They are obtained by condensing phenols with phthalic anhydride in the presence of zinc chloride, sulphuric acid, or anhydrous oxalic acid. Examples of this class are fluorescein, eosin, and rhodamine *B*.



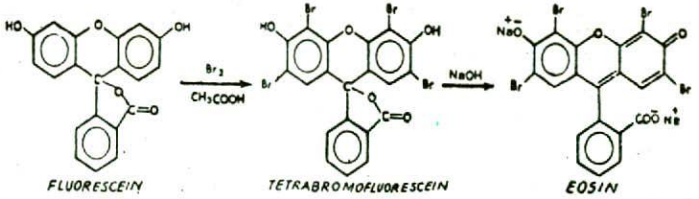
(*a*) **Fluorescein.** It is prepared by heating resorcinol (2 molecules) and phthalic anhydride (1 molecule) with zinc chloride at 190°C.



Fluorescein is of no value as a dye. It is a red powder, which is insoluble in water. A dilute solution of fluorescein in sodium hydroxide gives a strong yellow-green fluorescence when exposed to light. It is used to trace pollution of water supplies by sewrage, since if a small quantity of it is put in at the suspected source of pollution, the colour will be detectable at some distance from the source, even after extensive dilution. During World War II, fluorescein was used as a sea marker for airmen who had to bail out from aeroplanes over water. It also aided searchers in locating them. Fluorescein is also used as a mild purgative.

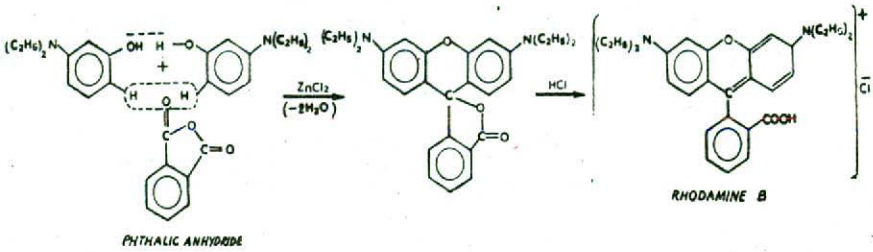
The sodium salt of fluorescein is called *Uranine*. It is used to dye wool and silk.

(*b*) **Eosin.** It is the disodium salt of tetrabromofluorescein. Eosin is obtained by brominating fluorescein in glacial acetic acid to give tetrabromofluorescein. Treatment of this with sodium hydroxide yields the dye.



Eosin is a red solid, which is soluble in water. Alkaline solutions of eosin show a yellow-green fluorescence. Eosin is used for dyeing wool, silk, and paper; for making red ink and as the colouring matter in lipsticks and nail polishes.

(*c*) **Rhodamine B.** It is prepared by condensing phthalic anhydride with *N*,*N*-diethyl-*m*-aminophenol in the presence of zinc chloride, and treating the product with hydrochloric acid.

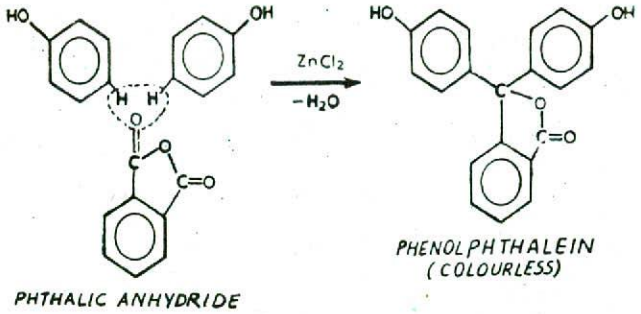


Rhodamine *B* is used for dyeing silk, wool and cotton.

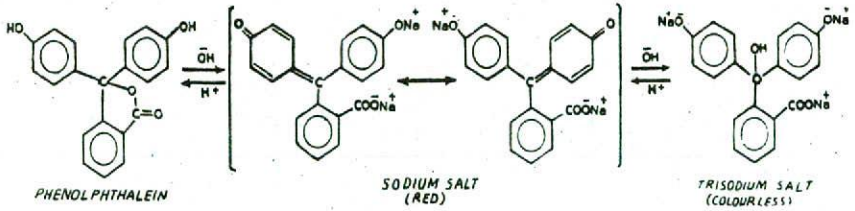
(6) **Phthaleins**

Phthaleins are related to xanthene dyes and are made in the same way.

Phenolphthalein. It is prepared by condensing phenol (2 molecules) with phthalic anhydride (1 molecule) in the presence of zinc chloride at 120°C



Phenolphthalein is not a dye. It is a colourless solid, mp 261°C. Phenolphthalein is insoluble in water, but dissolves in alkalis to form deep red solutions. This is due to the formation of a disodium salt, the ion of which is coloured because of resonance. When excess of strong alkali is added, the solution of phenolphthalein becomes colourless. This is attributed to the formation of a trisodium salt, the ion of which is colourless because of loss of resonance and quinoid structure.



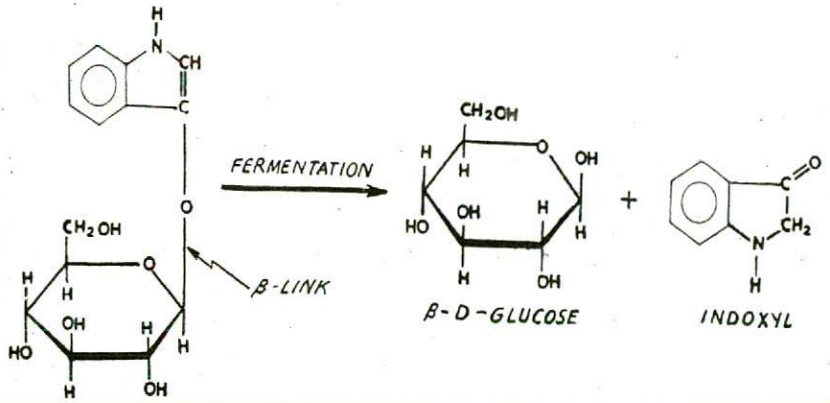
Because of the colour changes shown above, phenolphthalein is used as an indicator in acid-base titrations.

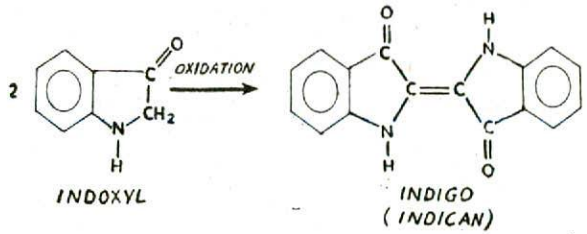
Phenolphthalein is an extremely powerful laxative, and this accounts for its widespread use as a denaturant for laboratory alcohol.

(7) **Indigoid and Thioindigoid Dyes**

Indigoid. It is the parent compound of indigoid dyes and has been used in this country from times immemorial. Egyptian mummy clothes, which are 5000 years old, were

dyed with it. Indigo was originally obtained from plants of *indigofera* group. The leaves from these plants were covered with water and allowed to stand for several hours. Enzymes present in the plants brought about fermentation, as a result of which the β-glucoside of indoxyl (known as indican) in the leaves was converted into indoxyl and glucose. Upon exposure to air the indoxyl was oxidised to indigo.

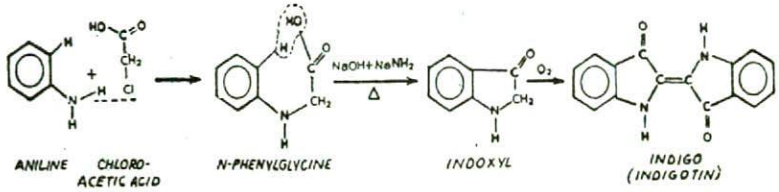




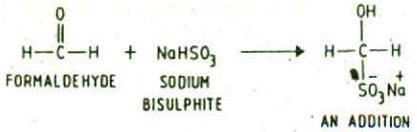
Natural indigo contains an isomer of indigo known as indirubin (Indigo Red), and other impurities in varying proportions. Most of the indigo used at the present time is a synthetic product. It has replaced the natural stuff because of cheapness, purity, and uniformity of the manufactured dye.

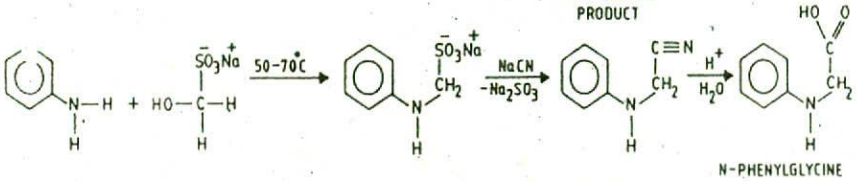
Preparation of Indigo. It may be obtained :

(1) *By Heumann's First Indigo Synthesis (1890).* This involves the condensation of aniline with chloroacetic acid to give *N*-phenylglycine. The phenylglycine is then fused with sodium hydroxide and sodamide at 250°C to form indoxyl, which on oxidation by air yields the dye.

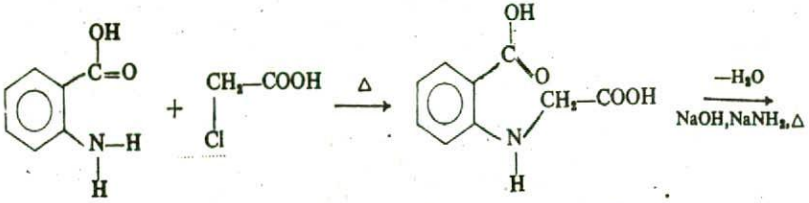


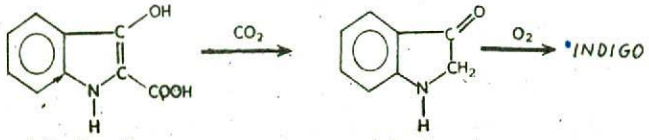
N-Phenylglycine is now obtained in much higher yield by interaction of aniline and the bisulphite compound of formaldehyde at 50-60°C, followed by treatment with aqueous sodium cyanide, and hydrolysis of the resulting nitrile.



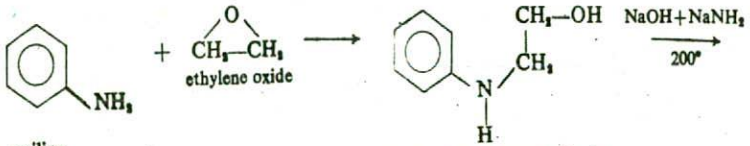


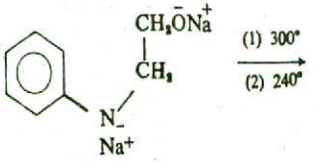
(2) *By Heumann's Second Indigo Synthesis (1896).* This involves the condensation of anthranilic acid with chloroacetic acid to form *N*-phenyl-*o*-carboxylic acid. This is then fused with sodium hydroxide and sodamide to produce unstable indoxylic acid, which decarboxylates to give indoxyl. Oxidation of indoxyl by air yields the dye.

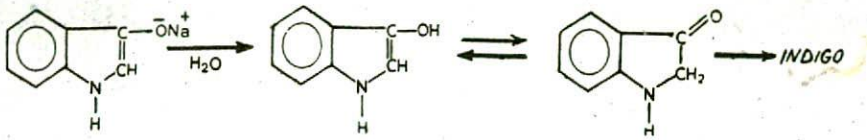




(3) *From Aniline and Ethylene Oxide (1943).* This involves treatment of aniline with ethylene oxide to form *N*-phenyl-2-hydroxyethylamine. Fusion of *N*-phenyl-2-hydroxyethylamine with sodium hydroxide and sodamide at 200°C produces its disodium derivative. The sodium derivative is heated rapidly to 300°C and then cooled to 240°C to yield the sodium salt of indoxyl. This on treatment with water and oxidation by air gives indigo.





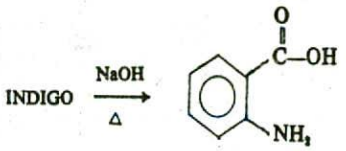


Indigo is a dark-blue crystalline compound, mp 390–2°. It is insoluble in water and most organic solvents, but soluble in aniline, nitrobenzene, and chloroform. It can be sublimed under reduced pressure to deep red vapours, which on cooling yield prismatic crystals Indigo is used very extensively for dyeing cotton by the Vat Process, and in printing inks.

Structure of Indigo. The structure of indigo has been deduced from consideration of facts and conclusions such as the following.

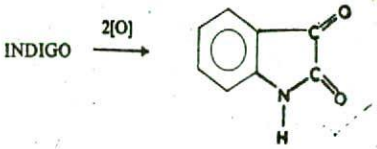
1. Elemental analysis and molecular weight determinations show that the molecular formula of indigo is $C_{16}H_{10}O_2N_2$.

2. Fusion of indigo with sodium hydroxide at low temperatures produces anthranilic acid. This indicates the presence of a benzene ring attached to one carbon atom and one nitrogen atom in the *ortho* position.

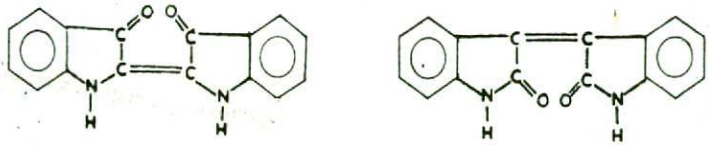


anthranilic acid

3. Oxidation of indigo with nitric acid yields only two molecules of isatin. This indicates that the indigo molecule contains two identical units joined together, and that each unit on oxidation produces a molecule of isatin.

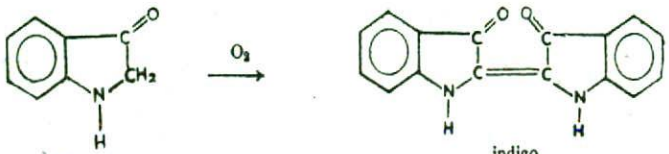


The following two possible structures of indigo meet this requirement.

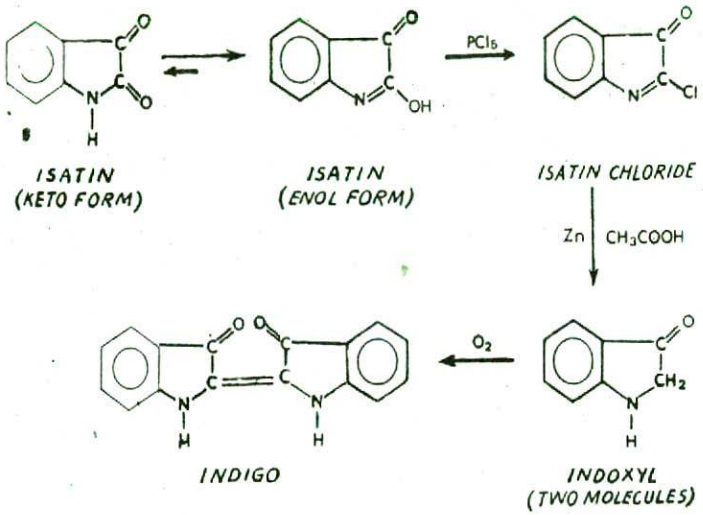


(*A*) (*B*)

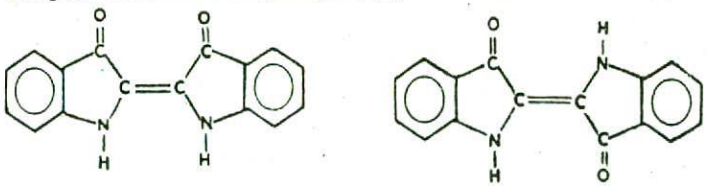
4. Oxidation of indoxyl by air yields indigo.



From above, it follows that (*A*) represents the structure of indigo. This has been confirmed by the following synthesis by Baeyer (1872).



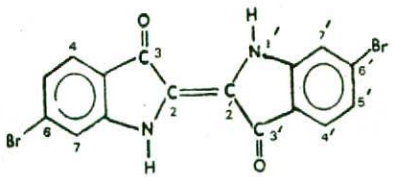
Two geometrical isomers are possible for (*A*).



Cis-form *Trans*-form

X-Ray analysis shows that mostly indigo exists in the more stable *trans*-form. However, derivatives of both are known.

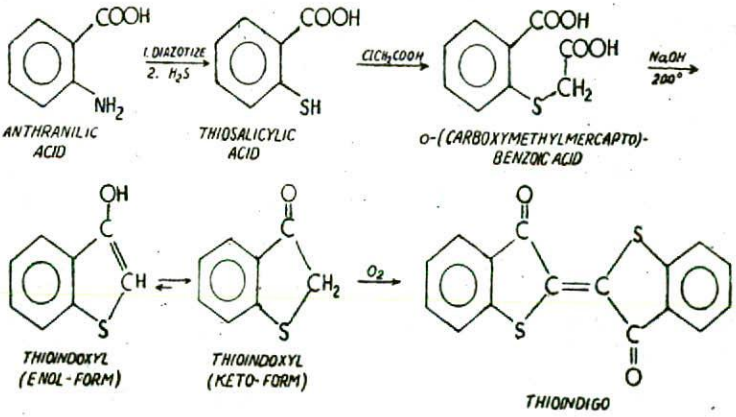
(*a*) **Tyrian Purple.** It is 6,6′-dibromoindigo. Its discovery was later than that of indigo, but it is believed to have been known in 1600 BC.



TYRIAN PURPLE
(6,6′-DIBROMOINDIGO)

Tyrian purple occurs naturally in the purple snail, *Murex Brandaris*. It takes about 12000 snails to produce 1·4 *g* of the dye. This explains its rarity and why the colour of purple came to be the symbol of royalty in the former times. The dye is no longer of commercial value.

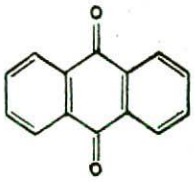
(*b*) **Thioindigo.** It is analogous to indigo in which the two —NH— groups are replaced by sulphur atoms. Thioindigo may be obtained by the reaction of thiosalicylic acid, with chloroacetic acid, followed by fusion with sodium hydroxide and oxidation by air. Thiosalicylic acid itself is made by diazotisation and reaction with hydrogen sulphide.



Thioindigo is used to dye cotton, wool and polyesters.

(8) Anthraquinoid Dyes

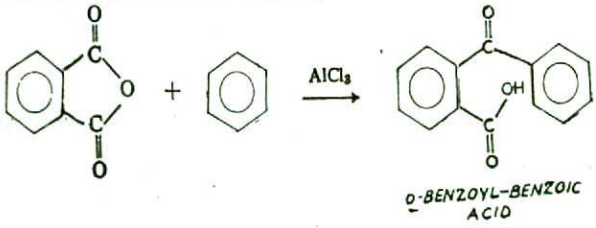
Anthraquinoid dyes can be identified by a common structural feature shown below. Notice that a *p*-quinoid group is fused to two other benzene rings.



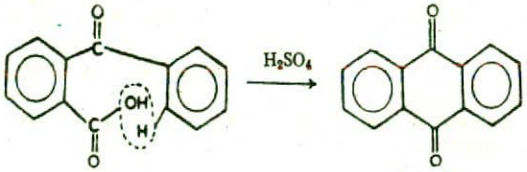
Anthraquinoid dyes are used for dyeing wool, silk, nylon, cotton, leather and paper. The most important dye in this group is alizarin.

Alizarin. It is 1, 2-dihydroxyanthraquinone. Alizarin derives its name from the fact that it was first obtained from the roots of the madder plant (Fr. *Alizari*, madder). It is now prepared from phthalic anhydride by the following *six* steps.

Step 1. Phthalic anhydride is treated with benzene in the presence of $AlCl_3$ to give *o*-benzoylbenzoic acid. (Friedel-Crafts Reaction)

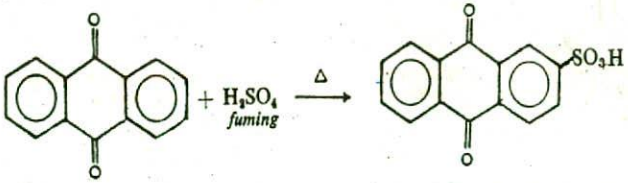


Step 2. *o*-Benzoylbenzoic acid is cyclized by treatment with concentrated sulphuric acid to form anthraquinone.



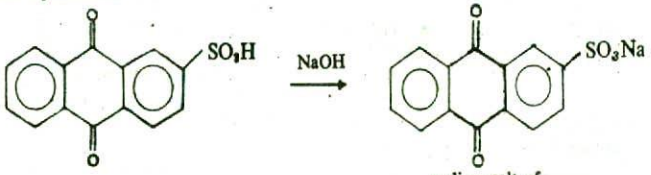
anthraquinone

Step 3. Anthraquinone is heated with fuming sulphuric acid at 180°C to give anthraquinone-2-sulphonic acid.



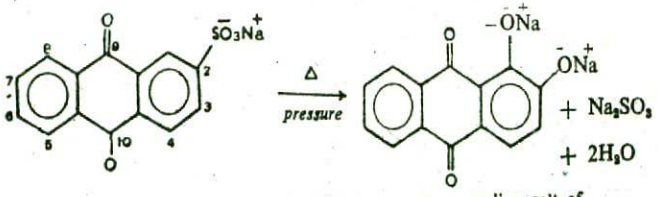
anthraquinone anthraquinone-2-sulphonic acid

Step 4. Anthraquinone-2-sulphonic acid is converted into its sodium salt by treatment with sodium hydroxide.



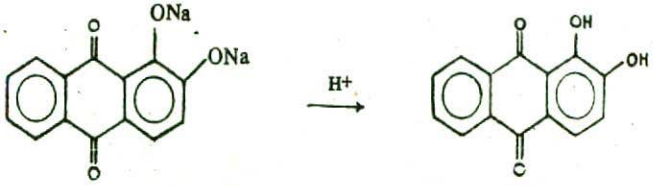
sodium salt of anthraquinone-2-sulphonic acid

Step 5. Sodium salt of anthraquinone-2-sulphonic acid is fused with sodium hydroxide in the presence of potassium chlorate at 200°C under pressure to give sodium salt of 1, 2-dihydroxyanthraquinone. The purpose of potassuim chlorate is to provide oxygen for the oxidation of the carbon atom at *C-1*.



sodium salt of 1, 2-dihydroxyanthraquinone

Step 6. Sodium salt of 1,2-dihydroxyanthraquinone is treated with sulphuric acid to yield 1, 2-dihydroxyanthraquinone (Alizarin).



Alizarin
(1, 2-dihydroxyanthraquinone)

Alizarin can also be made by condensing phathalic anhydride with catechol in the presence of sulphuric acid at 180°C (See Below).

Alzarin forms ruby red crystals, mp 290°C. It is insoluble in water and ethanol. It dissolves in alkalis to give purple solutions. Alizarin is used to dye cotton and wool. It is also used for making printing inks.

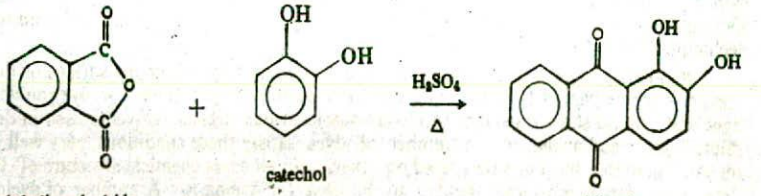
Structure of Alizarin. The structure of Alizarin has been deduced as follows.

1. Elemental analysis and molecular weight determinations show that the molecular formula of alizarin is $C_{14}H_8O_4$.

2. Reduction of alizarin with zinc dust at 400°C produces anthracene. This indicates that it has the same carbon skeleton as that of anthracene.

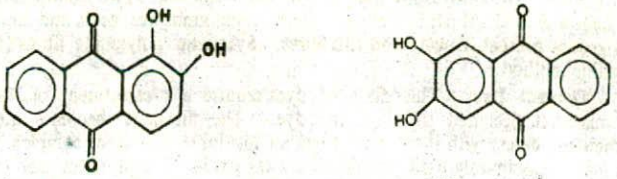
3. Alizarin reacts with acetic anhydride to form a diacetate. This indicates the presence of two hydroxyl groups in the molecule.

4. Alizarin can be prepared by condensing phthalic anhydride and catechol in the presence of sulphuric acid at 180°C. This shows that alizarin is a dihydroxy derivative of anthraquinone and both —OH groups are substituted in the same benzene ring.



phthalic anhydride catechol Alizarin (1, 2-dihydroxyanthraquinone)

The above facts limit our choice to two structural formulae for alizarin.



(A) (B)

5. Alizarin on nitration yields *two* isomeric mononitro derivatives, both of which on oxidation give phthalic acid. This shows that in each of these derivatives, the $-NO_2$ group is substituted on the hydroxylated benzene ring.

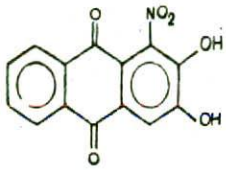
Let us now write down the possible mononitro derivatives from (*A*) and (*B*).

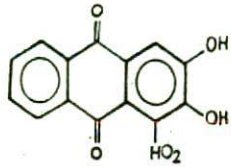
Mononitro derivatives from (*A*) :



DIFFERENT

Mononitro derivatives from (B)





IDENTICAL

Since only formula (*A*) permits the formation of two isomeric mononitro derivatives, it represents the structure of alizarin.

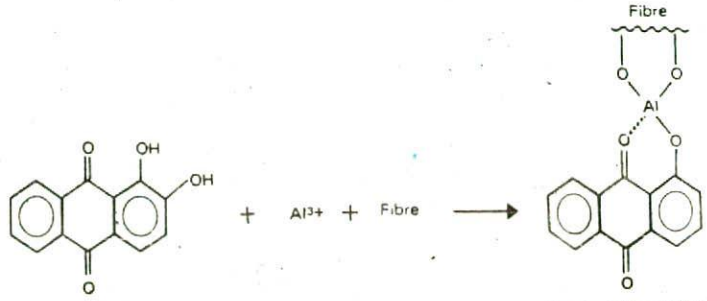
(B) CLASSIFICATION ACCORDING TO METHOD OF APPLICATION

Methods for dyeing vary with the chemical structure of the fibre to be dyed. A dye suitable for wool or silk may be entirely unsatisfactory for dyeing cotton or rayon. Wool and silk are protein substances. They contain many acidic and basic (polar) groups. These groups serve as points of attachment for a dye because it also has acidic or basic groups. On the other hand, cotton and rayon fibres are composed of cellulose in quite pure form and provide only neutral ether linkages and hydroxyl groups as points of attachment for hydrogen bonds. Polyolefin fibres are formed from products of polymerisation of unsaturated hydrocarbons, for example, propylene. They do not contain any polar groups and require still other techniques for dyeing.

As already mentioned, a dye must do more than simply colour the surface of the fibre. It should become part of the fibre, and wear and wash with the fibre. A dye should be fast to light and should show resistance to the action of various organic solvents used in dry-cleaning, dilute alkalis and acids, etc. A number of dyes satisfy these conditions very well when used on some material but not when used on others. In all cases chemical structure of the material determines the process and the dye to be used for dyeing it. A number of dyeing methods and dyes adaptable to each method are described below.

(1) **Direct Dyes.** These contain acidic or basic groups and combine with polar groups in the fibre. Such dyes colour a fabric directly when the fibre is immersed in a hot aqueous solution of the dye. Direct dyes are used to dye wool and silk. Two examples of this class are Naphthol Yellow *S* and Martius Yellow. Both compounds are acids and combine with the free amino groups present in wool and silk fibres. Synthetic polyamide fibres (*Nylon*) can also be dyed by this method.

(2) **Mordant Dyes.** This class of dyes require a pretreatment of the fibre with a mordant material designed to bind the dye. The mordant becomes attached to the fibre and then combines with the dye to form an insoluble coloured complex. This complex is called a *lake*. Commonly used mordants are the oxides of aluminium, iron and chromium. Mordant dyes may be used to dye wool, silk and cotton. Alizarin is an example of a mordant dye. It gives different colours when used with different mordants. It gives a red colour with aluminium and tin salts, brownish red tones with a chromium mordant, and black-violets with an iron mordant.

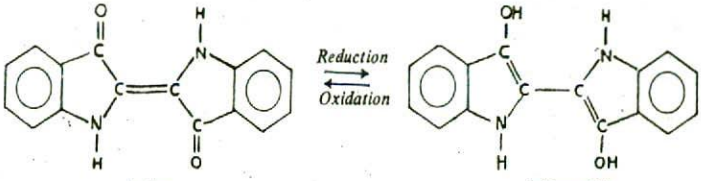


Alizarin

Mordant dye on fibre

Mordant dyes have been used for many centuries. They have lost their original importance because their use is no longer necessary. Equal or superior results can be obtained with other classes of dyes at less expense in time and labour.

(3) **Vat Dyes.** These dyes are insoluble in water, but on reduction with sodium hydrosulphite yield alkali soluble forms (*Leuco-compounds*) which may be colourless. It is in this form they are introduced into the fabric. The reducing operation was formerly carried out in wooden vats, giving rise to the name 'Vat Dyes'. After the reduced dye has been absorbed in the fibre, the original insoluble coloured dye is reformed by oxidation with air or chemicals. Vat dyes are used to dye cotton, and are very fast because of their insolubility in water. Indigo is an example of a vat dye.

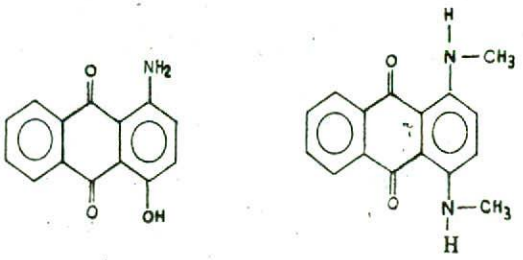


indigo
(blue ; water-insoluble)

indigo white
(colourless ; water-soluble)
a leuco-compound

(4) **Ingrain Dyes.** These dyes are synthesised within the fabric, and may be applied to any type of fibre. The azo dyes are good examples of ingrain dyes. The cloth to be dyed is first soaked in an alkaline solution of a phenol (usually naphthol) and dried. It is then immersed in a cold alkaline solution of a diazonium salt. Coupling reaction takes place within the fabric. Since these dyes are insoluble in water, they are very fast.

(5) **Disperse Dyes.** These dyes are insoluble in water, but are capable of dissolving certain synthetic fibres. Disperse dyes are usually applied in the form of a dispersion of finely divided dye in a soap solution in the presence of some solubilising agent such as phenol, cresol, or benzoic acid. The absorption into the fibre is carried out at high temperatures and pressures. Disperse dyes are used to dye acetate rayons, Dacron, Nylon and other synthetic fibres. *Celliton Fast Pink B* (1-amino-4-hydroxyanthraquinone) and *Celliton Fast Blue B* (1,4-*N*,*N*'-dimethylaminoanthraquinone) are examples of disperse dyes.



Celliton Fast Pink B
(1-amino-4-hydroxyanthraquinone)

Celliton Fast Blue B
(1,4-*N*,*N*'-dimethylaminoanthraquinone)

RAW MATERIALS FOR THE MANUFACTURE OF DYES

The raw materials for the manufacture of dyes are mainly aromatic compounds such as benzene, toluene, naphthalene, anthracene, and phenol. In the past, these compounds came exclusively from the distillation of coal-tar, but in recent years increasing quantities especially of benzene and toluene, have become available from petroleum and natural gas. A variety of

inorganic materials are also required by the dye industry. These include sulphuric acid, oleum, nitric acid, chlorine, bromine, caustic soda, sodium nitrite, hydrochloric acid, sodium carbonate, sodium hydrosulphite, sodium sulphide, aluminium chloride, sodium bicarbonate and manganese dioxide.

DYE INTERMEDIATES

The raw materials for dyes are almost never directly used in dye synthesis. It is necessary to convert them to a variety of derivatives which are in turn made into dyes. These derivatives are called *intermediates*. They are produced by reactions such as nitration, reduction, sulphonation, halogenation, oxidation, and condensation. Most of these reactions lead to the formation of substituted hydrocarbons which are functional in nature, that is, they bear groups capable of undergoing further chemical reaction. The number of dye intermediates available is very large, and the technology of their manufacture is an important part of industrial organic chemistry. Intermediates are used not only for dye manufacture but also for the manufacture of other important products such as pharmaceuticals.

NON-TEXTILE USES OF DYES

Dyes are used in many ways other than for dyeing fabrics. Large quantities of dyes are consumed by the paper industry. The most paper dyes contain acidic and basic groups, and belong to group of direct textile dyes. Natural leather is a protein substance and can also be dyed with direct dyes.

Dyes for many materials such as gasoline, lacquers, and varnishes are selected on the basis of solubility and fastness.

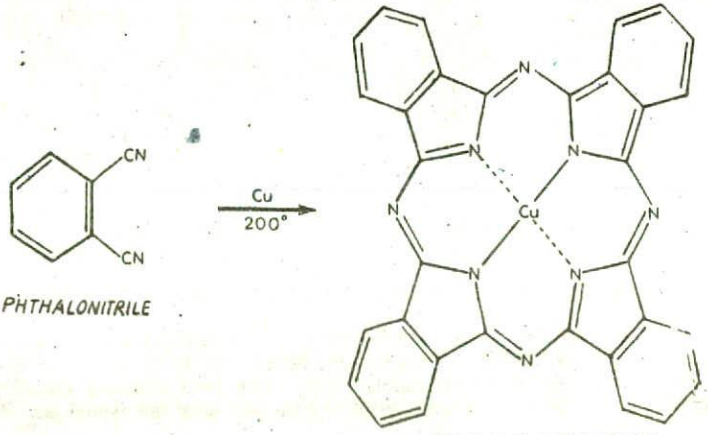
Important and growing markets for dyes are the plastic and metal industries. Dyed anodized aluminium, in particular, is finding increasing use in automotive and architectural applications.

Dyes are also used as indicators for the control of chemical processes. They are also used for staining biological substances, printing inks, and colour photography.

Dyes for food, drugs and cosmetics must be chosen with great care to avoid toxic effects. In India, dyes are certified by the government when judged safe for such uses. Only the certified dyes may legally be used. This restriction does not apply to natural dyes.

ORGANIC PIGMENTS

The difference between a dye and a pigment is that a dye is actually absorbed by the



PHTHALONITRILE

COPPER PHTHALOCYANINE

material to be coloured, whereas a pigment is applied to the surface. Pigments are highly insoluble powders of very fine particle size. They are applied in the form of dispersion in water or some other liquid. Pigments are used in paints, plastics, rubber, printing inks, and other materials for imparting colour, opaqueness, and other desirable properties. In paints, for example, pigments may also impart anticorrosive properties. Copper phthalocyanine is an example of an organic pigment. It may be obtained by heating phthalonitrile with copper at 200°C.

QUESTIONS

1. What is a dye ? How are dyes classified on the basis of their constitution ? *(South Gujarat BSc, 1993)*
2. Discuss the Theories of colour and constitution. *(Gulbarga BSc, 1993, Udaipur BSc, 1994)*
3. (*a*) Give the salient features of modern theory of colour and constitution.
   (*b*) How is natural indigo obtained from plants. Describe a synthesis of indigo. *(Poona BSc, 1993)*
4. (*a*) Explain the relationship between colour and chemical constitution.
   (*b*) Give a short account of the application of mordant and vat dyes of fabrics. *(Magadh BSc Hons, 1993)*
5. Define (*i*) Chromophore; and (*ii*) Auxochrome. *(Panjab BSc, 1993)*
6. Name one important azo dye and one important anthraquinone dye. Write their structures and uses.
7. Name and give structure of : (*a*) an azo dye ; (*b*) a triphenylmethane dye; (*c*) a vat dye ; and (*d*) a phenolphthalein dye.
8. How will you synthesise alizarin from anthracene ? *(Andhra BSc III, 1994)*
9. How will you convert resorcinol into a compound which dissolves in NaOH to give a reddish brown solution which on dilution with water exhibits yellowish green fluorescence. *(Dibrugarh BSc Hons, 1993)*
10. Give the synthesis and uses of :
    (*a*) Alizarin ;
    (*b*) Indigo *(Mangalore BSc, 1994)*
    (*c*) Malachite green
    (*d*) Phenolphthalein *(Bombay BSc, 1993)*
    (e) Fluorescein *(Kerala BSc, 1994)*
    (*f*) Methyl orange *(Madurai BSc, 1993)*
    (*g*) Congo red
    (*h*) Bismark brown
11. Given the classification of dyes according to their structure. Give examples for any three types. Indicate the synthesis of any one of the examples you have given. *(Berhampur BSc, 1994)*
12. Write a note on : Azo dyes *(Shivaji BSc, 1994)*
13. What is difference between mordant and vat dyes. *(Madras BSc, 1994)*
14. Write a note on: Vat dyes and the process of vat dyeing.
    (Udaipur BSc, 1994)