Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 2

(4) Uses

(a) As antifreeze in automobile radiator.

(b) In the preparation of good quality of soap-hand lotions shaving creams and tooth pastes.

(c) As a lubricant in watches.

(d) As a preservatives.

(e) As a sweetening agent in confectionary, beverages and medicines being non toxic in nature.

(f) In manufacture of explosives such as dynamite.

(5) Analytical tests of glycerol

(i) ***Acrolein test*** **:** When glycerol is heated with $KHSO_4$ a very offensive smell is produced due to formation of acrolein. Its aqueous solution restores the colour of schiff's reagent and reduces Fehling solution and Tollen's reagent.

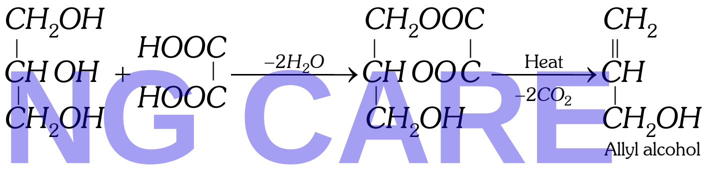
(ii) ***Dunstan's test*** **:** A drop of phenophthalein is added approximately 5 *ml* of borax solution. The pink colour appears on adding 2-3 drops of glycerol, pink colour disappears. The pink colour appears on heating and disappears on cooling again.

Unsaturated alcohols.

(1) Preparation (Allyl alcohol)

(i) ***From allyl halide*** **:** $CH_2 = CH - CH_2Br + H_2O \rightarrow \underset{\text{Allyl alcohol}}{CH_2 = CH - CH_2OH} + HBr$

(ii) ***By heating glycerol with oxalic acid*** **:**



$$\begin{array}{l} CH_2OH \\ | \\ CH\,OH \\ | \\ CH_2OH \end{array} + \begin{array}{l} HOOC \\ | \\ HOOC \end{array} \xrightarrow{-2H_2O} \begin{array}{l} CH_2OOC \\ | \qquad\quad | \\ CH\,OOC \\ | \\ CH_2OH \end{array} \xrightarrow[-2CO_2]{\text{Heat}} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array}$$

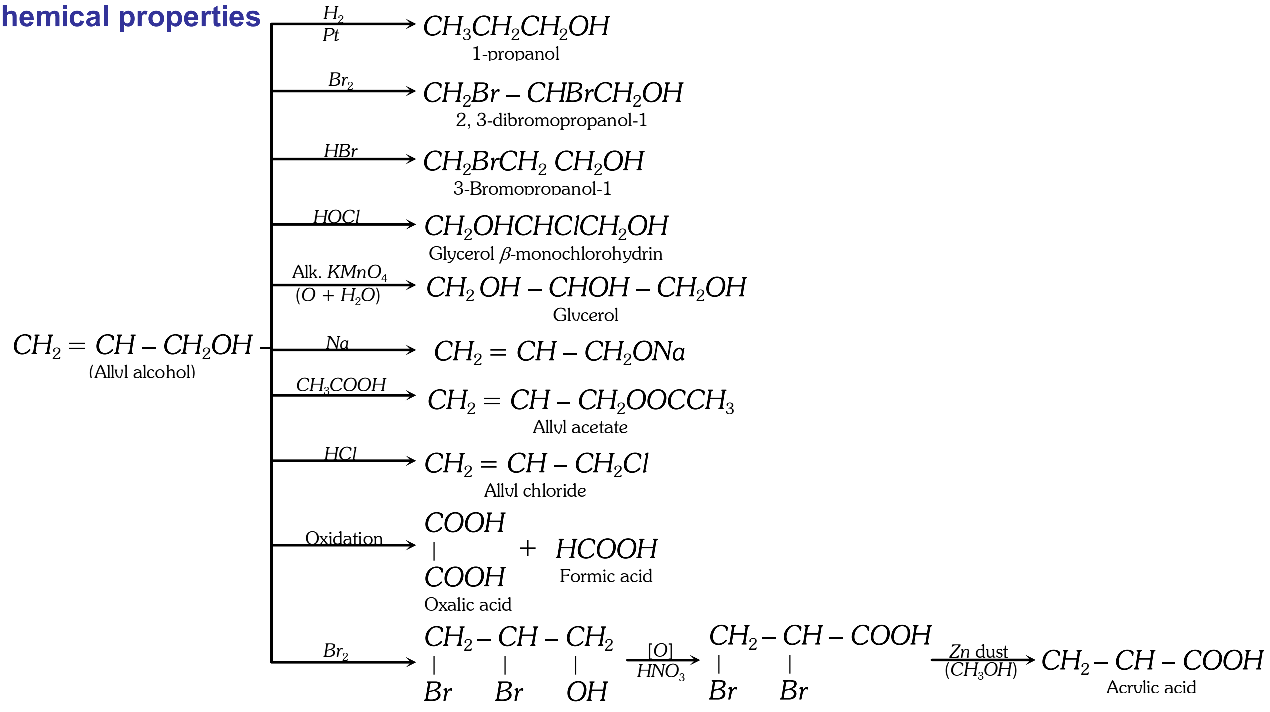
Allyl alcohol

(2) Physical properties

(a) It is colourless, pungent smelling liquid.

(b) It is soluble in water, alcohol and ether in all proportion.

(3) Chemical properties



$\underset{\text{(Allyl alcohol)}}{CH_2 = CH - CH_2OH}$

$\xrightarrow[Pt]{H_2} \underset{\text{1-propanol}}{CH_3CH_2CH_2OH}$

$\xrightarrow{Br_2} \underset{\text{2, 3-dibromopropanol-1}}{CH_2Br - CHBrCH_2OH}$

$\xrightarrow{HBr} \underset{\text{3-Bromopropanol-1}}{CH_2BrCH_2\ CH_2OH}$

$\xrightarrow{HOCl} \underset{\text{Glycerol } \beta\text{-monochlorohydrin}}{CH_2OHCHClCH_2OH}$

$\xrightarrow[(O + H_2O)]{\text{Alk. } KMnO_4} \underset{\text{Glycerol}}{CH_2\,OH - CHOH - CH_2OH}$

$\xrightarrow{Na} CH_2 = CH - CH_2ONa$

$\xrightarrow{CH_3COOH} \underset{\text{Allyl acetate}}{CH_2 = CH - CH_2OOCCH_3}$

$\xrightarrow{HCl} \underset{\text{Allyl chloride}}{CH_2 = CH - CH_2Cl}$

$\xrightarrow{\text{Oxidation}} \underset{\text{Oxalic acid}}{\begin{array}{l} COOH \\ | \\ COOH \end{array}} + \underset{\text{Formic acid}}{HCOOH}$

$\xrightarrow{Br_2} \begin{array}{lll} CH_2 - & CH - & CH_2 \\ | & | & | \\ Br & Br & OH \end{array} \xrightarrow[HNO_3]{[O]} \begin{array}{ll} CH_2 - & CH - COOH \\ | & | \\ Br & Br \end{array} \xrightarrow[(CH_3OH)]{\text{Zn dust}} \underset{\text{Acrylic acid}}{CH_2 - CH - COOH}$

Phenol (Carbolic acid), C_6H_5OH or Hydroxy benzene.

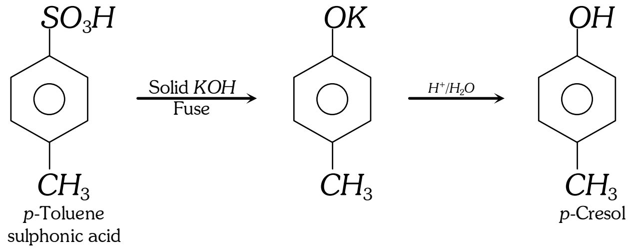
It was discovered by Runge in the middle oil fraction of coal-tar distillation and named it 'carbolic acid' (carbo = coal, oleum = oil) or phenol containing 5% water is liquid at room temperature and is termed as carbolic acid. It is also present in traces in human urine.

(1) Preparation

(i) ***From benzene sulphonic acid*** **:** Sodium salt of benzene sulphonic acid is fused with sodium hydroxide ($NaOH$) when sodium phenoxide is formed. Sodium phenoxide on treatment with dilute acid or carbon dioxide yields phenol. The start can be made with benzene.

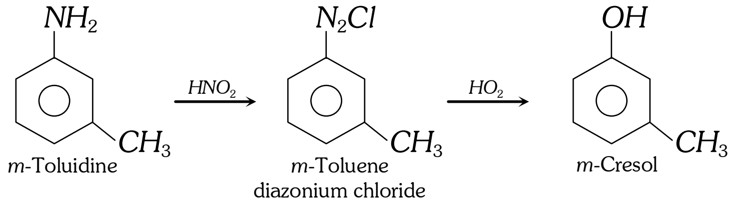
$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow{H_2SO_4\,(fuming)} \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} \xrightarrow{NaOH} \underset{\text{Sodium benzene sulphonate}}{C_6H_5SO_3Na} \xrightarrow[\text{Fuse}]{NaOH} \underset{\text{Sodium phenoxide}}{C_6H_5ONa} \xrightarrow[\text{or } CO_2/H_2O]{H^+/H_2O} \underset{\text{Phenol}}{C_6H_5OH}$$

This is one of the laboratory methods for the preparation of phenol. Similarly methyl phenols (cresols) can be prepared.



(ii) ***From benzene diazonium chloride*** **:** When benzene diazonium chloride solution is warmed, phenol is formed with evolution of nitrogen. The phenol from solution is recovered by steam distillation. In this case also, benzene can be taken as the starting material. This is also a laboratory method.

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[H_2SO_4,\,45^\circ C]{HNO_3} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[HCl,\,0-5^\circ C]{NaNO_2} \underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} \xrightarrow[\text{Warm}]{H_2O} \underset{\text{Phenol}}{C_6H_5OH}$$

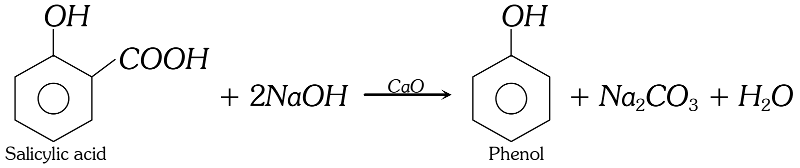


Note : ✸ *Diazonium salts are obtained from aniline and its derivatives by a process called **diazotisation.***

(iii) ***From Grignard reagent*** **:** Chlorobenzene or bromobenzene is first converted into phenyl magnesium halide in presence of dry ether. The Grignard reagent on reaction with oxygen and subsequent hydrolysis by a mineral acid, yields phenol.

$$\underset{\text{Bromobenzene}}{C_6H_5Br + Mg} \xrightarrow{\text{Ether}} \underset{\text{Phenyl magnesium bromide}}{C_6H_5MgBr} \xrightarrow{O_2} C_6H_5OMgBr \xrightarrow[H^+]{H_2O} \underset{\text{Phenol}}{C_6H_5OH}$$

(iv) ***From salicylic acid*** **:** When salicylic acid or its sodium salt is distilled with soda lime, decarboxylation occurs and phenol is formed.



(v) ***Middle oil of coal tar distillation*** **:** Middle oil of coal-tar distillation has naphthalene and phenolic compounds. Phenolic compounds are isolated in following steps.

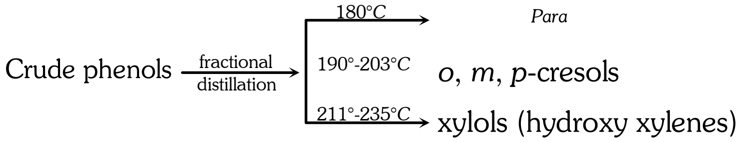
Step I **:** Middle oil is washed with H_2SO_4. It dissolves basic impurities like pyridine (base).

Step II : Excessive cooling separates naphthalene (a low melting solid)

Step III : Filtrate of step II is treated with aqueous $NaOH$ when phenols dissolve as phenoxides. Carbon dioxide is then blown through the solution to liberate phenols.

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \xrightarrow{CO_2, H_2O} C_6H_5OH + Na_2CO_3$$

Step IV : Crude phenol (of step III) is subjected to fractional distillation.



(vi) **Raschig's process :** Chlorobenzene is formed by the interaction of benzene, hydrogen chloride and air at 250°C in presence of catalyst cupric chloride and Ferric chloride it is hydrolysed by superheated steam at 425°C to form phenol and HCl. This is one of the latest methods for the synthesis of phenol. HCl may be again used to convert more of benzene into chlorobenzene.

$$\underset{\text{Benzene}}{C_6H_6} + HCl + \frac{1}{2}O_2 \xrightarrow[250^\circ C]{CuCl_2/FeCl_3} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + H_2O; \quad \underset{\text{Chlorobenzene}}{C_6H_5Cl} + \underset{\text{steam}}{H_2O} \xrightarrow{425^\circ C} \underset{\text{Phenol}}{C_6H_5OH} + HCl$$

(vii) **Dow process :** This process involves alkaline hydrolysis of chlorobenzene. Large quantities of phenol are formed by heating chlorobenzene with a 10% solution of caustic soda or sodium carbonate at 300°C under a very high pressure (200 *atm*).

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + 2NaOH \xrightarrow[\text{High pressure}]{300^\circ C} C_6H_5ONa + NaCl + H_2O$$

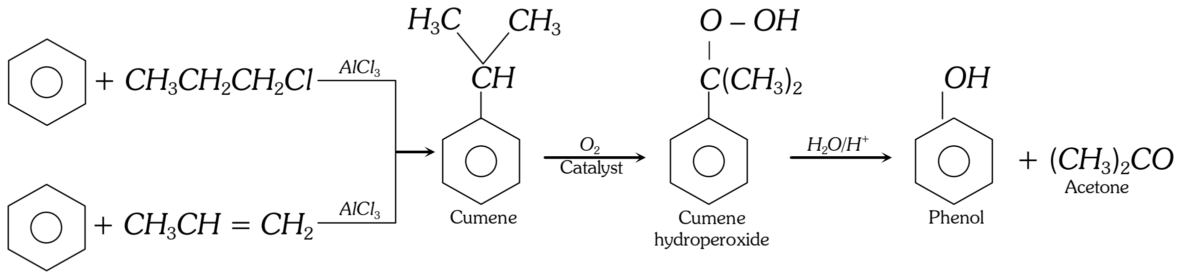
sodium phenoxide on treatment with mineral acid yields phenol.

$$2C_6H_5ONa + H_2SO_4 \rightarrow 2C_6H_5OH + Na_2SO_4$$

(viii) **Oxidation of benzene :** This is the latest method for the manufacture of phenol. The mixture of benzene and air is passed over vanadium pentaoxide at 315°C. Benzene is directly oxidised to phenol.

$$2C_6H_6 + O_2 \xrightarrow[315^\circ C]{V_2O_5} 2C_6H_5OH$$

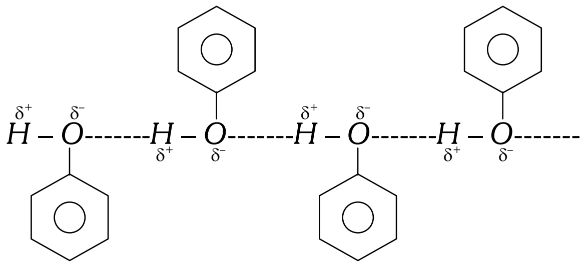
(ix) **Oxidation of isopropyl benzene** [Cumene] **:** Cumene is oxidised with oxygen or air into cumene hydroperoxide in presence of a catalyst. This is decomposed by dilute sulphuric acid into phenol and acetone.



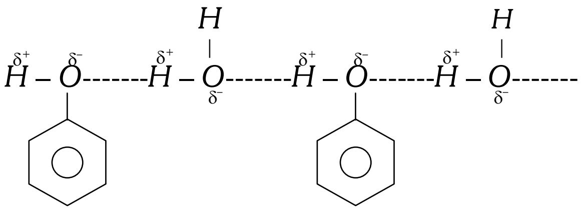
(2) Physical properties

(i) Phenol is a colourless crystalline, deliquescent solid. It attains pink colour on exposure to air and light.

(ii) They are capable of forming intermolecular H-bonding among themselves and with water. Thus, they have high b.p. and they are soluble in water.



(intermolecular H-bonding among phenol molecules)



(crossed intermolecular H-bonding between water and phenol molecules)

• Due to intermolecular *H*- bonding and high dipole moment, m.p. and b.p. of phenol are much higher than that of hydrocarbon of comparable molecular weights.

Compounds	**Molecular weight**	**Boiling point**	**Melting point**
Phenol	$94\ g\ mol^{-1}$	**182°C**	**41°C**
Toluene	$92\ g\ mol^{-1}$	**111°C**	**–95°C**

(iii) It has a peculiar characteristic smell and a strong corrosive action on skin.

(iv) It is sparingly soluble in water but readily soluble in organic solvents such as alcohol, benzene and ether.

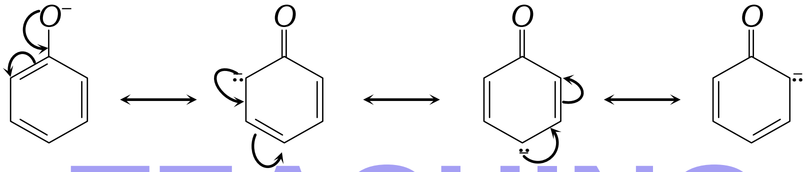
(v) It is poisonous in nature but acts as antiseptic and disinfectant.

(3) Chemical properties

(i) ***Acidic nature*** **:** Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution.

$$C_6H_5OH + H_2O \rightleftharpoons \underset{\text{Phenoxide ion}}{C_6H_5O^-} + H_3O^+$$

The phenoxide ion is stable due to resonance.



The negative charge is spread throughout the benzene ring. This charge delocalisation is a stabilising factor in the phenoxide ion and increase acidity of phenol. [No resonance is possible in alkoxide ions (RO^-) derived from alcohols. The negative charge is localised on oxygen atom. Thus alcohols are not acidic].

Note : ✹ *Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants. The relative acidity follows the following order*

$$K_a\text{(approx.)}\quad \underset{\text{Carboxylic acid}}{\underset{RCOOH}{(10^{-5})}} > \underset{\text{Carbonic acid}}{\underset{H_2CO_3}{(10^{-7})}} > \underset{\text{Phenol}}{\underset{C_6H_5OH}{(10^{-10})}} > \underset{\text{Water}}{\underset{HOH}{(10^{-14})}} > \underset{\text{Alcohols}}{\underset{ROH}{(10^{-18})}}$$

Effects of substituents on the acidity of phenols : Presence of electron attracting group, (*e.g.*, $-NO_2$, $-X$, $-NR_3^+$, $-CN$, $-CHO$, $-COOH$) on the benzene ring increases the acidity of phenol as it enables the ring to draw more electrons from the phenoxy oxygen and thus releasing easily the proton. Further, the particular effect is more when the substituent is present on *o*- or *p*-position than in *m*-position to the phenolic group.

The relative strengths of some phenols (as acids) are as follows :

p-Nitrophenol > *o*-Nitrophenol > *m*- Nitrophenol > Phenol

Presence of electron releasing group, (*e.g.*, $-CH_3$, $-C_2H_5, -OCH_3, -NR_2$) on the benzene ring decreases the acidity of phenol as it strengthens the negative charge on phenoxy oxygen and thus proton release becomes difficult. Thus, cresols are less acidic than phenol.

However, *m*-methoxy and *m*-aminophenols are stronger acids than phenol because of $-I$ effect and absence of $+R$ effect.

m-methoxy phenol > *m*-amino phenol > phenol > *o*-methoxy phenol > *p*-methoxy phenol

Greater the value of K_a or lower the value of pK_a, stronger will be the acid. Some other examples of acidic nature of phenols are,

Chloro phenols : *o*- > *m*- > *p*-
Cresols : *m*- > *p*- > *o*-
Dihydric phenol : *m*- > *p*- > *o*-

The acidic nature of phenol is observed in the following :

(a) Phenol changes blue litmus to red.

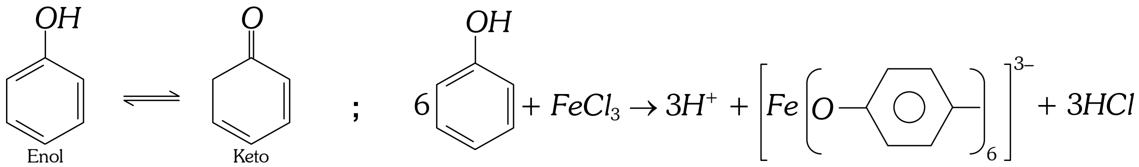
(b) Highly electropositive metals react with phenol. $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$

(c) Phenol reacts with strong alkalies to form phenoxides. $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

However, phenol does not decompose sodium carbonate or sodium bicarbonate, *i.e.*, CO_2 is not evolved because phenol is weaker than carbonic acid.

(ii) ***Reactions of –OH group***

(a) *Reaction with* $FeCl_3$ **:** Phenol gives violet colouration with ferric chloride solution (neutral) due to the formation of a coloured iron complex, which is a characteristic to the existence of keto-enol tautomerism in phenols (predominantly enolic form).



This is the test of phenol.

(b) *Ether formation* : Phenol reacts with alkyl halides in alkali solution to form phenyl ethers (Williamson's synthesis). The phenoxide ion is a nucleophile and will replace halogenation of alkyl halide.

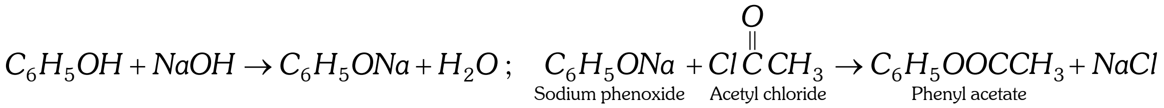
$$C_6H_5OH + NaOH \rightarrow \underset{\text{Sod. phenoxide}}{C_6H_5ONa} + H_2O\ ;\ C_6H_5ONa + ClCH_3 \rightarrow \underset{\text{Methyl phenyl ether (Anisole)}}{C_6H_5OCH_3} + NaCl$$

$$C_6H_5OK + IC_2H_5 \rightarrow \underset{\text{Ethoxy benzene (Phenetol)}}{C_6H_5-O-C_2H_5} + KI\ ;\ C_6H_5ONa + \underset{\text{Isopropyl chloride}}{Cl-HC(CH_3)_2} \rightarrow \underset{\text{Isopropyl phenyl ether}}{C_6H_5-O-HC(CH_3)_2}$$

Ethers are also formed when vapours of phenol and an alcohol are heated over thoria (ThO_2) or Al_2O_3.

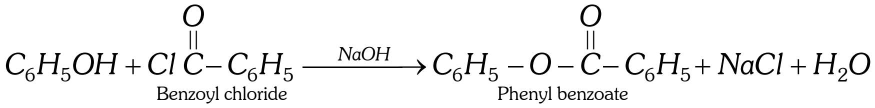
$$C_6H_5OH + HOCH_3 \xrightarrow{\Delta, ThO_2} \underset{\text{Methoxy benzene}}{C_6H_5-O-CH_3}$$

(c) *Ester formation* : Phenol reacts with acid chlorides (or acid anhydrides) in alkali solution to form phenylesters (**Acylation**). This reaction (**Benzoylation**) is called **Schotten-Baumann** reaction.



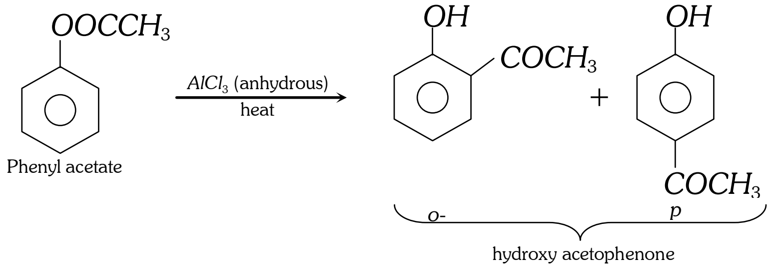
$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O\ ;\ \underset{\text{Sodium phenoxide}}{C_6H_5ONa} + \underset{\text{Acetyl chloride}}{Cl\overset{\overset{O}{\|}}{C}CH_3} \rightarrow \underset{\text{Phenyl acetate}}{C_6H_5OOCCH_3} + NaCl$$

$$C_6H_5OH + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow{NaOH} \underset{\text{Phenyl acetate (ester)}}{C_6H_5OOCCH_3} + CH_3COOH\ ;$$



$$C_6H_5OH + \underset{\text{Benzoyl chloride}}{Cl\overset{\overset{O}{\|}}{C}-C_6H_5} \xrightarrow{NaOH} \underset{\text{Phenyl benzoate}}{C_6H_5-O-\overset{\overset{O}{\|}}{C}-C_6H_5} + NaCl + H_2O$$

The phenyl esters on treatment with anhydrous $AlCl_3$ undergoes **Fries rearrangement** to give *o*- and *p*-hydroxy ketones.



(d) *Reaction with* PCl_5 : Phenol reacts with PCl_5 to form chlorobenzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

$$C_6H_5OH + PCl_5 \rightarrow C_6H_5Cl + POCl_3 + HCl; \quad 3C_6H_5OH + POCl_3 \rightarrow (C_6H_5)_3PO_4 + 3HCl$$

(e) *Reaction with zinc dust* **:** When phenol is distilled with zinc dust, benzene is obtained.

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

(f) *Reaction with ammonia* **:** Phenol reacts with ammonia in presence of anhydrous zinc chloride at 300°C or $(NH_4)_2SO_3 / NH_3$ at 150°C to form aniline. This conversion of phenol into aniline is called **Bucherer reaction.**

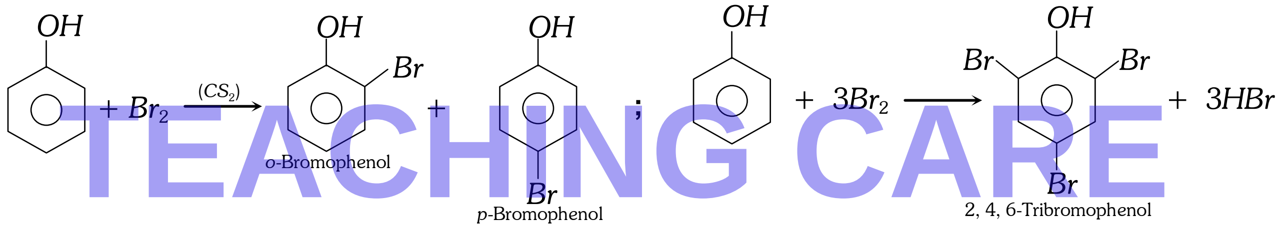
$$C_6H_5OH + NH_3 \xrightarrow[300^o C]{ZnCl_2} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

(g) *Action of* P_2S_5 : By heating phenol with phosphorus penta sulphide, thiophenols are formed.

$$5C_6H_5OH + P_2S_5 \rightarrow \underset{\text{Thiophenol}}{5C_6H_5SH} + P_2O_5$$

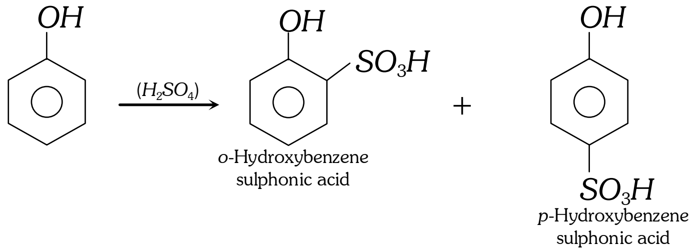
(iii) ***Reactions of benzene nucleus* :** The $-OH$ group is *ortho* and *para* directing. It activates the benzene nucleus.

(a) *Halogenation* **:** Phenol reacts with bromine in carbon disulphide (or $CHCl_3$) at low temperature to form mixture of *ortho* and *para* bromophenol.



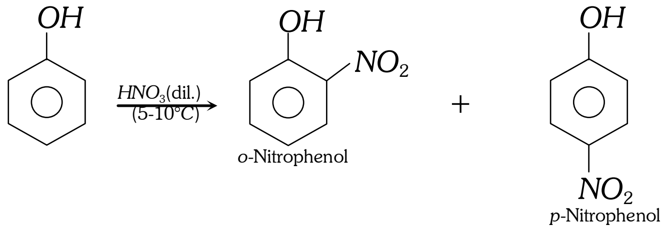
Phenol forms a white precipitate with excess of bromine water yielding 2, 4, 6-tribromophenol.

(b) *Sulphonation* : Phenol reacts with conc. H_2SO_4 readily to form mixture of *ortho* and *para* hydroxy benzene sulphonic acids.

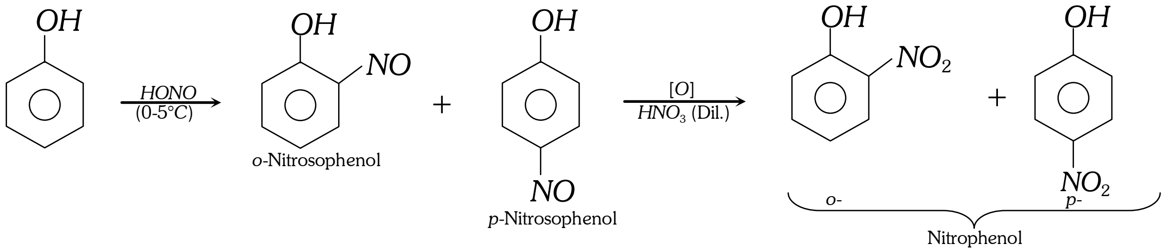


At low temperature (25°C), the *ortho*-isomer is the major product, whereas at 100°C, it gives mainly the *para*-isomer.

(c) *Nitration* : Phenol reacts with dilute nitric acid at 5-10°C to form *ortho* and *para* nitro phenols, but the yield is poor due to oxidation of phenolic group. The $-OH$ group is activating group, hence nitration is possible with dilute nitric acid.



It is believed that the mechanism of the above reaction involves the formation of *o*- and *p*- nitroso phenol with nitrous acid, $HNO_2 (NaNO_2 + HCl)$ at 0-5°C, which gets oxidised to *o*- and *p*- nitrophenol with dilute nitric acid.

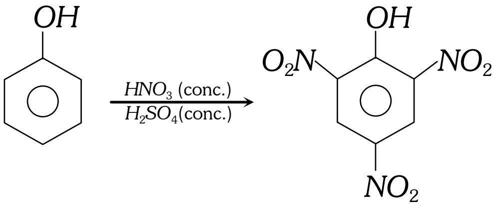


o-Nitrosophenol

p-Nitrosophenol

Nitrophenol

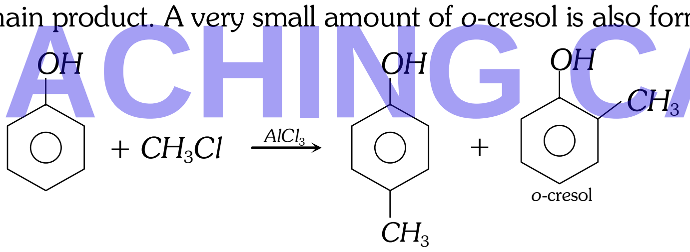
However, when phenol is treated with concentrated HNO_3 in presence of concentrated H_2SO_4, 2,4,6-trinitrophenol (**Picric acid**) is formed.



2, 4, 6-Trinitrophenol
(picric acid)

To get better yield of picric acid, first sulphonation of phenol is made and then nitrated. Presence of $-SO_3H$ group prevents oxidation of phenol.

(d) *Friedel-Craft's reaction* : Phenol when treated with methyl chloride in presence of anhydrous aluminium chloride, *p*-cresol is the main product. A very small amount of *o*-cresol is also formed.



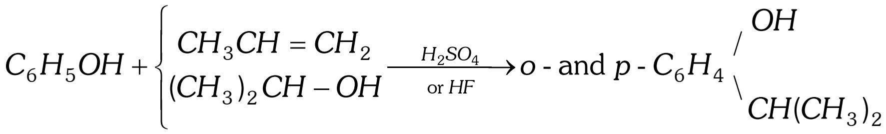
o-cresol

p-Cresol
(major product)

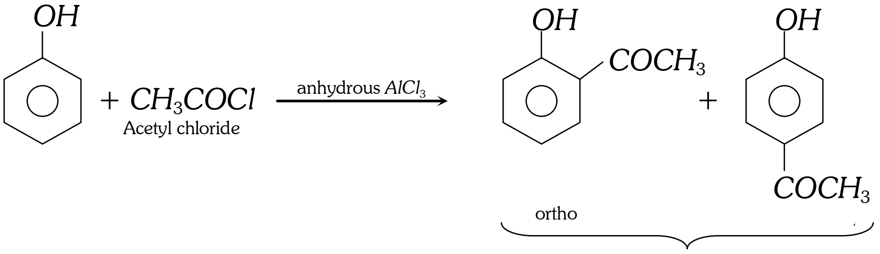
RX and $AlCl_3$ give poor yields because $AlCl_3$ coordinates with O. So Ring alkylation takes place as follows,

$$C_6H_5OH + AlCl_3 \rightarrow C_6H_5OAlCl_2 + HCl$$

Thus to carry out successful Friedel-Craft's reaction with phenol it is necessary to use a large amount of $AlCl_3$. The **Ring alkylation** takes place as follows :

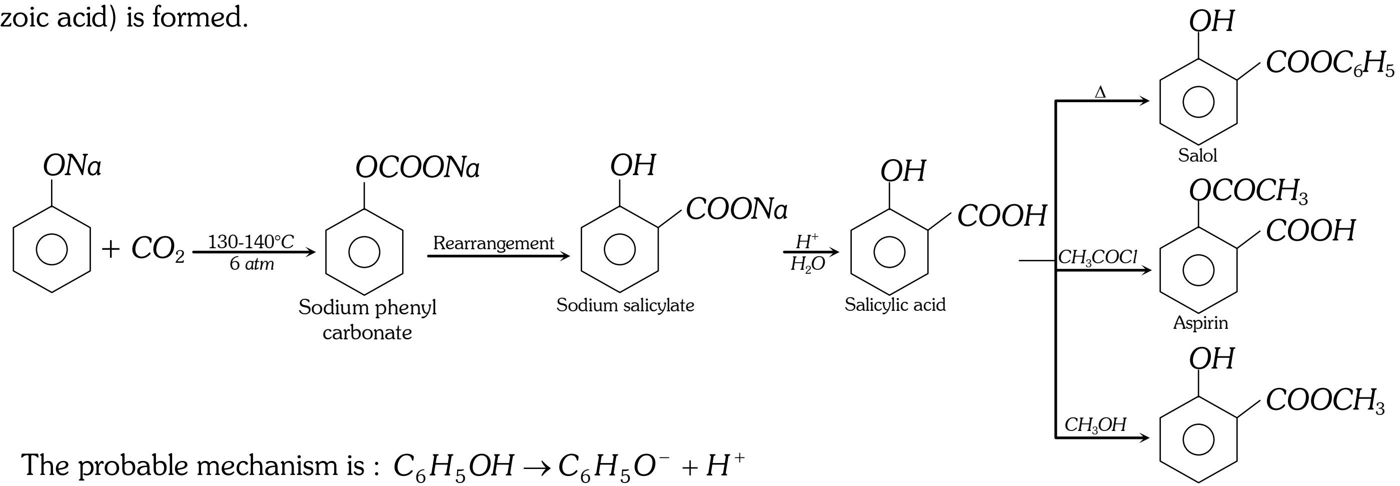


$$C_6H_5OH + \left\{ \begin{array}{l} CH_3CH = CH_2 \\ (CH_3)_2CH - OH \end{array} \right. \xrightarrow[\text{or } HF]{H_2SO_4} o\text{ - and } p\text{ - } C_6H_4 \begin{array}{l} / \; OH \\ \backslash \; CH(CH_3)_2 \end{array}$$

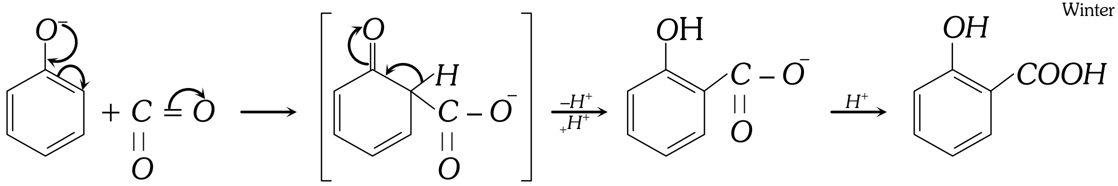


hydroxy acetophenone

(e) *Kolbe-Schmidt reaction* (Carbonation) : This involves the interaction of sodium phenoxide with carbon dioxide at 130-140°C under pressure of 6 atmospheres followed by acid hydrolysis, Salicylic acid (*o*-Hydroxy benzoic acid) is formed.

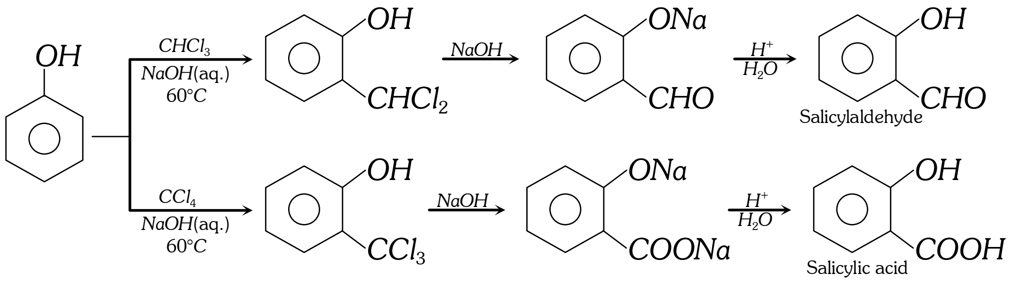


The probable mechanism is : $C_6H_5OH \rightarrow C_6H_5O^- + H^+$



At higher temperature (250-300°C), *p*-isomer is obtained.

(f) ***Reimer-Tiemann reaction*** **:** Phenol, on refluxing with chloroform and sodium hydroxide (aq.) followed by acid hydrolysis yields salicylaldehyde (*o*-hydroxy benzaldehyde) and a very small amount of *p*-hydroxy benzaldehyde. However, when carbon tetrachloride is used, salicylic acid (predominating product) is formed.



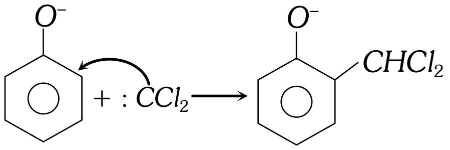
The electrophile is dichloromethylene $:CCl_2$ generated from chloroform by the action of a base.

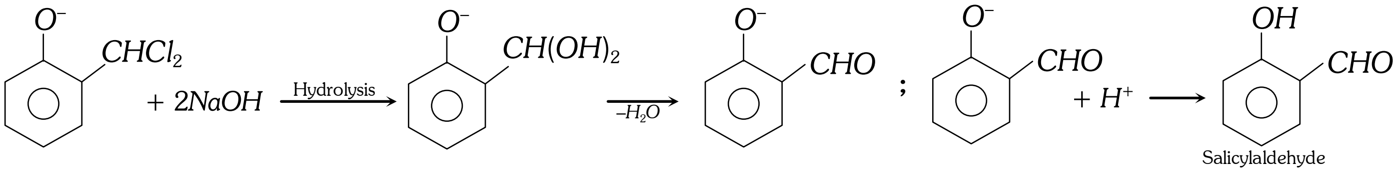
$$OH^- + CHCl_3 \rightleftharpoons HOH + :\bar{C}Cl_3 \rightarrow Cl^- + \underset{\text{Dichloro carbene}}{:CCl_2}$$

Reimer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring.

$$C_6H_5OH \rightarrow \underset{\text{Phenoxide}}{C_6H_5O^-} + H^+$$

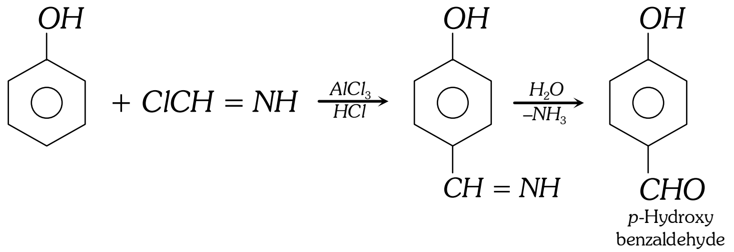
Attack of electrophile $(:CCl_2)$





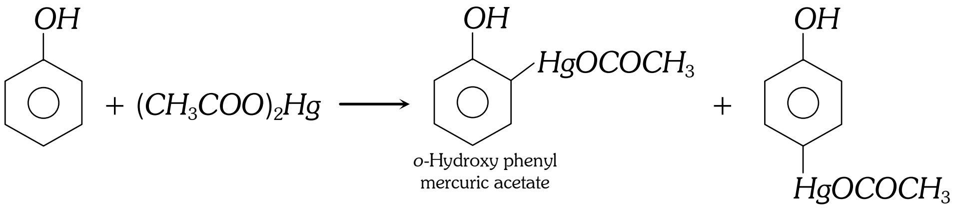
(g) *Gattermann's reaction* : Phenol, when treated with liquid hydrogen cyanide and hydrochloric acid gas in presence of anhydrous aluminium chloride yields mainly *p*-hydroxy benzaldehyde (Formylation).

$$HCl + HC \equiv N \xrightarrow{AlCl_3} ClCH = NH$$



p-Hydroxy benzaldehyde

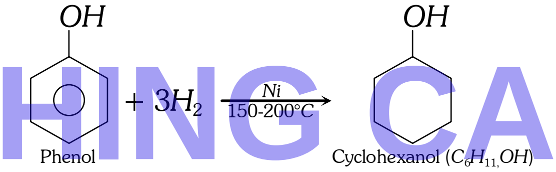
(h) *Mercuration* : Phenol when heated with mercuric acetate undergoes mercuration to form *o*- and *p*-isomers.



o-Hydroxy phenyl mercuric acetate

p-Hydroxy phenyl mercuric acetate

(i) **Hydrogenation :** Phenol, when hydrogenated in presence of a nickel catalyst at about 150-200°C, forms cyclohexanol.

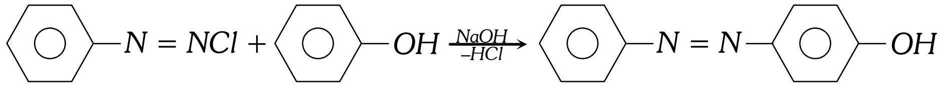


Phenol (C_6H_5OH)

Cyclohexanol ($C_6H_{11}OH$) (used as a good solvent)

(iv) **Miscellaneous reactions**

(a) *Coupling reactions* : Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a red dye (*p*-hydroxy azobenzene).

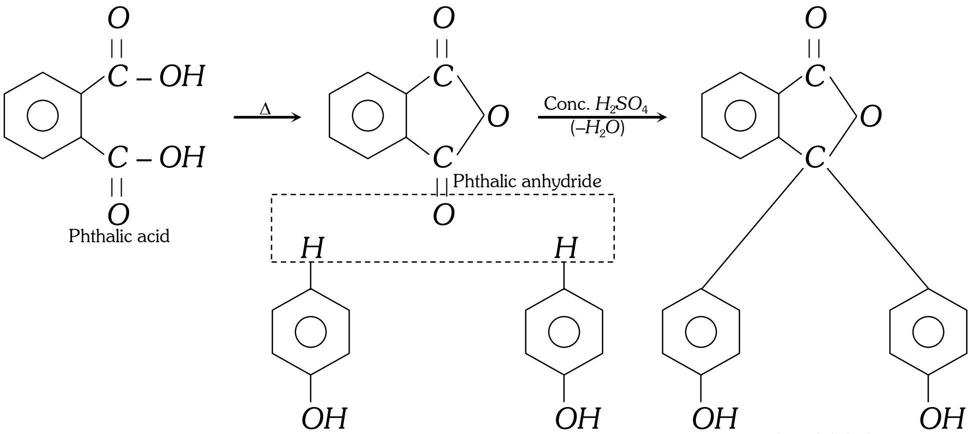


Benzene diazonium chloride

Phenol

p-Hydroxyazobenzene

Phenol couples with phthalic anhydride in presence of concentrated H_2SO_4 to form a dye, (phenolphthalein) used as an indicator.



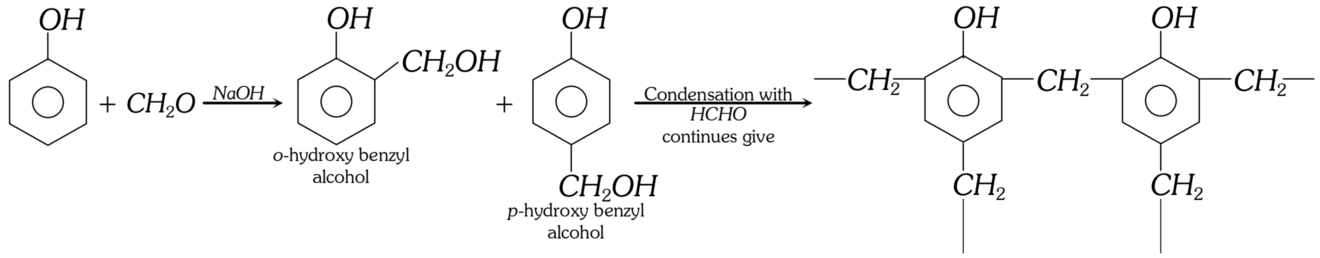
Phthalic acid

Phthalic anhydride

Phenol (2 molecules)

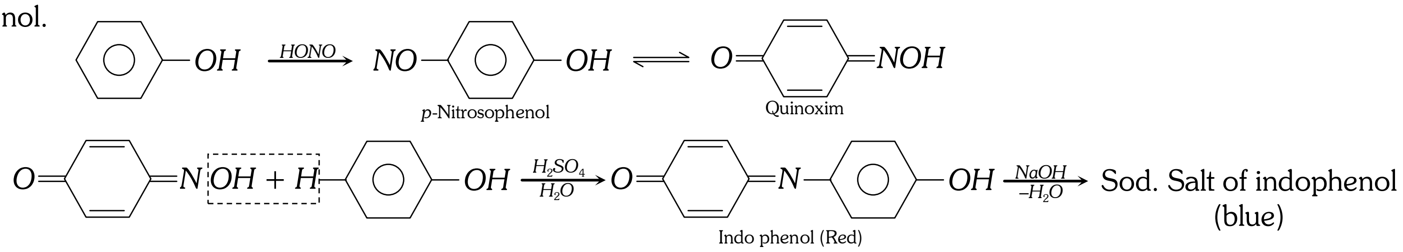
Phenolphthalein

(b) *Condensation with formaldehyde* : Phenol condenses with formaldehyde (excess) in presence of sodium hydroxide or acid (H^+) for about a week to form a polymer known as bakelite (a resin).

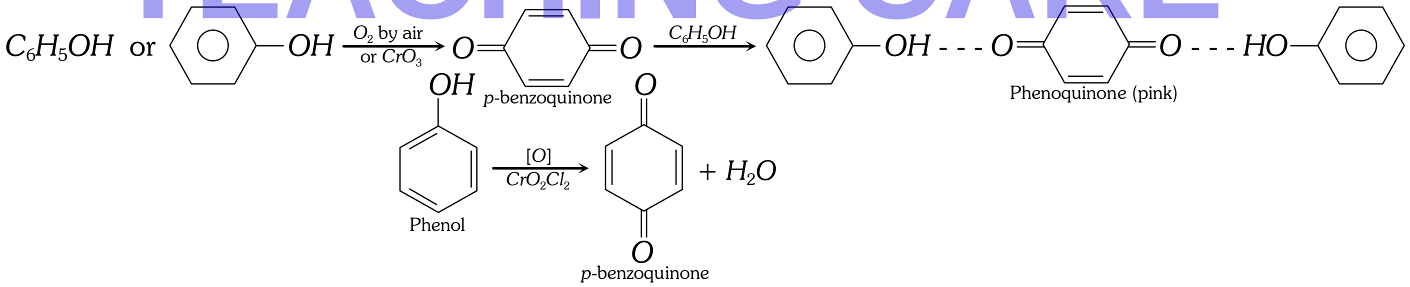


Polymer Bakelite (a resin)

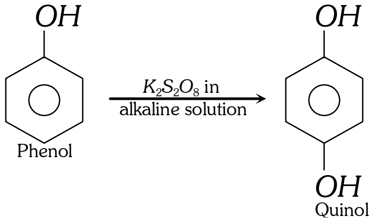
(c) *Liebermann's nitroso reaction* : When phenol is reacted with $NaNO_2$ and concentrated H_2SO_4, it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with *NaOH* original green or blue colour is restored. This reaction is known as Liebermann's nitroso reaction and is used as a test of phenol.



(d) *Oxidation* : Phenol turns pink or red or brown on exposure to air and light due to slow oxidation. The colour is probably due to the formation of quinone and phenoquinone.



But on oxidation with potassium persulphate in alkaline solution, phenol forms 1, 4-dihydroxy benzene (Quinol). This is known as **Elbs persulphate oxidation.**



(4) Uses : Phenol is extensively used in industry. The important applications of phenol are :

(i) As an antiseptic in soaps, lotions and ointments. A powerful antiseptic is "Dettol" which is a phenol derivative (2, 4-dichloro-3, 5-dimethyl phenol).

(ii) In the manufacture of azo dyes, phenolphthalein, etc.

(iii) In the preparation of picric acid used as an explosive and for dyeing silk and wool.

(iv) In the manufacture of cyclohexanol required for the production of nylon and used as a solvent for rubber and lacquers.

(v) As a preservative for ink.

(vi) In the manufacture of phenol-formaldehyde plastics such as bakelite.

(vii) In the manufacture of drugs like aspirin, salol, phenacetin, etc.

(viii) For causterising wounds caused by the bite of mad dogs.

(ix) As a starting material for the manufacture of nylon and artificial tannins.

(x) In the preparation of disinfectants, fungicides and bactericides.

(5) **Tests of phenol :** (i) Aqueous solution of phenol gives a violet colouration with a drop of ferric chloride.

(ii) Aqueous solution of phenol gives a white precipitate of 2, 4, 6-tribromophenol with bromine water.

(iii) Phenol gives **Liebermann's nitroso reaction.**

$$\text{Phenol in conc. sulphuric acid} \xrightarrow[\text{Excess of water}]{NaNO_2} \text{Red colour} \xrightarrow[\text{(Excess)}]{NaOH} \text{Blue colour}$$

(iv) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali, and used as an indicator.

(v) With ammonia and sodium hypochlorite, phenol gives blue colour.

Difference between phenol and alcohol

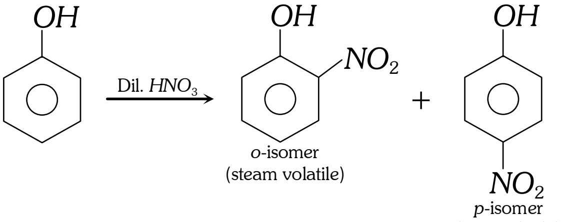
Property	*Phenol (C_6H_5OH)*	*Alcohol (C_2H_5OH)*
Odour	**Typical phenolic odour**	**Pleasant alcoholic odour**
Nature, reaction with alkali	**Acidic, dissolves in sodium hydroxide forming sodium phenoxide.**	**Neutral, no reaction with alkalies.**
Reaction with neutral $FeCl_3$	**Gives violet colouration due to formation of complex compound.**	**No reaction.**
Reaction with halogen acids	**No reaction with halogen acids.**	**Forms ethyl halides.**
Oxidation	**Pink or brown colour due to formation of quinone and phenoquinone.**	**Undergoes oxidation to give acetaldehyde and acetic acid.**
Reaction with HCHO	**Forms polymer (bakelite).**	**No reaction.**
Liebermann's nitroso reaction	**Positive.**	**Does not show.**
Coupling with benzene diazonium chloride	**Forms azo dye.**	**Does not form any dye.**
Reaction with PCl_5	**Mainly forms triphenyl phosphate.**	**Forms ethyl chloride**
Iodoform test	**Does not show.**	**Positive.**

Derivatives of phenol.

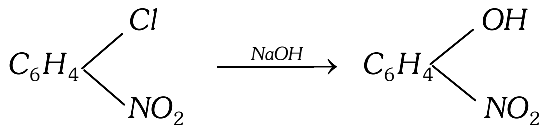
NITROPHENOLS

(1) Preparation

(i) Phenol easily undergoes nitration. Ortho and para nitrophenols are obtained by nitration of phenol with dilute HNO_3 in cold. Ortho isomer is separated by steam distillation as it is steam volatile.



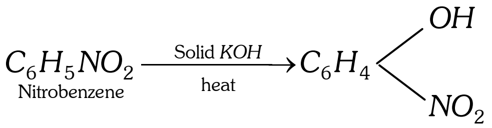
(ii) *o*- and *p*-forms are also obtained by treating chloro or bromo nitrobenzene with caustic alkali at 120°C.



$$C_6H_4\begin{matrix}Cl\\NO_2\end{matrix} \xrightarrow{NaOH} C_6H_4\begin{matrix}OH\\NO_2\end{matrix}$$

o- and *p*-chloro nitrobenzene — *o*- and *p*-nitrophenol

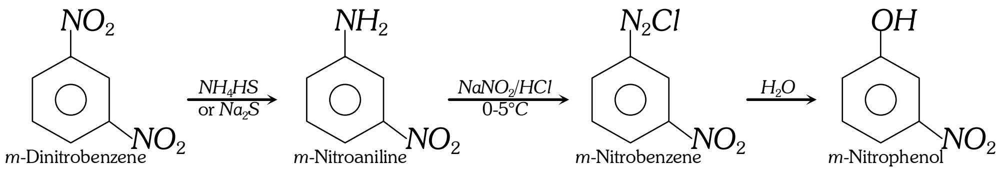
(iii) When heated with solid potassium hydroxide, nitrobenzene produces a mixture of *o*- and *p*-nitrophenols.



$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[\text{heat}]{\text{Solid } KOH} C_6H_4\begin{matrix}OH\\NO_2\end{matrix}$$

o- and *p*-nitrophenol

(iv) *m*-Nitrophenol is obtained from *m*-dinitrobenzene. One of the nitrogroup is converted into $-NH_2$ group which is diazotised. The diazonium compound on boiling yields *m*-nitrophenol.



m-Dinitrobenzene — *m*-Nitroaniline — *m*-Nitrobenzene diazonium chloride — *m*-Nitrophenol

(2) Properties : *o*-Nitrophenol is a yellow coloured crystalline compound, while *m*- and *p*-isomers are colourless crystalline compounds.

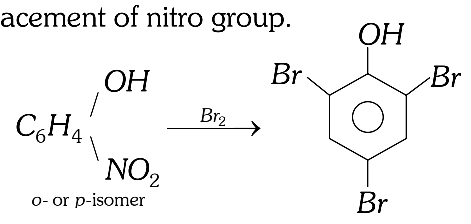
Isomer	*ortho*	*meta*	*para*
m.pt. (°C)	45	97	114

the lowest melting point of *o*-isomer is due to **intramolecular hydrogen bonding** whereas *meta* and *para* isomers possess **intermolecular hydrogen bonding** and thus, they have higher melting points.

They are stronger acids than phenol. The order is :

p-isomer > *o*-isomer > *m*-isomer > phenol

When reduced, they form corresponding aminophenols. *o*- and *p*-Nitrophenols react with bromine water to form 2, 4, 6-tribromophenol by replacement of nitro group.



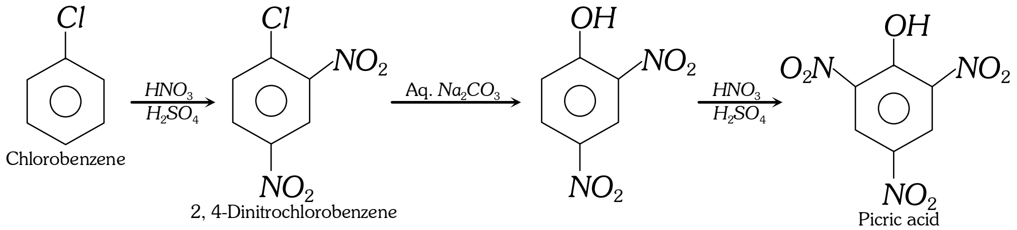
$$C_6H_4\begin{matrix}OH\\NO_2\end{matrix} \xrightarrow{Br_2}$$

o- or *p*-isomer — 2,4,6 Tribromophenol

Picric acid (2, 4, 6-trinitrophenol)

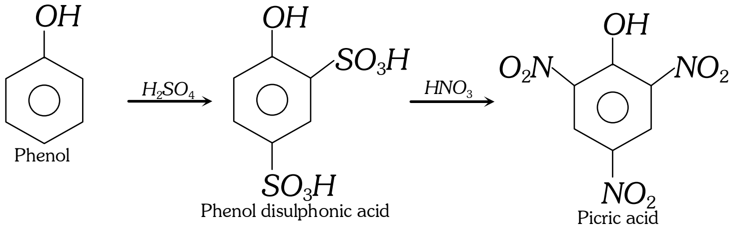
(1) Preparation : It is obtained when phenol is treated with conc. HNO_3. However, the yield is very poor. It is prepared on an industrial scale :

(i) ***From chlorobenzene***

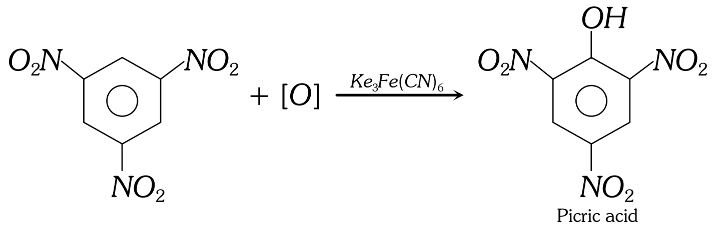


Chlorobenzene — 2, 4-Dinitrochlorobenzene — Picric acid (2, 4, 6-Trinitrophenol)

(ii) ***From phenol through disulphonic acid***

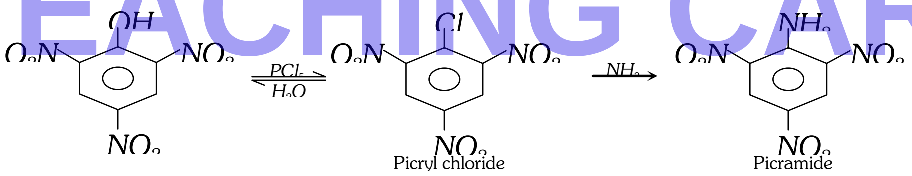


(iii) It may be prepared in the laboratory by oxidation of *s*-trinitrobenzene (TNB) with potassium ferricyanide.



(2) Properties : It is a yellow crystalline solid, m.pt. 122°C. it is insoluble in cold water but soluble in hot water and in ether. It is bitter in taste. Due to the presence of three electronegative nitro groups, it is a stronger acid than phenol and its properties are comparable to the carboxylic acid. It neutralises alkalies and decomposes carbonates with evolution of carbon dioxide.

Dry picric acid as well as its potassium or ammonium salts explode violently when detonated. It reacts with PCl_5 to form picryl chloride which on shaking with NH_3 yields picramide.



When distilled with a paste of bleaching powder, it gets decomposed and yields chloropicrin, CCl_3NO_2, as one of the products and is thus employed for the manufacture of tear gas.

It forms yellow, orange or red coloured molecular compounds called picrates with aromatic hydrocarbons, amines and phenols which are used for characterisation of these compounds.

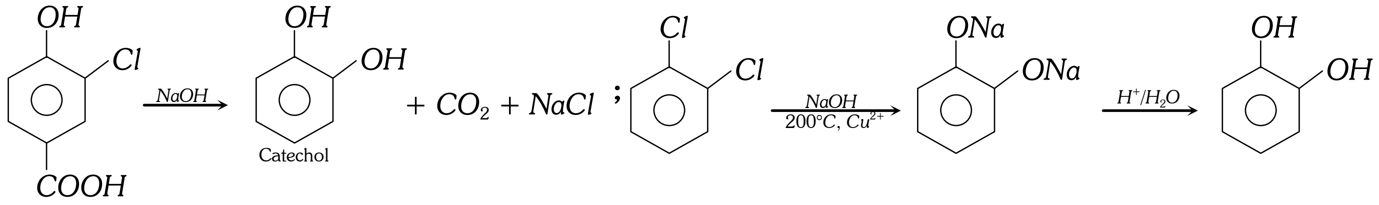
Note : ✹ *Picrates are explosive in nature and explode violently when heated. These are prepared carefully.*

(3) Uses : It is used as a yellow dye for silk and wool, as an explosive and as an antiseptic in treatment of burns.

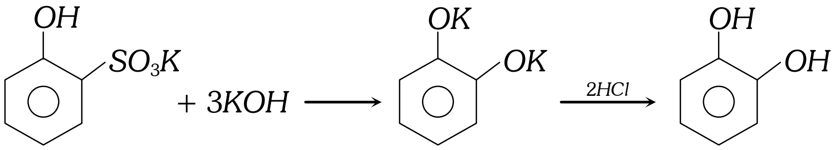
Catechol (1, 2-Dihydroxy benzene)

(1) Preparation

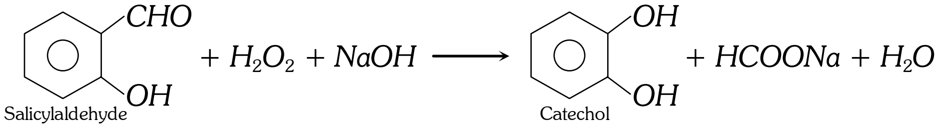
(i) By fusion of chlorosubstituted phenolic acid with caustic soda. or by hydrolysis of *o*-dichlorobenzene or *o*-chlorophenol with dilute *NaOH* solution at 200°C and in the presence of copper sulphate catalyst.



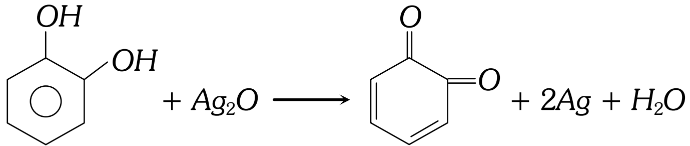
(ii) By fusing alkali salt of *o*-phenol sulphonic acid with caustic alkali and then hydrolysing the product with mineral acid.



(iii) It may be conveniently prepared in the laboratory by treating salicylaldehyde with alkaline H_2O_2.

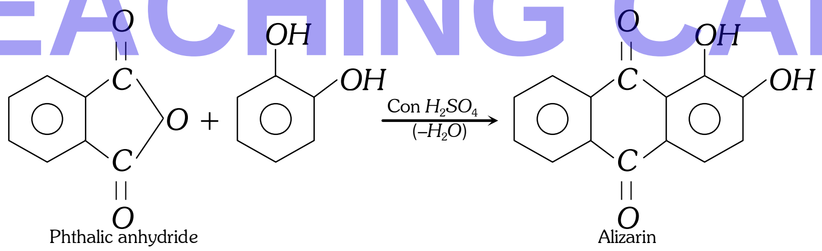


(2) **Properties :** It is a colourless crystalline solid, m.pt. 105°C. it is soluble in water. It is affected on exposure to air and light. It acts as a reducing agent as it reduces Tollen's reagent in cold and Fehling's solution on heating. With silver oxide it is oxidised to *o*-benzoquinone.



o-Benzoquinone

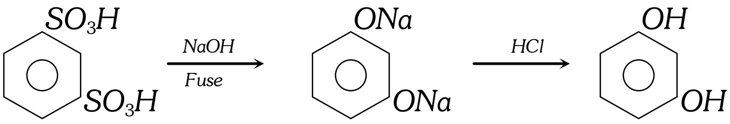
It forms insoluble lead salt (white ppt.) when treated with lead acetate solution and gives green colour with $FeCl_3$ which changes to red on adding Na_2CO_3 solution. It forms alizarin dye stuff when condensed with phthalic anhydride in the presence of sulphuric acid.



(iii) **Uses :** It finds use as photographic developer, in the manufacture of alizarin and adrenaline hormone and as an antioxidant (inhibitor in auto oxidation) for preserving gasoline.

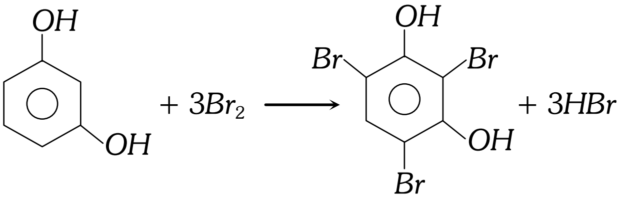
Resorcinol (1, 3-Dihydroxy benzene)

(1) **Preparation :** It is prepared by alkali fusion of 1,3, benzene disulphonic acid (Industrial method).

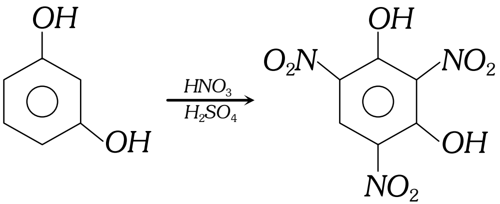


(2) **Properties :** It is a colourless crystalline solid, m.pt. 110°C. it is affected on exposure by air and light. It is soluble in water, alcohol and ether. It shows tautomerism. Its aqueous solution gives violet colour with $FeCl_3$. It reduces Fehling's solution and Tollen's reagent on warming.

With bromine water, it gives a crystalline precipitate, 2, 4, 6-tribromoresorcinol.

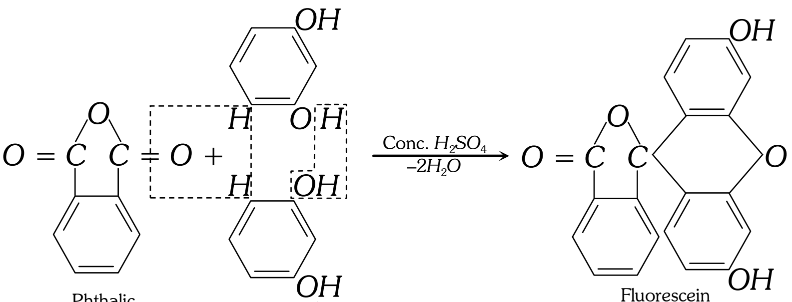


On nitration, it forms 2, 4, 6-trinitro-1, 3-dihydroxybenzene.



Styphnic acid

It condenses with phthalic anhydride and forms fluorescein.

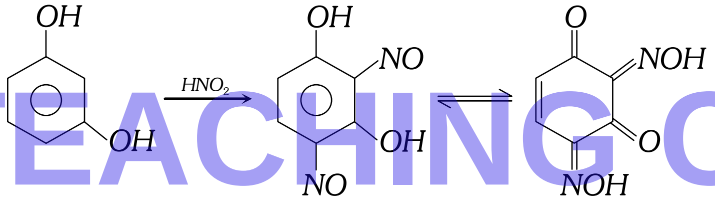


Phthalic anhydride

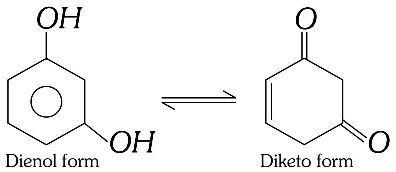
Resorcinol (2 moles)

Fluorescein

With nitrous acid, it forms 2, 4-dinitrosoresorcinol



Resorcinol behaves as a tautomeric compound. This is shown by the fact that it forms a dioxime and a bisulphite derivative.



Dienol form

Diketo form

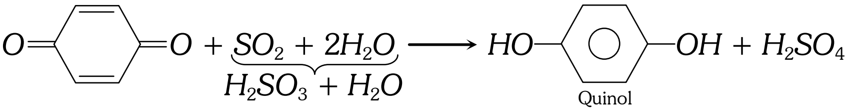
(3) **Uses**

(i) It is used as antiseptic and for making dyes.

(ii) It is also used in the treatment of eczema. 2, 4, 6-trinitroresorcinol is used as an explosive.

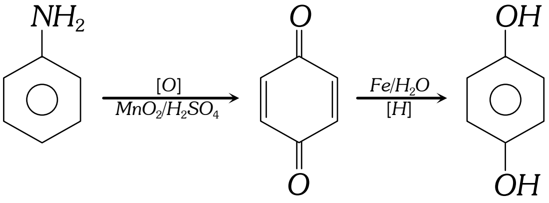
Hydroquinone or quinol (1, 4-Dihydroxy benzene)

(1) **Preparation :** It is formed by reduction of *p*-benzoquinone with sulphurous acid $(H_2SO_3 = H_2O + SO_2)$.



Quinol

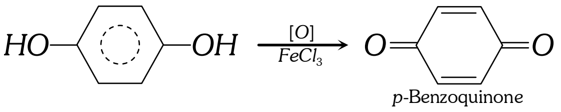
(*p*-Benzoquinone is obtained by oxidation of aniline)



Quinol

(2) **Properties :** It is a colourless crystalline solid, m.pt. 170°C. it is soluble in water. It also shows tautomerism. It gives blue colour with $FeCl_3$ solution.

It acts as a powerful reducing agent as it is easily oxidised to *p*-benzoquinone. It reduces Tollen's reagent and Fehling's solution.

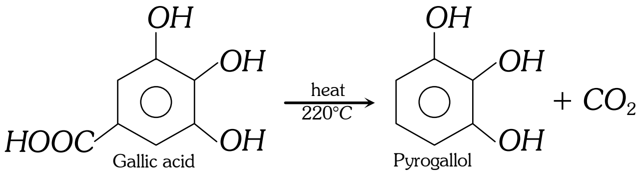


Due to this property, it is used as photographic developer.

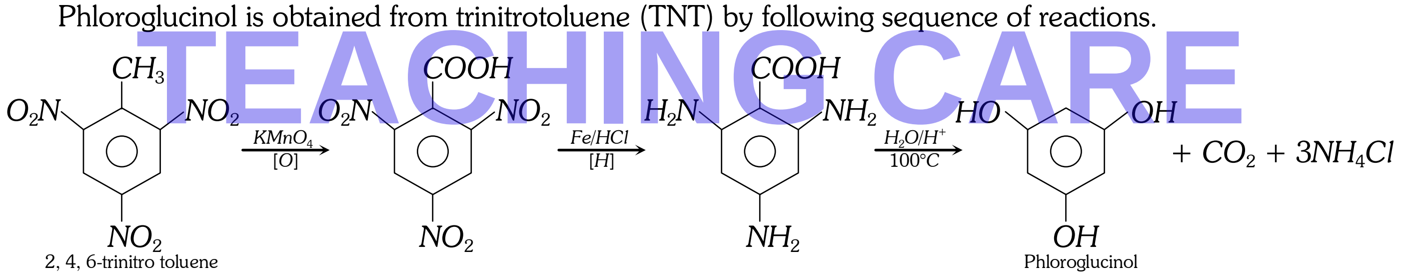
(3) **Uses :** It is used as an antiseptic, developer in photography, in the preparation of quinhydrone electrode and as an antioxidant.

Trihydric Phenols : Three trihydroxy isomeric derivatives of benzene are Pyrogallol (1, 2, 3), hydroxy quinol (1, 2, 4) and phloroglucinol (1, 3, 5).

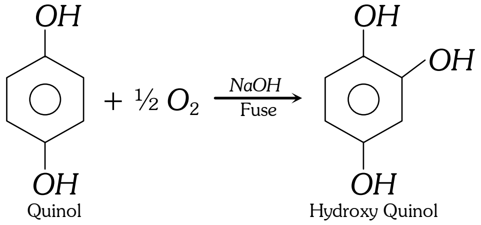
Pyrogallol is obtained by heating aqueous solution of gallic acid at 220°C.



Phloroglucinol is obtained from trinitrotoluene (TNT) by following sequence of reactions.



Hydroxyquinol is prepared by the alkaline fusion of hydroquinone in air.



The three isomers are colourless crystalline compounds. All are soluble in water and their aqueous solutions give characteristic colour with $FeCl_3$. For example, Pyrogallol-red; Hydroxy quinol-greenish brown; Phloroglucinol-bluish violet. Alkaline solutions absorb oxygen rapidly from air.

Uses of pyrogallol

(i) As a developer in photography.

(ii) As a hair dye.

(iii) In treatment of skin diseases like eczema.

(iv) For absorbing unreacted oxygen in gas analysis.