

ORGANIC CHEMISTRY

Topic-10

PHENOL

LONG ANSWER QUESTIONS

1. Explain the methods of preparation of phenol.

Introduction of phenols: A phenol contains -OH group(s) directly attached to an aryl carbon atom(s). The simplest phenol is hydroxybenzene also called phenol with formula C_6H_5OH . Simple phenol is an antiseptic. A phenolic compound hexachlorophene is a constituent of several mouthwashes, deodorant soaps and medicinal skin cleansers.

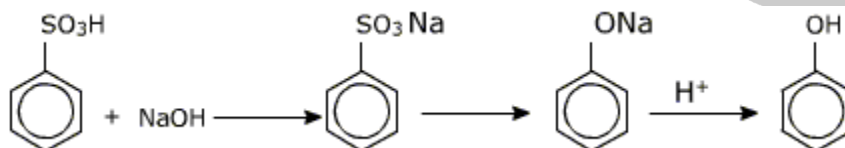
It must be noted that the aromatic compounds in which -OH group is not directly attached to benzene ring are not phenols but are called aromatic alcohols. These may be regarded as aryl derivatives of aliphatic alcohols.

Preparation of phenol

In the early nineteenth century, phenol was selected from coal tar by destructive distillation. Now phenol is commercially produced synthetically. The laboratory methods of preparation of phenols are:

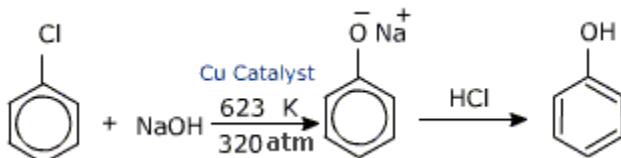
i) From aryl sulphonic acids

An aryl sulphonic acid yields the corresponding phenol on heating it with molten sodium hydroxide at 570 - 620 K. The sodium salt is obtained which is hydrolysed with acid to obtain free phenol.



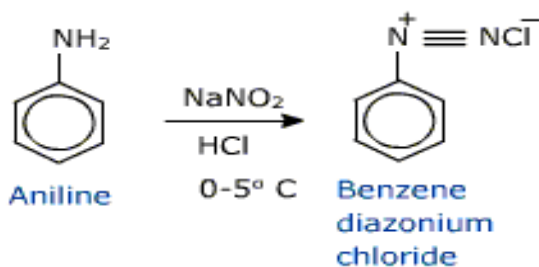
ii) From haloarenes

Chlorobenzene (an haloarene) is hydrolysed by treating it with 10% NaOH at 623 K and 320 atmospheric pressure in presence of Cu catalyst. Phenol is obtained by acidification of sodium phenoxide.

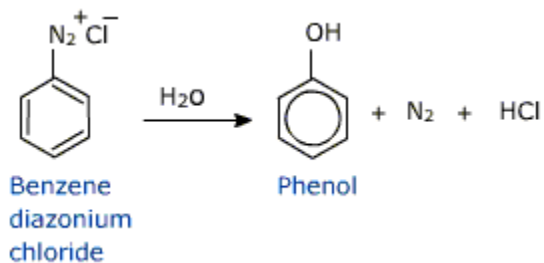


iii) Hydrolysis of diazonium salts

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid (obtained from a mixture of NaNO_2 and HCl) at low temperature of 273 K to 278 K.



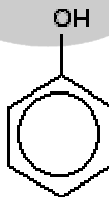
Diazonium salts are hydrolysed to phenols treating with dilute acids.



2. Explain the physical properties, structure and acidic nature of Phenol.

a) The structure of phenol

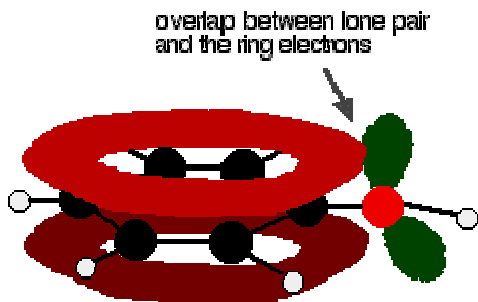
The simplest way to draw the structure of phenol is:



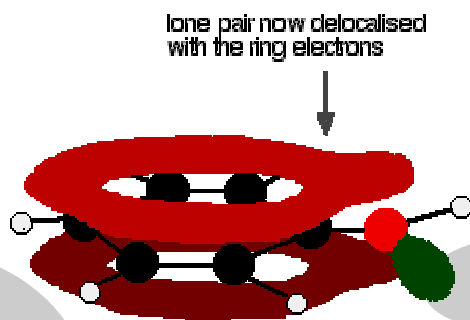
... But to understand phenol properly, you need to dig a bit deeper than this.

There is an interaction between the delocalised electrons in the benzene ring and one of the lone pairs on the oxygen atom. This has an important effect on both the properties of the ring and of the -OH group.

One of the lone pairs on the oxygen overlaps with the delocalised ring electron system . .



... giving a structure rather like this:



The donation of the oxygen's lone pair into the ring system increases the electron density around the ring. That makes the ring much more reactive than it is in benzene itself. That is explored in another page in this phenol section.

It also helps to make the -OH group's hydrogen a lot more acidic than it is in alcohols. That will also be explored elsewhere in this section.

b) Physical properties:

1. Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discoloured.

2. Melting and boiling points: It is useful to compare phenol's melting and boiling points with those of methylbenzene (toluene). Both molecules contain the same number of electrons and are a very similar shape. That means that the intermolecular attractions due to Van der Waals dispersion forces are going to be very similar.

| | melting point (°C) | boiling point (°C) |
|--------------|--------------------|--------------------|
| C_6H_5OH | 40 - 43 | 182 |
| $C_6H_5CH_3$ | -95.0 | 111 |

The reason for the higher values for phenol is in part due to permanent dipole-dipole attractions due to the electronegativity of the oxygen - but is mainly due to hydrogen bonding.

Hydrogen bonds can form between a lone pair on an oxygen on one molecule and the hydrogen on the -OH group of one of its neighbours.

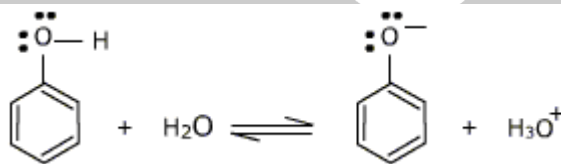
3. Solubility in water

Phenol is moderately soluble in water - about 8 g of phenol will dissolve in 100 g of water. If you try to dissolve more than this, you get two layers of liquid. The top layer is a solution of phenol in water, and the bottom one a solution of water in phenol. The solubility behaviour of phenol and water is complicated. Phenol is somewhat soluble in water because of its ability to form hydrogen bonds with the water.

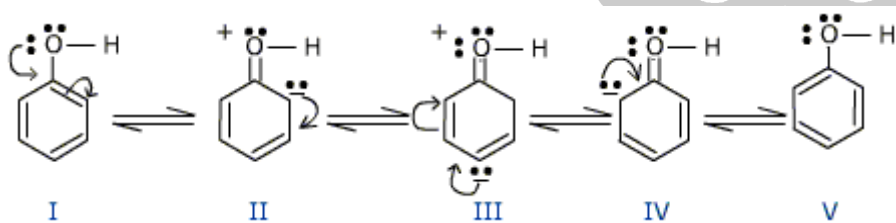
c) Acidic nature of phenol

Phenols turn blue litmus red and react with metals liberating hydrogen. However they do not react with carbonates or bicarbonates.

Phenols behave as acids because of the presence of polar O-H group in them. They ionise in aqueous solutions to give H^+ ions.



Phenols as well as phenoxide ion both are resonance stabilised. The various contributing structures of phenol and phenoxide ion are given below:



3. Explain the chemical properties of phenol.

I. Action with PCl_5 , PX_3 , NH_3 , Zn , Na benzene diazonium chloride and phthalic anhydride

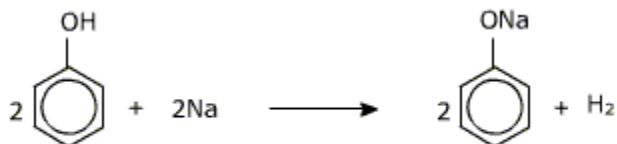
In alcohols and phenols, -OH group is the functional group. Thus the chemical properties of alcohols generally involve the reactions of -OH group. They can undergo substitution as well as elimination reaction.

Reactions of alcohols are classified into three types.

1) Reactions involving cleavage of -OH bond.

Reaction with metals

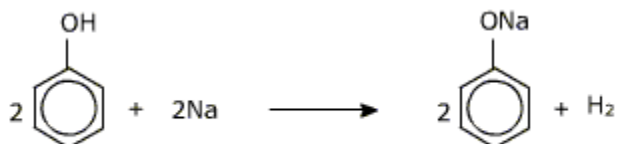
Phenols react with metals such as sodium, potassium and aluminium to yield corresponding alkoxides and hydrogen.



Phenol

Sodium phenoxide

In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



Phenol

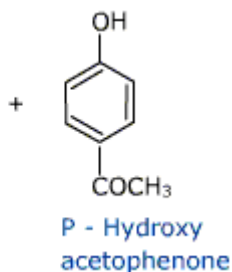
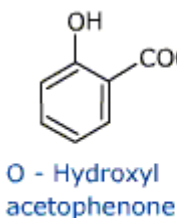
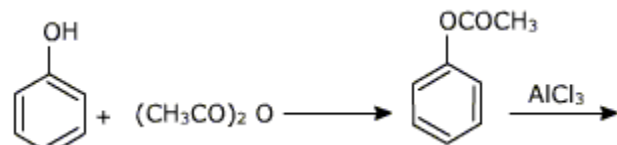
Sodium phenoxide

The above reactions show that phenols are acidic in nature. In fact, phenols are Bronsted acids i.e., they can donate a proton to a strong base (B:).

II. Acylation reaction, Kolbe's reaction, Reimer Tiemann's reaction

Acylation

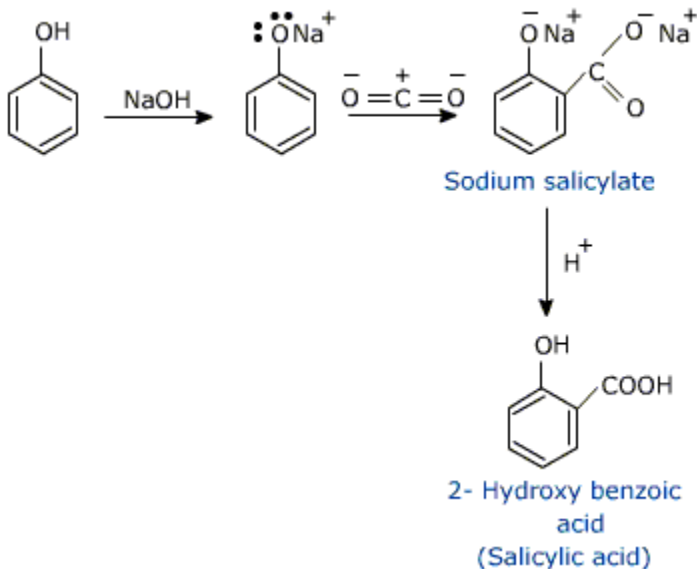
Esters of phenols yields phenolic ketones on treatment with anhydrous aluminium chloride.



Phenyl ethanoate yields ortho and para hydroxy acetophenones. It involves migration of an acyl group from phenolic oxygen to ortho and para positions of the aromatic ring.

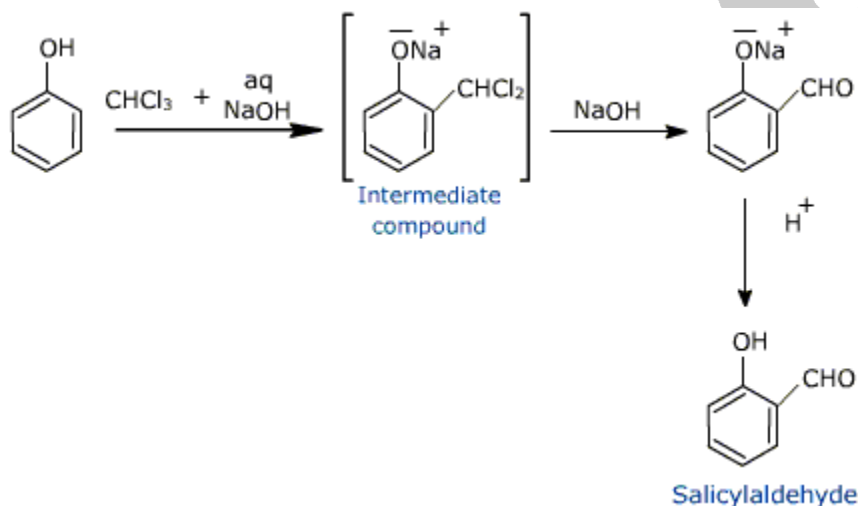
Kolbe's reaction

On reaction sodium salt of phenol with carbon dioxide gas, ortho hydroxy benzoic acid is formed as the main product. The temperature is 400 K and a pressure of 4-7 atm is required. Sodium salicylate is formed which on acidification yields salicylic acid (ortho hydroxy benzoic acid).



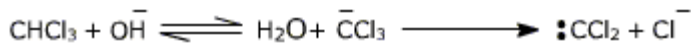
Reimer Tiemann's reaction

On treating phenol with chloroform in presence of sodium hydroxide at 340 K, a -CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction. This results in the formation of o - hydroxybenzaldehyde (salicylaldehyde) and para-hydroxybenzaldehyde, the ortho isomer being the major product.



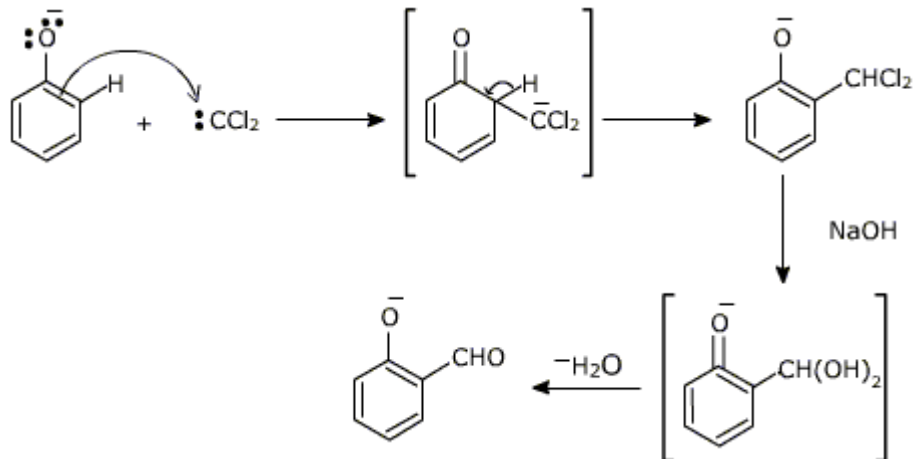
The intermediate substituted benzal chloride is hydrolysed in presence of alkali to produce salicylaldehyde.

Reimer Tiemann reaction is an electrophilic substitution reaction. The first step is generation of electrophile.



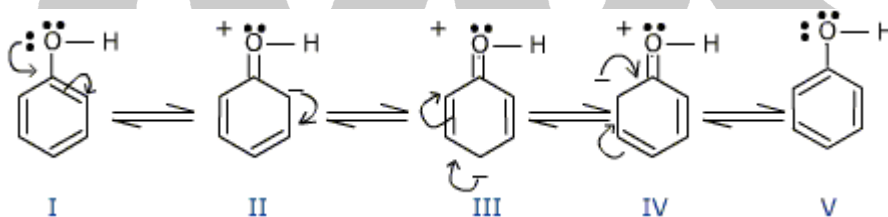
Dichloro carbene
(electrophile)

Dichlorocarbene contains a sextet of electrons and thus is a strong electrophile.



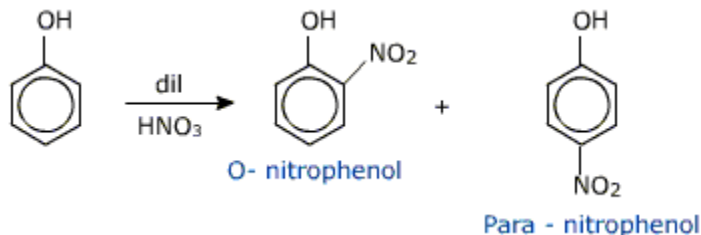
III. Electrophilic substitution of phenol

The -OH group attached to the benzene ring in phenol activates, it towards electrophilic substitution. It directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to electronic effect (also mesomeric effect) caused by -OH group.

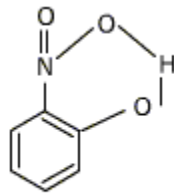


Common electrophilic aromatic substitution reactions taking place in phenol are as follow:

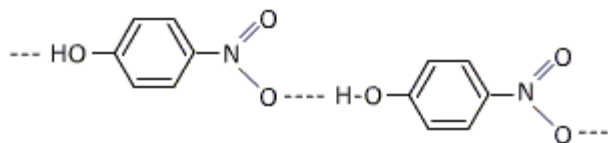
(i) **Nitration** - with dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitro phenols.



The ortho and para isomers can be separated by steam distillation O-Nitro phenol is steam volatile due to intra molecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding, which causes association of molecules.

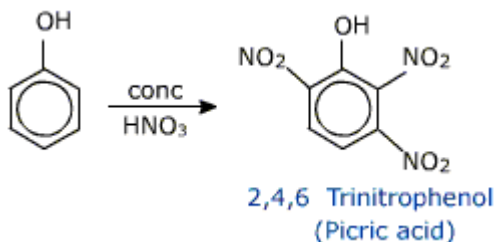


Intra molecular hydrogen bonding in O-nitro phenol



P- Nitrophenol with inter molecular hydrogen bonding

With concentrated nitric acid, phenol is converted to 2,4,6 trinitrophenol. This reaction involves nitration accompanied by oxidation of Phenol.

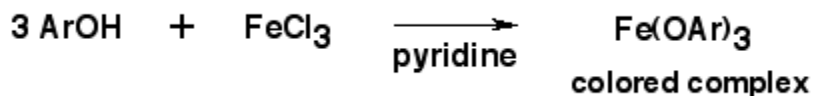


Industrially, picric acid is prepared by treating phenol first with conc. H_2SO_4 which converts it to phenol 2, 4 disulphonic acid. This yields picric acid on treatment with conc. HNO_3 .

4. Explain the tests and uses of phenol.

a) Laboratory test of phenol

Phenol



Standard Phenol

Procedure (for water-soluble phenols)

The iron (III) chloride test for phenols is not completely reliable for acidic phenols, but can be administered by dissolving 15 mg of the unknown compound in 0.5 mL of water or water-alcohol mixture and add 1 to 2 drops of 1% aqueous iron (III) chloride solution.

Positive Test

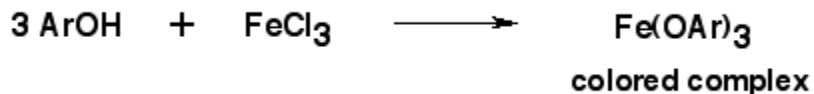
A red, blue, green, or purple color is a positive test.

Cleaning up

Since the quantity of material is extremely small, the test solution can be diluted with water and flushed down the drain.

Iron(III) Chloride - Pyridine Test for Water-Insoluble Phenols

Phenol



b) Uses of phenol

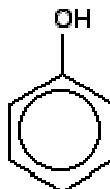
- The main use of phenol is as a feedstock for phenolic resins, bisphenol A and caprolactam (an intermediate in the production of nylon-6).
- It is used in the manufacture of many products including insulation materials, adhesives, lacquers, paint, rubber, ink, dyes, illuminating gases, perfumes, soaps and toys.
- Also used in embalming and research laboratories.
- It is a product of the decomposition of organic materials, liquid manure, and the atmospheric degradation of benzene.
- It is found in some commercial disinfectants, antiseptics, lotions and ointments.
- Phenol is active against a wide range of microorganisms, and there are some medical and pharmaceutical applications including topical anesthetic and ear drops, sclerosing agent.
- It is also used in the treatment of ingrown nails in the "nail matrix phenolization method".
- Another medical application of phenol is its use as a neurolytic agent, applied in order to relieve spasms and chronic pain.
- It is used in dermatology for chemical face peeling

SHORT ANSWER QUESTIONS

1. Explain the structure of phenol.

The structure of phenol

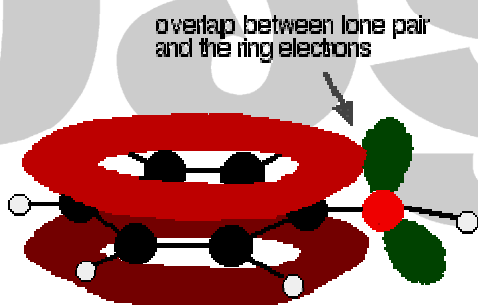
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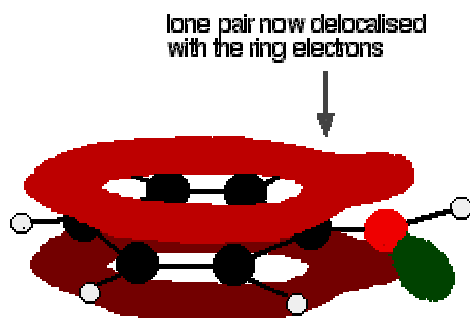
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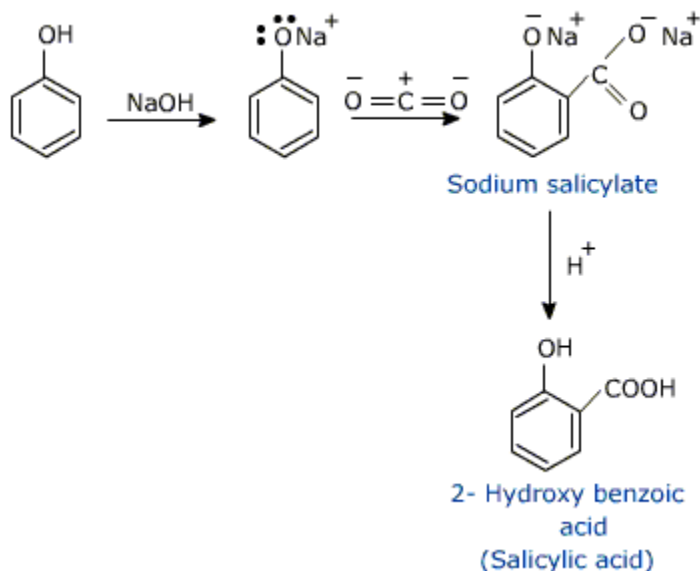
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Kolbe's reaction

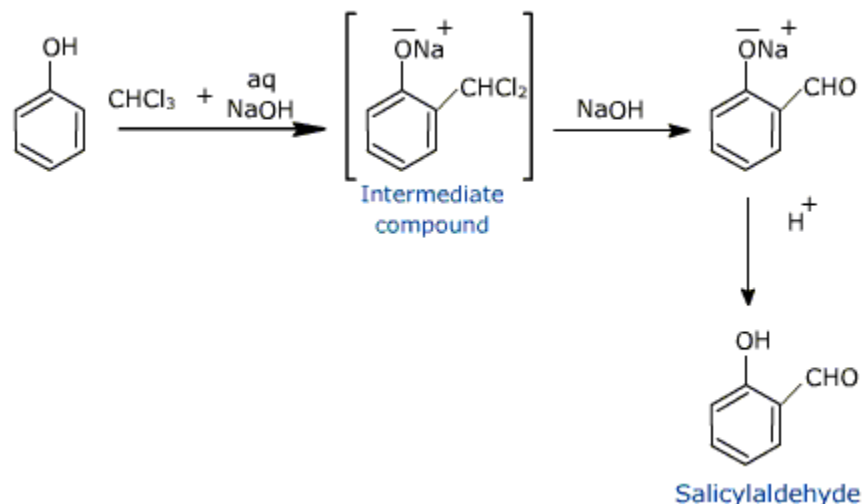
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4. Explain Reimer Tiemann's reaction

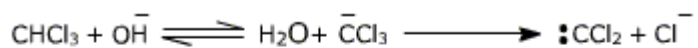
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