JEE Main Chemistry

Short Notes

Phenol and Reimer Tiemann Reaction

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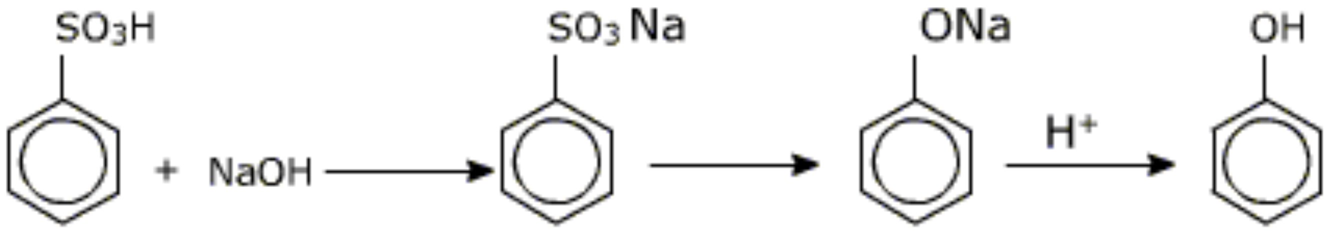
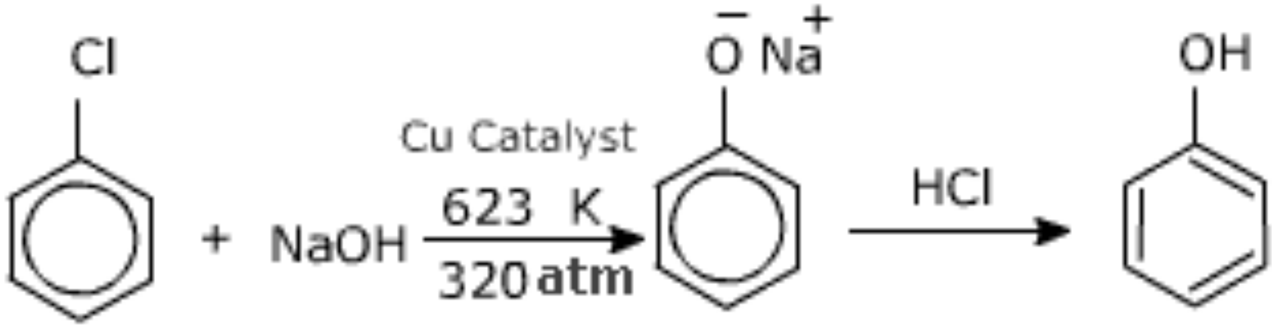
Preparation of Phenols

The laboratory methods of preparation of phenols are:

1. From aryl sulphonic acids

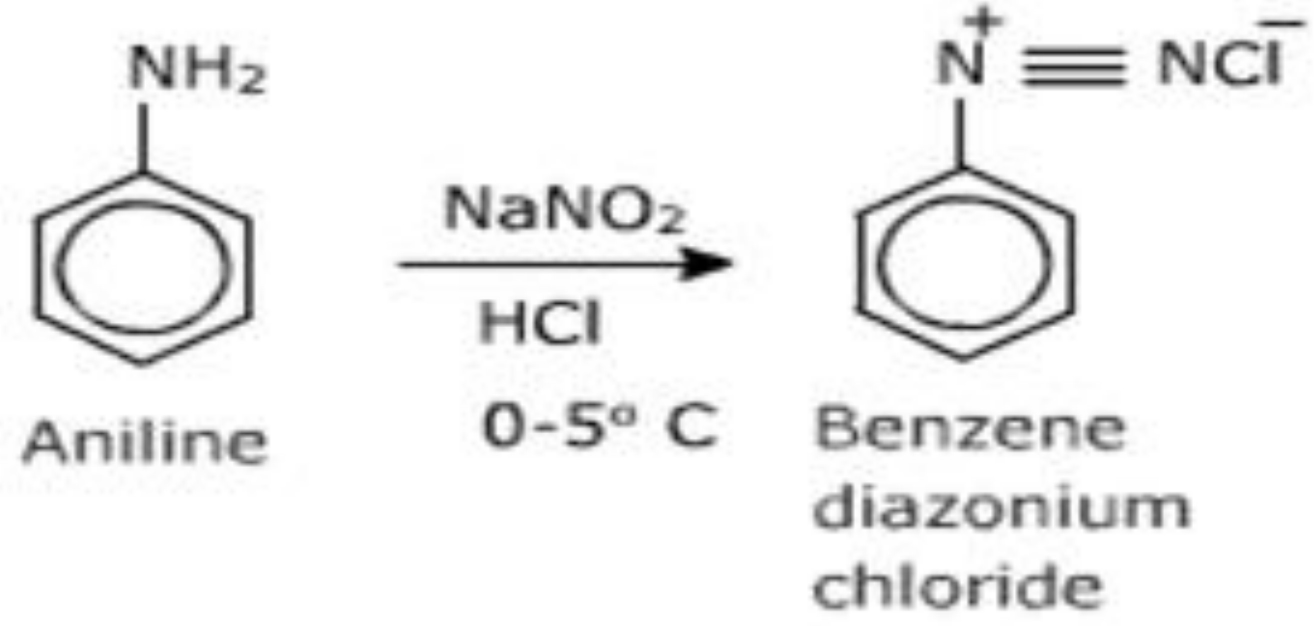


2. From haloarenes

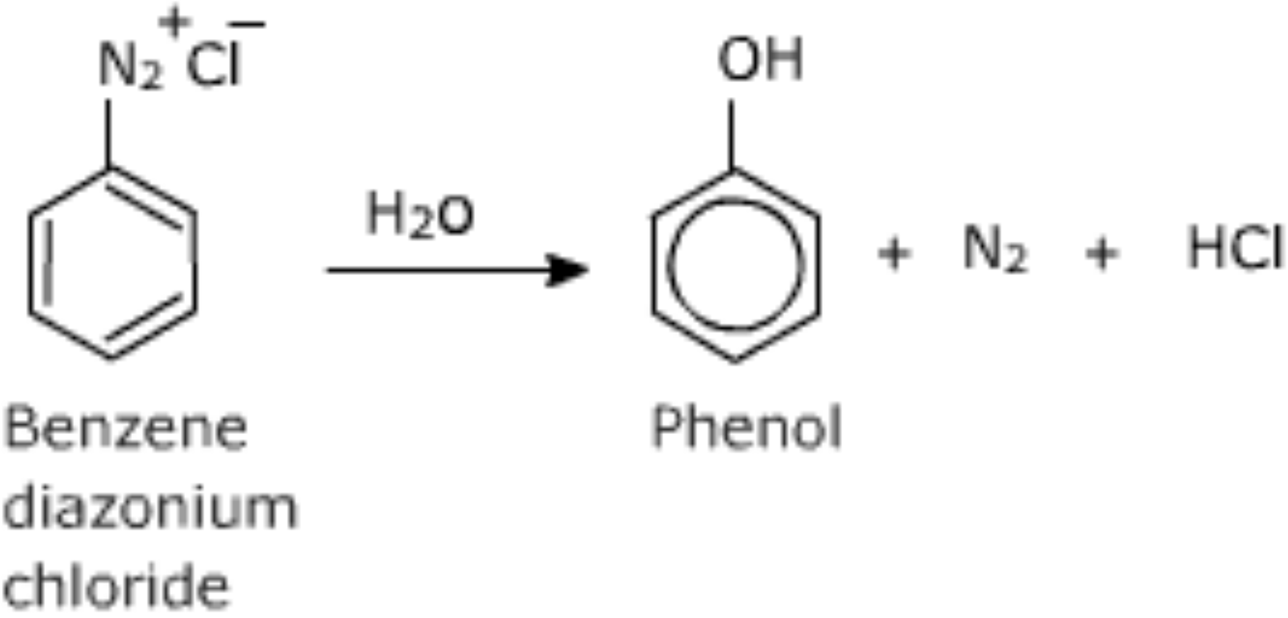


3. Hydrolysis of diazonium salts

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



Diazonium salts are hydrolysed to phenols by treating them with dilute acids.



Properties

Physical Properties of Alcohols & Phenols:

The alkyl and aryl groups modify these properties.

1. The lower members of alcohols are colourless, volatile liquids with a characteristic alcoholic smell and burning taste whereas higher alcohols are odourless and tasteless.

Higher alcohols having 12 or more carbon atoms are colourless waxy solids. Phenols are colourless, crystalline solids or liquids. (They may become coloured due to slow oxidation in presence of air).

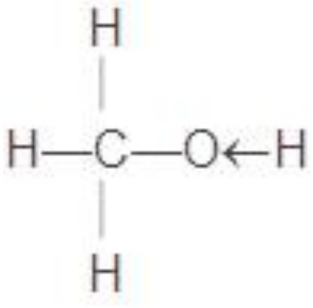
2. **Solubility of alcohols**
   The first three members are completely miscible with water. The solubility rapidly decreases with increase in molecular mass. The higher members are almost insoluble in water but are soluble in organic solvents like benzene, ether etc.
   The solubility of lower alcohols is due to the existence of hydrogen bonds between water and polar -OH group of alcohol molecules. Phenols too are sparingly soluble in water.
   In addition, among the isomeric alcohols, the solubility increases with the branching of the chain as surface area decreases.Phenols are sparingly soluble in water but readily soluble in organic solvents such as alcohol and ether.
3. **Boiling Point of alcohols**
   Boiling point of alcohols are much higher than those of alkenes, haloalkenes or ethers of comparable molecular masses due to intermolecular hydrogen bonding
   Phenols boil at higher temperatures them the arenes of comparable molecular masses. due to the intermolecular hydrogen bonding.
   Among isomeric alcohols, the boiling point decreases with increase in branching in the alkyl group.
   For isomeric alcohols, the boiling points decrease with increase in branching in the alkyl group.

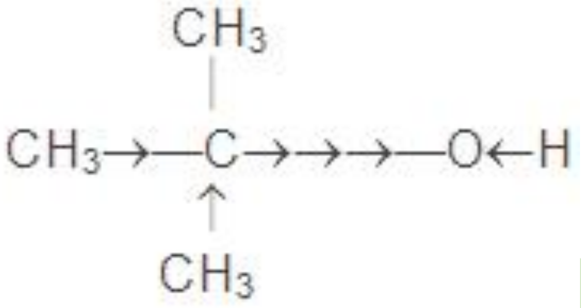
Chemical Properties

Reactions involving cleavage of -OH group : The Bronsted acid nature shows the order :

methyl alcohols > $1^{o} > 2^{o} > 3^{o}$ alcohol

The tendency to release H atom decreases in tertiary alcohols due to increasing partial negative charge over O atom due to inductive effect.





Following reactions of this category are noticed.

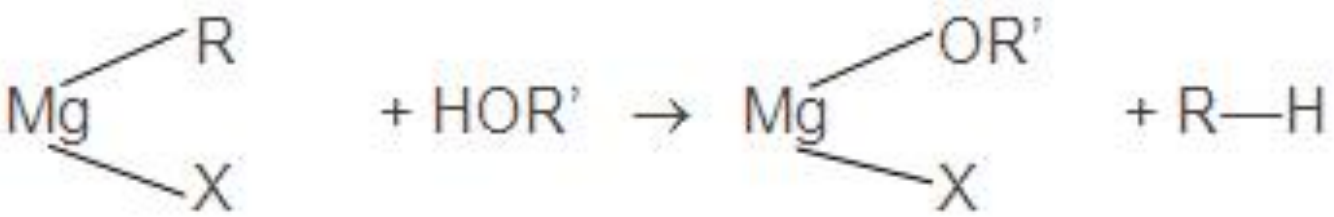
(a) The action of active metals: By strong electropositive metals like Na, K, Ca & Mg.

$R\text{-}OH + Na \rightarrow R\text{-}ONa + 1/2H_2.$

(b) The action of carboxylic acids or esterification:

$$R\text{-}OH + HOOCR' \xrightarrow[H_2SO_4]{\Delta} R'COOR + H_2O$$

(c) The action of Grignard reagent:



All these reactions show the reactivity order P.A. > S.A.> T.Alcohol

Reactions involving replacement of -OH gp of alcohols:

T.A. > S.A. > P. Alcohol

or 3° > 2° > 1° > methyl alcohol

In tertiary alcohols the partial -ve charge on oxygen atom is intensified due to + I.E. of CH_3 gps. This increases the tendency of oxygen atom to donate electron pair or to show cleavage of C-O bond.

(a) The action of phosphorus halides:

$3ROH + PCl_3 \rightarrow 3RCl + H_3PO_3$

$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$

Similar reactions are obtained by using $P + Br_2$ and $P + I_2$ for alkyl bromide and iodide preparation because of less stable nature of PBr_3 & PI_3

Also,

$$R-OH + SOCl_2 \xrightarrow{Pyridine} R-Cl + SO_2 + HCl$$

(b) The action of halogen acids:

$$R{-}OH + HCl \xrightarrow[\text{secondary alcohols are used}]{ZnCl_2 \text{ or } H_2SO_4 \text{ if}} R{-}Cl$$

$$R{-}OH + HBr \xrightarrow[\text{primary alcohols are used}]{ZnCl_2 \text{ or } H_2SO_4 \text{ if}} R{-}Br$$

$$R{-}OH + HI \rightarrow R{-}I$$

The reactivity order for halogen acids is : HI > HBr > HCI

Note:

1. If alcohols are heated with conc. HI and red P, alkanes are formed

$$R-OH+2HI \xrightarrow{Phosphorus} R-H+H_2O+I_2$$

2. For getting bromo and iodo derivatives from alcohols, a mixture of KBr + $H_2SO_4$and KI + H_2SO_4 respectively can be used.

3. Primary alcohols follow S_N2 mechanism during replacement of OH gp by halogen atom

$$R-OH+HX \rightleftharpoons R-O+H_2+\overline{X}:$$

$$\text{R-O}^+\text{H}_2+\overline{\text{X}}: \xrightarrow{\text{Slow}} [\text{X}......\text{R}-\text{OH}_2] \xrightarrow{\text{Fast}} \text{X}-\text{R}+\text{H}_2\text{O}$$

Secondary and tertiary alcohols follow S_N1 mechanism during replacement of OH group by halogen atom.

$$R\text{-}OH + HX \rightleftharpoons RO^{+}H_2 + \bar{X}$$

$$R\text{-}OH_2 \overset{slow}{\Leftrightarrow} R^{+} + H_2O$$

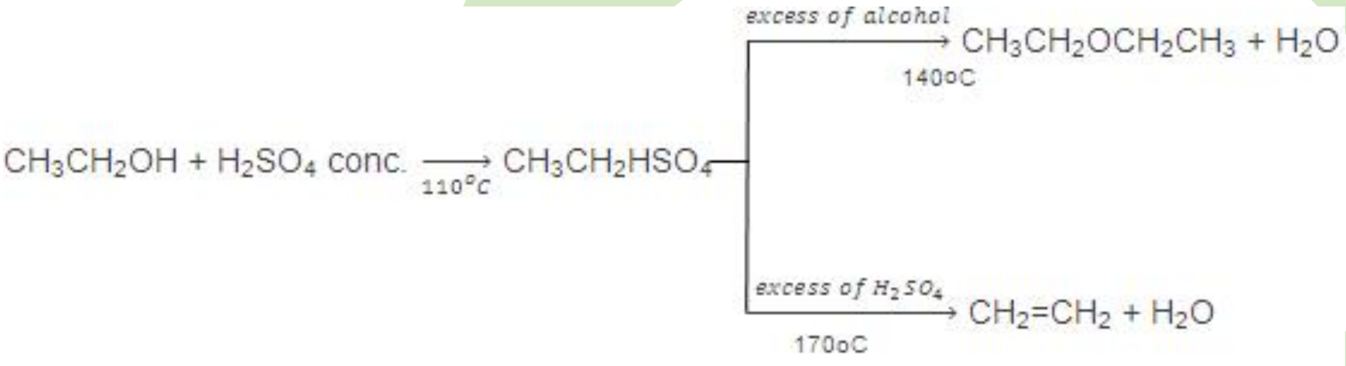
$$R^{+} + \bar{X}: \overset{fast}{\Leftrightarrow} R - X$$

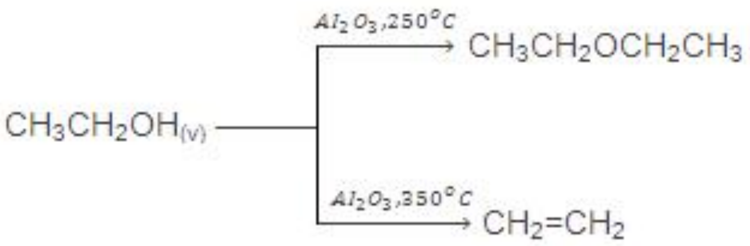
(c) The action of NH_3:

$$\underset{\text{vapours}}{R{-}OH} + NH_{3(g)} \xrightarrow[250oC]{Al_3O_3} \underset{\text{amines}}{R{-}NH_2} + H_2O$$

Reactions involving complete molecule of alcohols:

(a) Dehydration: Dehydration (removal of H_2O) of alcohols yields alkene or ether depending up-on the experimental conditions. The dehydration of alcohol favour the order T.A. > S.A. > P. Alcohol. The action of various dehydrating agents used are given below.



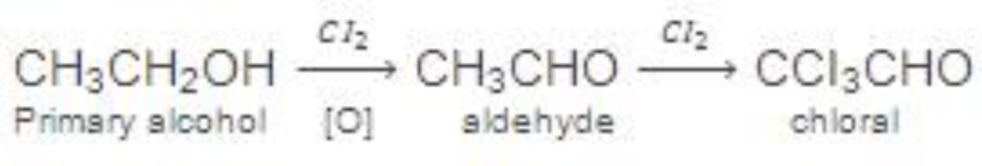


Note:

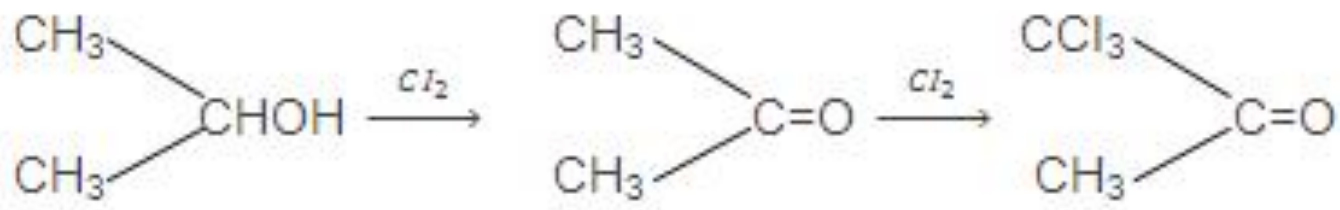
Normally secondary & tertiary alcohols give alkene as main product on dehydration.

(b) The action of halogens (Haloform reaction):

1. Alcohols are oxidised in the first step.
2. After oxidation, substitution takes place at the α-carbon atom of products.



$$\underset{\text{Primary alcohol}}{CH_3CH_2OH} \xrightarrow[\text{[O]}]{Cl_2} \underset{\text{aldehyde}}{CH_3CHO} \xrightarrow{Cl_2} \underset{\text{chloral}}{CCl_3CHO}$$

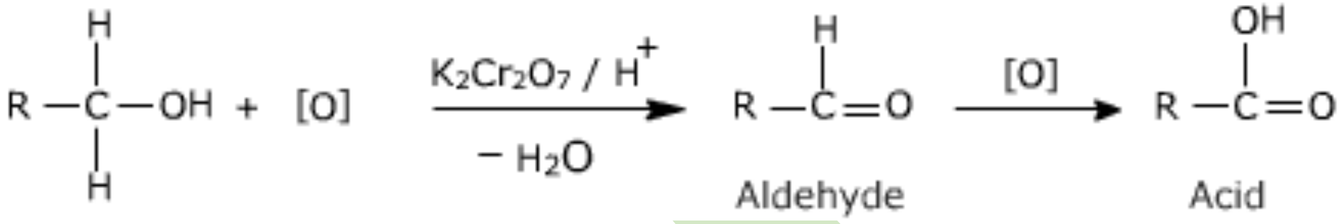


Note: Tertiary alcohols are not oxidised by halogens and thus tertiary butyl alcohol does not give iodoform if heated with halogens and alkali.

(c) Acetal formation:

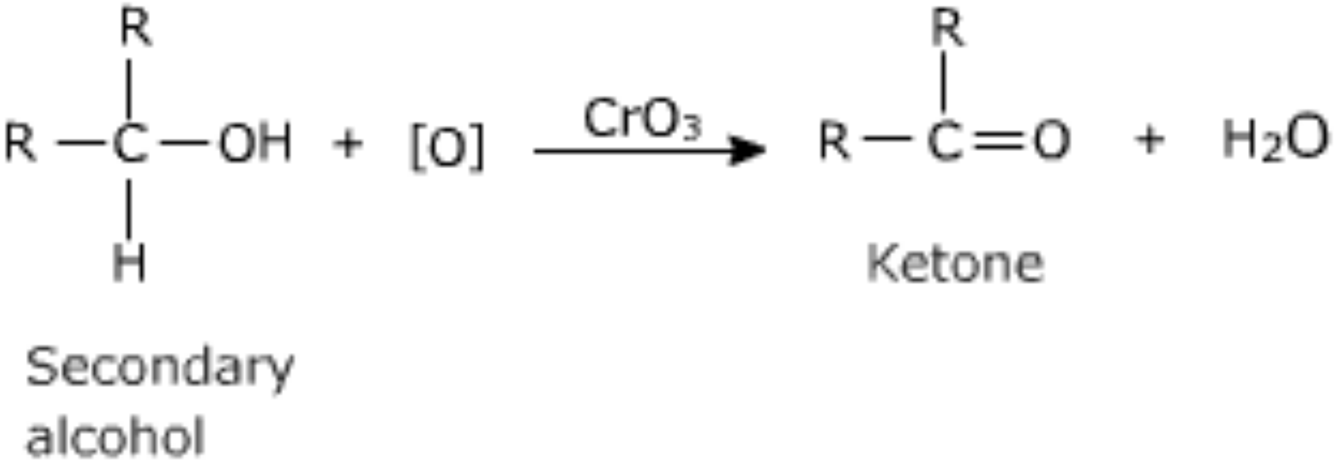
Oxidation

A primary alcohol on oxidation with acidified potassium dichromate first gives an aldehyde, which on further oxidation gives an acid with the same number of carbon atoms as the original alcohol.



Strong oxidising agents such as acidified $KMnO_4$ are used for getting carboxylic acids directly. Cr(VI) in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3). The Ketone has the same number of carbon atoms as the original alcohol.

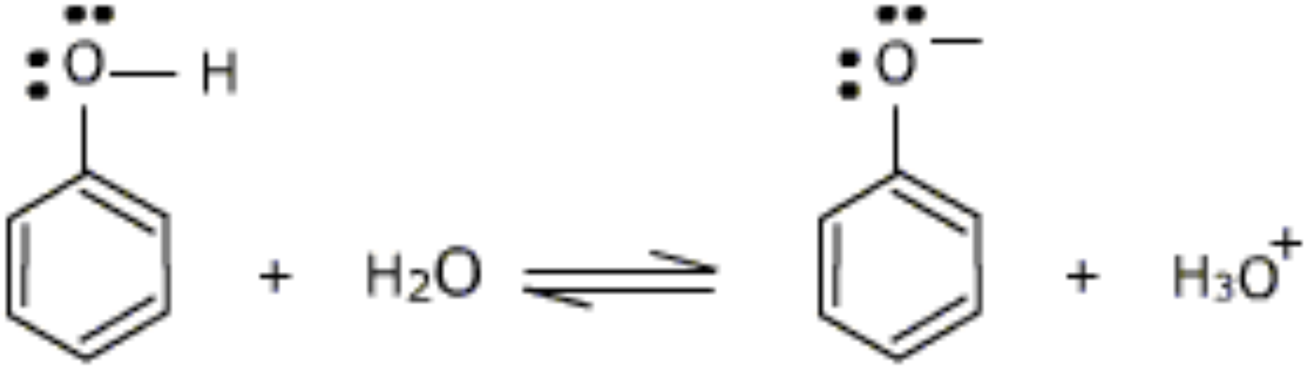


Ketones are quite resistant to further oxidation. But upon prolonged treatment with the oxidising agent. They get oxidised to acids with lesser number of carbon atoms then the alcohol.

Tertiary alcohols do not undergo oxidation reaction.

Chemical Properties of Phenols

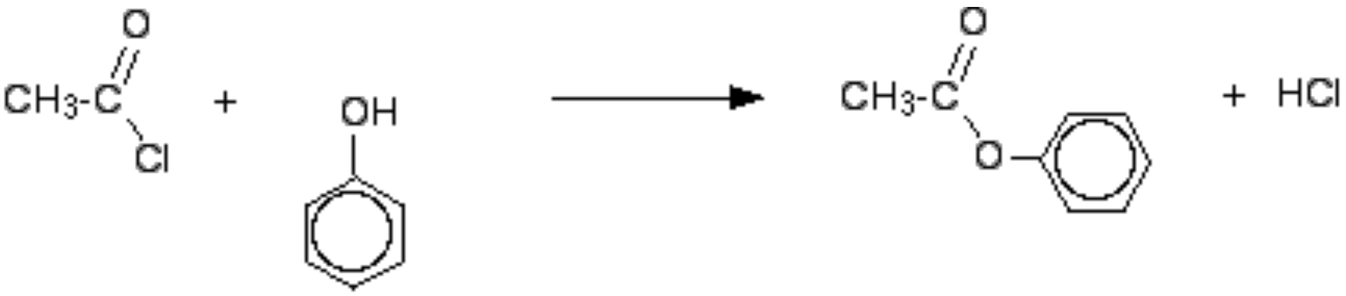
Phenols behave as acids because of the presence of polar O-H group in them. They ionise in aqueous solutions to give H^+ ions.



Phenols as well as phenoxide ion both are resonance stabilised.

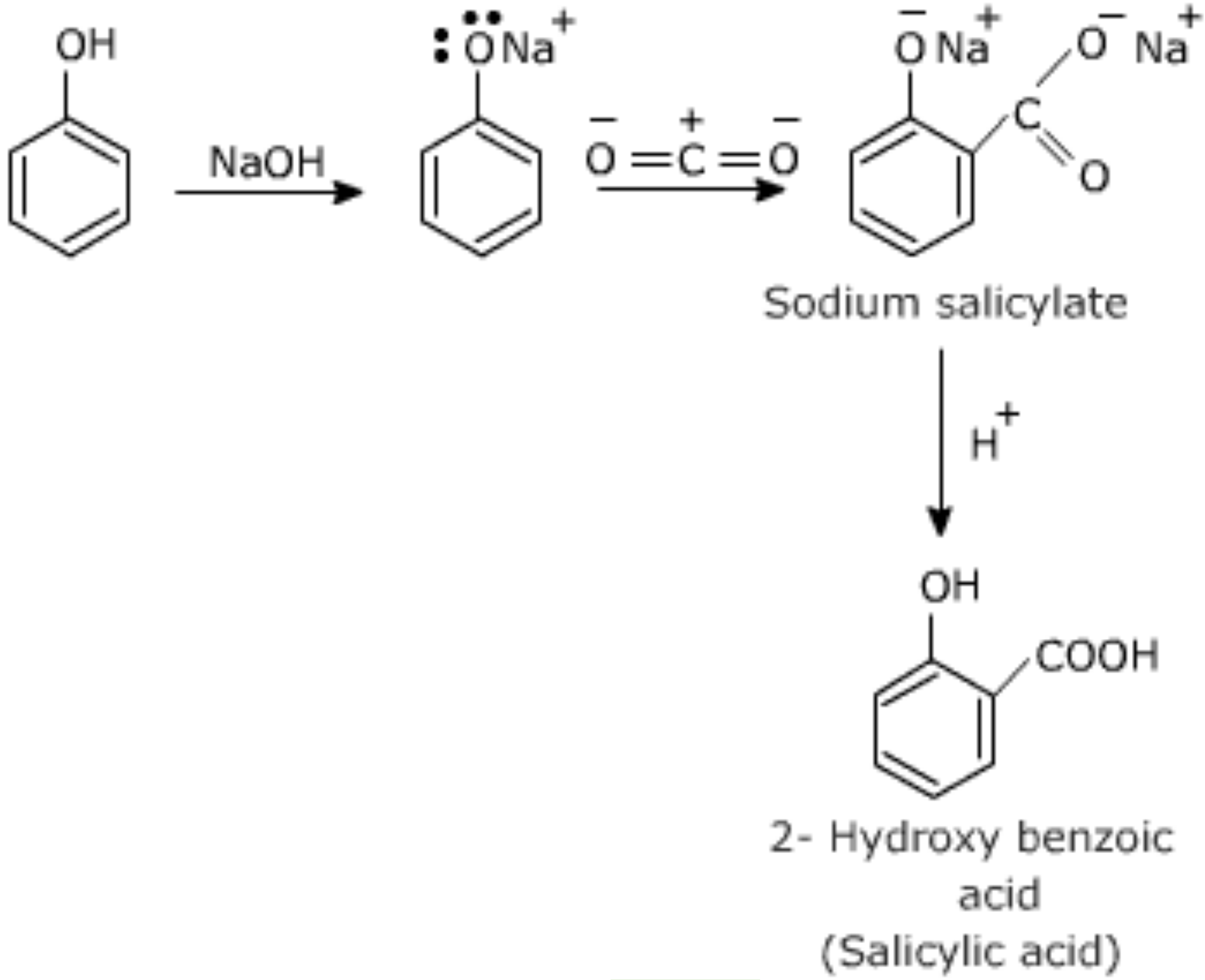
Making esters from phenol using an acyl chloride

A typical acyl chloride is ethanoyl chloride, CH_3COCl.



Kolbe's Reaction

On reaction sodium salt of phenol with carbon dioxide gas, ortho hydroxy benzoic acid is formed as the main product.



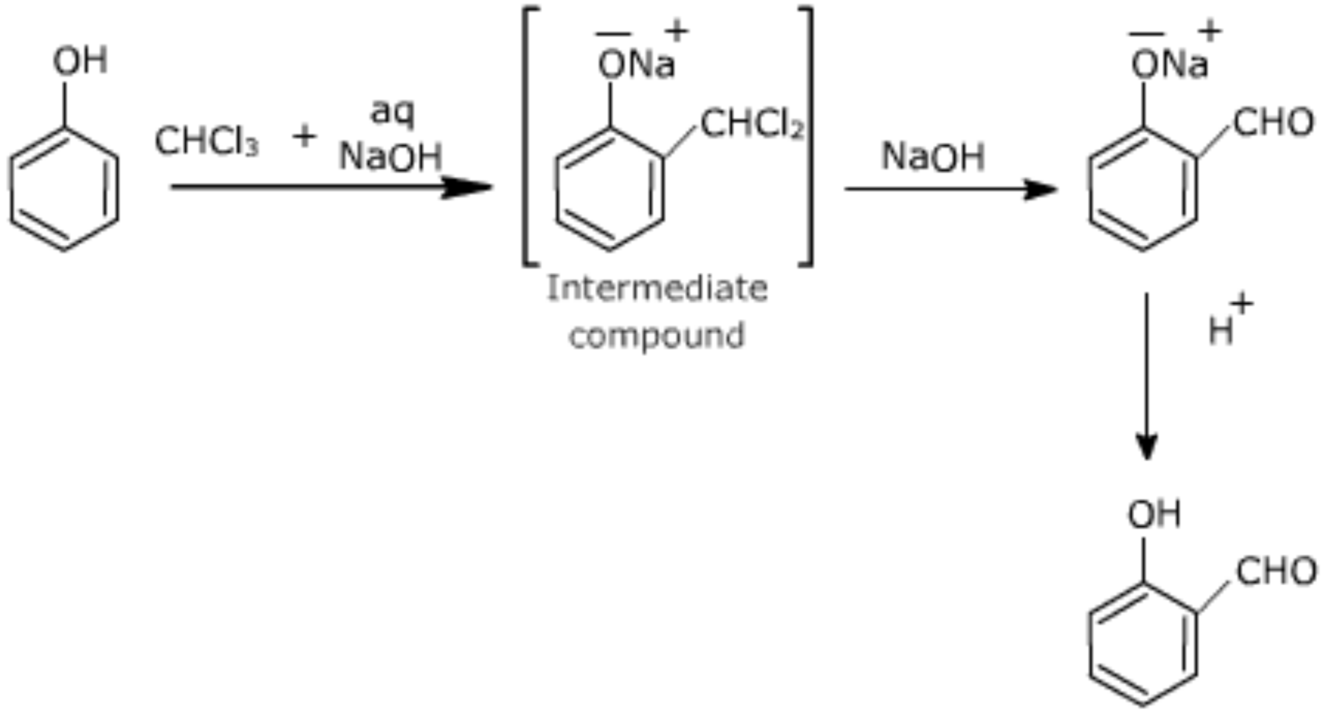
Riemer-Tiemann Reaction

On treating phenol with chloroform in presence of sodium hydroxide at 340 K, a - CHO group is introduced at the ortho position of the benzene ring.

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

$$CHCl_3 + O\overline{H} \rightleftharpoons H_2O + \overline{C}Cl_3 \longrightarrow :CCl_2 + Cl^{-}$$

Dichloro carbene
(electrophile)



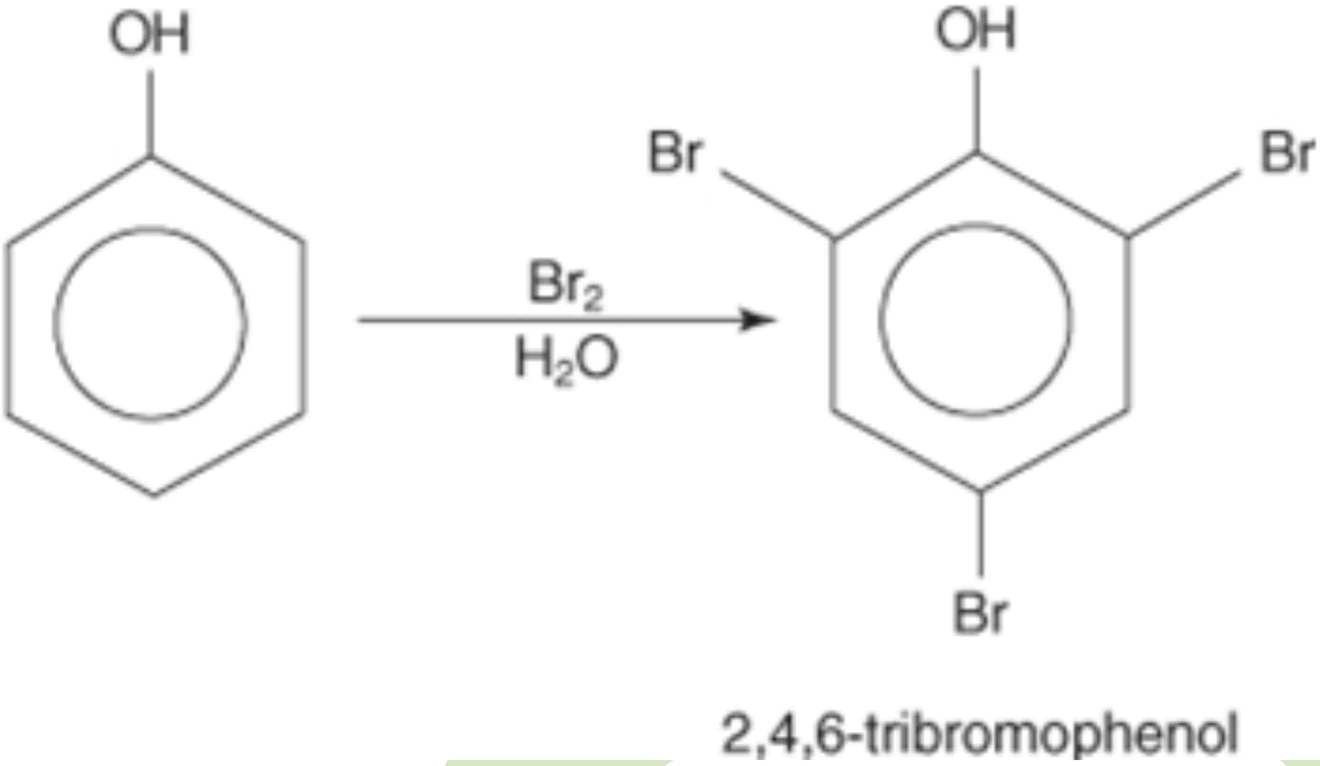
Salicylaldehyde

Electrophilic Aromatic Substitution Reaction

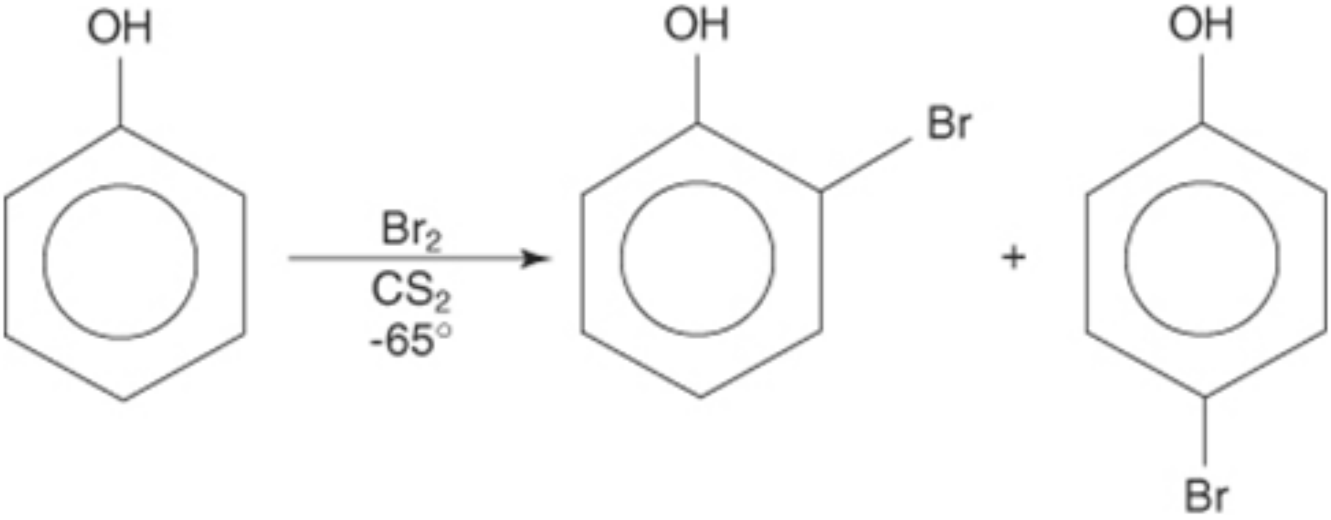
The -OH group attached to the benzene ring in phenol activates, it towards electrophilic substitution. It directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to electronic effect (also mesomeric effect) caused by -OH group. Thus all the substitution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

Halogenation

Phenols react with halogens to yield mono-, di-, or tri-substituted products, depending on reaction conditions. For example, an aqueous bromine solution brominates all ortho and para positions on the ring.

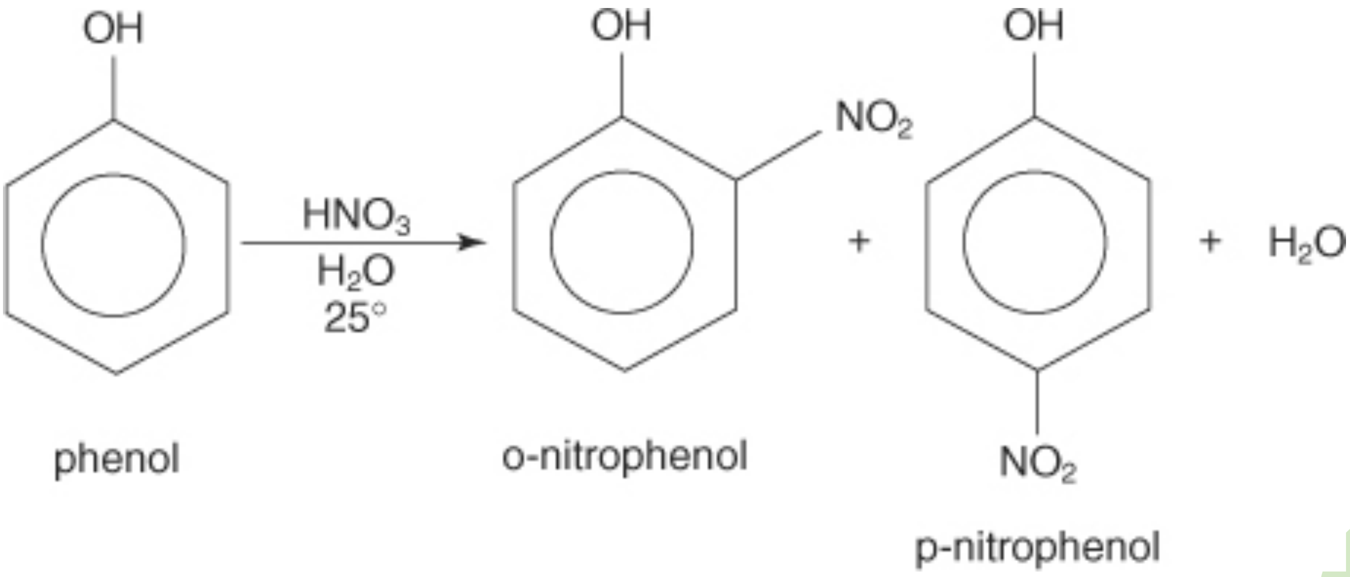


Likewise, you can accomplish monobromination by running the reaction at extremely low temperatures in carbon disulfide solvent.



Nitration

Phenol, when treated with dilute nitric acid at room temperature, forms ortho- and para-nitrophenol.



Sulfonation

The reaction of phenol with concentrated sulfuric acid is thermodynamically controlled. At 25°C, the ortho product predominates while at 100°C, the para product is the major product.

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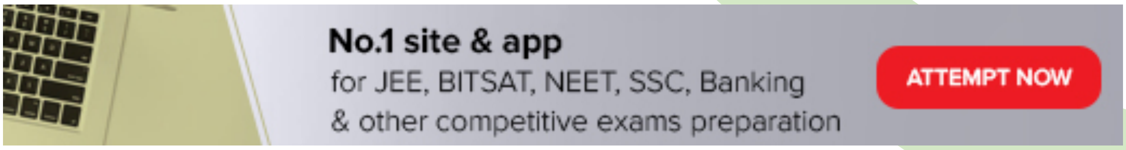

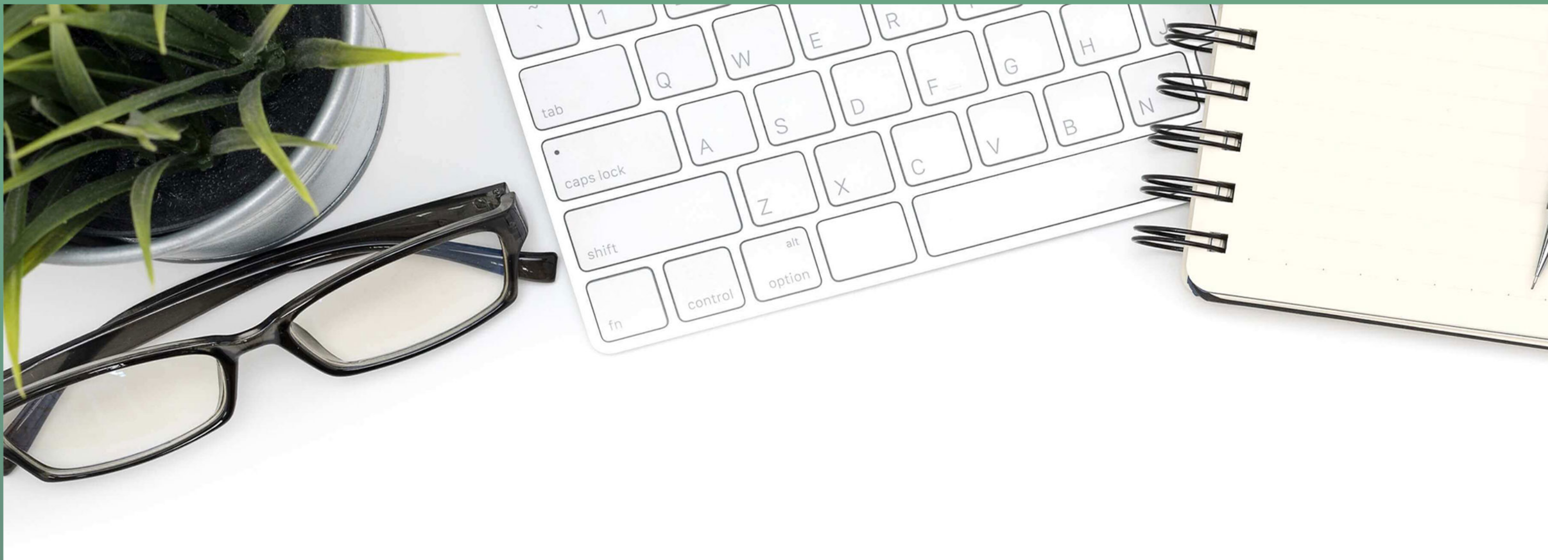

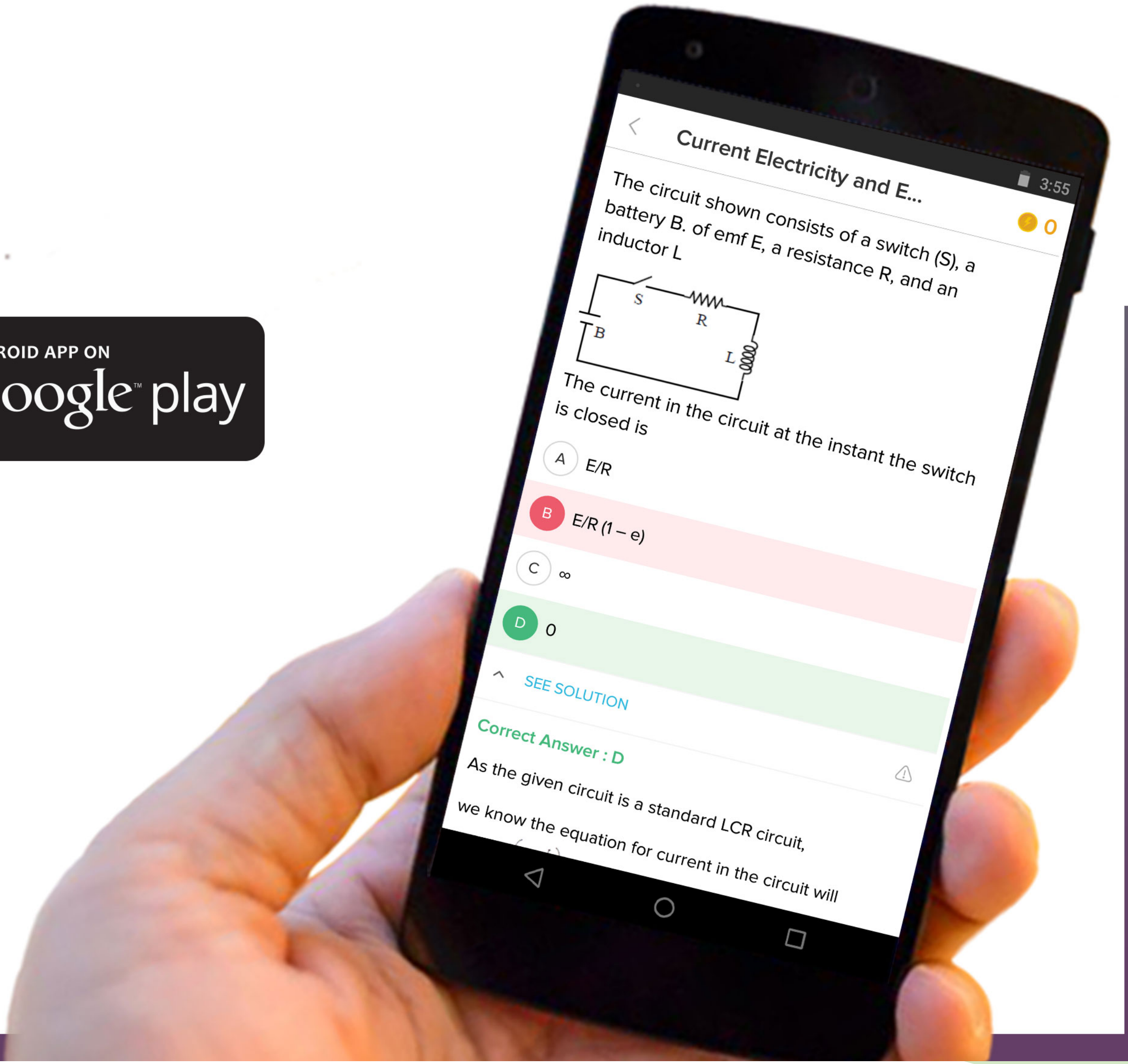
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