

Organic Compounds Containing C, H and O

Long Answer Questions:

****1. i. Explain the acidic nature of phenol and Compare with that of alcohols.**

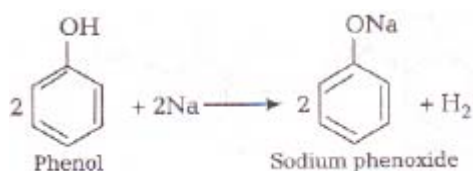
ii. Describe the following

a. Cannizaro reaction

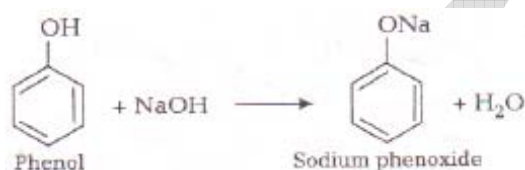
b. Decarboxylation.

Sol. i. Phenol is acidic in nature and is represented by the following reactions.

i) . It reacts with sodium metal to liberate H₂ gas .

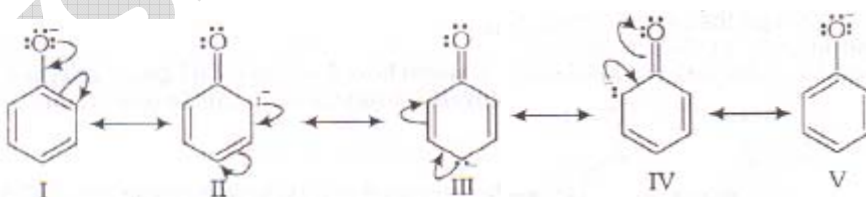


(ii) It reacts with sodium hydroxide to form sodium salt and water.



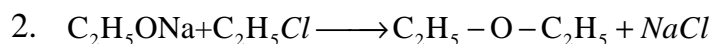
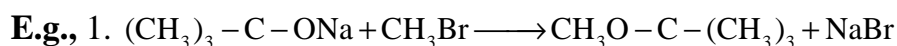
Comparison of acidic character of phenol and alcohol.

Phenol is more acidic than alcohol because after losing a proton (H⁺) phenol forms phenoxide ion which is stabilized by resonance whereas alkoxide (RO⁻) ion is stabilized by inductive effect but not by resonance.



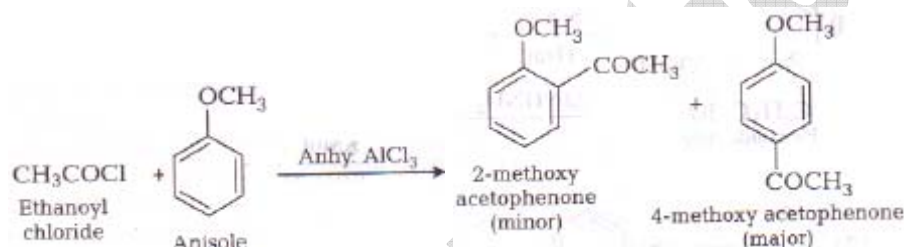
ii. a. Cannizaroreaction : Aldehydes which do not have any α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. This reaction is called Cannizaro reaction. As a result, one molecule of aldehyde is reduced to alcohol while another is oxidized to carboxylic acid salt.

(iii) **Williamson ether synthesis:** Alkyl halides react with sodium alkoxides to form ethers is called as Williamson synthesis. Both symmetrical and unsymmetrical ethers are prepared by this method. $R-X + R'-ONa \longrightarrow R-O-R' + NaX$



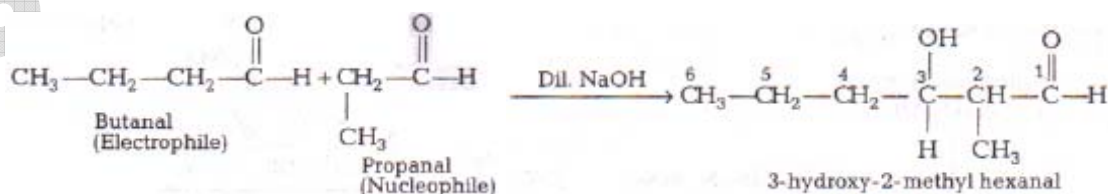
b) i. **Acetylation:** When active hydrogen atom of alcohol, phenol or an amine is replaced by acetyl (CH_3CO-) group to form corresponding ester or amide then the reaction is known as acetylation. Reagents used are acid chloride or acid anhydride in presence of a base like pyridine or dimethyl aniline.

For Example:



ii. **Cross aldol condensation:** Aldol condensation carried out between two different aldehydes or ketones is called cross aldol condensation. If both the reactants contain α -hydrogen atoms, it gives a mixture of four products.

E.g.: condensation between butanal and propanal



*3.a) Account for the statement: Alcohols boils at higher temperature than hydrocarbons and ethers of comparable molecular masses.

b) Explain the following terms. Give an example of the reaction in each case.

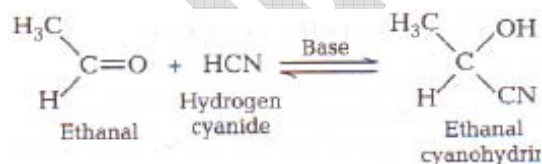
- (i) Cyanohydrin (ii) Acetal (iii) Semicarbazone
 (iv) Aldol (v) Hemiacetal (vi) Oxime

Ans. a) Alcohols boils at higher temperature than hydrocarbons and ethers of comparable molecular masses because of inter molecular H-bonding is present in alcohol but not in hydrocarbons and ethers



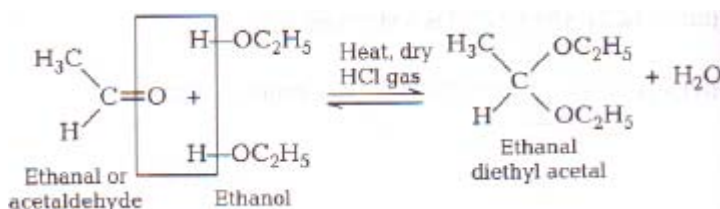
b) (i) **Cyanohydrin:** Addition product formed by the reaction of aldehydes and ketones with hydrogen cyanide (HCN) are known as cyanohydrins.

E.g.:



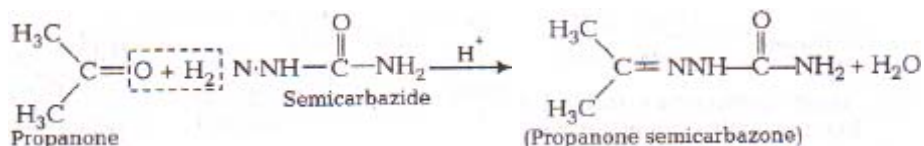
ii).Acetal: Gem-dialkoxy compounds formed when an aldehyde reacts with two equivalents of a monohydric alcohol in the presence of dry HCl gas are known as acetals. In acetal, two alkoxy groups are present on the terminal C-atom.

E.g.:



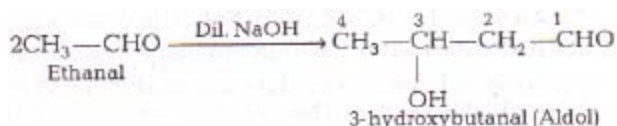
(iii) Semicarbazone: The compounds formed when an aldehyde or a ketone reacts with semicarbazide are called semicarbazones.

Ex:



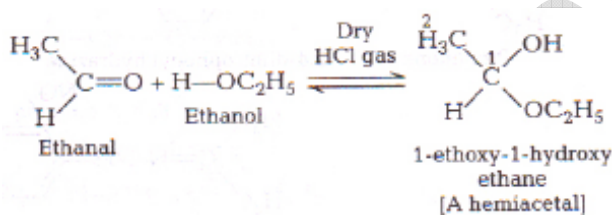
(iv) **Aldol:** An aldehyde or ketone having at least one α -hydrogen atom undergoes self condensation to form aldol or β -hydroxy aldehydes (or ketals in case of ketones) on reaction with dilute alkali. This reaction is called aldol condensation.

E.g.:



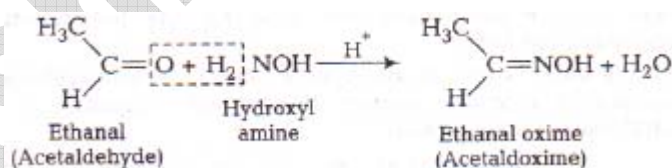
(v) **Hemiacetal:** The product formed when an aldehyde reacts with one molecule of a monohydric alcohol in presence of dry HCl gas is known as hemiacetal.

E.g.:



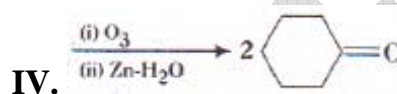
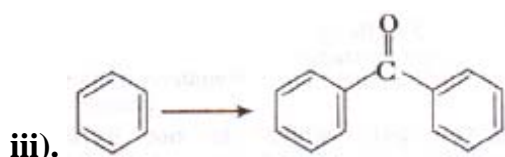
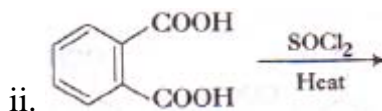
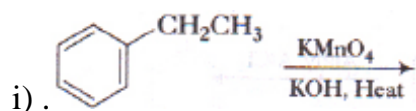
(vi) **Oxime:** The product obtained when an aldehyde or ketone reacts with hydroxylamine in weak acidic medium is known as oxime.

E.g.:

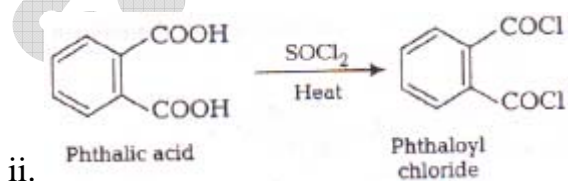
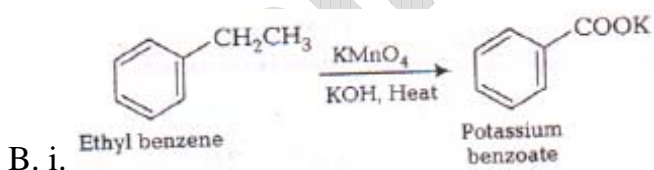
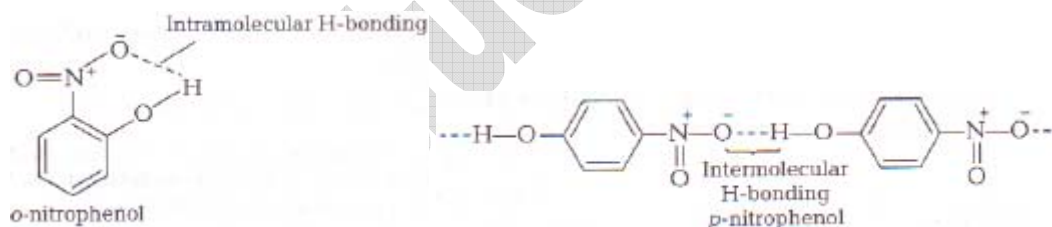


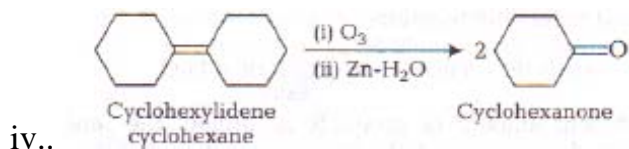
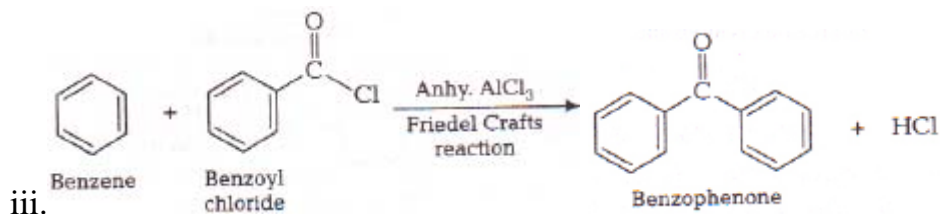
*4. A. While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

B. Complete each synthesis by giving missing starting material, reagent or products.



Ans. A. Ortho-nitro phenol is steam volatile. The reason is chelation due to intramolecular H-bonding. So, it can be separated by steam distillation from p-nitrophenol. Para-nitrophenol is not steam volatile as it contains intermolecular H-bonding.



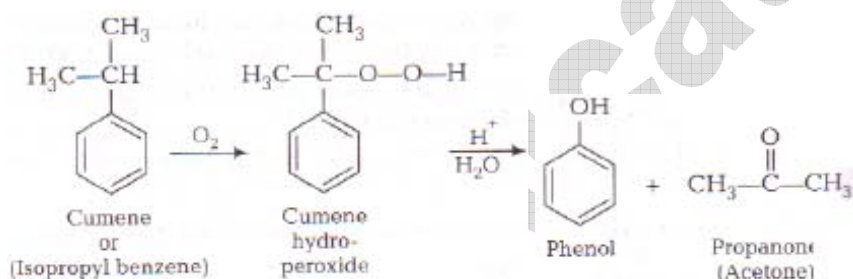


****5.i. Give the equations for the preparation of phenol from**

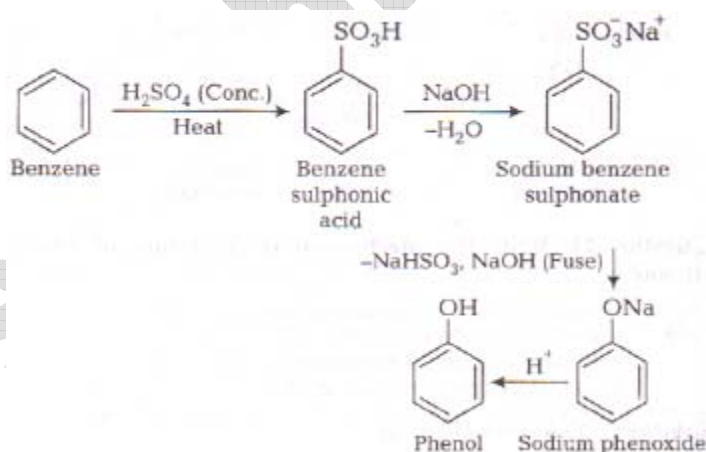
- a) Cumene b) benzene, Conc.H₂SO₄ and NaOH

ii. write the oxidation products of acetaldehyde, acetone and Acetophenone.

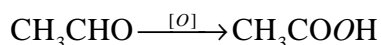
Ans. i. a). This method is used for the preparation of phenol on commercial scale by air oxidation of cumene followed by acid hydrolysis..



b.



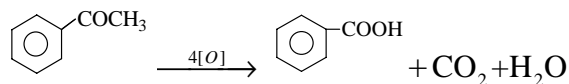
ii. Acetaldehyde on oxidation with common oxidising agents like HNO₃ or KMnO₄ or with mild oxidising agents like Tollen's reagent or Fehling solution give acetic acid.



Acetone on oxidation with strong oxidising agents at elevated temperatures involve carbon-carbon bond cleavage to give acetic acid [one carbon atom less by acetone].

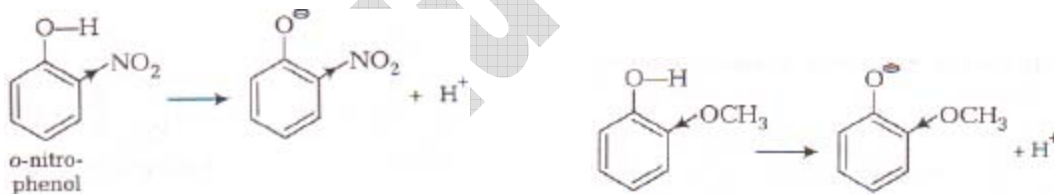


Acetophenone on drastic oxidation with chromic acid gives Benzoic acid.

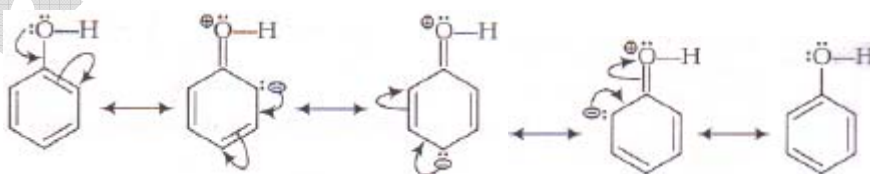


- **6. i. a. Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?**
b. Explain how does the OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?
ii. What is Tollen's reagent? Explain its reaction with aldehydes.

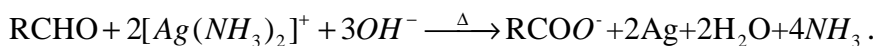
Ans. i. a. Nitro (-NO₂) group is an electron withdrawing whereas methoxy (-OCH₃) group is electron releasing in nature. o-nitrophenol produces H⁺ ions easily but methoxyphenol does not. This is because o-nitrophenoxide ion is stabilised due to resonance. This is not true with o-methoxyphenoxide ion. The two negative charges repel each other thereby destabilising it.



- b.** In the presence of attacking electrophile, -OH group exerts +R effect on the benzene ring. So, electron density in the ring increases and activates benzene ring toward electrophilic substitution particularly at the ortho and para positions.



- ii.** Ammonical silver nitrate solution is called Tollen's reagent. It acts as a mild oxidising agent. Any aldehyde on warming with Tollen's reagent gives a bright silver mirror due to formation of metallic silver and the aldehydes are oxidised to corresponding carboxylic acids.



Ketones do not give silver mirror. Hence Tollen's reagent is used to distinguish aldehydes from ketones.

*7.i. Write the mechanism of hydration of ethene to yield ethanol.

ii. Predict the products formed when cyclohexane carbaldehyde reacts with following reagents.

(i) PhMgBr and then H_3O^+

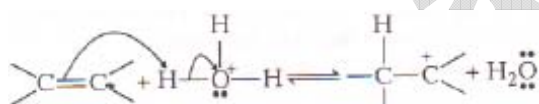
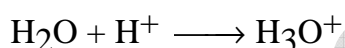
(ii) Tollen's reagent

(iii) Semi carbazide and weak acid

(iv) Zinc amalgam and dilute hydrochloric acid

Ans. i. The mechanism involves 3 steps

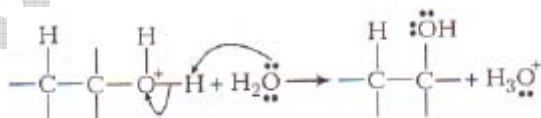
Step I: Protonation of alkene to form carbocation by electrophile attack of H_3O^+



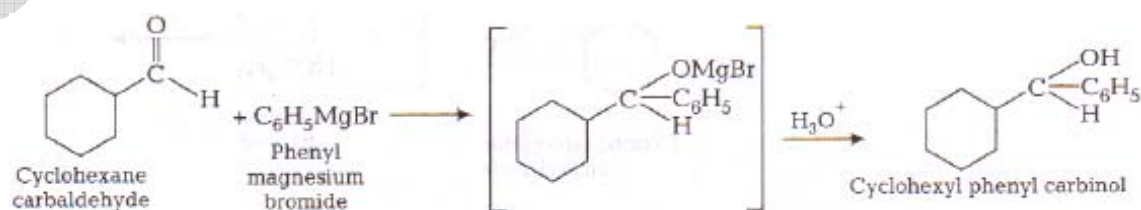
Step II: Nucleophilic attack of water on carbocation formed.



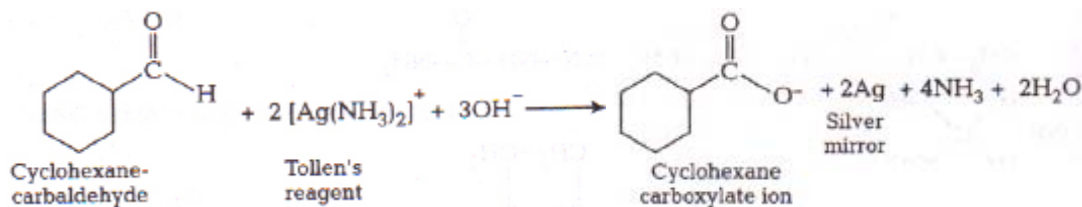
Step III: De protonation to form corresponding alcohol



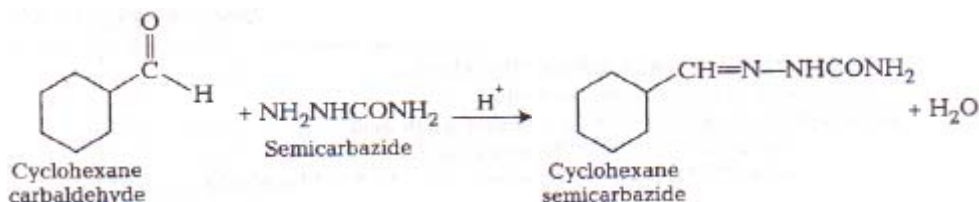
ii. I



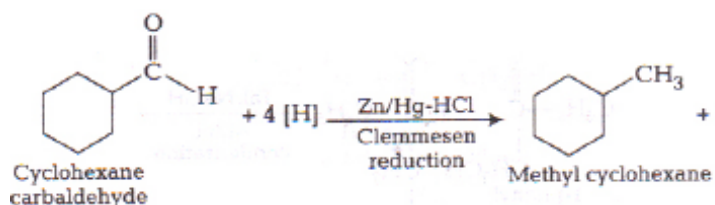
II)



III)



IV)



Short Answer Questions

1. Arrange the following in the increasing order of their acid strength.

Benzoic acid, 4-nitrobenzoic acid, 3, 4-dinitro benzoic acid, 4-methoxy benzoic acid.

Ans. Increasing order of acidic strength is:

4-methoxy benzoic acid < benzoic acid < 4-nitrobenzoic acid < 3, 4-dinitrobenzoic acid.

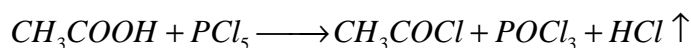
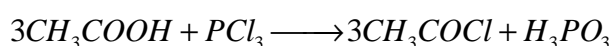
reason: -NO₂ group is electron withdrawing group while -OCH₃ is an electron releasing group.

2. Write equations showing the conversion of

i. Acetic acid to acetyl chloride

ii. Benzoic acid to Benzamide.

Ans. i

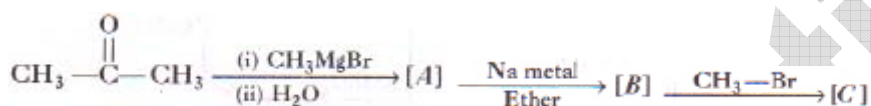


****3. Write reaction showing α -halogenation of carboxylic acids and give its name?**

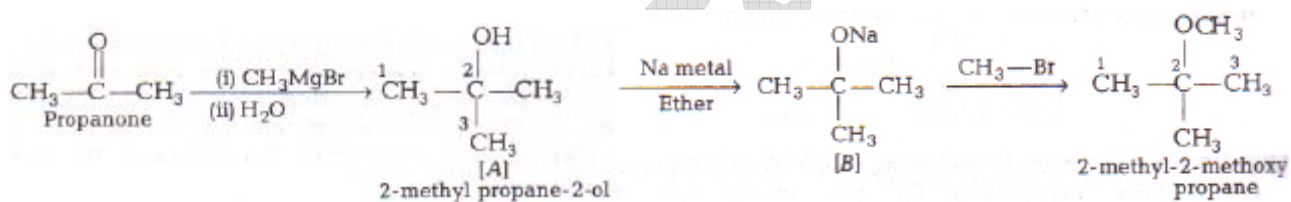
Ans. $R\overset{\alpha}{C}H_2COOH + Cl_2 \xrightarrow{redP} R\overset{\alpha}{C}H(Cl)COOH$. This reaction is known as H.V.Z

i.e. Hell-volhard-Zelinsky reaction. carboxylic acids having α -hydrogens only give this reaction. $HCOOH, C_6H_5COOH, CCl_3COOH$ etc do not give HVZ reaction as there is no α -hydrogens in them.

4. Complete the following reaction sequence?

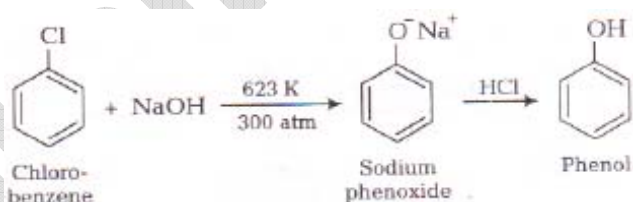


Ans.



5. Write chemical reaction for the preparation of phenol from chlorobenzene?

Ans. chlorobenzene reacts with sodium hydroxide followed by acidification give phenol.



6. What is meant by hydroboration-oxidation reaction? Illustrate it with an example?

Ans. The addition of diborane to alkenes to form trialkyl boranes followed by their oxidation by alkaline H_2O_2 to form alcohols is known as hydro boration-oxidation reaction. For example

