Chapter No.

11 Alcohols, Phenols and Ethers

Subtopics

Why do old books turn yellow???

Paper, as it is made from wood, contains carbohydrates like cellulose and lignin. As the time passes, lignin converts to many phenolic acids which are yellow in colour; thus making the paper yellow. Moreover, these acids react with cellulose which makes the paper brittle. Now-a-days acid-free paper is used for printing books in which paper manufacturers remove lignin from wood-pulp by chemical reactions.

Quick Review

Classification of alcohols:

Alcohols

Monohydric alcohol
Alcohol with one hydroxyl (–OH) group present in its structure.
e.g. $CH_3 - CH_2OH$
Ethanol

Dihydric alcohol
Alcohol with two hydroxyl (–OH) groups present in its structure.
e.g. $CH_2 - OH$ / $CH_2 - OH$
Ethylene glycol

Trihydric alcohol
Alcohol with three hydroxyl (–OH) groups present in its structure.
e.g. $CH_2 - OH$ / $CH - OH$ / $CH_2 - OH$
Glycerol

Polyhydric alcohol
Alcohol with more than three hydroxyl (–OH) groups present in their structure.

C_{sp^3} – OH bond
…H group is attached to sp^3 …ridised carbon atom of an …d, allyl or benzylic group.
$CH_2 = CH - CH_2OH$
Allylic alcohol

C_{sp^2} – OH bond
–OH group is bonded to a C=C double bond, i.e., to a vinylic carbon.
e.g. $CH_2 = CH - OH$
Vinyl alcohol

➢ **Classification of monohydric alcohols based on attachment of –OH group to sp^3 hybridised carbon:**

Classification of monohydric alcohols based on attachment of –OH group

Primary alcohol

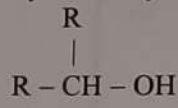
–OH group is attached to primary carbon atom of an alkyl, allyl or benzylic group.

e.g. $R-CH_2-OH$

Secondary alcohol

–OH group is attached to secondary carbon atom of an alkyl, allyl or benzylic group.

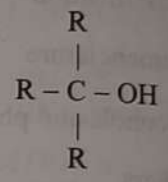
e.g.



Tertiary alcohol

–OH group is attached to tertiary carbon atom of an alkyl, allyl or benzylic group.

e.g.

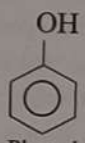


➢ **Classification of phenols:**

Phenols

Monohydric phenols

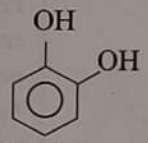
e.g.



Phenol

Dihydric phenols

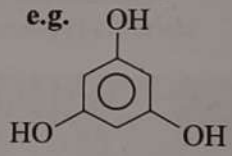
e.g.



Catechol
(Benzene-1,2-diol)

Trihydric phenols

e.g.



Phloroglucinol
(Benzene-1,3,5-triol)

➢ **Classification of ethers:**

Ethers

Simple ethers OR Symmetrical ethers
(R – O – R, Ar– O –Ar)
e.g.

CH_3-O-CH_3 Dimethyl ether

$C_6H_5-O-C_6H_5$ Diphenyl ether

Mixed ethers OR Unsymmetrical ethers
(R – O – R′, R – O –Ar, Ar– O –Ar′)
e.g.

$CH_3-O-C_2H_5$ Ethyl methyl ether

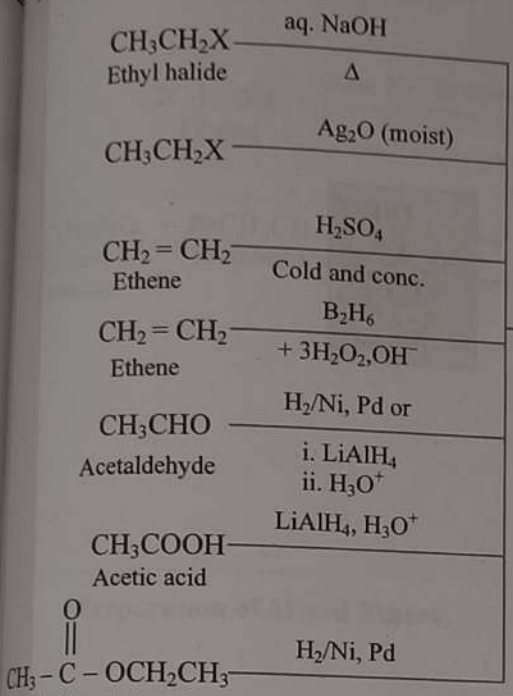
$C_2H_5-O-C_6H_5$ Ethyl phenyl ether

$C_5H_5-O-C_6H_5$ Cyclopentyl phenyl ether

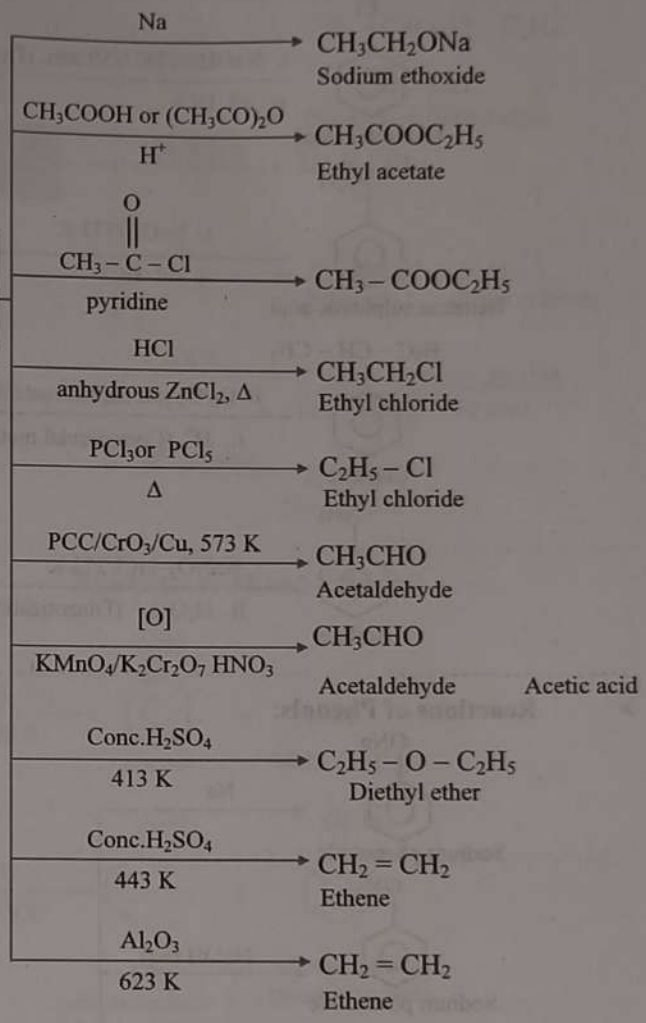
➢ **Physical properties of alcohols, phenols and ethers:**

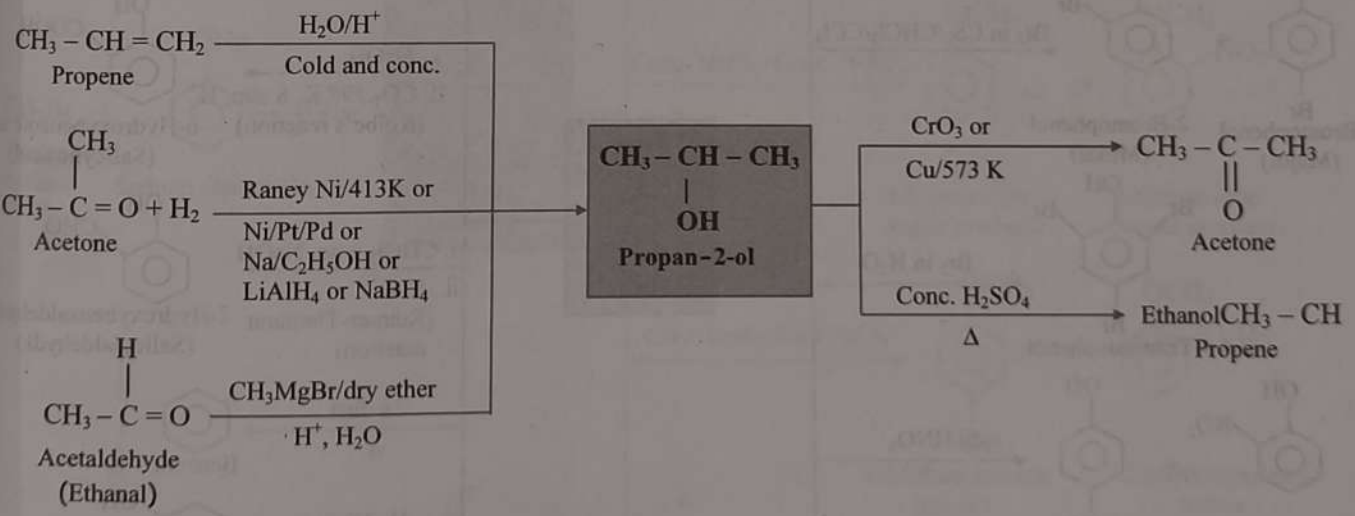
Alcohols and phenols	**Polarity**	Polar compounds
	Boiling point	Boiling point increases as the number of carbon atom increases. Boiling point of isomeric alcohols decreases with increased branching.
	Solubility	Phenols and lower alcohols (having upto three carbons) show appreciable solubility in water. **Note:** p-nitrophenol (strong intermolecular hydrogen bonding with solvent water) has higher solubility in water than that of o-nitrophenol (strong intramolecular hydrogen bonding).
Ethers	**Polarity**	Weakly polar
	Boiling point	Boiling point increases as the number of carbon atom increases.
	Solubility	Ethers show appreciable solubility in water.

Preparation of alcohols:

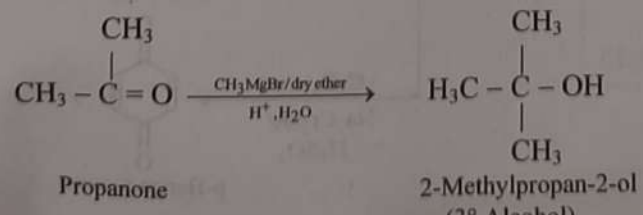


Reactions of alcohols:

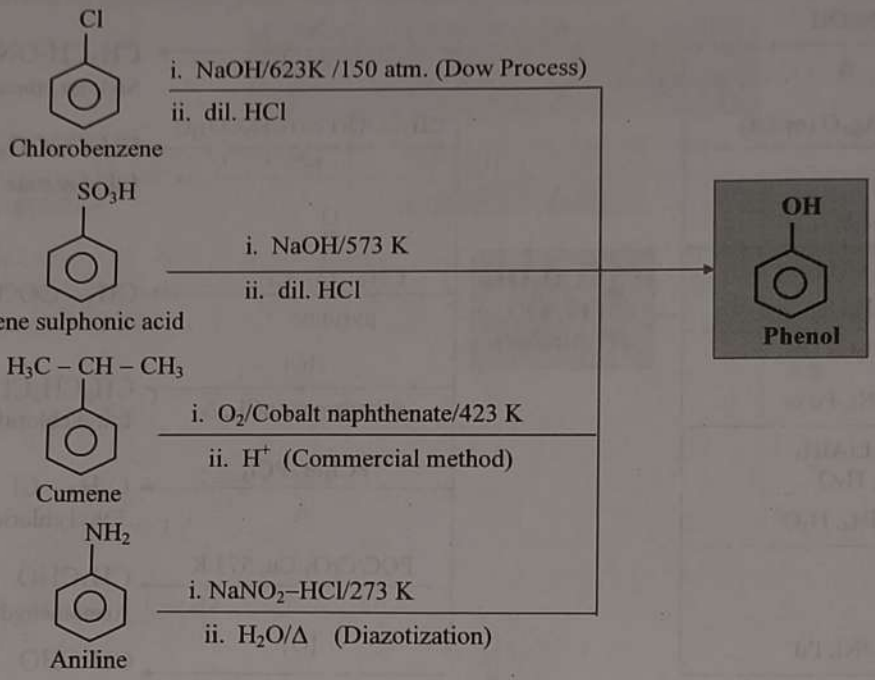




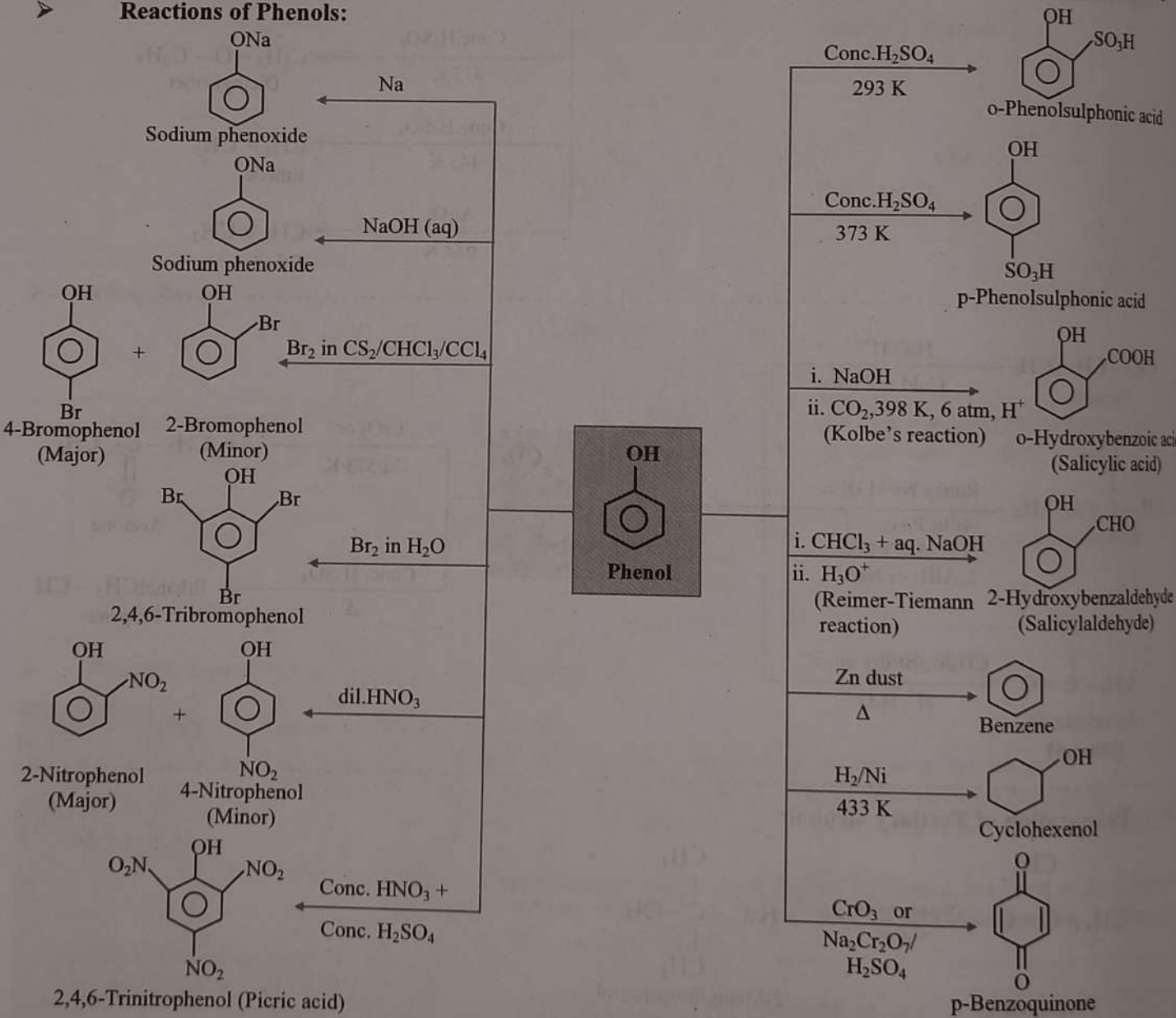
Preparation of Tertiary alcohol:



➢ Preparation of Phenols:



➢ Reactions of Phenols:



Preparation of Simple Ethers:

$2C_2H_5OH$ (Ethanol) $\xrightarrow[413\ K]{\text{Conc. } H_2SO_4 \text{ or } H_3PO_4}$

C_2H_5ONa (Sodium ethoxide) + $BrCH_2CH_3$ (Bromoethane) $\xrightarrow{\Delta}$ (Williamson's synthesis)

$\rightarrow$ **$C_2H_5 - O - C_2H_5$ Diethyl ether**

Reactions of Simple Ethers:

- $\xrightarrow[\text{Long contact with air}]{O_2}$ $CH_3 - CH(O-OH) - O - C_2H_5$ — Peroxide of diethyl ether
- $\xrightarrow[\Delta]{\text{dil.}H_2SO_4}$ $2C_2H_5OH$
- $\xrightarrow[\Delta]{PCl_5}$ $2C_2H_5OH$ (Ethanol) + C_2H_5Cl (Ethyl chloride)
- $\xrightarrow{\text{Hot HI}}$ C_2H_5I (Ethyl iodide) + C_2H_5OH (Ethanol)
- $\xrightarrow{\text{HI (excess)}}$ $2C_2H_5I$ (Ethyl iodide)

Preparation of Mixed Ethers:

CH_3Br (Bromo-methane) + C_6H_5ONa (Sodium phenoxide) $\xrightarrow{\Delta}$ **$C_6H_5OCH_3$ Methyl phenyl ether (Anisole)**

Reactions of Mixed Ethers:

- $\xrightarrow[398\ K]{HI}$ Phenol + CH_3I (Methyl iodide)
- $\xrightarrow[CH_3COOH]{Br_2 \text{ in}}$ p-Bromoanisole (major product) + o-Bromoanisole (minor product)
- $\xrightarrow{\text{Conc. } HNO_3 + \text{Conc. } H_2SO_4}$ 4-Nitroanisole (major product) + 2-Nitroanisole (minor product)
- $\xrightarrow{CH_3Cl/\text{anhydrous } AlCl_3}$ 4-Methoxytoluene (major) + 2-Methoxytoluene (minor)
- $\xrightarrow{CH_3COCl/\text{anhydrous } AlCl_3}$ 4-Methoxy-acetophenone (major product) + 2-Methoxy-acetophenone (minor product)

o-Phenolsulphonic acid

SO_3H ...enolsulphonic acid

o-Hydroxybenzoic acid (Salicylic acid)

...Hydroxybenzaldehyde (Salicylaldehyde)

...zene

...lohexenol

...quinone