ALCOHOLS

- Alcohols are the hydroxyl derivatives of alkanes having general formula, $C_nH_{2n+1}OH$.

NOMENCLATURE

- In common system, alcohols are named as alkyl alcohol.
- According to IUPAC system, alcohols are called '*alkanols*', by replacing '-*e*' of alkane by '-*ol*'.

Compound	Common name	IUPAC name
$CH_3-CH_2-CH_2-CH_2-OH$	*n*-Butyl alcohol	Butan-1-ol
$CH_3-CH(OH)-CH_2-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
$CH_3-CH(CH_3)-CH_2-OH$	*Iso*-butyl alcohol	2-Methylpropan-1-ol
$CH_3-C(CH_3)_2-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
$CH_2(OH)-CH(OH)-CH_2(OH)$	Glycerol	Propane -1, 2, 3-triol

PREPARATION

- **From alkyl halides :**

$$\underset{\text{Alkyl halide}}{RX} \xrightarrow[\text{Moist AgOH or aq. } K_2CO_3]{\text{Aq. KOH}} \underset{\text{Alcohol}}{ROH}$$

- **From alkenes :**

$$\underset{\text{Alkene}}{H_2C=CH_2} \xrightarrow{\text{conc. } H_2SO_4/H_2O} CH_3CH_2OH$$

$$H_2C=CH_2 \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } B_2H_6 \text{ in THF}} CH_3CH_2OH$$

$$H_2C=CH_2 \xrightarrow[\text{(ii) } NaBH_4,\ OH^-]{\text{(i) } Hg(OAc)_2 \text{ in THF-}H_2O} CH_3CH_2OH$$

- **From amines :**

$$\underset{1^\circ \text{ Amine}}{RNH_2} \xrightarrow{NaNO_2/\text{dil. HCl}} ROH + N_2 + H_2O$$

- **From ethers :**

$$\underset{\text{Ether}}{ROR} \xrightarrow[\Delta]{H_2O/\text{dil. } H_2SO_4} 2ROH$$

$$\underset{\text{Oxirane}}{CH_2-CH_2 \ (\text{–O– bridged})} \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } RMgX/\text{Dry ether}} \underset{1^\circ \text{ Alcohol}}{RCH_2CH_2OH}$$

- **From carbonyl compounds :**

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[NaBH_4 \text{ or } LiAlH_4]{H_2/Pt \text{ or Pd or Ni}} \underset{1^\circ \text{ Alcohol}}{RCH_2OH}$$

$$\underset{\text{Ketone}}{R_2C=O} \xrightarrow{NaBH_4 \text{ or } LiAlH_4 \text{ or } Na/C_2H_5OH} \underset{2^\circ \text{ Alcohol}}{R_2CHOH}$$

$$\underset{\text{Ketone}}{R_2C=O} \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } RMgX/\text{Dry ether}} \underset{3^\circ \text{ Alcohol}}{R_3COH}$$

- **From acids and their derivatives :**

$$\underset{\text{Carboxylic acid}}{RCOOH} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4 \text{ or } B_2H_6/\text{ether}} RCH_2OH$$

$$\underset{\text{Ester}}{RCOOR} \xrightarrow{H_2O/H^+ \text{ or } OH^-} RCOOH + ROH$$

$$RCOOR \xrightarrow[\text{(Saponification)}]{\text{Aq. NaOH}} RCOONa + ROH$$

$$RCOOR \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} RCH_2OH + ROH$$

$$\underset{\text{Acid anhydride}}{(RCO)_2O} \xrightarrow[\text{ether}]{LiAlH_4} 2RCH_2OH$$

$$\underset{\text{Acid chloride}}{RCOCl} \xrightarrow{LiAlH_4} RCH_2OH + HCl$$

Physical Properties

- Lower alcohols are liquid at room temperature while higher ones are solid.
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.
- Alcohols have high boiling points. Order of boiling point : 1° alcohols > 2° alcohols > 3° alcohols

Chemical Properties

- The hydroxyl group present in alcohols is a very reactive group. The reactions of the hydroxyl group consists of either cleavage of C — O bond or the cleavage of O — H bond as both are highly polarised with negative end of the dipoles at oxygen.
- In O — H cleavage, the order of reactivity :
  Primary > Secondary > Tertiary
- In C — O cleavage, the order of reactivity :
  Tertiary > Secondary > Primary

ALCOHOLS

$\xrightarrow{Na} RONa + H_2$

$\xrightarrow[\text{Conc. } H_2SO_4]{RCOOH} RCOOR + H_2O$

$\xrightarrow[\text{Base}]{RCOCl} RCOOR + HCl$

$\xrightarrow[\text{Base}]{(RCO)_2O} RCOOR + RCOOH$

$\xrightarrow{R'MgX} R'H + Mg(OR)X$

$\xrightarrow{HX} RX + H_2O$

$\xrightarrow{PX_3} RX + H_3PO_3$

$\xrightarrow{PCl_5} RCl + POCl_3 + HCl$

$\xrightarrow{SOCl_2} RCl + SO_2\uparrow + HCl\uparrow$

$\xrightarrow[443\text{ K}]{\text{Conc. } H_2SO_4} RCH{=}CH_2 + H_2O$

$\xrightarrow[413\text{ K}]{\text{Conc. } H_2SO_4} ROR + H_2O$

$\xrightarrow[\text{or } KMnO_4/OH^-]{K_2Cr_2O_7/H^+} R{-}COOH$

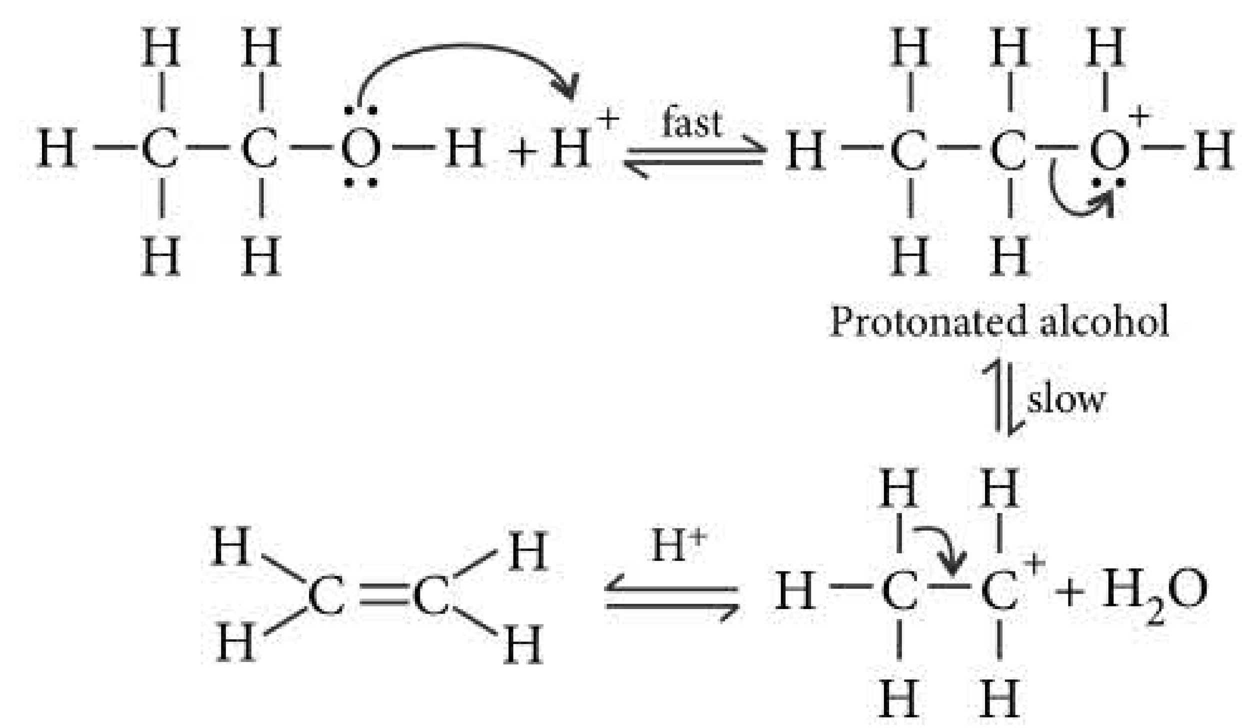
$\xrightarrow[-H_2]{Cu/573\text{ K}}$ RCHO (from 1° alcohol) or RCOR (from 2° alcohol) or alkene (from 3° alcohol)

$\xrightarrow[\text{or } CrO_3\cdot C_5H_5N\cdot HCl]{PCC} RCHO$

- **Dehydration of alcohols :**

$$C_2H_5OH \xrightarrow[443\text{ K}]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

  - **Mechanism :**



Formation of carbocation

  - The order of stability of carbocations :
    3° > 2° > 1°
  - It always occurs in accordance with the Saytzeff rule *i.e.*, the more substituted alkene is the major product.

Distinction between 1°, 2° and 3° Alcohols

- **Lucas test :** Alcohols + $ZnCl_2$ + HCl
  - **1° Alcohol :** $RCH_2OH + ZnCl_2 + HCl \longrightarrow$ No reaction at room temperature
  - **2° Alcohol :** $R_2CHOH + ZnCl_2 \longrightarrow R_2CHCl$; White turbidity appeared after 5-10 min.
  - **3° Alcohol :** $R_3COH + ZnCl_2 + HCl \longrightarrow R_3CCl$; White turbidity appeared immediately.
- **Victor Meyer test :**
  - **1° Alcohol :**

$$RCH_2OH \xrightarrow{P/I_2} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow{HNO_2} R{-}\underset{\underset{NOH}{\|}}{C}{-}NO_2$$

(Nitrolic acid)

Nitrolic acid on treatment with alkali gives blood red colouration.

  - **2° Alcohol :**

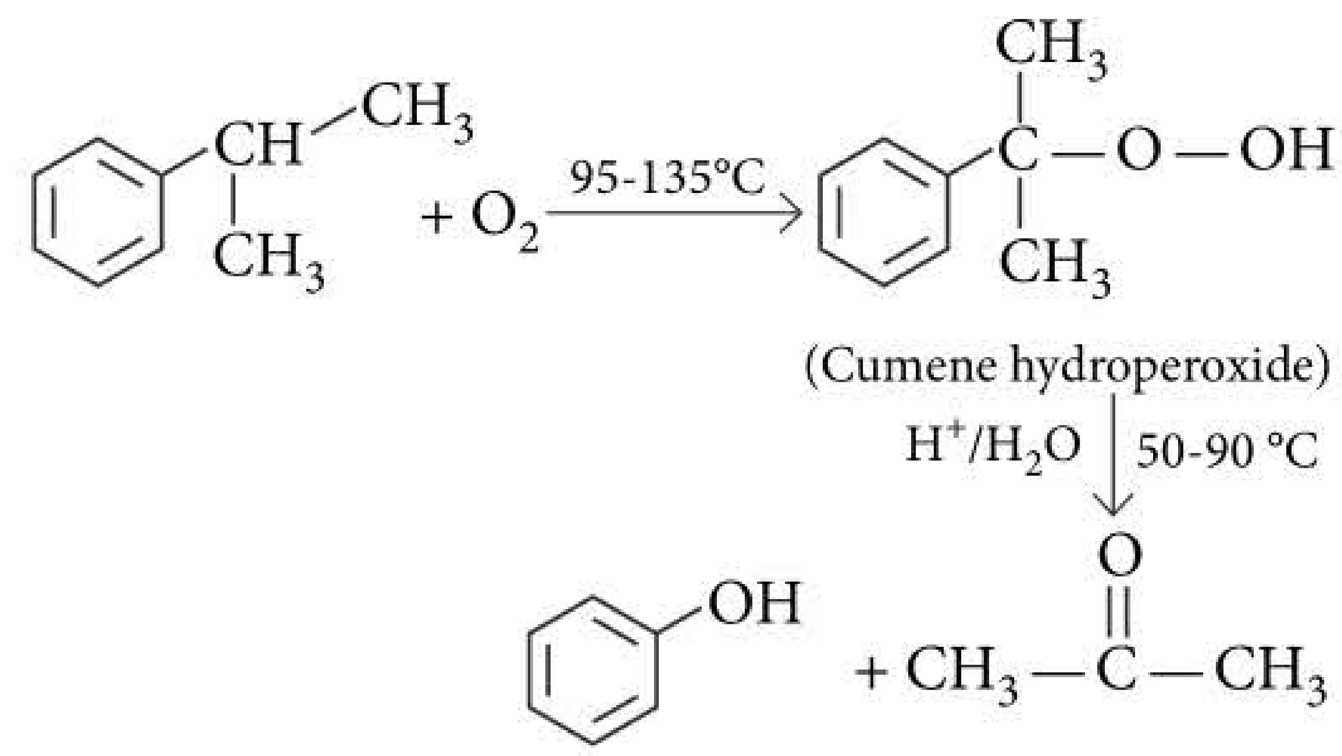
$$R_2CHOH \xrightarrow{P/I_2} R_2CHI \xrightarrow{AgNO_2} R_2CHNO_2 \xrightarrow{HNO_2} R_2C(NO_2){-}N{=}O$$

(Pseudonitrol)

Pseudonitrol on treatment with alkali gives blue colouration.

- **3° Alcohol :**

$$R_3C-OH \xrightarrow{P/I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2} \text{No reaction}$$

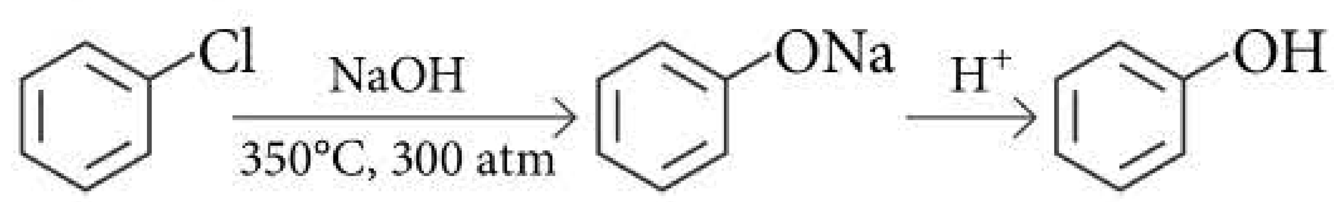


PHENOLS

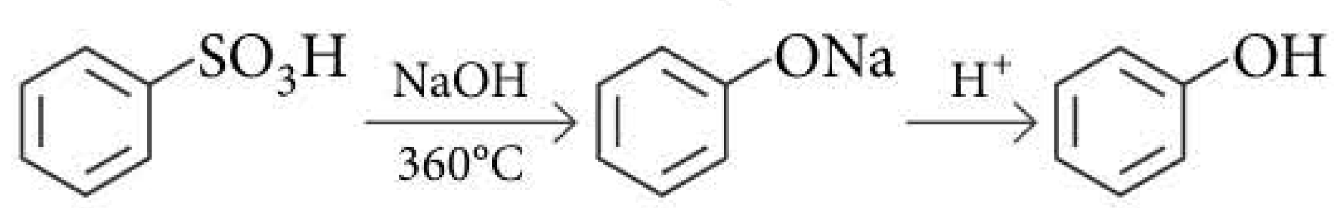
- Phenols are derivatives of benzene in which a ring hydrogen is replaced by —OH group.

PREPARATION

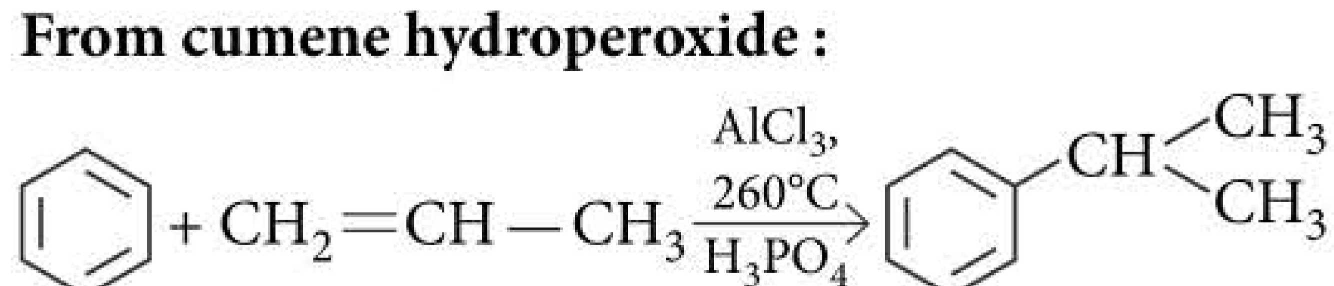
- **Hydrolysis of chlorobenzene (Dow's process) :**



- **From benzene sulphonic acid (alkali fusion of sodium benzene sulfonate) :**



- **From cumene hydroperoxide :**

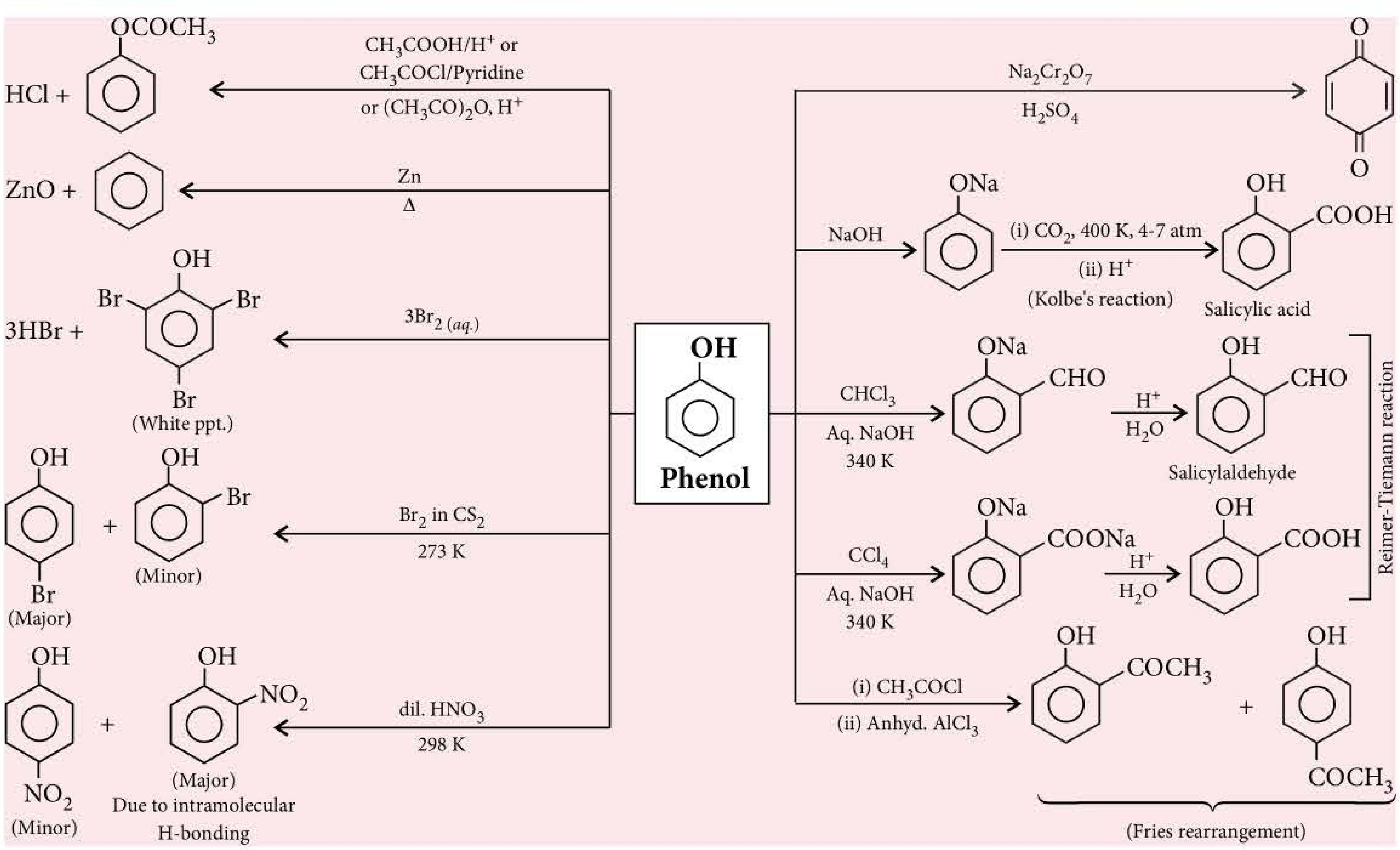


(Cumene)

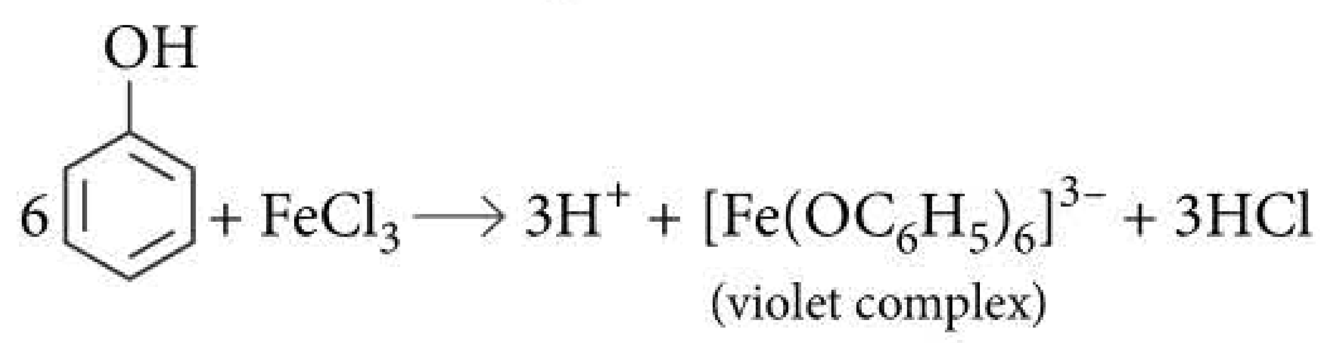
PHYSICAL PROPERTIES

- Phenol is a colourless, crystalline, deliquescent solid, attains pink colour on exposure to air and light.
- Its melting point is 315 K and boiling point 455 K. The boiling point of phenol is much higher than the corresponding aromatic hydrocarbons and the haloarenes.
- It is soluble in water due to inter-molecular H-bonding among themselves and with water.
- It is poisonous in nature but acts as antiseptic and disinfectant.

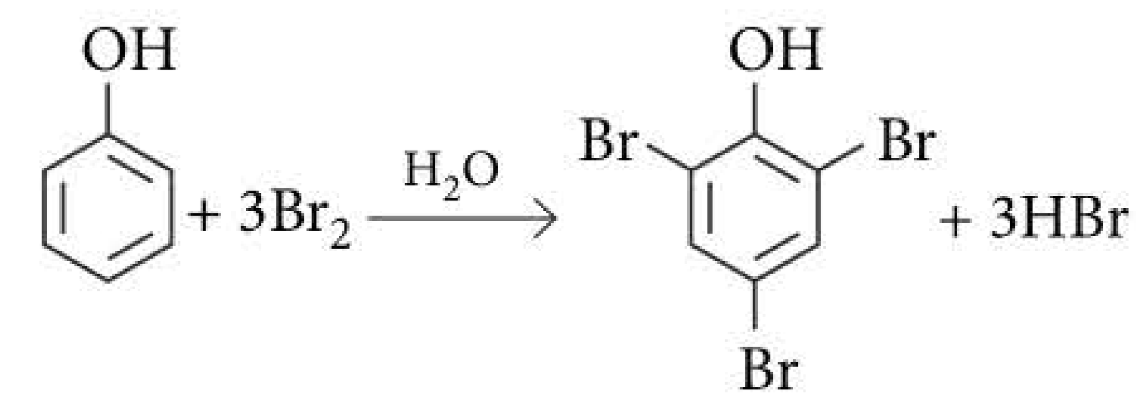
CHEMICAL PROPERTIES



- **Test for phenols :**
  - **Ferric chloride test :** Phenol gives violet colour with neutral $FeCl_3$ solution.



  - **Bromine water test :** Phenol gives white ppt. with Br_2-water due to the formation of 2, 4, 6-tribromophenol.



(white ppt.)

- **Acidity of phenol :** Phenols are much more acidic than alcohols but less than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants (K_a) or pK_a. Smaller the pK_a value, stronger the acid. The relative acidity follows the following order:

	K_a (approx.)	pK_a value
Acidic strength decreases ↓	(10^{-5}) *R*COOH Carboxylic acid	5
	(10^{-7}) H_2CO_3 Carbonic acid	7
	(10^{-10}) C_6H_5OH Phenol	8-10
	(10^{-14}) HOH Water	14
	(10^{-18}) *R*OH Alcohols	16-18

ETHERS

- **General formula :** $C_nH_{2n+2}O$ ($R-O-R'$)
- **Symmetrical ether :** When R and R' are same groups. *e.g.*, CH_3-O-CH_3, $C_2H_5-O-C_2H_5$
- **Unsymmetrical ether :** When R and R' are different groups. *e.g.*, $CH_3-O-C_6H_5$, $CH_3-O-C_2H_5$

Preparation

From alcohols by dehydration :

$$2ROH \xrightarrow[\text{or } Al_2O_3,\ 523\text{ K}]{\text{conc. } H_2SO_4,\ 413\text{ K}} ROR \text{ Ether}$$

From alkyl halides :

$$RX + RONa \xrightarrow[-NaX]{\Delta} ROR \text{ Ether}$$

(Williamson synthesis)

$$2RX + Ag_2O(\text{dry}) \xrightarrow[-AgX]{\Delta} ROR \text{ Ether}$$

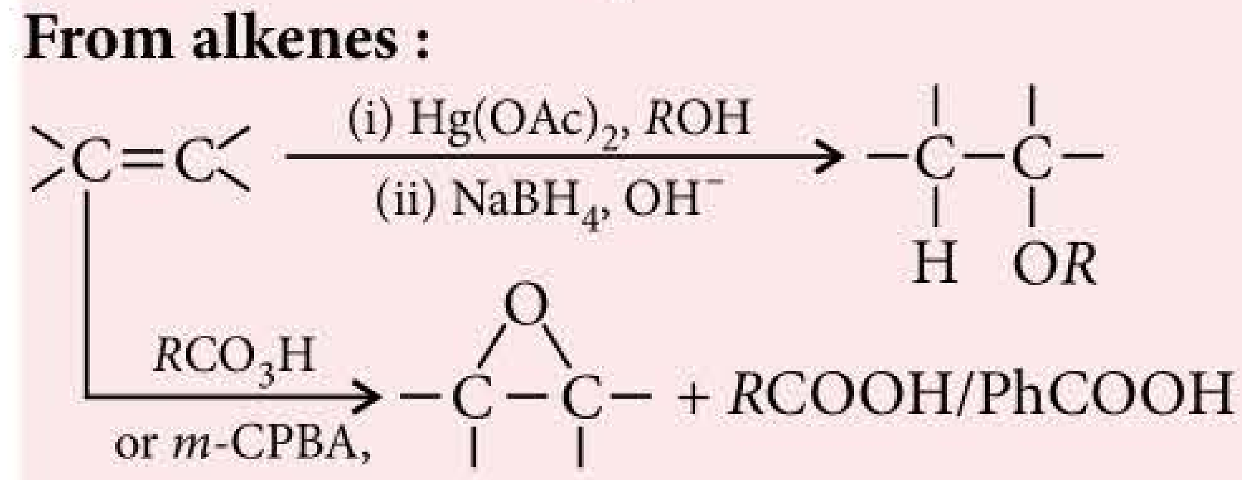
From Grignard reagent :

$$ROCH_2X + R'MgX \xrightarrow[-MgX_2]{\text{Dry ether}} ROCH_2R'$$

From diazomethane :

$$ROH + CH_2N_2 \xrightarrow[-N_2]{HBF_4,\ \Delta} ROCH_3$$

From alkenes :



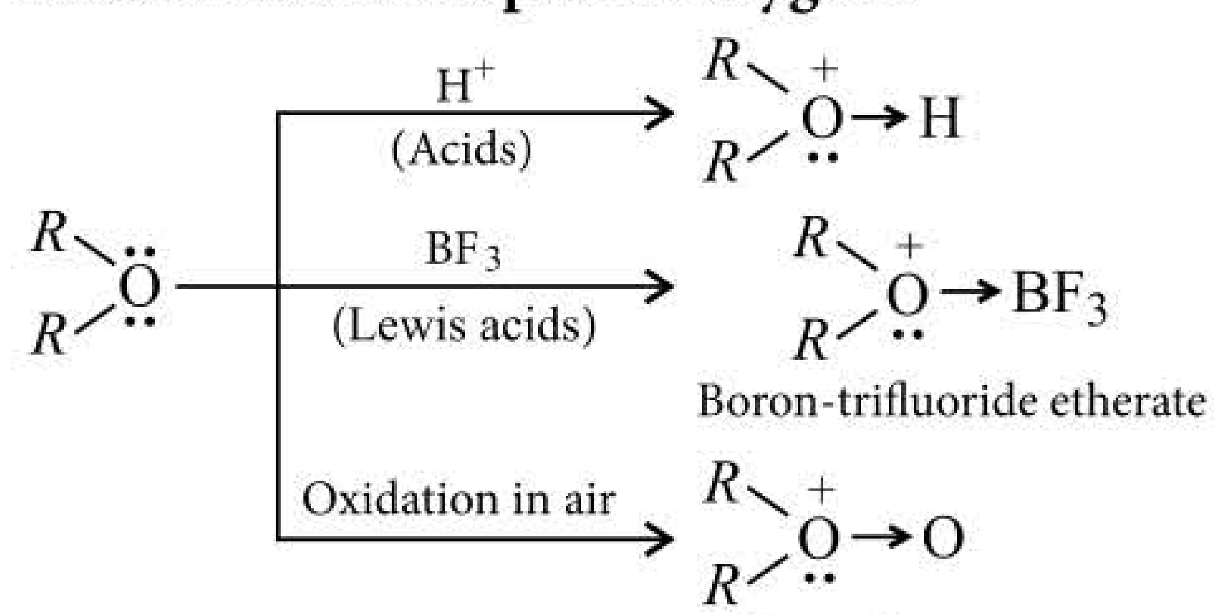
Epoxide (Cyclic ether)

Physical Properties

- Ethers have a bent structure and are dipolar in nature.
- Boiling points of ethers show a gradual increase with increase in molecular mass.
- They are lighter than water. Lower ethers are highly volatile and very inflammable.
- They are sparingly soluble in water but readily soluble in organic solvents.
- Dimethyl ether and ethyl methyl ether are gases. All ethers are colourless liquids with characteristic ether smell.

Chemical Properties

- **Reactions of lone pair of oxygen :**

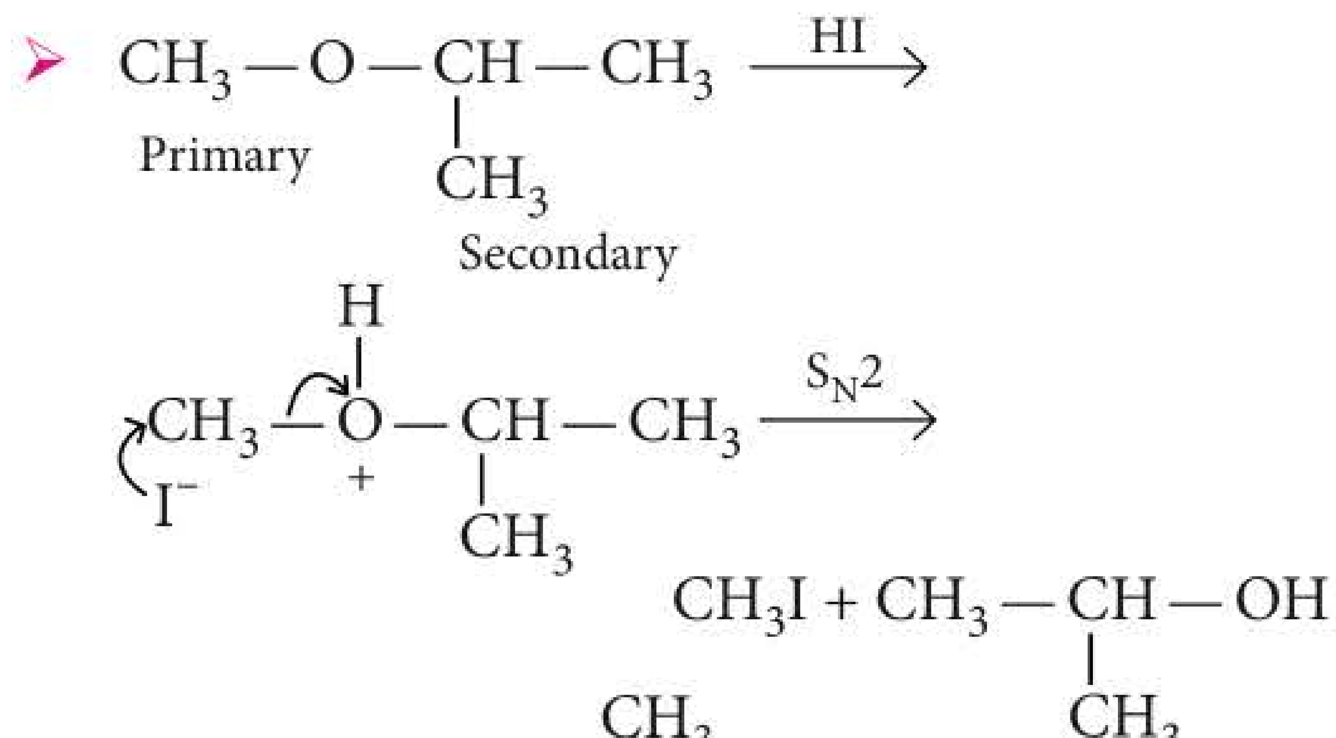


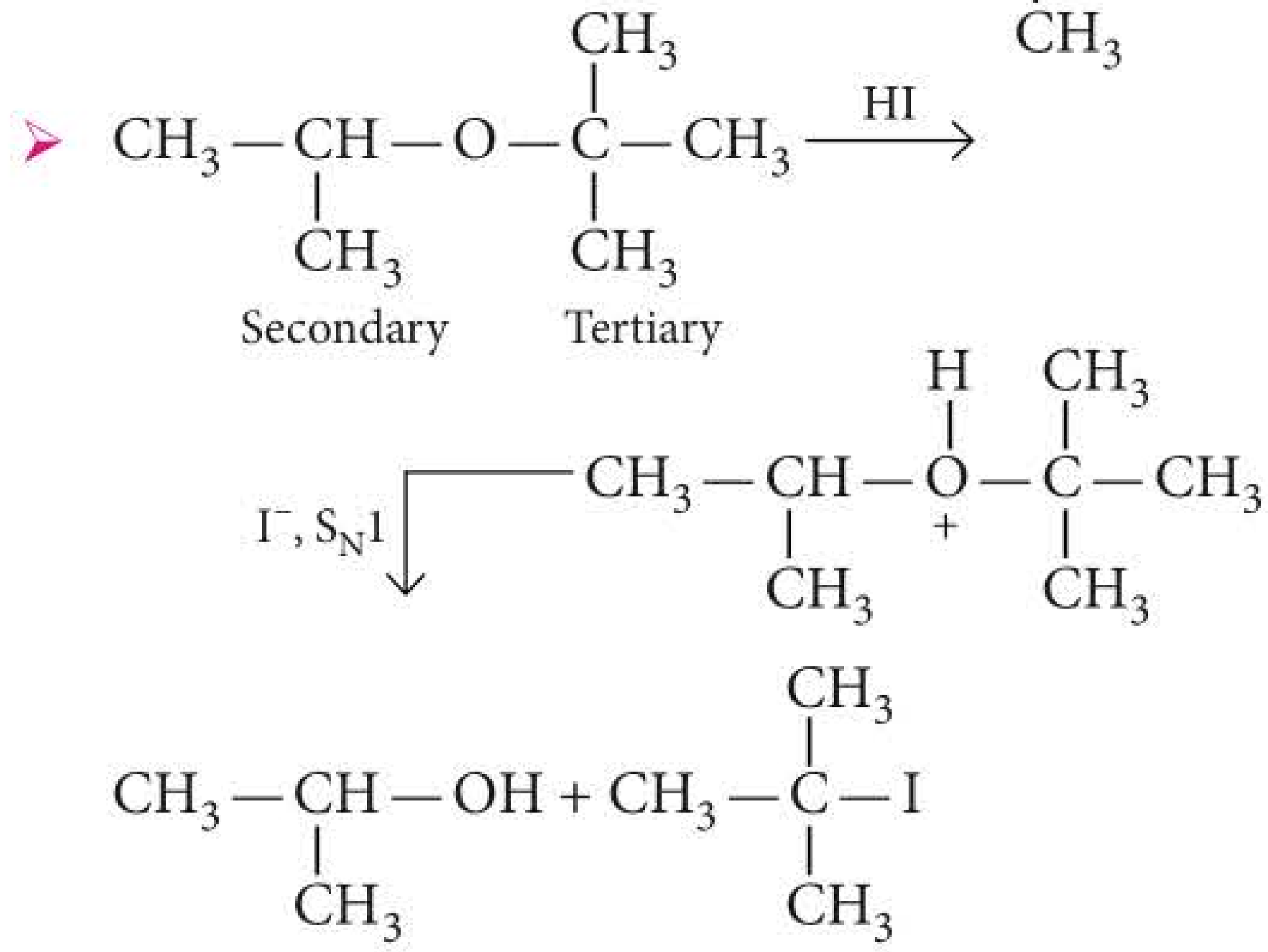
- **Cleavage of $R-O-R$ bond :**

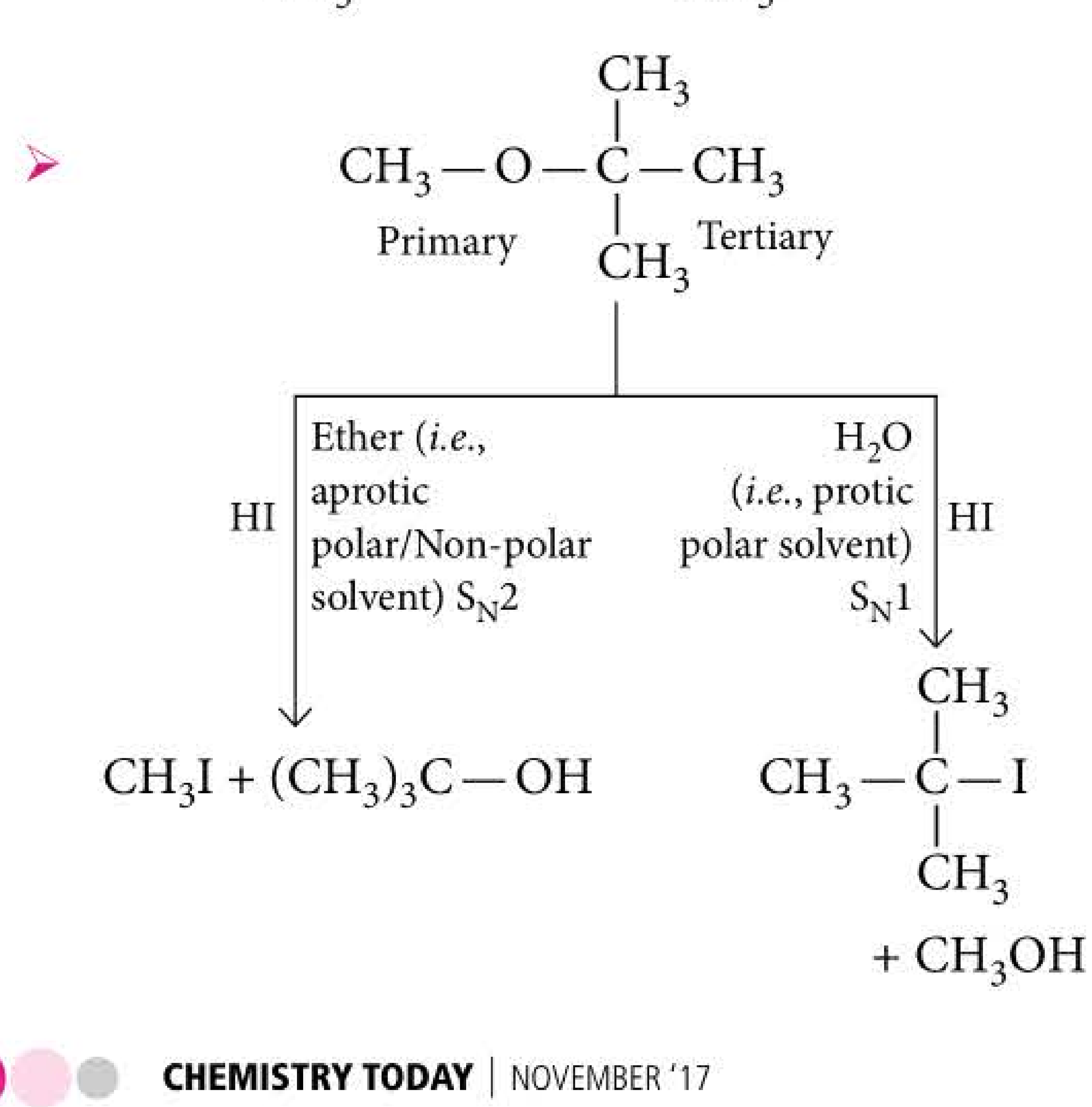
$$R-O-R \xrightarrow[\Delta]{PCl_5} 2R-Cl + POCl_3$$
$$R-O-R \xrightarrow[H_2O]{dil.\ H_2SO_4/\Delta} 2ROH$$
$$R-O-R \xrightarrow[(excess)]{HX} 2R-X + H_2O$$

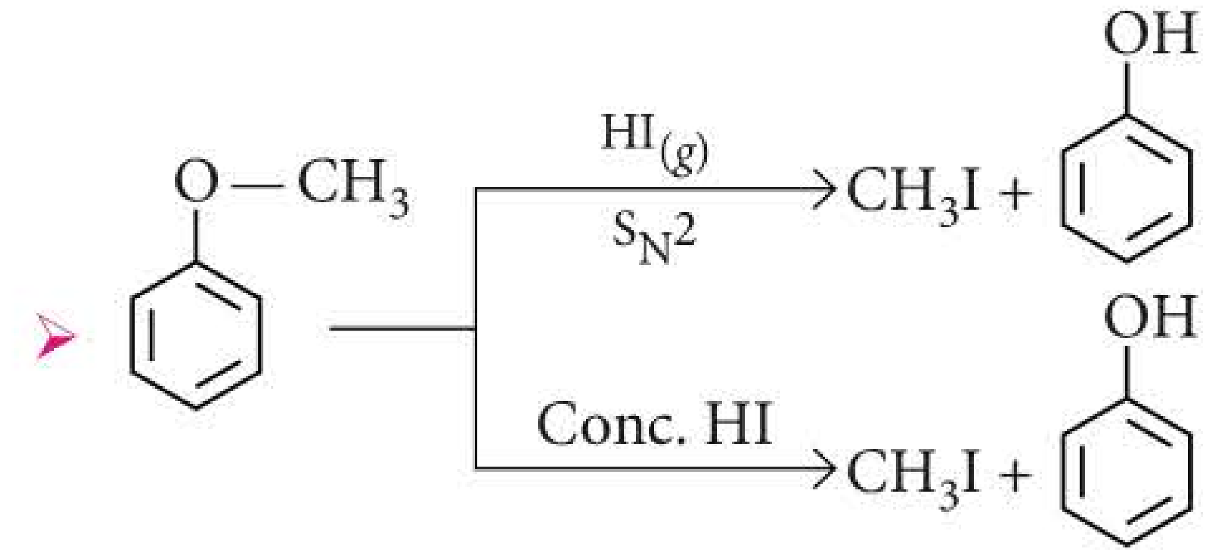
$$R-O-R' \xrightarrow{Cold\ conc.\ HI} R-OH + R'I$$
$$R-O-R' \xrightarrow{Hot\ conc.\ HI} R-I + R'I + H_2O$$

- **Different possibilities of reaction of ether with HI :**

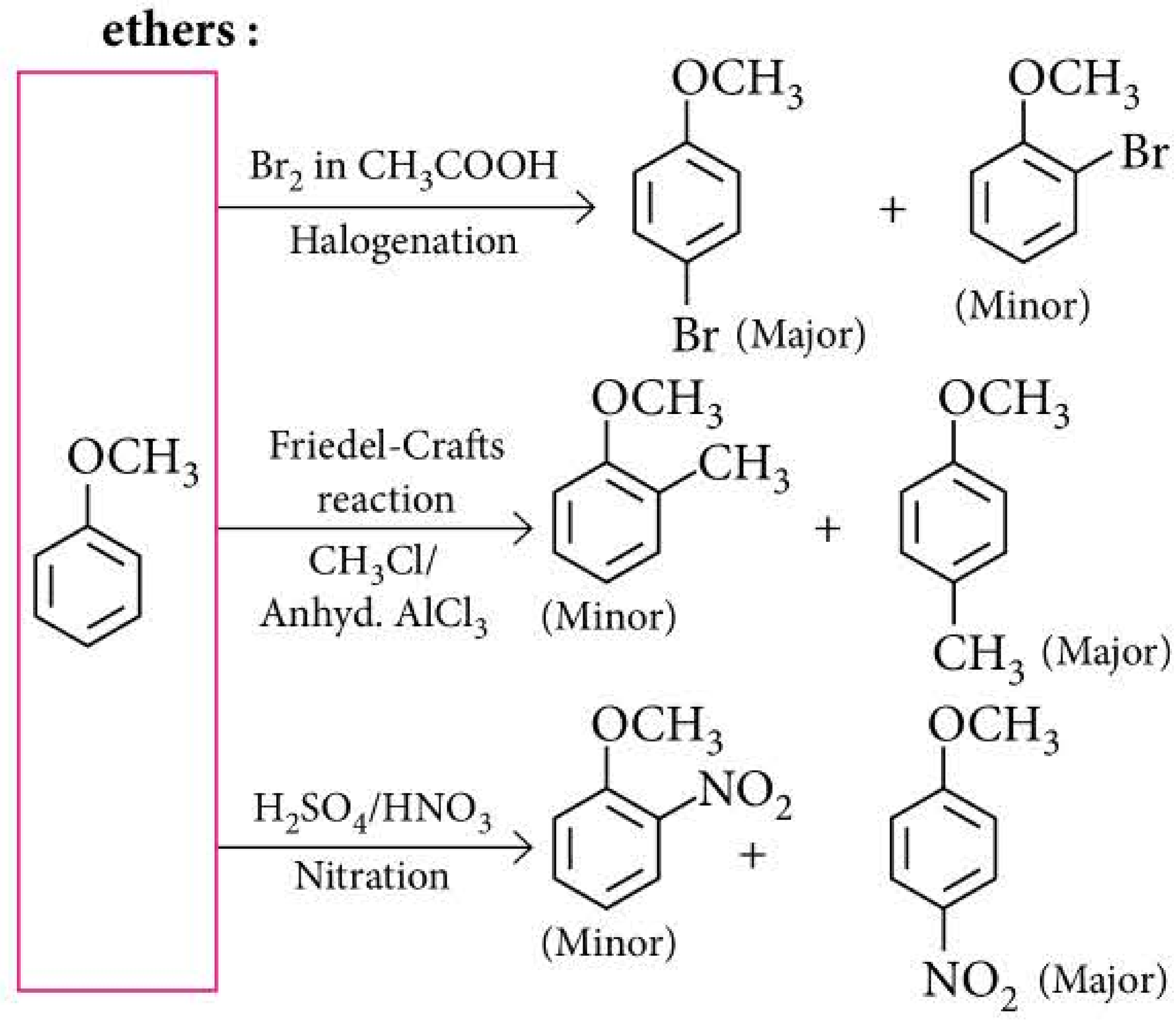








- **Electrophilic substitution reactions of aromatic ethers :**



USES

- Diethyl ether is used as solvent for oils, fats, waxes, plastics and lacquers.
- Provide inert medium for reactions.
- Used in surgery as an anaesthetic.
- Used in perfumery and in the manufacture of smokeless powder.

INFO SHOTS

A bioinspired *ortho*-sulfiliminyl phenol synthesis!

A variety of synthetic methods have been developed to construct the *ortho*-functionalized phenols which are highly useful in chemical industry, functional materials and medicines. These methods mainly include three kind of strategies (*a*) rearrangement of aromatic O—*X* bonds (*b*) directing group-assisted *ortho* C—H hydroxylation of arenes and (*c*) *ortho* C—H functionalization of phenols.