CLASS-XII

BRUSH UP for NEET/JEE 2021

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 5

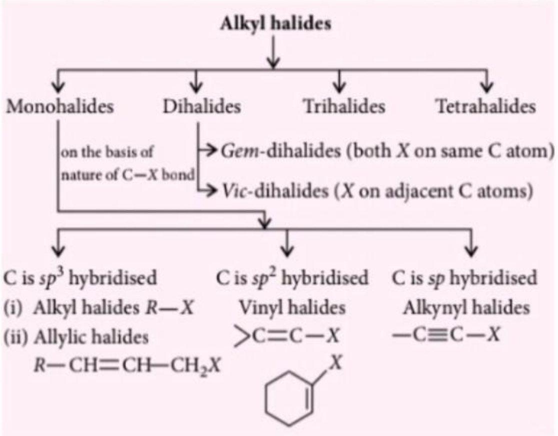
Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers

Haloalkanes and Haloarenes

HALOALKANES

- Compounds derived from alkanes by the replacement of one or more hydrogen atoms by corresponding number of halogen atoms (fluorine, chlorine, bromine or iodine) are termed as *haloalkanes*.
- Alkyl halides are represented by general formula $C_nH_{2n+1}X$, where X is the halogen atom.

CLASSIFICATION



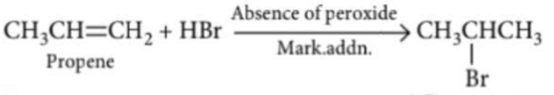
METHODS OF PREPARATION

- **From alcohols :**

$$\left.\begin{array}{r} RCH_2OH + HX \xrightarrow[-H_2O]{ZnCl_2} \\ RCH_2OH + PX_5 \xrightarrow[-HX]{-POX_3} \\ RCH_2OH + SOX_2 \xrightarrow[-SO_2]{\text{pyridine}} \\ RCH_2OH \xrightarrow[X_2 = Br_2,\, I_2]{\text{Red P}/X_2} \end{array}\right\} \rightarrow RCH_2X$$

- **From hydrocarbons :**

$$\underset{\text{Methane}}{CH_4} \xrightarrow[\text{or 520-670 K}]{Cl_2\,/\,h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$



$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow[\text{Mark.addn.}]{\text{Absence of peroxide}} \underset{\text{2-Bromopropane}}{CH_3\underset{|\atop Br}{C}HCH_3}$$

- **Hunsdiecker reaction :**

$$RCH_2COO^-Ag^+ + X_2 \xrightarrow[\Delta]{CCl_4} RCH_2X + CO_2 + AgBr$$

- **Finkelstein reaction :**

$$RCH_2Cl + NaX \xrightarrow{\text{Acetone}} RCH_2X + NaCl$$

- **Swarts reaction :**

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

PHYSICAL PROPERTIES

Physical properties

Physical state and smell : Lower members are colourless gases at room temperature, alkyl halides up to C_{18} are colourless sweet smelling liquids while higher members are colourless solids.

Dipole moment : Haloalkanes are polar compounds and their polarity depends on electronegativity of halogen. Dipole moment of halomethanes are

$CH_3Cl > CH_3F > CH_3Br > CH_3I$
1.86 D 1.84D 1.83D 1.63D

Boiling point : The boiling point increases from R—F to R—I

$R—F < R—Cl < R—Br < R—I$

- Boiling point increases with increase in size of alkyl group *i.e.*, $CH_3X < C_2H_5X < C_3H_7X$ etc.
- For isomeric alkyl halides, boiling point decreases with branching.

Density : The density increases with atomic mass of halogen and decreases with increase in size of alkyl group.

- For same alkyl group, density follows the order $R—I > R—Br > R—Cl > R—F$
- For same halogen atom, density follows the order $CH_3X > C_2H_5X > C_3H_7X$

Solubility : Haloalkanes are insoluble in water but soluble in organic solvents.

Bond strength : Bond strength of carbon-halogen bond decreases with increase in the bond length as we move from fluorine to iodine.
C—F > C—Cl > C—Br > C—I

CHEMICAL PROPERTIES

Nucleophilic Substitution Reactions

H A L O A L K A N

$\xrightarrow{KOH_{(aq.)}} R—OH + KX$

$\xrightarrow{\text{Moist } Ag_2O \text{ or } AgOH} R—OH + AgX$

$\xrightarrow{\text{Dry } Ag_2O} R'—O—R + 2AgX$

$\xrightarrow{R'ONa} R—O—R' + NaX$ **(Williamson's Synthesis)**

$\xrightarrow{R'—C\equiv C^-Na^+} R—C\equiv C—R' + NaX$

$\xrightarrow{NH_{3(alc.)} \text{ excess}} R_4N^+X^-$

$\xrightarrow{R'COOAg} R'COOR + AgX$

$\xrightarrow{KNO_2} R—O—N{=}O + KX$

$\xrightarrow{AgNO_2} R—N\overset{O}{\underset{O}{\lessgtr}} + AgX$

$\xrightarrow{AgCN} R—N\equiv C$

$\xrightarrow{KCN} R—C\equiv N$

E S

Dehydrohalogenation

$\xrightarrow{\text{Alc. KOH}} CH_3—CH{=}CH_2$

Reduction

$R—Cl \xrightarrow[\text{or Zn/HCl or } LiAlH_4]{Zn\text{-}Cu/C_2H_5OH} CH_3—CH_3$

$R—I \xrightarrow[150°C]{\text{HI/Red P}} CH_3—CH_3$

REACTION WITH METALS

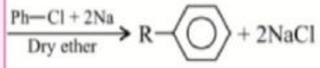
HALOALKANES

$\xrightarrow[\text{Ether}]{Mg} RMgX$

Wurtz reaction

$\xrightarrow[\text{Dry ether}]{2Na} R—R + 2NaX$

Wurtz-Fittig Reaction



Corey House reaction

$\xrightarrow[\text{(ii) CuI}]{\text{(i) Li/}Et_2O} R_2CuLi \xrightarrow{R'X} R'R + RCu + LiX$

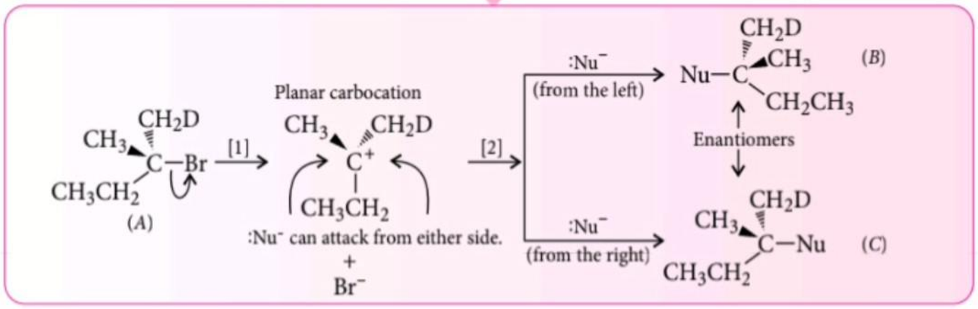
S_N1 reaction

The mechanism involves two steps and rate of reaction depends only upon the concentration of halides because it is only participating in slow or rate determining step.

Order of reactivity towards S_N2 reaction :

$CH_3-X < RCH_2-X < R_2CH-X < R_3C-X$

Methyl 1° 2° 3°



COMPARISON BETWEEN S_N1 AND S_N2

Unimolecular (S_N1)	Bimolecular (S_N2)
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile, or DMF.
Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : 3° > 2° > 1° > $^+CH_3$ (Fastest) (Slowest) Greater the stability of carbocation, faster will be the reaction.	Rate of reaction : CH_3 > 1° > 2° > 3° halides (Fastest) (Slowest) Less the steric hindrance in *T.S.*, faster will be the reaction.
Tends to proceed with weak nucleophiles *e.g.*; CH_3OH, H_2O, CH_3CH_2OH, etc.	Tends to proceed with strong nucleophiles, *e.g.*; CH_3O^-, CN^-, OH^-, etc.
Configuration is retained but in front attack inversion takes place (racemisation and inversion).	Inversion of configuration takes place (Walden inversion).

HALOARENES

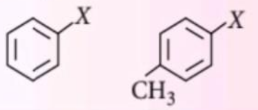
- Compounds in which the halogen atom is linked directly to the carbon atom of benzene ring are called aryl halides or haloarenes.

CLASSIFICATION OF HALOARENES

Classification of Haloarenes

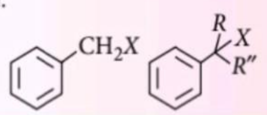
Compounds containing sp^2 C–X bond

Aryl halides : These are the compounds in which the halogen atom is bonded to sp^2-hybridised carbon atom of an aromatic ring.

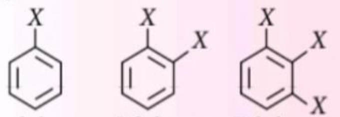


Compounds containing sp^3 C–X bond

Benzylic halides : In these halides, the halogen atom is attached to a benzylic carbon.

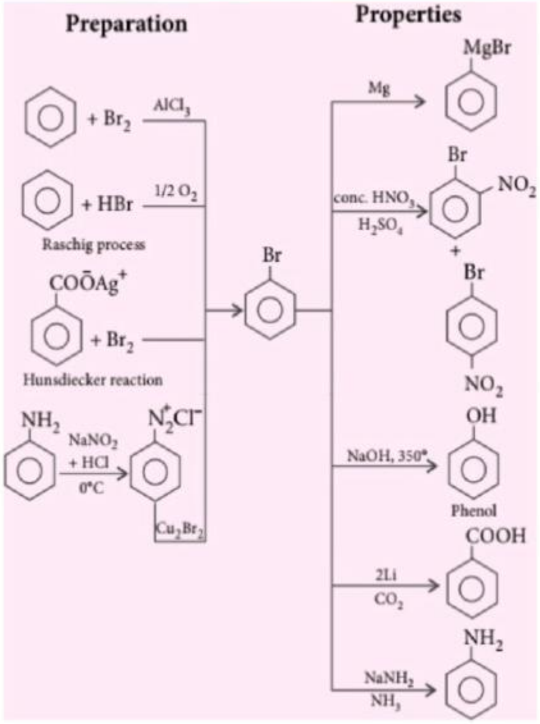


On the basis of number of halogen atoms



Monohaloarene Dihaloarene Trihaloarene

PREPARATION AND PROPERTIES



PHYSICAL PROPERTIES

Physical properties

Physical state and smell : Haloarenes are generally colourless liquids with pleasant odour or are crystalline solids with characteristic smell.

Boiling point : The boiling points of monohalogen derivatives of benzene are in order

Iodo > Bromo > Chloro > Fluoro

- Boiling and melting points increase as the size of the aryl group increases.

Solubility : Aryl halides are insoluble in water but readily miscible with organic solvents.

Density : Aryl halides are heavier than water. Their density follows the order

Aryl iodide > aryl bromide > aryl chloride

Dipole moment : The dipole moment of haloarenes follows the order

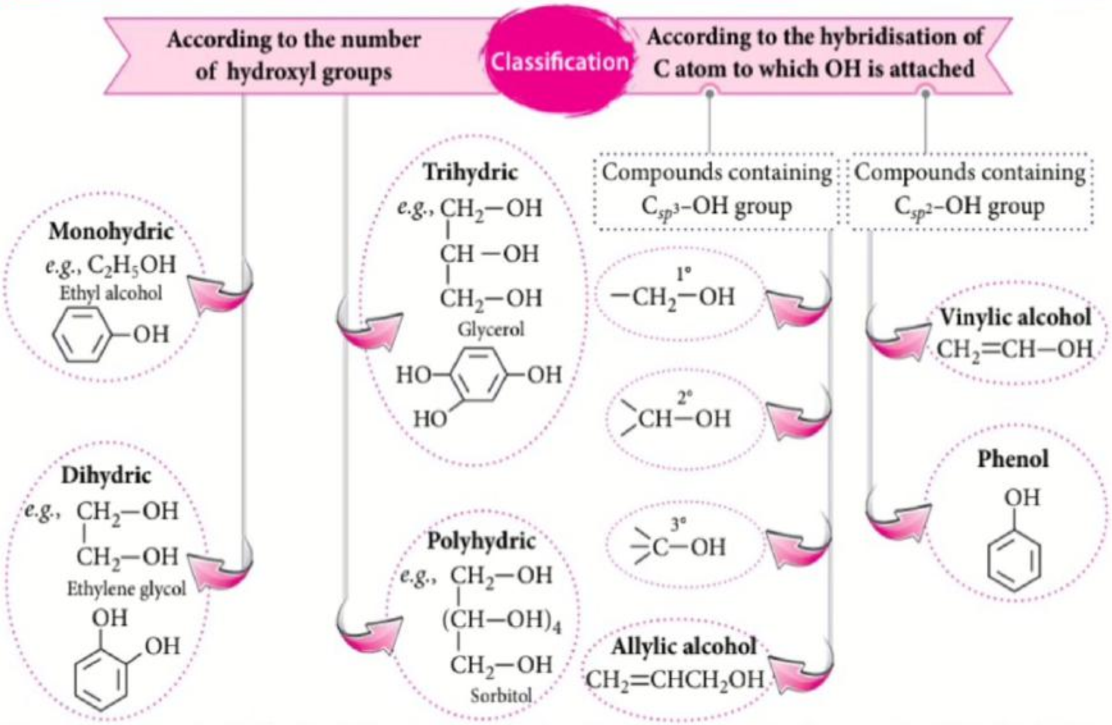
Flurobenzene < Chlorobenzene < Bromobenzene ≈ Iodobenzene

Alcohols, Phenols and Ethers

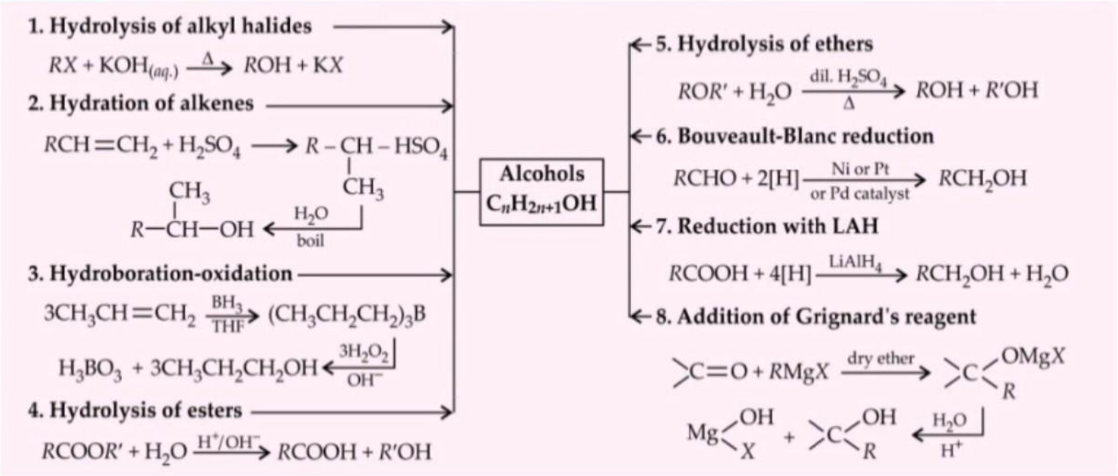
ALCOHOLS AND PHENOLS

- Alcohols and phenols are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by – OH group. Compounds in which hydroxyl group – OH is directly linked with the aromatic ring are known as phenols.
  - General formula of alcohols : $C_nH_{2n+2}O$.

CLASSIFICATION OF ALCOHOLS AND PHENOLS



PREPARATION OF ALCOHOLS



1. Hydrolysis of alkyl halides

$RX + KOH_{(aq.)} \xrightarrow{\Delta} ROH + KX$

2. Hydration of alkenes

$RCH{=}CH_2 + H_2SO_4 \longrightarrow R-\underset{CH_3}{CH}-HSO_4 \xrightarrow[boil]{H_2O} R-\overset{CH_3}{CH}-OH$

3. Hydroboration-oxidation

$3CH_3CH{=}CH_2 \xrightarrow[THF]{BH_3} (CH_3CH_2CH_2)_3B \xrightarrow[OH^-]{3H_2O_2} H_3BO_3 + 3CH_3CH_2CH_2OH$

4. Hydrolysis of esters

$RCOOR' + H_2O \xrightarrow{H^+/OH^-} RCOOH + R'OH$

Alcohols $C_nH_{2n+1}OH$

5. Hydrolysis of ethers

$ROR' + H_2O \xrightarrow[\Delta]{dil.\ H_2SO_4} ROH + R'OH$

6. Bouveault-Blanc reduction

$RCHO + 2[H] \xrightarrow[or\ Pd\ catalyst]{Ni\ or\ Pt} RCH_2OH$

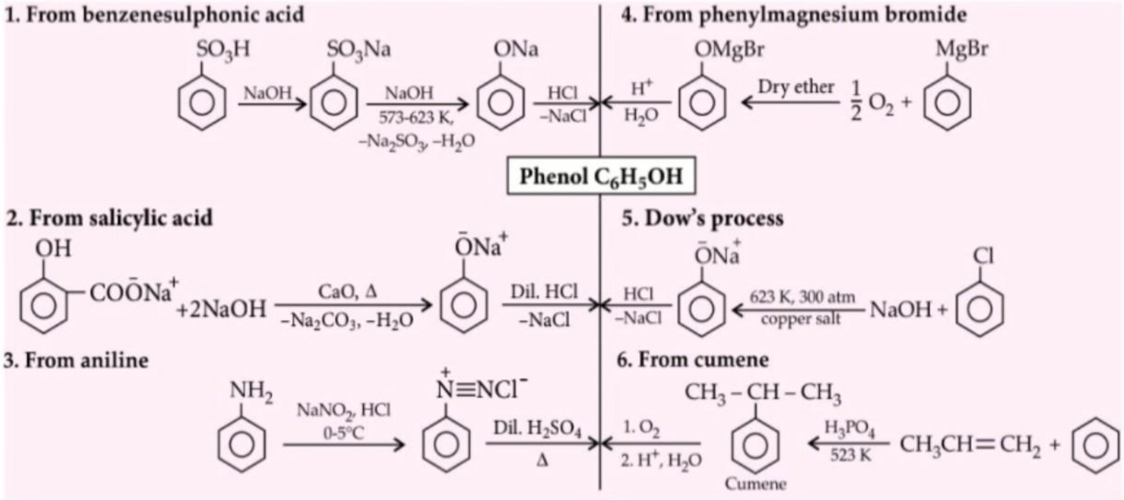
7. Reduction with LAH

$RCOOH + 4[H] \xrightarrow{LiAlH_4} RCH_2OH + H_2O$

8. Addition of Grignard's reagent

$>C{=}O + RMgX \xrightarrow{dry\ ether} >C<^{OMgX}_{R} \xrightarrow[H^+]{H_2O} Mg<^{OH}_{X} + >C<^{OH}_{R}$

PREPARATION OF PHENOL

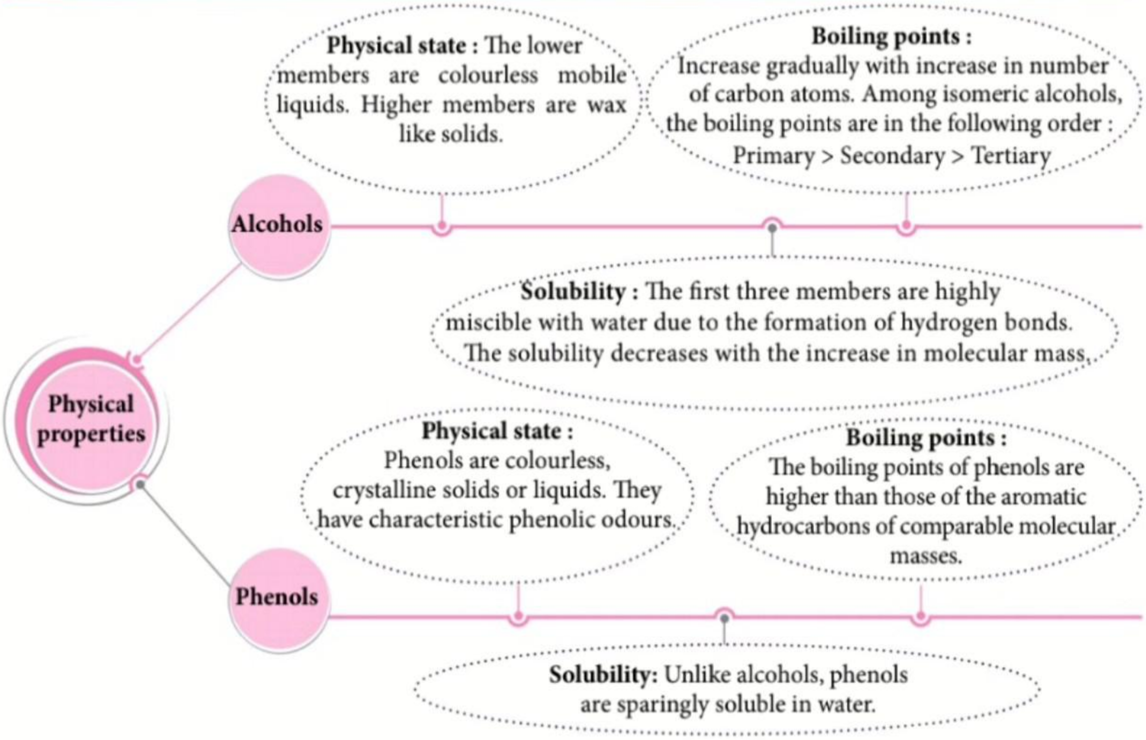


INFOSHOTS

Application of plant phenolics in skin therapy

Phenolic compounds constitute a group of secondary metabolites which have important functions in plants. Besides the beneficial effects on the plant host, phenolic metabolites (polyphenols) exhibit a series of biological properties that influence the human in a health-promoting manner. Evidence suggests that people can benefit from plant phenolics obtained either by the diet or through skin application because, they can alleviate symptoms and inhibit the development of various skin disorders. Due to their natural origin and low toxicity, phenolic compounds are a promising tool in eliminating the causes and effects of skin aging, skin diseases, and skin damage, including wounds and burns. Polyphenols also act protectively and help prevent or attenuate the progression of certain skin disorders, both minor problems *e.g.*, wrinkles, acne or serious, potentially life-threatening diseases such as cancer.

PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS



Physical state : The lower members are colourless mobile liquids. Higher members are wax like solids.

Boiling points : Increase gradually with increase in number of carbon atoms. Among isomeric alcohols, the boiling points are in the following order : Primary > Secondary > Tertiary

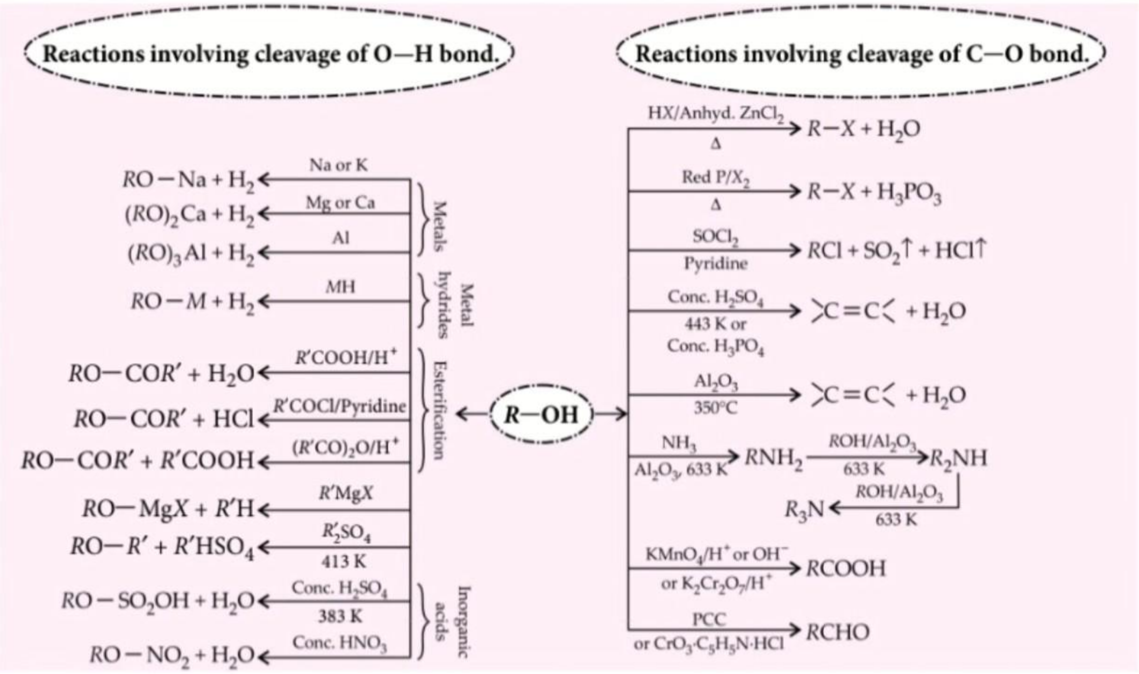
Solubility : The first three members are highly miscible with water due to the formation of hydrogen bonds. The solubility decreases with the increase in molecular mass.

Physical state : Phenols are colourless, crystalline solids or liquids. They have characteristic phenolic odours.

Boiling points : The boiling points of phenols are higher than those of the aromatic hydrocarbons of comparable molecular masses.

Solubility: Unlike alcohols, phenols are sparingly soluble in water.

CHEMICAL PROPERTIES OF ALCOHOLS



Reactions involving cleavage of O—H bond.

$$R\text{—OH} \xrightarrow{\text{Na or K}} RO\text{—Na} + H_2$$

$$R\text{—OH} \xrightarrow{\text{Mg or Ca}} (RO)_2Ca + H_2$$

$$R\text{—OH} \xrightarrow{\text{Al}} (RO)_3Al + H_2$$

$$R\text{—OH} \xrightarrow{MH} RO\text{—}M + H_2$$

$$R\text{—OH} \xrightarrow{R'COOH/H^+} RO\text{—}COR' + H_2O$$

$$R\text{—OH} \xrightarrow{R'COCl/\text{Pyridine}} RO\text{—}COR' + HCl$$

$$R\text{—OH} \xrightarrow{(R'CO)_2O/H^+} RO\text{—}COR' + R'COOH$$

$$R\text{—OH} \xrightarrow{R'MgX} RO\text{—}MgX + R'H$$

$$R\text{—OH} \xrightarrow[413\text{ K}]{R'_2SO_4} RO\text{—}R' + R'HSO_4$$

$$R\text{—OH} \xrightarrow[383\text{ K}]{\text{Conc. } H_2SO_4} RO\text{—}SO_2OH + H_2O$$

$$R\text{—OH} \xrightarrow{\text{Conc. } HNO_3} RO\text{—}NO_2 + H_2O$$

Reactions involving cleavage of C—O bond.

$$R\text{—OH} \xrightarrow[\Delta]{HX/\text{Anhyd. } ZnCl_2} R\text{—}X + H_2O$$

$$R\text{—OH} \xrightarrow[\Delta]{\text{Red } P/X_2} R\text{—}X + H_3PO_3$$

$$R\text{—OH} \xrightarrow[\text{Pyridine}]{SOCl_2} RCl + SO_2\uparrow + HCl\uparrow$$

$$R\text{—OH} \xrightarrow[443\text{ K or Conc. } H_3PO_4]{\text{Conc. } H_2SO_4} >C=C< + H_2O$$

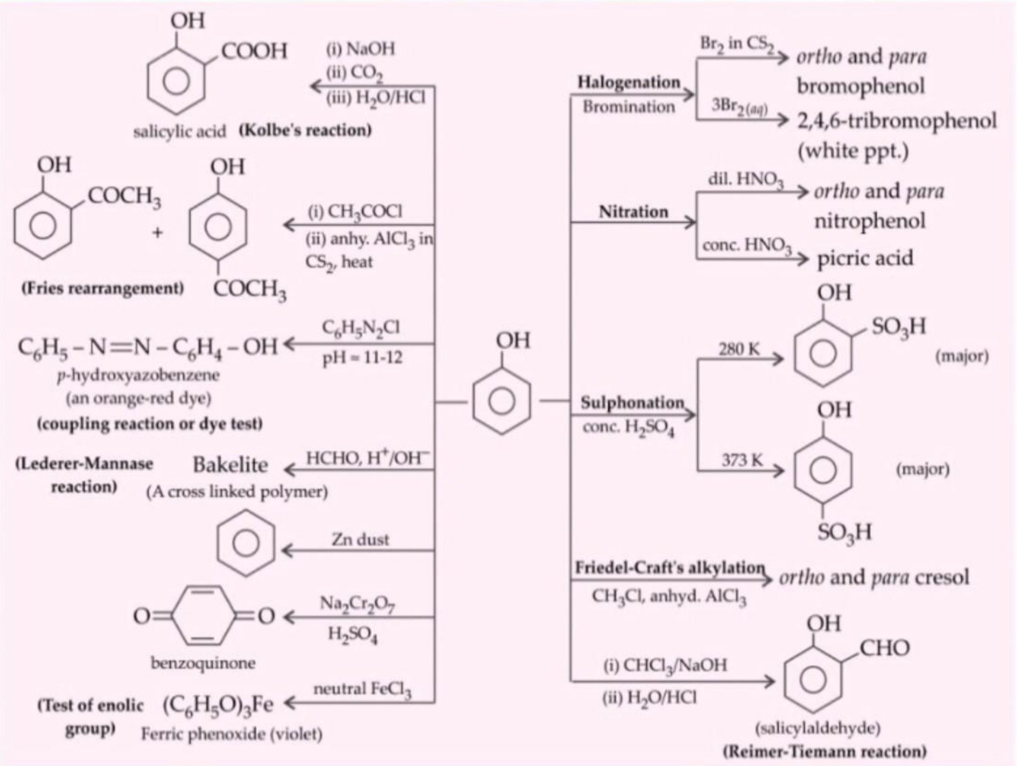
$$R\text{—OH} \xrightarrow[350^\circ C]{Al_2O_3} >C=C< + H_2O$$

$$R\text{—OH} \xrightarrow[Al_2O_3,\ 633\text{ K}]{NH_3} RNH_2 \xrightarrow[633\text{ K}]{ROH/Al_2O_3} R_2NH \xrightarrow[633\text{ K}]{ROH/Al_2O_3} R_3N$$

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

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

CHEMICAL PROPERTIES OF PHENOL



ETHERS

- Substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group ($R-O/Ar-O$) yields 'ethers' having general formula $C_nH_{2n+2}O$ ($n > 1$).

CLASSIFICATION OF ETHERS

Classification

- **Simple or symmetrical :** Having same R attached to O atom *e.g.*, $C_2H_5OC_2H_5$
- **Mixed or unsymmetrical :** Two R groups are different *e.g.*, $CH_3OC_2H_5$
- **Aliphatic ethers :** R and R' are both alkyl groups. *e.g.*, $CH_3-O-CH_2CH_3$
- **Aromatic ethers :** Either one or both R and R' are aryl groups. *e.g.*, $C_6H_5-O-CH_3$

ISOMERISM

Isomerism

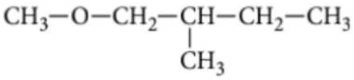
Functional

(i) CH_3-O-CH_3
Dimethyl ether

(ii) CH_3-CH_2-OH
Ethyl alcohol

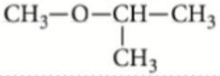
Chain

(i) $CH_3-O-C_5H_{11}$
Methoxy pentane

(ii) 
$$CH_3-O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$
1-Methoxy-2-methylbutane

Metamerism

Attachment of different alkyl groups.

(i) $CH_3CH_2OCH_2CH_3$
(ii) $CH_3OCH_2CH_2CH_3$
(iii) 
$$CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

PHYSICAL PROPERTIES

Physical properties

Physical state : Dimethyl ether and ethyl methyl ether are exceptionally gases at room temperature whereas all other ethers are colourless liquids with characteristic ethereal smell.

Solubility : Ethers are soluble in water to a certain extent due to hydrogen bonding. However, solubility decreases with increase of molecular mass *i.e.*, increase in the hydrocarbon part.

Boiling points : Ethers have lower boiling points than isomeric alcohols due to their inability to form hydrogen bonds and get associated.

Dipole moment : Ethers are polar in nature with a dipole moment varying from 1.15 D to 1.30 D. Since ethers have a bent structure, the polarities of two C—O bonds do not cancel each other.

METHODS OF PREPARATION

ETHERS

By dehydration of alcohols

$$ROH + HOR \xrightarrow[413\ K]{Conc.\ H_2SO_4}$$

$$ROH + HOR \xrightarrow{Al_2O_3,\ 633\ K}$$

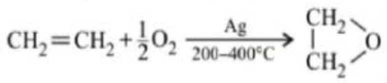
$$ROH + CH_2N_2 \xrightarrow{HBF_4}$$

From alkyl halides

$$2R-X + Ag_2O \xrightarrow{\Delta}$$

$$R-X + RONa \xrightarrow{\Delta}$$

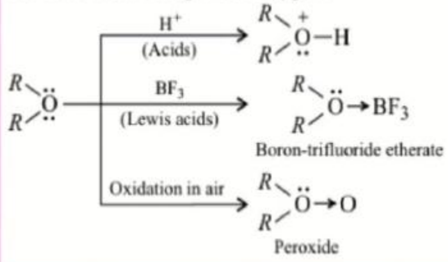
Preparation of cyclic ethers (or epoxides)



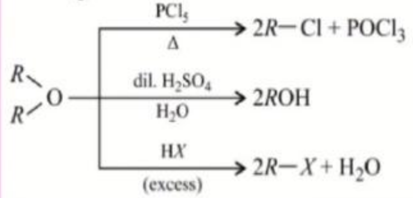
CHEMICAL PROPERTIES

ETHERS

Reactions of lone pair of oxygen



Cleavage of R—O—R bond



WRAP it up!

1. Identify *A* and *B* in the given reactions :

$$B \xleftarrow[H^+]{KMnO_4} (CH_3)_3COH \xrightarrow{KMnO_4/OH^-} A$$

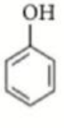
(a) *A* and *B* both are $(CH_3)_2C=CH_2$

(b) *A* and *B* both are $(CH_3)_2CO + CH_2O$

(c) *A* is $(CH_3)_3COH$, while *B* is $(CH_3)_2C=CH_2$ or $(CH_3)_2CO$

(d) *A* and *B* both are $(CH_3)_3COH$, *i.e.*, there is no reaction

2. Which one is the most acidic compound?

(a)


(b)