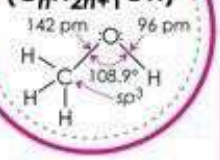
CONCEPT MAP

ALCOHOLS, PHENOLS AND ETHERS

Alcohols, phenols and ethers are the basic compounds of organic chemistry and they find wide applications in industry as well as in day-to-day life.

ALCOHOLS ($C_nH_{2n+1}OH$)



Physical properties

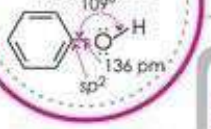
$$\text{B.pt.} \propto \text{No. of C-atoms} \propto \frac{1}{\text{Branching}}$$

$$\text{Solubility} \propto \frac{1}{\text{Size}} \propto \text{Branching}$$

Preparation

- $RX + KOH_{(aq.)} \rightarrow ROH + KX$
- $>C=C<$ (Alkene) $\xrightarrow[\text{(Markovnikov's addition)}]{\text{conc. } H_2SO_4/H_2O}$ $\xrightarrow[\text{(ii) } H_2O_2, OH^-]{\text{(i) } B_2H_6 \text{ in THF}}$ RCH_2OH (Anti-Markovnikov's addition)
- HCHO or $RCHO$ or $\begin{matrix}R\\R\end{matrix}>C=O$ (Carbonyl compounds)
  - Reduction: H_2/Pt or Pd or Ni; $NaBH_4$ or $LiAlH_4$ or Na/C_2H_5OH → RCH_2OH (1° Alcohol)
  - Grignard's reagent: (i) $RMgX$/Dry ether, (ii) H_2O/H^+ → $R-CH(OH)-R$ (2° Alcohol) or R_3C-OH (3° Alcohol)
- $RCOOH$ (Carboxylic acids) $\xrightarrow[\text{(ii) } H_2O^+]{\text{(i) } LiAlH_4 \text{ or } B_2H_6/\text{ether}}$ RCH_2OH

PHENOLS (C_6H_5OH)



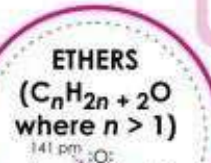
Physical properties

- Pure phenols are colourless liquids or solids.
- Form intermolecular hydrogen bonds hence, soluble in water.

Preparation

- $C_6H_5SO_3H \xrightarrow[-H_2O]{NaOH} C_6H_5SO_3Na \xrightarrow[573-623\ K]{NaOH} C_6H_5ONa \xrightarrow[-NaCl]{dil.\ HCl} C_6H_5OH$ (Phenol) ($-Na_2SO_3, -H_2O$)
- $C_6H_5N_2^+Cl^- + H_2O \xrightarrow[-N_2, -HCl]{dil.\ H_2SO_4,\ \Delta} C_6H_5OH$ (Phenol)
- $C_6H_5Cl + NaOH \xrightarrow[-NaCl, -H_2O]{623\ K,\ 320\ atm} C_6H_5ONa \xrightarrow[-NaCl]{dil.\ HCl} C_6H_5OH$ (Phenol)
- $C_6H_5CH(CH_3)_2$ (Cumene) $\xrightarrow[2.\ H^+, H_2O]{1.\ O_2}$ C_6H_5OH (Phenol) + CH_3COCH_3

ETHERS ($C_nH_{2n+2}O$ where $n > 1$)



Classification

- **Simple or symmetrical :** Same alkyl groups are attached to oxygen, *ROR*.
- **Mixed or unsymmetrical :** Different alkyl groups are attached to oxygen, *ROR'*.
- **Aliphatic ethers :** *R* and *R'* both are alkyl groups.
- **Aromatic ethers :** Either one or both *R* and *R'* are aryl groups.

Chemical properties

- **Reaction of ethereal oxygen :**

$$ROR + HCl(\text{conc.}) \longrightarrow \left[\begin{matrix}R\\R\end{matrix}>\overset{+}{O}-H\right] Cl^-$$

- **Cleavage of C – O bond :**

$R-OR + HX \xrightarrow{373\ K} R-OH + R-X$

– In case of alkyl aryl ethers, phenol and an alkyl halide are obtained.

$ROR + H_2O \xrightarrow[\Delta]{dil.\ H_2SO_4} 2R-OH$

$ROR + PCl_5 \xrightarrow{\Delta} 2R-Cl$

- **Reactions involving alkyl group :**
  – Formation of peroxides with air and light.
  – Substitution products obtained on halogenation.
- **Electrophilic substitution reactions :**
  Aryl alkyl ethers give *o*- and *p*-substituted products due to +*R* effect of alkoxy group (–*OR*).

Chemical properties

- **Cleavage of O—H bond :** Ease of reaction depends on stability of alkoxide ion.
  Acidity: Phenols > Water > 1° alcohol > 2° alcohol > 3° alcohol
- **Cleavage of C—OH bond :** Ease of reaction depends on stability of carbocations.
  Order of reactivity: 3° alcohol > 2° alcohol > 1° alcohol
- **Reactions involving whole alcohol molecule :**

Dehydration : $R-OH + \text{conc. } H_2SO_4 \xrightarrow[413\ K]{443\ K} >C=C<$ / ROR / $RO-SO_2OH$ (383 K)

$R-OH + Al_2O_3 \xrightarrow[633\ K]{513\ K} ROR$ / $>C=C<$

Oxidation : Alcohol $\xrightarrow{[O]}$ Aldehyde/Ketone $\xrightarrow{[O]}$ Carboxylic acid

Dehydrogenation : 1° alcohol $\xrightarrow{Cu/573\ K}$ Aldehyde

2° alcohol $\xrightarrow{Cu/573\ K}$ Ketone

Dehydration : 3° alcohol $\xrightarrow{Cu/573\ K} >C=C<$

Distinction tests

- **Dichromate test (oxidation) :** 1° alcohol → Acid with same number of C-atoms; 2° alcohol → Ketone with same number of C-atoms; 3° alcohol → No reaction under normal conditions.
- **Victor Meyer's test :** 1° alcohol → Blood red colour; 2° alcohol → Blue colour; 3° alcohol → Colourless.
- **Lucas test :** 1° alcohol → No turbidity; 2° alcohol → Turbidity in 5 minutes; 3° alcohol → Turbidity appears immediately.

Some important alcohols

- **Methanol :** Prepared by catalytic hydrogenation of carbon monoxide or water gas. It is used as a solvent, preservative, substitute for petrol, etc.
- **Ethanol :** Prepared by the hydration of ethene or by the fermentation of molasses. It is used as an antiseptic, power alcohol, in beverages, etc.

Chemical properties

- **Electrophilic substitution of phenols :** Halogenation, sulphonation, nitration, Friedel—Crafts alkylation, etc. occur at *o*- and *p*- positions due to activating effect of —OH group.

Tests to distinguish phenols from alcohols

- **$FeCl_3$ test :** Gives violet colour
- **$Br_2 - H_2O$ test :** Gives white ppt.
- **Liebermann's nitroso test :** Gives blue colour which turns red on dilution
- **Ammonia/Sodium hypochlorite test :** Gives blue colour
- **Azo dye test :** Gives orange colour

Physical properties

- Dipolar due to slightly polar C—O bonds.
- B.pts. are lower than isomeric alcohols due to lack of hydrogen bonding.
- Solubility in water $\propto \frac{1}{\text{Molecular mass}}$ (soluble due to formation of H–bonds with water)
- Fairly soluble in organic solvents.
- Lighter than water.

Preparation

- $2ROH \xrightarrow[\text{or } Al_2O_3,\ 523\ K]{\text{conc. } H_2SO_4,\ 413\ K}$ ROR (Ether)
- $RX + RONa \xrightarrow[-NaX]{\Delta}$ ROR (Ether) (Williamson synthesis)
- Williamson synthesis involves S_N2 mechanism in case of 1° alkyl halides.
- In the case of 2° and 3° alkyl halides, elimination takes place.
- Dehydration of alcohols for the formation of ethers follows the order : 1° > 2° > 3°

Uses

Ethers are used as industrial solvents, heat transfer medium (diphenyl ether), flavouring agents and in perfumes.