Acohal

Aliphatic organic compounds containing OH group as F.G. (R–OH)

$C_nH_{2n+1}OH$

- **Monohydric alcohols** — having one OH group
  - E.g.: CH_3CH_2OH Ethanol
  - $CH_3CH_2CH_2OH$ Propanol
- **Polyhydric alcohols**
  - **Dihydric** — Alcohol having 2 (OH) groups
    - E.g. CH_2-CH_2 (OH, OH) Ethylene (Ethane 1,2 diol) glycol
  - **Trihydric** — Alcohol having 3 (OH) groups
    - E.g. $CH_2-CH_2-CH_2$ (OH, OH, OH) Propane 1,2,3 triol (glycerol)

Classification of Monohydric

- **Primary alcohol** — OH is attach with primary carbon.
  - E.g. CH_3-CH_2-OH (1° carbon) Primary alcohol
  - $CH_3CH_2CH_2OH$ Primary alcohol
- **Secondary alcohol** — OH is attach with secondary carbon.
  - E.g. $CH_3-CH(OH)-CH_3$ (2° carbon) Secondary alcohol (Propan-2-ol)
- **Tertiary alcohol** — OH is attach with tertiary carbon.
  - E.g. $CH_3-C(CH_3)(OH)-CH_3$ (3° carbon) Tertiary alcohol (2-methyl propan-2-ol)

Reactions of alcohols:-

(a) Combustion:- Burn completely in air to form $CO_2 + H_2O$ + heat

$CH_3-OH + 2O_2 \longrightarrow CO_2 + 2H_2O$ + heat

(b) Rxn with $SOCl_2$, PX_3 to produce R–X:-

$R-CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} RCH_2Cl + SO_2 + HCl$

$3R-OH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$

$5R-OH + PCl_5 \longrightarrow 5R-Cl + H_3PO_4 + H_2O$

(c) Reaction with HX:-

$R-OH + HBr \longrightarrow R-Br + H_2O$ (alkyl halide)

Lucas test:-

(a) 3° alcohol:- → immediately oily layer

$CH_3-C(CH_3)_2-OH + HCl \longrightarrow CH_3-C(CH_3)_2-Cl + H_2O$

(Tertiary alcohol) (Tertiary butyl alcohol)

(b) 2° alcohol:- → oily layer after 5 minutes

$CH_3-CH(CH_3)-OH + HCl \xrightarrow[\text{anhydrous}]{ZnCl_2} CH_3-CH(CH_3)-Cl + H_2O$

Secondary alcohol

(c) 1° alcohol:- → oily layer on heating.

$CH_3-CH_2-OH + HCl \xrightarrow[\text{anhydrous}]{ZnCl_2} CH_3-CH_2-Cl + H_2O$

Primary alcohol

3° alcohol > 2° Alcohol > 1° alcohol

(d) Reaction with KBr

$R-OH + KBr + H_2SO_4 \longrightarrow R-Br + H_2O + KHSO_4$

(e) Dehydration of alcohol:-

$CH_3CH_2OH \xrightarrow[180°C]{\text{conc } H_2SO_4} CH_2=CH_2 + H_2O$ Elimination alkene

$2CH_3CH_2OH \xrightarrow[140°C]{\text{conc } H_2SO_4} CH_3CH_2O-CH_2CH_3 + H_2O$ Diethyl ether

(f) Formation of Ester:-

$CH_3-C(=O)-OH + C_2H_5OH \underset{\text{conc}}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3-C(=O)-OC_2H_5 + H_2O$

Acetic acid

Carboxylic + alcohol ⟶ Ester

Preparations:-

(a) By electrophilic addition of steam to alkene

$CH_2=CH_2 + H-OH \xrightarrow{H^+} CH_3-CH_2-OH$

(b) By the reaction of alkene with $KMnO_4$

$5CH_2=CH_2 + 2H_2O + 2MnO_4^- + 6H^+ \longrightarrow 5CH_2(OH)-CH_2(OH) + 2Mn^{2+}$

alkene ⟶ oxidized ⟶ alcohol (1,2 ethanediol)

(c) By the substitution of haloalkane:-

$R-Br + OH^- \xrightarrow{NaOH} R-OH + Br^-$

(d) By Reduction of carbonyl compound:-

$H-C(=O)-H + 2[H] \xrightarrow{LiAlH_4} H-CH(OH)-H$

Methanal → Methanol

Aldehyde ⟶ Reduced ⟶ 1° Alcohol

$R-C(=O)-R + 2[H] \xrightarrow{LiAlH_4} R-CH(OH)-R$

Ketone ⟶ Reduced to ⟶ 2° Alcohol

(e) By the reduction of carboxylic acid:-

$R-COOH + 4[H] \xrightarrow{NaBH_4/LiAlH_4} R-CH_2-OH + H_2O$

carboxylic acid ⟶ reduced to ⟶ 1° alcohol

(f) Hydrolysis of Ester:-

$CH_3-C(=O)-OC_2H_5 \underset{H^+ \text{(acid)}}{\overset{H-OH}{\rightleftharpoons}} CH_3-C(=O)-OH + C_2H_5OH$

Ethyl acetate → Acetic acid + alcohol (Ethanol)

$CH_3-C(=O)-OC_2H_5 \xrightarrow[\text{dilute alkali}]{NaOH} CH_3-C(=O)-ONa + C_2H_5OH$

Ethyl acetate → Sodium acetate + alcohol (Ethanol)

Acidity of Alcohol:-

$2R-OH + 2Na^+ \longrightarrow 2R-ONa + H_2$

$2H^{+\delta}-OH^{-\delta} + Na^+ \longrightarrow NaOH + H_2$

$R-O^{-\delta}H^{+\delta}$ — alkyl weak e⁻ donor (H^+ weak acid) (alcohol is less polar)

$H^{+\delta}-OH^{-\delta}$ — (water is more polar) H^+ good acid. Polarity & acidic nature

(a) Oxidation of Alcohol:-

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

orange → Green

(a) Primary alcohol:-

$$CH_3-CH_2-OH + [O] \xrightarrow[50^\circ c]{K_2Cr_2O_7 + H_2SO_4} CH_3-C(=O)-H$$

remove

1° alcohol ⟶ aldehyde

$$CH_3-C(=O)-H + [O] \xrightarrow[50^\circ c]{K_2Cr_2O_7 + H_2SO_4} CH_3-C(=O)-H$$

Aldehyde —oxidized→ carboxylic acid

(b) Secondary alcohol:-

$$CH_3-CH(CH_3)-OH + [O] \xrightarrow[50^\circ c]{K_2Cr_2O_7,\ H_2SO_4} CH_3-C(=O)-CH_3 + H_2O$$

2° alcohol —oxidized→ ketone

(c) Tertiary alcohol:-

- does not oxidized

$$CH_3-CH_2-C(CH_3)_2-OH \xrightarrow[\Delta]{K_2Cr_2O_7,\ H_2SO_4} CH_3-CH=C(CH_3)_2 + H_2O$$

2-Methyl-2-butanal — 2-Methyl-2-butene

3° alcohol —X not oxidized→ alkene

(b) Iodoform reaction:- (Ppt yellow)

1° alcohol ⟶ Ethanol

2° alcohol ⟶ one CH_3 group (CH_3-CH

3° alcohol ⟶ do not give this test

- Alcohol treated I_2 and Excess NaOH

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O$$

- 2° alcohol having $-CH_3$ group on one side give this test (46 → 55)

$$R-CH(OH)-CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + RCOONa + 5NaI + 5H_2O$$

3° alcohol does not give this test.

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