Alcohols/Alkanols

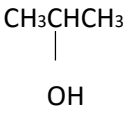
These are organic compounds that contain at least one hydroxyl group (-OH) attached to saturated carbon atom.

Classification

(a) According to the number of –OH group

(i) Monohydric alcohols have one hydroxyl (-OH) group Example

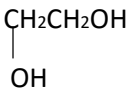
CH_3CH_2OH ethanol

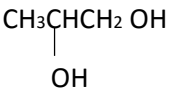


Propan-2-ol

(ii) Dihydric alcohols or glycols have two hydroxyl groups

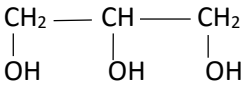
Examples





Ethan-1,2-diol Propane-1,2-diol

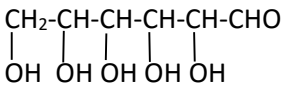
(iii) Trihydric alcohols have three hydroxyl groups.



Propane-1,2,3-triol

(iv) Polyhydric alcohols or polyol contain more than three hydroxyl groups

e.g. Sugar



(b) Classification of monohydric alcohols

They are classified according to the number of alkyl groups attached to the carbon atom that bear a hydroxyl (OH) group.

(i) Primary alcohols have one alkyl group attached to the carbon atom that carry OH group, i.e. ROH.

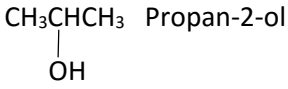
Example

CH_3CH_2OH Ethanol

$CH_3CH_2CH_2OH$ Propan-1-ol

(ii) Secondary alcohol: have two alkyl groups attached to the carbon atom that bear OH group, i.e. R_2CHOH

Example

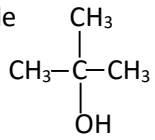


Propan-2-ol

(iii) Tertiary alcohols: have three alkyl groups attached to a carbon atom that bear OH group

i.e. R_3COH

Example

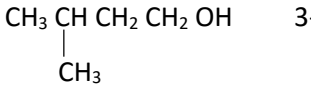


2-Methylpropan-2-ol

Nomenclature

(a) Are named by replacing the final "e" in the corresponding alkanes with "ol"

(b) The hydroxyl group is taken as a substituent group, and its position is given by numbering the carbon atoms in the chain from from the side nearest to the carnon atom tha t carry OH group.
Examples



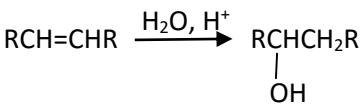
3-Methybutan-1-ol

Physical properties

1. Alcohols have high melting and boiling points than corresponding hydrocarbon of similar molecular masses due to intermolecular hydogen bonds.consequently alcohols ate either liquids or solids.
   Example
   Propane (44) Bpt = -42^0C
   Ethanol (46) Bpt = 78^0C
2. Lower members are completely soluble in water due to the formation of hydrogen bonds withwater. But solubility of alcohols decrease as alkyl group leghths increase due to increase in "alkane like" character.

Preparation of alcohols

(a) Industrial preparation
   (i) From petroleum products,e.g. alkenes



(ii) Fermentation of sugars

Ethanol can be made by fermentation of sugars. Fermentation is usually carried out by adding yeast to a mixutre of sugar and water.

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2CH_3CH_2OH + 2CO_2(g)$$

(iii) Methanol is produced by catalytic reduction of carbon mono xide.

$$CO(g) + 3H_2(g) \xrightarrow[300\text{-}400^0/200\text{-}300atm]{Cr_2O_3/ZnO} CH_3OH$$

(b) Laboratory preparation

(i) Hydration of alkenes in presence of acid catalyst

$$CH_3CH_2CH{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

(ii) By hydrolysis of alkyl halides using aqueous alkali

$$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \xrightarrow[\text{Reflux}]{\text{-OH}} CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

(iii) By reduction of carbonyl compounds (aldehyde and ketones) using lithium aluminium hydride ($LiAlH_4$) in presence of dry ether.

$$CH_3CH_2CHO \xrightarrow{LiAlH_4,\ \text{dry ether}} CH_3CH_2CH_2OH$$

$$CH_3CH_2COCH_3 \xrightarrow{LiAlH_4,\ \text{dry ether}} CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

(iv) Reduction of carboxylic acids using $LiAlH_4$ in dry ether

$$CH_3CH_2COOH \xrightarrow{LiAlH4,\ \text{dry ether}} CH_3CH_2CH_2OH$$

Absolute ethanol

All aqueous solutions of ethanol yield, on fractional distillation a constant boiling mixture (azeotrope) of 96% ethanol and 4% water known as rectified spirit.

(i) In the laboratory rectified spirit is stored over quick lime overnight. Quick lime dehydrates the mixture; then pure ethanol called absolute ethanol is distilled.

$$CaO\ (s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

(ii) In industry, benzene is added to the rectified spirit. Distillation yields three fractions
At 65^0C a constant boiling mixture of ethanol, benzene and water.
At 68^0C a constant boiling mixture of ethanol and water
At 78^0C pure ethanol distills of

Reactions of monohybrid alcohol

a. Cleavage of O-H bond
b. Cleavage od C-O bond
c. Oxidation
d. Dehydration

(a) Cleavage of O-H bond

(i) Behavior as a weak acid

$$2ROH + 2Na \longrightarrow RO^-Na^+ + H_2(g)$$

Acidity: primary alcohol> secondary alcohol>tertiary alcohol

(ii) Behavior as a base

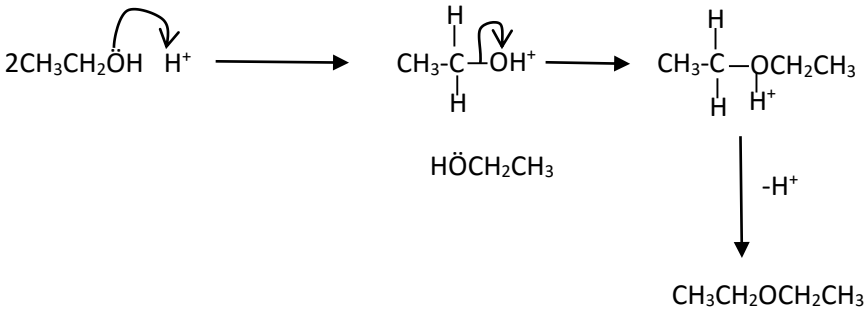
$$ROH + H^+ \longrightarrow RO^+H_2$$

(iii) Formation of ether

Ethanol reacts presence of concentrated sulphuric acid at 140^0C to form diethyl ether.

$$2CH_3CH_2OH \xrightarrow[140^0C]{\text{Conc. } H_2SO_4} CH_3CH_2OCH_2CH_3$$

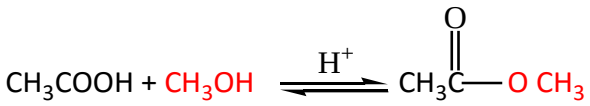
Mechanism



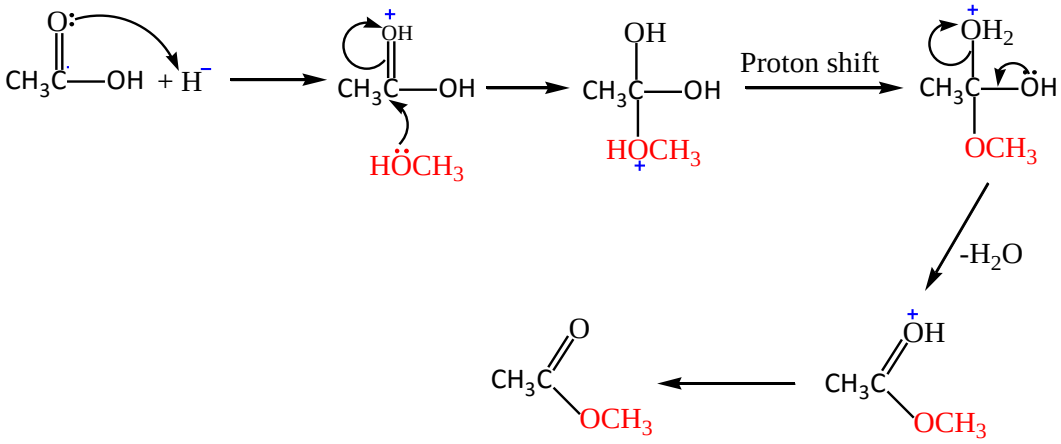
(iv) Formation of esters

(a) Alcohols react with carboxylic acids in the presence of a mineral acid (phosphoric or sulphuric acid) to form esters. However, this is not a good method because the reaction is reversible and does not go to completion.

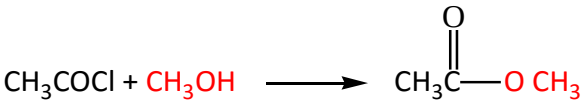
Example



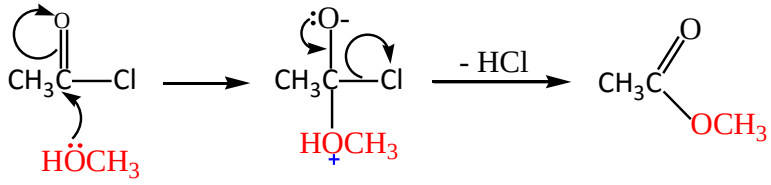
Mechanism



(b) Alcohols react with acid halides to form esters.

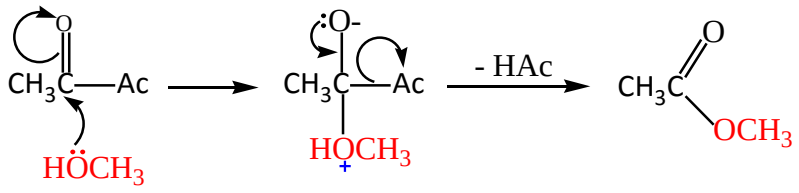


Mechanism



(c) Alcohols react with acid anhydride to form esters.

Mechanism



(b) Cleavage of C-O bond

Formation of alkyl halide

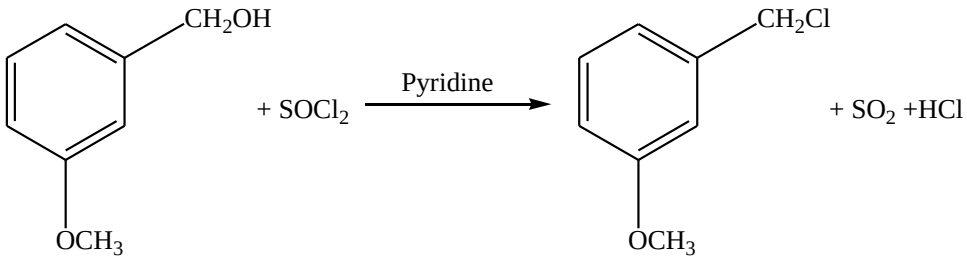
Alcohols react with a variety of reagents to yield alkyl halides. The most commonly used reagents are hydrogen halides (HCl, HBr and HI) phosphorus tribromide (PBr_3) and thionyll chloride.

Examples

(i) $CH_3-C(CH_3)_2-OH + HCl(conc.) \xrightarrow{25^0} CH_3-C(CH_3)_2-Cl + H_2O)$

(ii) $CH_3CH_2CH_2CH_2OH + HBr\ (conc.) \xrightarrow{reflux} CH_3CH_2CH_2CH_2Br$

(iii) $3CH_3-CH(CH_3)CH_2OH + PBr_3 \longrightarrow 3CH_3-CH(CH_3)CH_2Br + H_3PO_3$

(iv) 

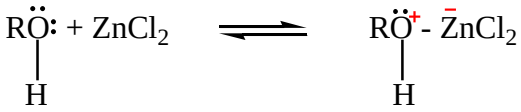
The order of reactivity of hydrogen halides is HI> HBr> HCl whereas the order of reactivity of alcohols is 3^0> 2^0> 1^0. The reaction of HCl with alcohol is catalyzed by anhydrous zinc chloride. The reaction is used to distinguish between primary, secondary and tertiary alcohols.

Tertiary alcohol react readily with HCl in presence of anhydrous zinc chloride to form an insoluble chloride giving two layers immediately.

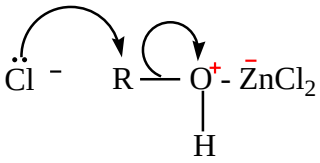
Secondary alcohols form two layer in 50 -10minutes

Primary alcohol do not form layers at room temperature.

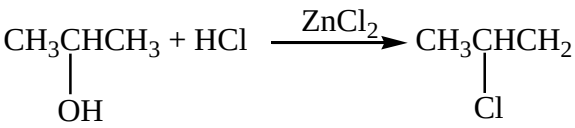
Mechanism



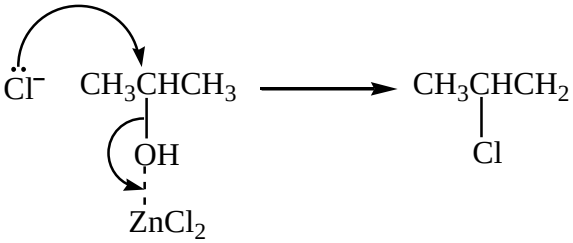
Then,



Example



Mechanism



(c) Oxidation

(i) Alcohols are burnt in oxygen to produce carbon dioxide, water and heat. Due to production of heat on combustion, alcohols are used as fuel.

(ii) Mild oxidizing agents like acidified potassium dichromate oxidize primary alcohols to aldehydes and then, to carboxylic acids. Secondary alcohols are oxidized to ketones.

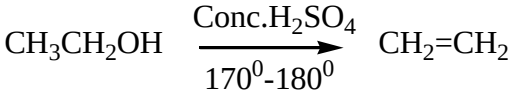
Tertiary alcohols are not oxidized by potassium dichromate and therefore acidified potassium dichromate is used to distinguish tertiary alcohols from primary or secondary alcohols. When reacted with primary or secondary alcohol, the color of acidified potassium dichromate changes from orange to green.

(d) Dehydration of alcohol

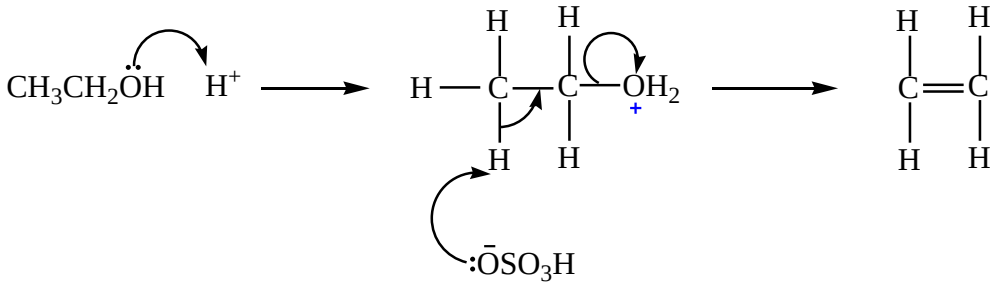
Alcohols are dehydrated by hot concentrated sulphuric or phosphoric acid to form alkenes. The mechanisms depend on the class of alcohols.

(i) Primary alcohol undergo elimination bimolecular; E2.

Example

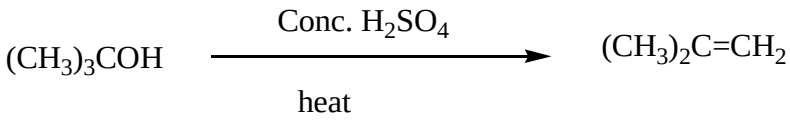


Mechanism

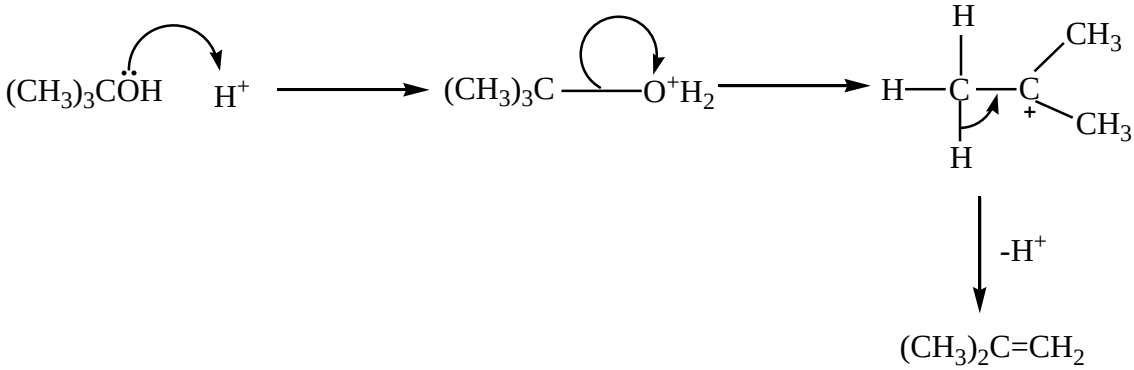


(ii) Tertiary alcohols undergo elimination unimolecular; E1.

Example



Mechanism



(iii) Secondary alcohol undergo either E2 or E1 mechanism

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