ALCOHOLS

They have a general molecular formula $C_nH_{2n+1}OH$ where n=1, 2, 3…
It can be generally represented by ROH where R is an alkyl group.
The functional group is the hydroxyl group (-OH group).

Classes of alcohols

There are three classes of alcohols namely;

(i) **Primary alcohols (1^o)**. These have one alkyl group attached to the carbon atom with a hydroxyl group.i.e. RCH_2OH e.g. CH_3CH_2OH (Ethanol). $CH_3CH_2CH_2OH$ (Propan-1-ol),etc

(ii) **Secondary alcohols (2^o).**These have two alkyl groups attached to the carbon atom with a hydroxyl group.i.e. $R\underset{\underset{OH}{|}}{C}HR$ e.g $CH_3\underset{\underset{OH}{|}}{C}HCH_3$ (Propan-2-ol)

$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3$ (Butan-2-ol), etc

(iii) Tertiary alcohols (3^o). These have three alkyl groups attached to the carbon atom with a hydroxyl group. i.e. $R-\overset{\overset{R}{|}}{\underset{\underset{OH}{|}}{C}}-R$ e.g $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_3$

(2-methylpropan-2-ol)

Nomenclature of alcohols

- The longest continuous carbon chain bearing the hydroxyl group should be chosen as the parent chain
- The ending "e" in alkanes is replaced with "ol" in the corresponding alcohols.
- The carbon atom with the hydroxyl group is given the smallest number possible following either right to left or left to right numbering.
- The alkyl groups present are identified by nature and position. If they are more than one similar, prefixes di, tri, tetra-etc are used. If the alkyl groups are more than one and different, alphabetical orders are followed .

Examples

CH_3OH Methanol

CH_3CH_2OH Ethanol

CH_3CHCH_3 (with OH on C-2) Propan-2-ol

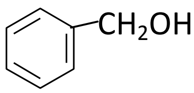
$\quad\;\; OH$

$CH_3CH_2CH_2OH$ propan-1-ol

$\qquad\qquad\quad CH_3$

$CH_3CH_2CH_2CHCHCH_3$ 3-methylhexan-2-ol

$\qquad\qquad\qquad\quad OH$



Phenyl methanol

N.B

- If there is more than one hydroxyl groups in a compound, then the suffix di, tri, tetra, etc are used to represent how many they are and also locate their positions.e.g

CH_2CH_2 Ethane-1,2-diol

$OH\ OH$

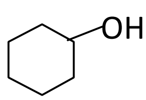
CH_3CHCH_2OH Propane-1,2-diol

$\quad\;\; OH$

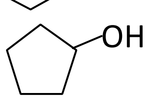
CH_2CHCH_2 Propane-1,2,3-triol

$OH\ OH OH$

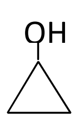
- Alcohols with one hydroxyl group are called monohydric alcohols while those with many hydroxyl groups are called polyhydric alcohols.
- Cyclic alcohols are named with a prefix “cyclo” before the parent chain.e.g



Cyclohexanol



Cyclopentanol



Cyclopropanol

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Isomerism in organic compounds

Alcohols exhibit chain, position and functional group isomerism.

Qn. Write the structural formulae and IUPAC names of all the possible isomers of $C_4H_{10}O$.

Solution

$CH_3CH_2CH_2CH_2OH$ Butan-1-ol

$CH_3CH_2\underset{|}{C}HCH_3$ Butan-2-ol
$\qquad\qquad OH$

$\qquad CH_3$
$\qquad\ |$
$CH_3\underset{|}{C}CH_3$ 2-methylpropan-2-ol
$\qquad OH$

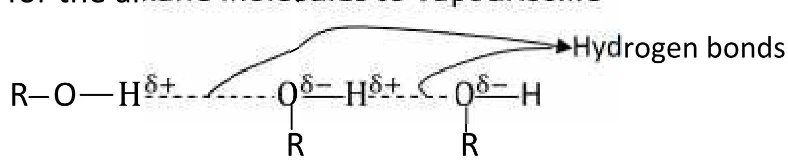
$CH_3\underset{|}{C}HCH_2OH$ 2-methylpropan-1-ol
$\qquad CH_3$

$CH_3CH_2OCH_2CH_3$ Ethoxyethane (diethyl ether)

$CH_3CH_2CH_2OCH_3$ methoxypropane (methylpropyl ether)

PHYSICAL PROPERTIES OF ALCOHOLS

1. Physical state.
   Lower members are liquids while higher members are solids with a characteristic alcohol smell.
2. Boiling points.
   (a) The boiling of alcohols is higher than those of alkanes of similar molecular masses.
   Explaination
   This is because in liquid phase the alcohol molecules associates via intermolecular hydrogen bonds which are stronger and requires much energy to be broken for the molecules to vapourise. Alkane molecules are held by the weak Vander Waals forces of attraction and these requires less energy to be broken for the alkane molecules to vapourise.i.e



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Qn. Explain the following observation.

Ethanol boils at a higher temperature than ethane of almost similar molecular mass.

(b) The boiling point of alcohols increases with increase in molecular weight.

Explaination

This is because the magnitude of the vander waals forces of attraction increases with increase in molecular weight. As the magnitude of vander waals forces of attraction increases,the energy required to break these forces increases and hence the boiling point increases.

Qn. Explain the following observation.

Propan-1-ol boils at a higher temperature than ethanol.

(c) The boiling point of alcohols decreases with increase in branching.

Qn. Explain the following observation

Butan-1-ol boils at 118^{o}C while 2-methylpropan-2-ol boils at 83^{o}C.

Explaination

In both cases the forces holding the molecules together are the vander waals forces of attraction and the hydrogen bonds.Butan-1-ol molecules are in a straight chain and therefore closely packed thus the vander waals forces of attraction between these molecules are stronger than those between the 2-methylpropan-2-ol molecules which are branched and far apart.

3. Solubility

The low molecular weight alcohols are soluble in water e.g methanol and ethanol. This is because they form hydrogen bonds with water molecules. However the solubility in water decreases with increase in the molecular weight of the alcohol.

N.B

Solutions of alcohols are neutral to litmus.i.e in alcohol solutions, the blue litmus paper remains blue and the red litmus paper remains red.

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METHODS OF PREPARATION OF ALCOHOLS

1. Hydration of alkenes.

   Warming of alkenes with concentrated sulphuric acid in presence of water forms alcohols e.g

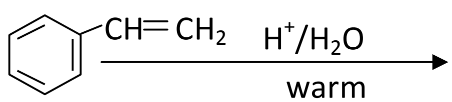
$$CH_3CH{=}CH_2 \xrightarrow[\text{warm}]{\text{Conc } H_2SO_4\ /\ H_2O} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$CH_3CH{=}CH_2 \xrightarrow{\quad} H^+ \qquad CH_3\overset{+}{C}HCH_3 \quad H_2O{:} \xrightarrow{\quad} CH_3\underset{\displaystyle \overset{}{\underset{+}{O}}H_2}{\underset{|}{C}}HCH_3 \xrightarrow{-H^+} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

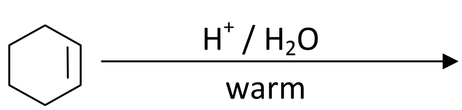
Qn. Complete the following equations and in each case outline the mechanism for the reaction that took place.

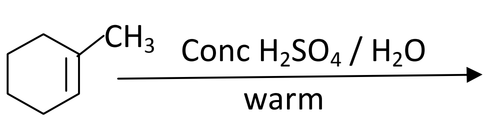
(a) 

(b) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow[\text{heat}]{\text{Conc } H_2SO_4\ /\ H_2O}$

(c) $CH_3CH{=}CHCH_3 \xrightarrow[\text{warm}]{H^+\ /\ H_2O}$

(d) $CH_2{=}CH_2 \xrightarrow[\text{(ii) } H_2O\text{ , warm}]{\text{(i) Conc } H_2SO_4}$

(e) 

(f) 

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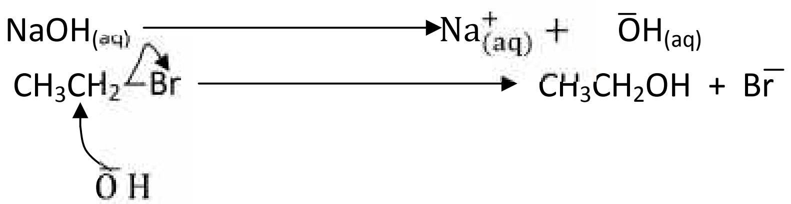
2. Reaction of alkyl halides with hot sodium or potassium hydroxide solution.

Examples

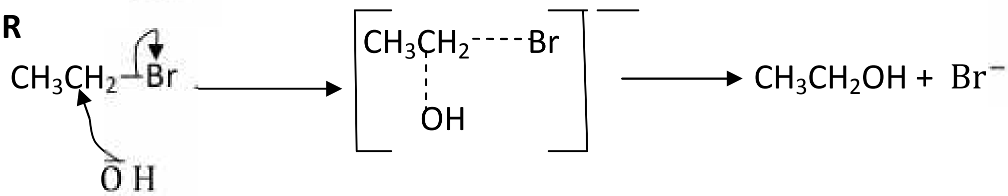
(a) With primary alkyl halides the reaction is S_N2 e.g

$$CH_3CH_2Br \xrightarrow[\text{Heat}]{NaOH_{(aq)}} CH_3CH_2OH + NaBr$$

Mechanism



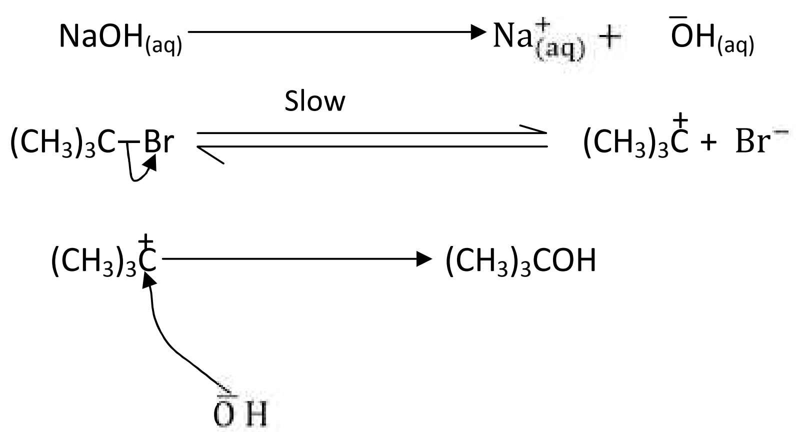
OR



(b) With tertiary alkyl halides the reaction is S_N1 e.g

$$(CH_3)_3CBr \xrightarrow[\text{Heat}]{NaOH_{(aq)}} (CH_3)_3COH + NaBr$$

Mechanism



3. Reaction of Grignard reagents with carbonyl compounds.

(a) Primary alcohols are obtained by reacting Grignard reagents with methanal (HCHO) and the product hydrolysed.i.e

$$CH_3Br \xrightarrow[\text{dry ether}]{Mg} CH_3MgBr \xrightarrow[\text{(ii) } H^+ / H_2O]{\text{(i) HCHO / dry ether}} CH_3CH_2OH$$

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(b) Secondary alcohols are obtained by reacting Grignard reagents with other aldehydes and the product hydrolysed.i.e

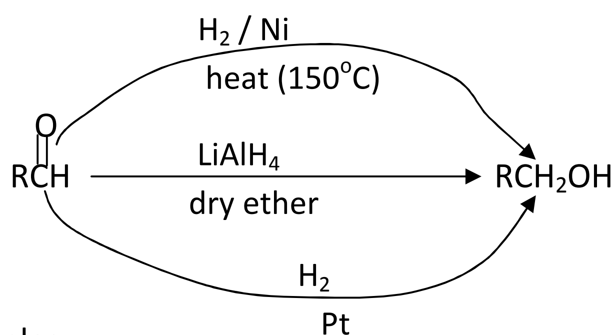
$$CH_3I \xrightarrow[\text{dry ether}]{Mg} CH_3MgI \xrightarrow[\text{(ii) } H^+ / H_2O]{\text{(i) } CH_3CHO \text{ / dry ether}} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

(c) Tertiary alcohols are obtained by reacting Grignard reagents with ketone and the product formed hydrolysed.i.e

$$CH_3Cl \xrightarrow[\text{dry ether}]{Mg} CH_3MgCl \xrightarrow[\text{(ii) } H^+ / H_2O]{\text{(i) } CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3 \text{ / dry ether}} CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle \overset{|}{OH}}{\overset{|}{C}}}CH_3$$

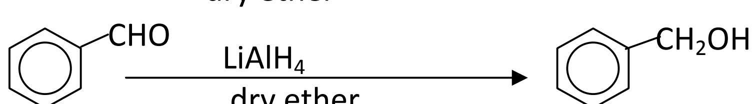
4. Reduction of carbonyl compound using lithium aluminium hydride (Lithium tetrahydridoaluminate, $LiAlH_4$) in presence of dry ether or hydrogen in presence of platinum or heated nickel at 150^{o}C.

(a) Aldehydes are reduced to primary alcohols i.e



Examples

$$CH_3CHO \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2OH$$



Benzaldehyde

Phenylmethanol

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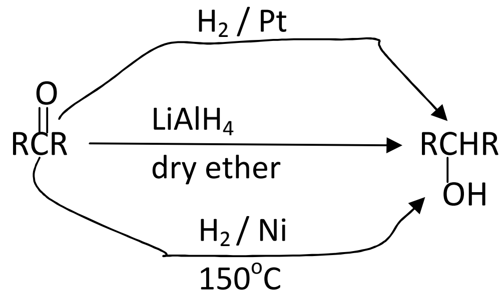
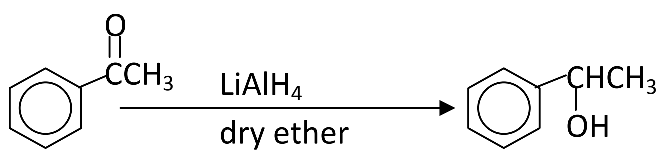
(b) Ketones are reduced to secondary alcohols.



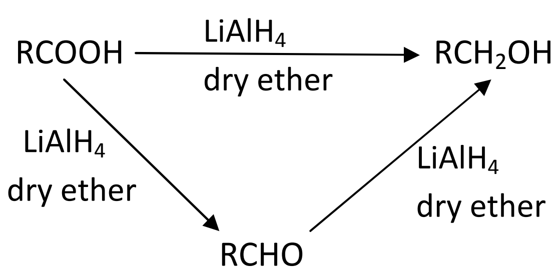
Examples

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3\underset{OH}{\underset{|}{C}}HCH_3$$

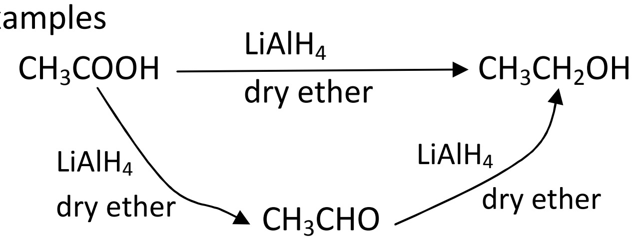


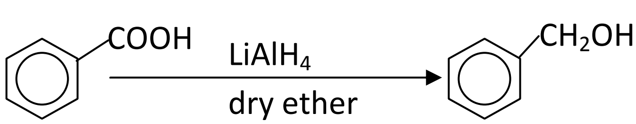
Phenylethanone Phenylethanol

5. Reduction of carboxylic acids using lithium aluminium hydride.
   Carboxylic acids are reduced to primary alcohols.i.e



Examples





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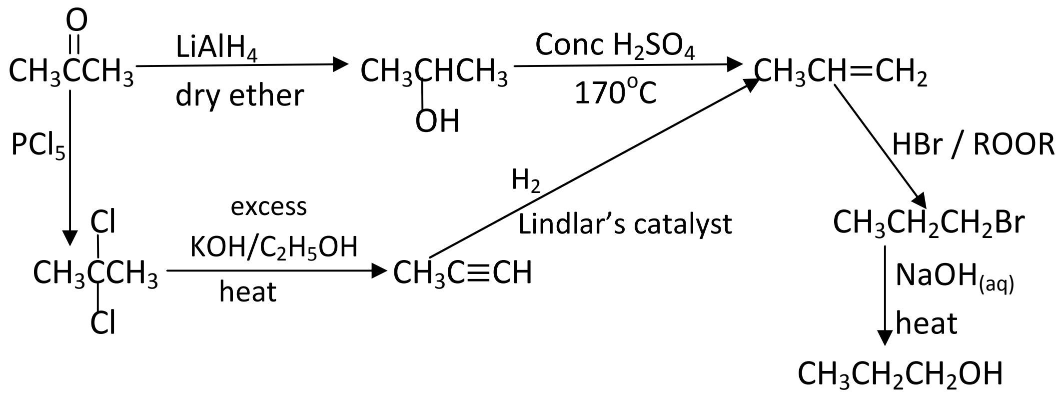
Qn. Using equations only show how the following conversions can be made.

(a) $CH_3\overset{\overset{O}{||}}{C}CH_3$ to $CH_3CH_2CH_2OH$

Solution



(b) CH_3COOH to $CH_3C\equiv CH$

Solution

$$CH_3COOH \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2OH \xrightarrow[180^oC]{Conc\ H_2SO_4} CH_2{=}CH_2 \xrightarrow[CCl_4]{Cl_2} \underset{\underset{Cl}{|}}{C}H_2\underset{\underset{Cl}{|}}{C}H_2$$

$$\underset{\underset{Cl}{|}}{C}H_2\underset{\underset{Cl}{|}}{C}H_2 \xrightarrow[\text{heat}]{KOH/C_2H_5OH} HC\equiv CH \xrightarrow{Na/Liquid\ NH_3} HC\equiv\bar{C}Na^+ \xrightarrow{CH_3Cl} CH_3C\equiv CH$$

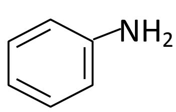
Qn. Use equations to show how the following conversions can be made.

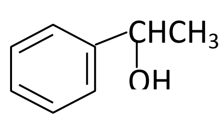
(i) CH_3CHO to $CH_3\underset{\underset{Br}{|}}{C}HCH_2Br$

(ii) Benzene to phenylmethanol

(iii) Ethanoic acid to propan-2-ol

(iv) Butan-1-ol to propanone

(v) 

to 

(vi) Propanone to But-2-yne

(i) Phenylethanone to phenylethene

(ii) Carbon to butan-2-ol

(iii) Butanoic acid to ethanol

(iv) Cyclohexanone to cyclohexane.

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INDUSTRIAL MANUFACTURE OF ETHANOL

Ethanol is mainly prepared by fermentation process.

Fermentation is the process by which carbohydrates (starch or sugar) is converted to ethanol by yeast enzyme.

The main sources of starch materials include millet, sorghum, cassava, banana, rice, potatoes, maize, wheat, etc and molasses is the main source of sugars.

(a) Fermentation of starch

Maize grains, millet, wheat, barley or cassava are soaked in water. They are then removed from water and allowed to dry in warm air for a few days. This allows them to germinate and malt is formed (malt is germinated cereal grains that have been dried)

The malt is then crushed and mixed with a mash of starch materials in water at a temperature of about 55°C.

The malt contains an enzyme called diastase which catalyses the hydrolysis of starch to maltose.

$$\underset{\text{Starch}}{2C_6H_{10}O_5} + H_2O \xrightarrow{\text{Diastase}} \underset{\text{maltose}}{C_{12}H_{22}O_{11}}$$

Yeast is added to the mixture at room temperature (or temperatures of about 35°C) and one of the enzymes in yeast called maltase catalyses the hydrolysis of maltose to glucose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Another enzyme in yeast called zymase catalyses the conversion of glucose to ethanol and carbon dioxide.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

The ethanol obtained is only about 11% ethanol and can be concentrated to about 96% ethanol by fractional distillation.

(b) Fermentation of sugars.

Molasses containing sugar (sucrose) is mixed with hot water. Yeast is added to the mixture. The mixture is allowed to ferment for several days.
One of the enzymes in yeast called Sucrose catalyses the hydrolysis of sucrose to glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Sucrase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Another enzyme in yeast called zymase catalyses the decomposition of glucose to ethanol and carbon dioxide.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

The ethanol obtained is only about 11% ethanol and can be concentrated to about 96% ethanol by fractional distillation.

Uses of ethanol

- Used as a drink (a beverage)
- Used as a disinfectant
- Used as fuel
- Used as a liquid in the thermometer
- Used as a solvent for perfumes ,vanishes ,paints
- Used in the manufacture of organic compounds such as ethanoic acid

Disadvantage of drinking ethanol

- It is a drug and affects the central nervous system.
- Leads to loss of coordination when consumed in large amounts which may even cause death.

N.B

Methanol can be prepared industrially as follows.

- Methane obtained from natural gas is mixed with steam and passed over heated catalyst of nickel at 900^oC and 30 atmosphere pressure to form synthesis gas (water gas i.e a mixture of carbon monoxide and hydrogen gas)

$$CH_{4(g)} + H_2O_{(g)} \xrightarrow[900^oC\text{ , 30 atm}]{\text{Ni catalyst}} CO(g) + 3H_{2(g)}$$

Or

- Steam is passed through white hot coke to form water gas'

$$C_{(s)} + H_2O_{(g)} \xrightarrow{1300^oC} CO_{(g)} + H_{2(g)}$$

The mixture (water gas) is passed over heated catalyst of zinc oxide and chromium (III) oxide at a temperature of 300^oC and pressure of 300 atm to form methanol.

$$CO + 2H_2 \xrightarrow[300^oC\ ,\ 300\ atm]{ZnO\ /\ Cr_2O_3\ cat} CH_3OH$$

Qn.

(a) Name the locally available raw materials from which ethanol can be manufactured.
(b) Describe briefly how ethanol can be manufactured from one of the named material in (a) above. Include the equations of reaction that takes place if any.
(c) State briefly how the purification of the ethanol produced in (b) above can be done.
(d) State four uses of ethanol.
(e) State two effects of over consumption of ethanol on the human body.

OTHER METHODS OF PREPARING ALCOHOLS FROM ESTERS

(a) Base catalysed hydrolysis of esters i.e

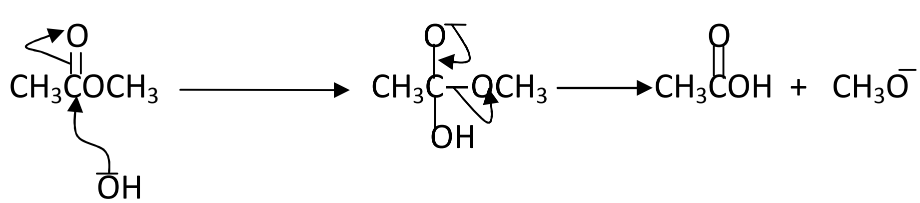
$$R\overset{\overset{O}{||}}{C}OR^I + H_2O \underset{heat}{\overset{\bar{O}H_{(aq)}}{\rightleftharpoons}} R\overset{\overset{O}{||}}{C}OH + R^IOH$$

Example

$$CH_3\overset{\overset{O}{||}}{C}OCH_3 + H_2O \underset{heat}{\overset{\bar{O}H_{(aq)}}{\rightleftharpoons}} CH_3COOH + CH_3OH$$

Methylethanoate

Mechanism



$$CH_3\bar{O} + H_2O \longrightarrow CH_3OH + \bar{O}H$$

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Qn. Complete the equation below and outline a mechanism for the reaction.

$$CH_3COOCH_2CH_3 \xrightleftharpoons[\text{heat}]{\bar{O}H_{(aq)}}$$

(b) Acid catalysed hydrolysis of esters. i.e

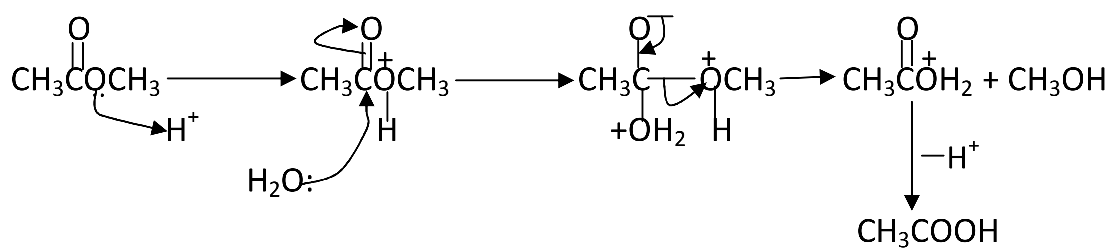
$$R\overset{\overset{O}{||}}{C}OR^I + H_2O \xrightleftharpoons[\text{heat}]{H^+} R\overset{\overset{O}{||}}{C}OH + R^IOH$$

Example

$$CH_3\overset{\overset{O}{||}}{C}OCH_3 + H_2O \xrightleftharpoons[\text{heat}]{H^+} CH_3COOH + CH_3OH$$

Methylethanoate

Mechanism



(c) Reduction of esters using either sodium in ethanol (Na/C_2H_5OH) or Lithium aluminium hydride ($LiAlH_4$).

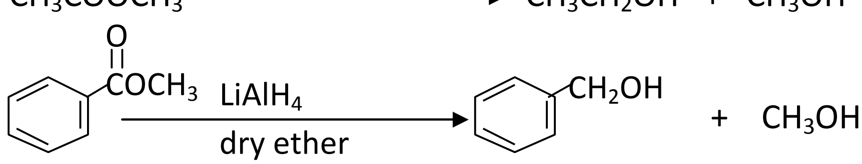
$$R\overset{\overset{O}{||}}{C}OR^I \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2OH + R^IOH$$

$$Na/C_2H_5OH$$

Examples

$$CH_3\overset{\overset{O}{||}}{C}OCH_2CH_3 \xrightarrow[\text{dry ether}]{LiAlH_4} 2CH_3CH_2OH$$

$$CH_3COOCH_3 \xrightarrow{Na/C_2H_5OH} CH_3CH_2OH + CH_3OH$$



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(d) Reaction of esters with ammonia.

Esters react with ammonia, in either concentrated aqueous or alcoholic solution to form amides and alcohols.i.e

$$RCOOR^{I} \xrightarrow[\text{heat}]{NH_{3(aq)}\ /\ \text{alcohol}} RCONH_2 + R^{I}OH$$

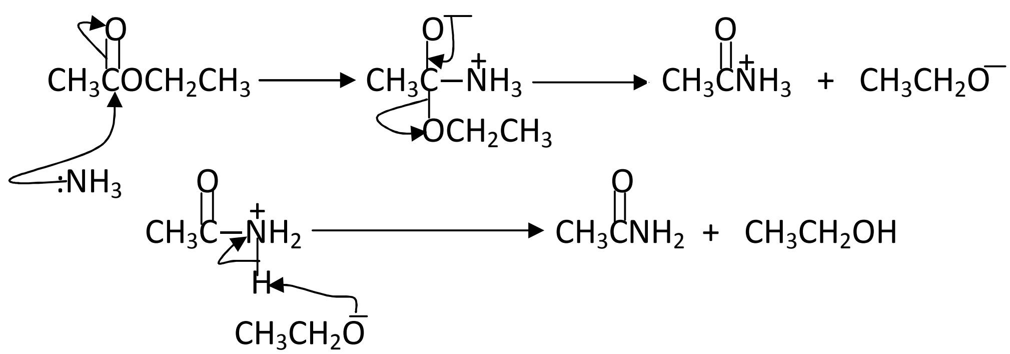
$$RCOOR^{I} \xrightarrow[\text{heat}]{\text{Conc } NH_3} RCONH_2$$

Example

$$CH_3COOCH_2CH_3 \xrightarrow[\text{heat}]{NH_3\ /\ \text{alcohol}} CH_3CONH_2 + CH_3CH_2OH$$

Ethylethanoate Ethanamide Ethanol

Mechanism



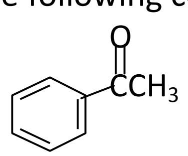
Qn. Synthesize

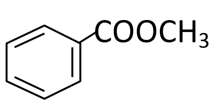
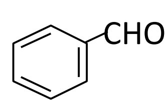
Ethylethanoate to 1,2-dichloroethane.

Solution

$$CH_3COOCH_2CH_3 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3CH_2OH \xrightarrow[180^{o}C]{\text{Conc } H_2SO_4} CH_2{=}CH_2 \xrightarrow[CCl_4]{Cl_2} CH_2ClCH_2Cl$$

Qn. Write equations to show how the following compounds can be synthesized.

(a) $CH_3COOCH_2CH_3$ to 

(b)  to 

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REACTIONS OF ALCOHOLS.

The reactions of the alcohols are grouped in three classes.

(a) Reactions of the $-OH$ group.i.e
   (i) Reactions involving cleavage of O—H bond.
   (ii) Reactions involving cleavage of C—O bond.

(b) Oxidation reactions which depends on whether the alcohol is primary, secondary or tertiary.

(c) Elimination reactions.

(a) Reactions of the $-OH$ bond

(i) Reactions involving cleavage of O—H bond.

1. Alcohols react with sodium to form salts (sodium alkoxides) and hydrogen gas. i.e

$$ROH + 2Na \longrightarrow R\overline{O}Na^+ + H_2$$

Example

$$2CH_3CH_2OH + 2Na \longrightarrow CH_3CH_2\overline{O}Na^+ + H_2$$

Sodium ethoxide

2. Esterification.

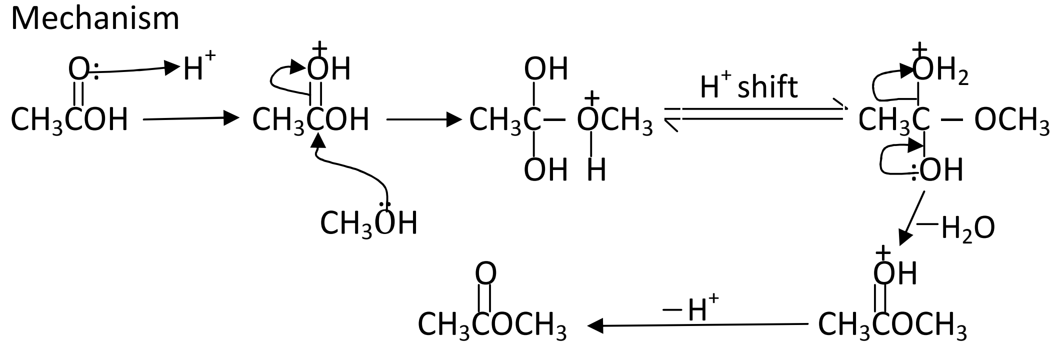
(a) Alcohols react with organic acids (RCOOH) in presence of concentrated sulphuric acid as a catalyst to form esters.i.e

$$RCOOH + R^IOH \underset{\text{warm}}{\overset{\text{Conc } H_2SO_4}{\rightleftharpoons}} RCOOR^I + H_2O$$

Example

$$CH_3COOH + CH_3OH \overset{H^+}{\rightleftharpoons} CH_3COOCH_3 + H_2O$$

Mechanism



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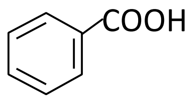
Qn. Complete the following equations and in each case outline the acceptable mechanism for the reaction.

(i) $CH_3CH_2OH + CH_3COOH \xrightleftharpoons{H^+}$

(ii) 

$+ \; CH_3OH \xrightleftharpoons{H^+}$

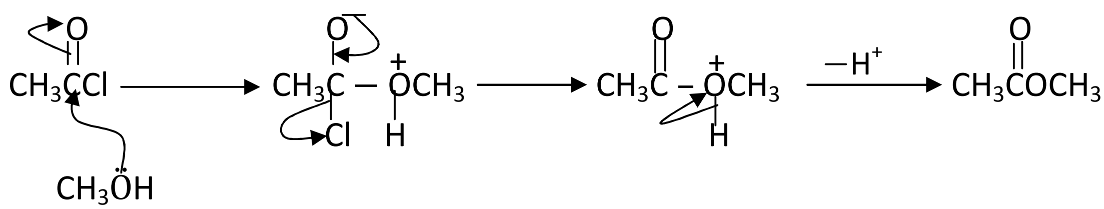
(b) Alcohols react with acid halides to form esters.i.e

$$R^IOH + R\overset{\overset{O}{||}}{C}X \longrightarrow R\overset{\overset{O}{||}}{C}OR^I + HX$$

Example

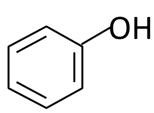
$$CH_3OH + CH_3COCl \longrightarrow CH_3\overset{\overset{O}{||}}{C}OCH_3 + HCl$$

Mechanism

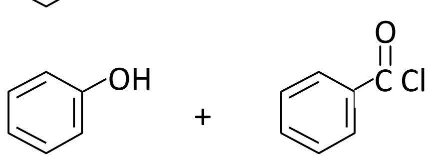


Qn. Complete the following equations and in each case outline the mechanism.

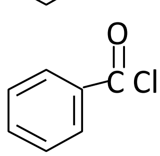
(i) $CH_3CH_2OH + CH_3COCl \longrightarrow$

(ii) 

$+ \; CH_3COCl \longrightarrow$

(iii) 

$\longrightarrow$

(iv) 

$+ \; CH_3CH_2OH \longrightarrow$

(c) Alcohols react with acid anhydrides ($(RCO)_2O$)forming esters and carboxylic acids.i.e

$$R^IOH + R\overset{\overset{O}{||}}{C}\text{-O-}\overset{\overset{O}{||}}{C}R \longrightarrow R\overset{\overset{O}{||}}{C}OR^I + RCOOH$$

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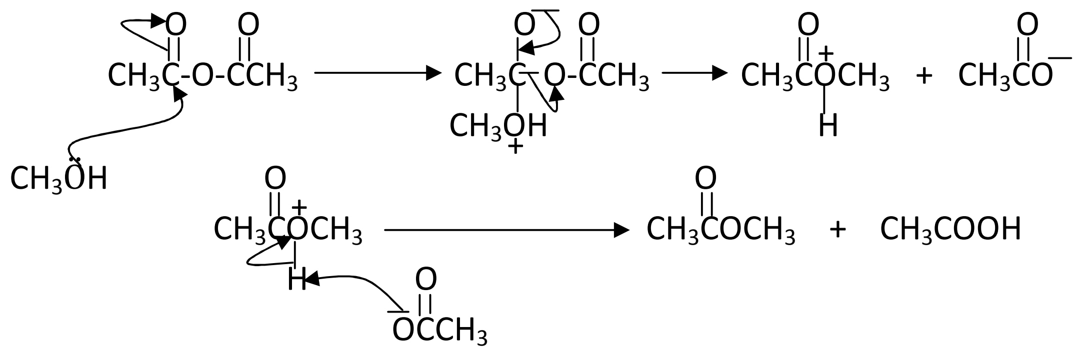
Example

$$CH_3OH + CH_3\overset{\overset{O}{||}}{C}\text{-}O\text{-}\overset{\overset{O}{||}}{C}CH_3 \longrightarrow CH_3\overset{\overset{O}{||}}{C}OCH_3 + CH_3COOH$$

Ethanoic anhydride

Mechanism



Qn. Complete and outline the mechanism

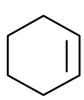
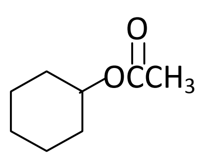
$$CH_3CH_2OH + (CH_3CO)_2O \longrightarrow$$

3. Reactions with dialkyl sulphates.

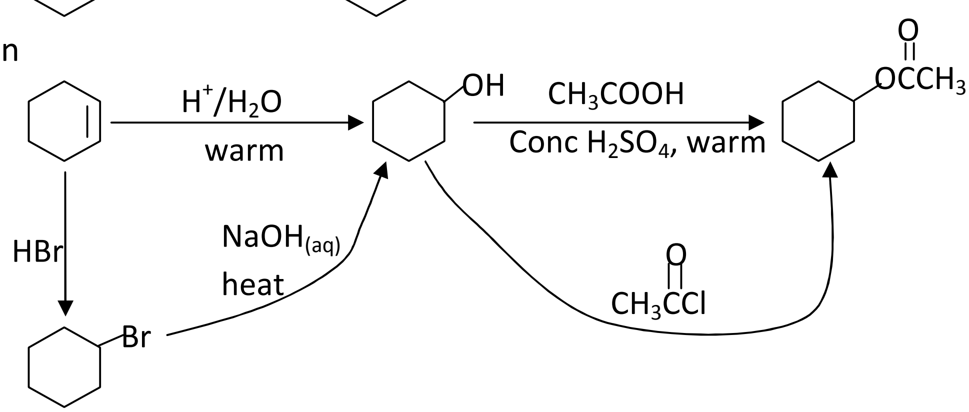
   Alcohols react with dialkyl sulphates forming ethers and alkyl hydrogen sulphates.e.g

   $$\underset{\text{dimethyl sulphate}}{CH_3OH + (CH_3)_2SO_4} \longrightarrow CH_3OCH_3 + \underset{\text{methyl hydrogen sulphate}}{CH_3OSO_3H}$$

Qn. Synthesize

 to 

Solution



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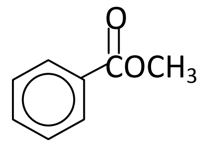
Qn. Using equations only show how the following conversions can be made.

(a) $CH_2{=}CH_2$ to Ethylethanoate

(b) CH_3CH_2OH to 

(c) CH_3OH to $CH_3COOCH_2CH_3$

(d) $CH_3CH_2CH_2CH_2OH$ to methylethanoate

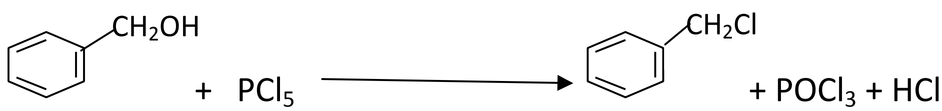
(e) Benzene to phenylbenzoate

(ii) Reactions involving cleavage of C−O bond.

1. Alcohols react with halides of phosphorus e.g. PCl_5 ,PCl_3 ,PBr_3 and PI_3 forming alkyl halides

Examples

$$3CH_3CH_2OH + PI_3 \longrightarrow 3CH_3CH_2I + H_3PO_3$$



$$3CH_3CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2Br + H_3PO_3$$

2. Alcohol react with thionyl chloride (Sulphur dichloride oxide ,$SOCl_2$) in presence of pyridine (C_5H_5N) forming alkyl chlorides.(pyridine absorbs the hydrogen chloride)

$$CH_3CH_2OH \xrightarrow{SOCl_2\ /\ \text{Pyridine}} CH_3CH_2Cl + SO_2 + HCl$$

3. Alcohols react with the hydrogen halides to form alkyl halides.i.e

$$ROH + HX \longrightarrow RX + H_2O \quad \text{where X=Br, Cl or I.}$$

Examples

$$CH_3CH_2OH \xrightarrow[\text{heat}]{\text{Conc HI}} CH_3CH_2I + H_2O$$

$$CH_3CH_2OH \xrightarrow[\text{heat}]{\text{Conc HBr}} CH_3CH_2Br + H_2O$$

$$CH_3CH_2OH \xrightarrow[\text{anhydrous } ZnCl_2]{\text{Conc HCl}} CH_3CH_2Cl + H_2O$$

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N.B. The mixture of concentrated hydrochloric acid and anhydrous zinc chloride is Known as **Lucas reagent** and is used to distinguish between primary, secondary and tertiary alcohols. e.g

Qn. Name a reagent that can be used to distinguish the following compound and in each case state what is observed if each compound is treated with the reagent.

$$\text{(a)}\quad CH_3CH_2CH_2OH\ ,\quad CH_3\underset{\large OH}{\underset{|}{C}}HCH_3\quad \text{and}\quad CH_3\overset{\large CH_3}{\overset{|}{\underset{\large OH}{\underset{|}{C}}}}CH_3$$

Reagent

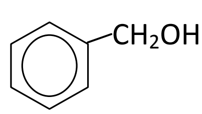
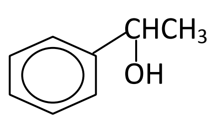
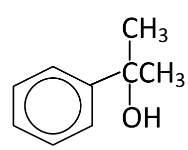
Concentrated hydrochloric acid in presence of anhydrous zinc chloride.

Observations

$CH_3CH_2CH_2OH$ (primary alcohol) ; No observable change at room temperature

$CH_3\underset{\large OH}{\underset{|}{C}}HCH_3$ (secondary alcohol); forms a cloudy solution between 5-10 minutes. i.e after 5 minutes

$CH_3\overset{\large CH_3}{\overset{|}{\underset{\large OH}{\underset{|}{C}}}}CH_3$ (tertiary alcohol); forms a cloudy solution immediately i.e within 5 minutes

(b)  ,  and 

4. Reactions with concentrated sulphuric acid.

(i) Alcohols react with concentrated sulphuric acid at 0^oC to form alkyl hydrogen sulphate.i.e

$$ROH \xrightarrow[0^oC]{\text{Conc } H_2SO_4} ROSO_3H + H_2O$$

Example

At 0^oC, ethanol reacts with concentrated sulphuric acid forming ethyl hydrogen sulphate.

$$CH_3CH_2OH \xrightarrow[0^oC]{\text{Conc } H_2SO_4} \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_3H} + H_2O$$

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Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + \bar{O}SO_3H$$

$$CH_3CH_2\ddot{O}H \xrightarrow{H^+} CH_3CH_2-\overset{+}{O}H_2 \longrightarrow CH_3\overset{+}{C}H_2 \xrightarrow{\bar{O}SO_3H} CH_3CH_2OSO_3H$$

(ii) Excess of a primary alcohol reacts with concentrated sulphuric acid when heated at about 140°C forming an ether.i.e

$$2ROH \xrightarrow[140^oC]{Conc\ H_2SO_4} ROR + H_2O$$

Example

At 140°C, concentrated sulphuric acid react with excess ethanol to form Ethoxyethane (diethyl ether)

$$2CH_3CH_2OH \xrightarrow[140^oC]{Conc\ H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

Ethoxyethane (diethyl ether)

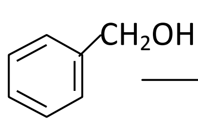
Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + \bar{O}SO_3H$$

$$CH_3CH_2\ddot{O}H \xrightarrow{H^+} CH_3CH_2-\overset{+}{O}H_2 \longrightarrow CH_3\overset{+}{C}H_2 \xrightarrow{CH_3CH_2\ddot{O}H} CH_3CH_2\overset{+}{\underset{H}{O}}CH_2CH_3$$

$$\xrightarrow{-H^+} CH_3CH_2OCH_2CH_3$$

Qn. Complete the equations below and in each case outline the mechanism.

(a)  $\xrightarrow[140^oC]{Conc\ H_2SO_4}$

(b) $CH_3OH \xrightarrow[140^oC]{Conc\ H_2SO_4}$

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(b) Elimination reactions

Alcohols are dehydrated by concentrated sulphuric acid at a temperature of about 170^oC or 180^oC to form alkenes.

Example

Ethanol reacts with concentrated sulphuric acid at a temperature of about 170^oC to form ethane.

$$CH_3CH_2OH \xrightarrow[170^oC]{Conc\ H_2SO_4} CH_2{=}CH_2 + H_2O$$

Mechanism

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

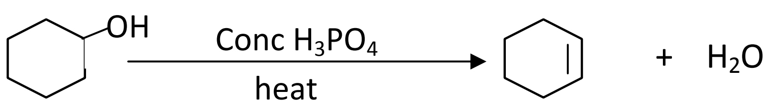
$$CH_3CH_2\ddot{O}H \xrightarrow{H^+} CH_3CH_2-\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3\overset{+}{C}H_2$$

$$\underset{|\atop H}{C}H_2-\overset{+}{C}H_2 \xrightarrow{HSO_4^-} CH_2{=}CH_2$$

Qn. Discuss the reactions of ethanol with sulphuric acid. In each case outline a mechanism for the reaction that takes place.

N.B

- The dehydrations of liquid alcohols can be done using concentrated phosphoric acid in presence of heat.i.e



- Alcohols can also be dehydrated by passing their vapour over aluminium oxide catalyst at about 300^oC.

$$CH_3CH_2OH \xrightarrow[300^oC]{Al_2O_3} CH_2{=}CH_2 + H_2O$$

- Secondary or tertiary alcohols form alkenes when heated at temperatures of about 140^oC or $170^oC – 180^oC$.

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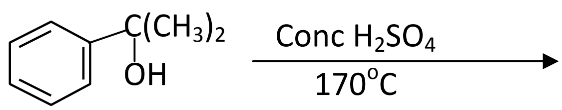
Qn. Complete the following equations and in each case outline the mechanism for the reaction.

(i) $CH_3CH_2CH_2CH_2OH \xrightarrow[180^oC]{Conc\ H_2SO_4}$

(ii) $CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}CH_3 \xrightarrow[140^oC]{Conc\ H_2SO_4}$

(iii) $CH_3\underset{\displaystyle OH}{C}HCH_3 \xrightarrow[heat]{Conc\ H_2SO_4}$

(iv) 

(v) $CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} - \underset{\displaystyle OH}{C}HCH_3 \xrightarrow[heat]{Conc\ H_2SO_4} CH_3\underset{\displaystyle CH_3}{C}=\overset{\displaystyle CH_3}{C}CH_3 + H_2O$

Mechanism;

Qn. Using equations only show how the following conversions can be made.

(a) CaO to CH_3OCH_3

(b) $CH_3CH_2CH_2CH_2OH$ to $CH_3CH_2OCH_2CH_3$

(c) CH_3Br to Ethoxyethane

(c) Oxidation reactions

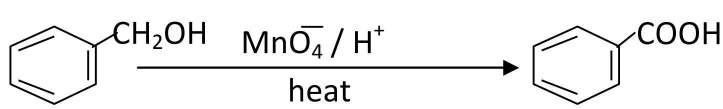
(i) Primary alcohols are oxidized to carboxylic acids using strong oxidizing agents such as acidified potassium or sodium dichromate ($Cr_2O_7^{2-}/H^+$) and acidified potassium permanganate solution (MnO_4^-/H^+)

This oxidation takes place in two stages via an aldehydes i.e

$$RCH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} RCHO \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} RCOOH$$

Example

$$CH_3CH_2OH \xrightarrow[heat]{\substack{excess \\ Cr_2O_7^{2-}/H^+}} CH_3COOH$$



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N.B

Primary alcohols are oxidized to aldehydes if mild oxidizing agents such as acidified chromium (VI) oxide (CrO_3/H^+) or acidified manganase (IV) oxides (MnO_2/H^+) are used. However if the mild oxidizing agent is used in excess the primary alcohol is still oxidized to a carboxylic acid.

$$CH_3CH_2OH \xrightarrow[\text{heat}]{MnO_2/H^+} CH_3CHO$$

$$CH_3CH_2OH \xrightarrow[\text{heat}]{CrO_3/H^+} CH_3CHO$$

(ii) Secondary alcohols are oxidized to ketones i.e

$$R\underset{\underset{OH}{|}}{C}HR^I \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/\ H^+} R\overset{\overset{O}{||}}{C}R^I$$

Example

$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[\text{heat}]{Cr_2O_7^{2-}\ /\ H^+} CH_3\overset{\overset{O}{||}}{C}CH_3$$

(iii) Tertiary alcohols are not oxidized i.e. they are resistant to oxidation.

In vapour phase, oxidation of alcohols can be brought about by either;

(a) Passing alcohol vapour and oxygen over silver catalyst at 500^{o}C.

Examples

$$CH_3OH + \frac{1}{2}O_2 \xrightarrow[500^oC]{\text{Ag as catalyst}} HCHO + H_2O$$

$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 + \frac{1}{2}O_2 \xrightarrow[500^oC]{\text{Ag as cat}} CH_3\overset{\overset{O}{||}}{C}CH_3 + H_2O$$

Or

(b) Passing alcohol vapour alone over heated copper at 500^{o}C.

$$CH_3CH_2OH \xrightarrow[500^oC]{\text{Cu as cat}} CH_3CHO + H_2$$

$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[500^oC]{Cu} CH_3\overset{\overset{O}{||}}{C}CH_3 + H_2$$

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(iv) Iodoform reaction (Iodoform test)

Ethanol and methyl secondary alcohols ($CH_3\underset{\overset{|}{OH}}{C}HR$) are oxidised by iodine solution in the presence of sodium hydroxide solution to **a yellow precipitate** of tri-iodomethane (CHI_3).

Therefore Iodoform test can be used to distinguish between;

(a) CH_3CH_2OH and $CH_3CH_2CH_2OH$

Reagent

Iodine solution in the presence of sodium hydroxide solution.

(Iodine solution and sodium hydroxide solution)

Observation

CH_3CH_2OH ; forms a yellow precipitate.

$CH_3CH_2CH_2OH$; No observable change

Equation

$$CH_3CH_2OH_{(l)} + 4I_{2\,(aq)} + 6NaOH_{(aq)} \longrightarrow CHI_{3\,(s)} + HCO\bar{O}Na^+_{(aq)} + 5NaI_{(aq)} + 5H_2O_{(l)}$$

Or

$$CH_3CH_2OH_{(l)} \xrightarrow{I_{2(aq)}\ /\ NaOH_{(aq)}} CHI_{3(s)} + HCO\bar{O}Na^+_{(aq)}$$

(b) $CH_3\underset{\overset{|}{OH}}{C}HCH_3$ and $CH_3CH_2CH_2OH$

Reagent

Iodine solution in the presence of sodium hydroxide solution.

(Iodine solution and sodium hydroxide solution)

Observation

$CH_3\underset{\overset{|}{OH}}{C}HCH_3$; forms a yellow precipitate.

$CH_3CH_2CH_2OH$; No observable change

Equation

$$CH_3\underset{\overset{|}{OH}}{C}HCH_{3(l)} + 4I_{2\,(aq)} + 6NaOH_{(aq)} \longrightarrow CHI_{3\,(s)} + CH_3CO\bar{O}Na^+_{(aq)} + 5NaI_{(aq)} + 5H_2O_{(l)}$$

Or $$CH_3\underset{\overset{|}{OH}}{C}HCH_{3\,(l)} \xrightarrow{I_{2(aq)}\ /\ NaOH_{(aq)}} CHI_{3(s)} + CH_3CO\bar{O}Na^+_{(aq)}$$

N.B

- In the reaction above the propan-2-ol is first oxidised to propanone which is a methyl ketone by the iodine solution.i.e

$$CH_3\underset{OH}{\underset{|}{C}}HCH_{3(l)} + I_{2\,(aq)} + 2NaOH_{(aq)} \longrightarrow CH_3\overset{O}{\overset{||}{C}}CH_{3(l)} + 2NaI_{(aq)} + 2H_2O_{(l)}$$

- The methyl ketone (propanone) formed is further oxidised to tri-iodomethane which is the yellow precipitate.i.e

$$CH_3\overset{O}{\overset{||}{C}}CH_{3(l)} + 3I_{2\,(aq)} + 4NaOH_{(aq)} \longrightarrow CHI_{3\,(s)} + CH_3CO\bar{O}Na^+_{(aq)} + 3NaI_{(aq)} + 3H_2O_{(l)}$$

Therefore ethanal and methyl ketones (CH_3COR) reacts with iodine solution and sodium hydroxide solution forming a yellow precipitate of tri-iodomethane and hence Iodoform test can also be used to distinguish between;

$$CH_3CH_2\overset{O}{\overset{||}{C}}CH_3 \quad \text{and} \quad CH_3CH_2\overset{O}{\overset{||}{C}}CH_2CH_3$$

Reagent

Iodine solution in the presence of sodium hydroxide solution.

Observation

$CH_3CH_2\overset{O}{\overset{||}{C}}CH_3$; forms a yellow precipitate

$CH_3CH_2\overset{O}{\overset{||}{C}}CH_2CH_3$; No observable change

Equation

$$CH_3CH_2\overset{O}{\overset{||}{C}}CH_3 + 3I_{2\,(aq)} + 4NaOH_{(aq)} \longrightarrow CHI_{3\,(s)} + CH_3CH_2CO\bar{O}Na^+_{(aq)} + 3NaI_{(aq)} + 3H_2O_{(l)}$$

Qn. Explain why ethanol boils at a lower temperature than ethane-1,2-diol.

Explaination;

Both ethanol and ethane-1,2-diol molecules associate via hydrogen bonds. However because ethane-1,2-diol has two hydroxyl groups, the hydrogen bonds formed are very extensive(i.e ethane-1,2-diol molecules form more hydrogen bonds) and these requires more energy to be broken for boiling to take place.

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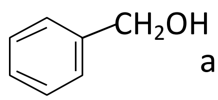
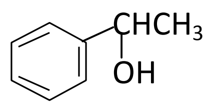
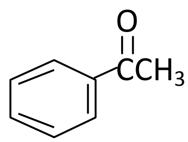
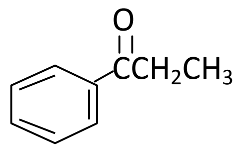
Qn. Name a reagent(s) that can be used to distinguish between the following pairs of compounds. In each case state any observations that can be made and write an equation of reaction that takes place.

(a) CH_3CHO and CH_3CH_2CHO

(b) CH_3OH and CH_3CH_2OH

(c) $CH_3CH(OH)CH_3$ and $(CH_3)_3COH$

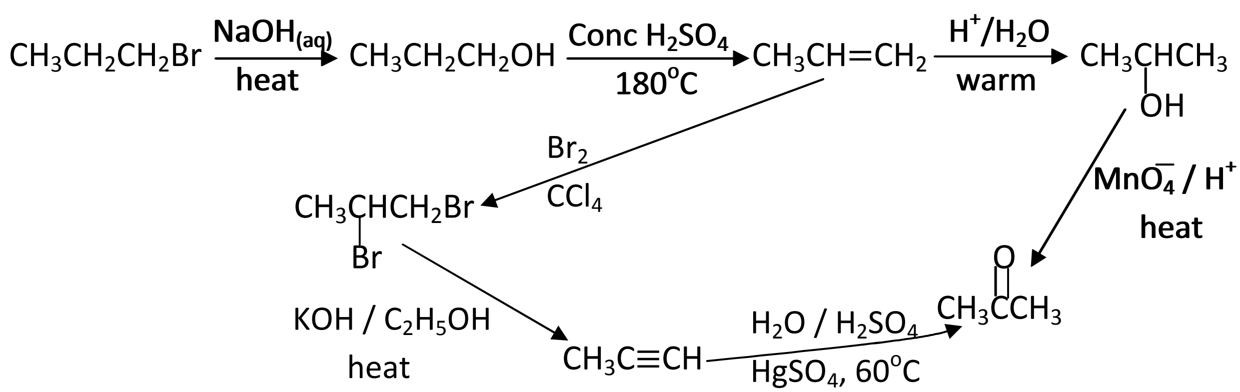
(d)  and 

(e)  and 

Example

Synthesize; $CH_3\overset{O}{\overset{\|}{C}}CH_3$ from $CH_3CH_2CH_2Br$

Solution;



Qn. Using equations only show how the following conversions can be made.

(a) $CH_3CH_2CH_2Cl$ to CH_3CH_2COCl

(b) 2,3-dibrobutane to methylethanoate

(c) Chlorophenyl methane to Phenylethanone

(d) CaC_2 to CH_3COOH

(e) 2-bromopropane to propanoic acid

(f) CH_3CH_2CHO to CH_3COCH_3

(g) CH_3CH_2COOH to 2,2-dichloropropane.

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PHENOL (HYDROXY BENZENE)

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