ALKYL HALIDES (HALOGENOALKANES)

They have a general molecular formula $C_nH_{2n+1}X$ where n =1, 2, 3,…and X is Cl, Br or I

The halide (X) is their functional group.

Classes of alkyl halides

There are three classes of alky halides namely;

(i) **Primary alkyl halides (1^o)**. These have one alkyl group attached to the carbon atom with a halogen atom. i.e. RCH_2X e.g. CH_3CH_2Br (Bromoethane). $CH_3CH_2CH_2Cl$ (1-chloropropane),etc

(ii) **Secondary alkyl halides (2^o).**These have two alkyl groups attached to the carbon atom with a halogen. i.e. $\begin{matrix}R\\|\\CHR\\|\\X\end{matrix}$ e.g $\begin{matrix}CH_3\\|\\CHCH_3\\|\\Br\end{matrix}$ (2-bromopropane),

$\begin{matrix}CH_3CH_2\\|\\CHCH_3\\|\\Cl\end{matrix}$ (2-chlorobutane), etc

(iii) Tertiary alkyl halides (3^o). These have three alkyl groups attached to the carbon atom with a halogen atom. i.e. $\begin{matrix}R\\|\\R\text{-}C\text{-}R\\|\\X\end{matrix}$ e.g $\begin{matrix}CH_3\\|\\CH_3CCH_3\\|\\Br\end{matrix}$

(2-bromo-2-methylpropane)

Nomenclature of alkyl halides

- They are named as derivatives of alkanes
- The longest continuous carbon chain bearing the halogen atom should be chosen as the parent chain
- The carbon atom with the halogen atom is given the smallest number possible from 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 .e,g

$CH_3CH_2CH_2CH_2Br$ 1-bromobutane

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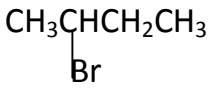
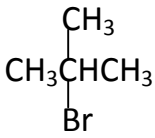
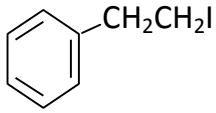


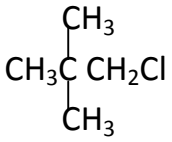
2-bromobutane



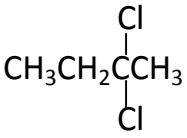
2-bromo-2-methylpropane



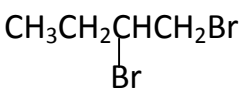
1-iodo-2-phenylethane



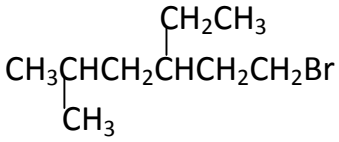
1-choro-2,2-dimethylpropane



2,2-dichlorobutane



1,2-dibromobutane



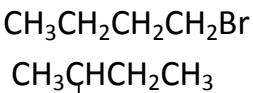
1-bromo-3-ethyl-5-methylhexane

Isomerism in alkyl haildes

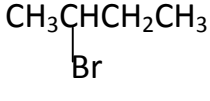
Alkyl halides exhibits chain isomerism and position isomerism

Qn. Write the structural formulae and IUPAC names of all the possible isomers of C_4H_9Br.

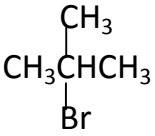
Solution



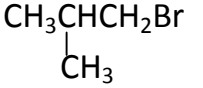
1-bromobutane



2-bromobutane



2-bromo-2-methylpropane



1-bromo-2-methylpropane

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METHODS OF PREPARATION OF ALKYL HALIDES

1. From alcohols

   (a) Reacting an alcohol with concentrated hydrochloric acid.

   This reaction occurs in presence of anhydrous zinc chloride.

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.

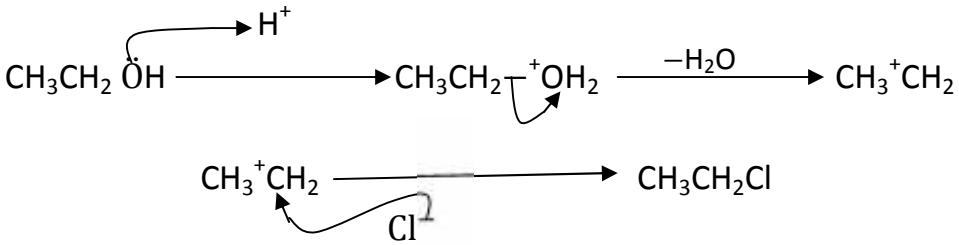
Examples

(i) Primary alcohols give no observable change when treated with Lucas reagent at room temperature.

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

Mechanism

$$HCl \longrightarrow H^+ + Cl^-$$



(ii) Secondary alcohols form a cloudy solution within 5-10 minutes i.e. after 5 minutes.

$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow[\text{anhydrous } ZnCl_2]{\text{Conc. HCl}} CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 + H_2O$$

(iii) Tertiary alcohols form a cloudy solution immediately i.e within 5 minutes

$$(CH_3)_3COH \xrightarrow[\text{anhydrous } ZnCl_2]{\text{Conc. HCl}} (CH3)_3CCl + H_2O$$

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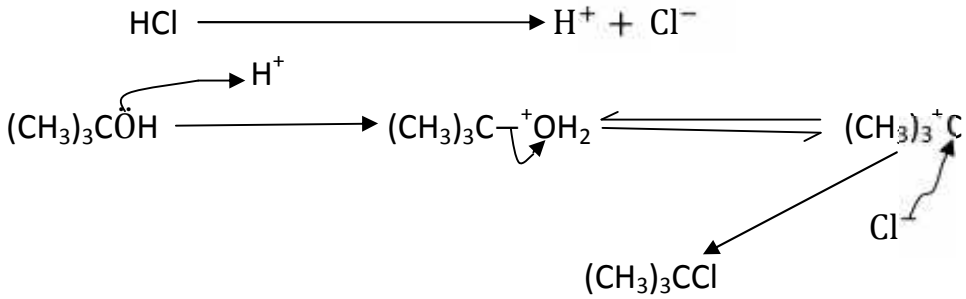
Mechanism



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.

✓ $CH_3CH_2CH_2OH$, $CH_3\underset{\underset{OH}{|}}{C}HCH_3$ and $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_3$

Reagent

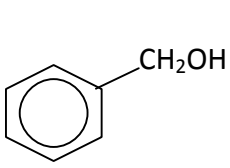
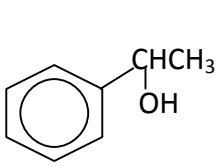
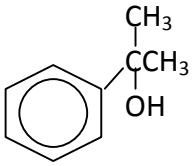
Concentrated hydrochloric acid in presence of anhydrous zinc chloride.

Observations

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

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

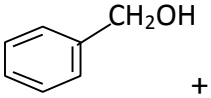
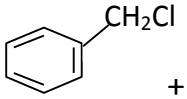
$CH3\overset{\overset{CH3}{|}}{\underset{\underset{OH}{|}}{C}}CH3$ (tertiary alcohol); forms a cloudy solution immediately
i.e within 5 minutes

✓  ,  and 

(b) Reacting an alcohol with halides of phosphorus e.g. PCl_5 ,PCl_3 and PBr_3

Examples

$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

 + PCl_5  + $POCl_3$ + HCl

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

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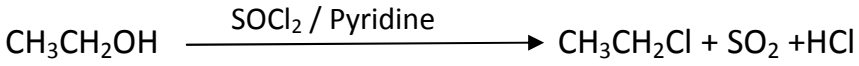
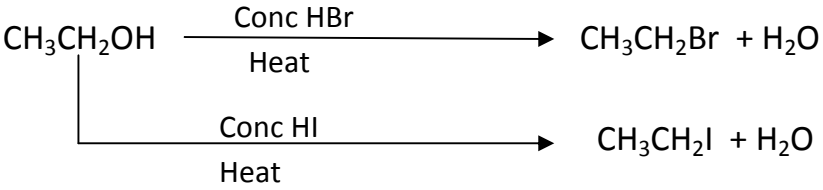
(c) Reacting an alcohol with thionyl chloride (Sulphur dichloride oxide ,$SOCl_2$) in presence of pyridine.

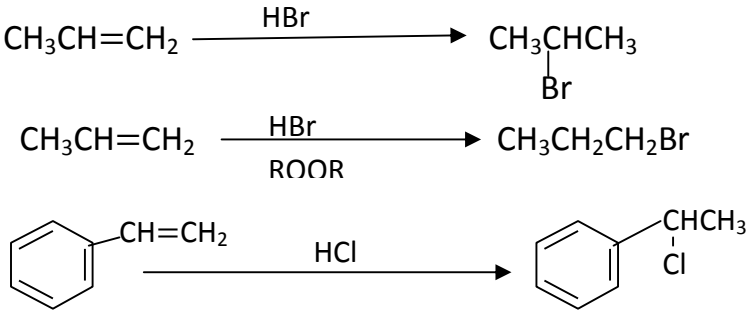


N.B Evolution of white fumes of hydrogen chloride gas when a compound is treated with phosphorus pentachloride and thionyl chloride is used as a test for the presence of hydroxyl group in a compound.

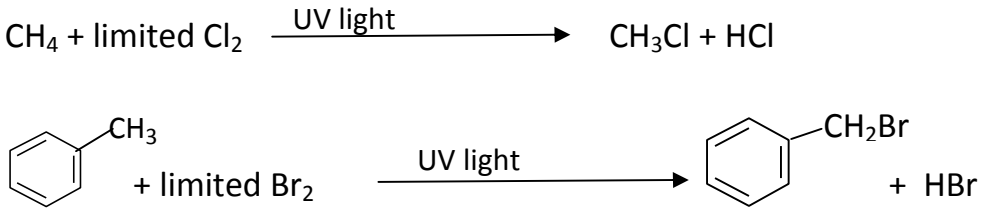
(d) Heating an alcohol with a halogen acid e.g HBr , HI



2. Hydrohalogenation alkenes



3. Reacting alkanes with chlorine or bromine in presence of ultra violet light



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With this method however, a mixture of products is formed if the halogen used is in excess i.e

$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Generally

$$CH_4 + \underset{\text{excess}}{4Cl_2} \xrightarrow{\text{UV light}} CCl_4 + 4HCl$$

REACTIONS OF ALKYL HALIDES

The reactions of alkyl halides are divided into three categories namely;

(i) Nucleophilic substitution reactions (S_N reactions)
(ii) Elimination reactions (E- reactions)
(iii) Reaction with metals

(1) **Nucleophilic substitution reactions**

This is a reaction in which a nucleophile replaces an atom or a group of atoms in a compound to form a compound with a different functional group.
These are of two types namely

- **Bimolecular nucleophilic substitution reactions (S_N2 reactions)**

This is a reaction in which a nucleophile replaces an atom or a group of atoms in a compound to form a compound with a different functional group and two species take place in the rate determining step to form an unstable intermediate (activated complex) that then breaks down fast to form the products.
This reaction is undergone by primary alkyl halides.

- **Unimolecular nucleophilic substitution reactions (S_N1 reactions)**

This is a reaction in which a nucleophile replaces an atom or a group of atoms in a compound to form a compound with a different functional group and one species take place in the rate determining step (slow step).
This reaction is undergone by tertiary alkyl halides

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Examples

(a) Alkyl halides react with hot aqueous sodium or potassium hydroxide solutions to form alcohols.

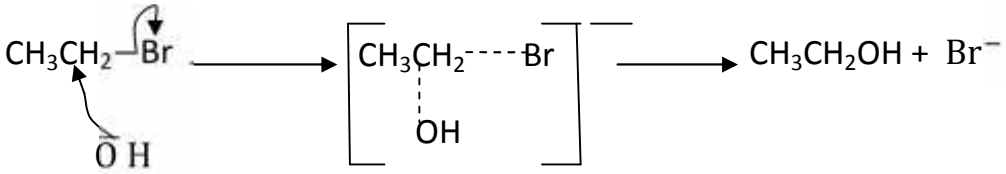
- With primary alkyl halides the reaction is S_N2 e.g

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

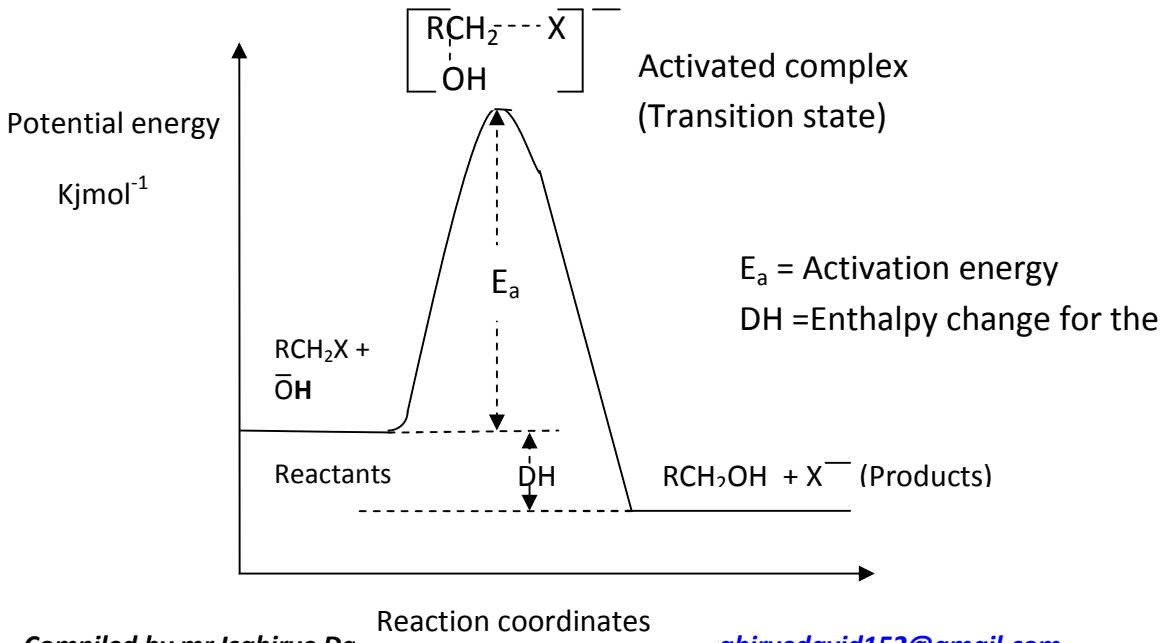
Mechanism

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + \bar{O}H_{(aq)}$$

OR



ENERGY PROFILE DIAGRAM FOR S_N2 REACTION



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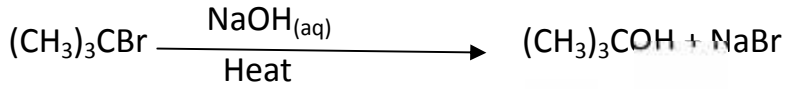
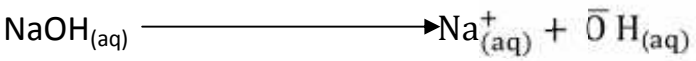
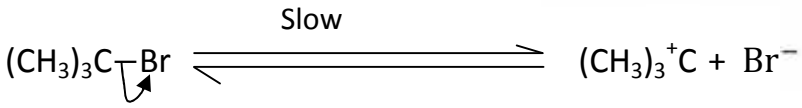
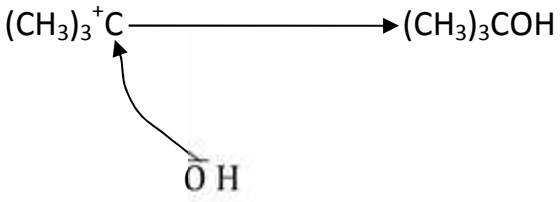
- With tertiary alkyl halides the reaction is S_N1 e.g



Mechanism

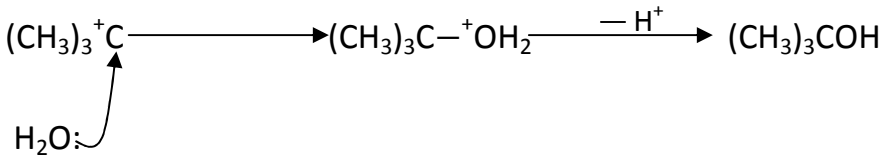




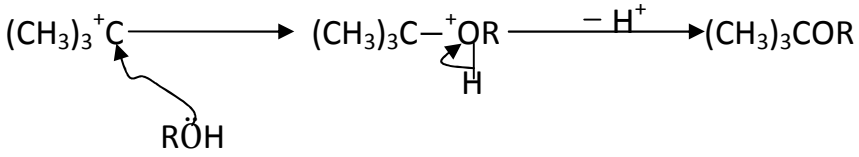


The carbonium ion is very reactive and is attacked by other nucleophile i.e

(i) If water is the solvent, itself acts as the nucleophile and an alcohol is formed.



(ii) If an alcohol is the solvent, alcohol itself acts as the nucleophile ether is formed.



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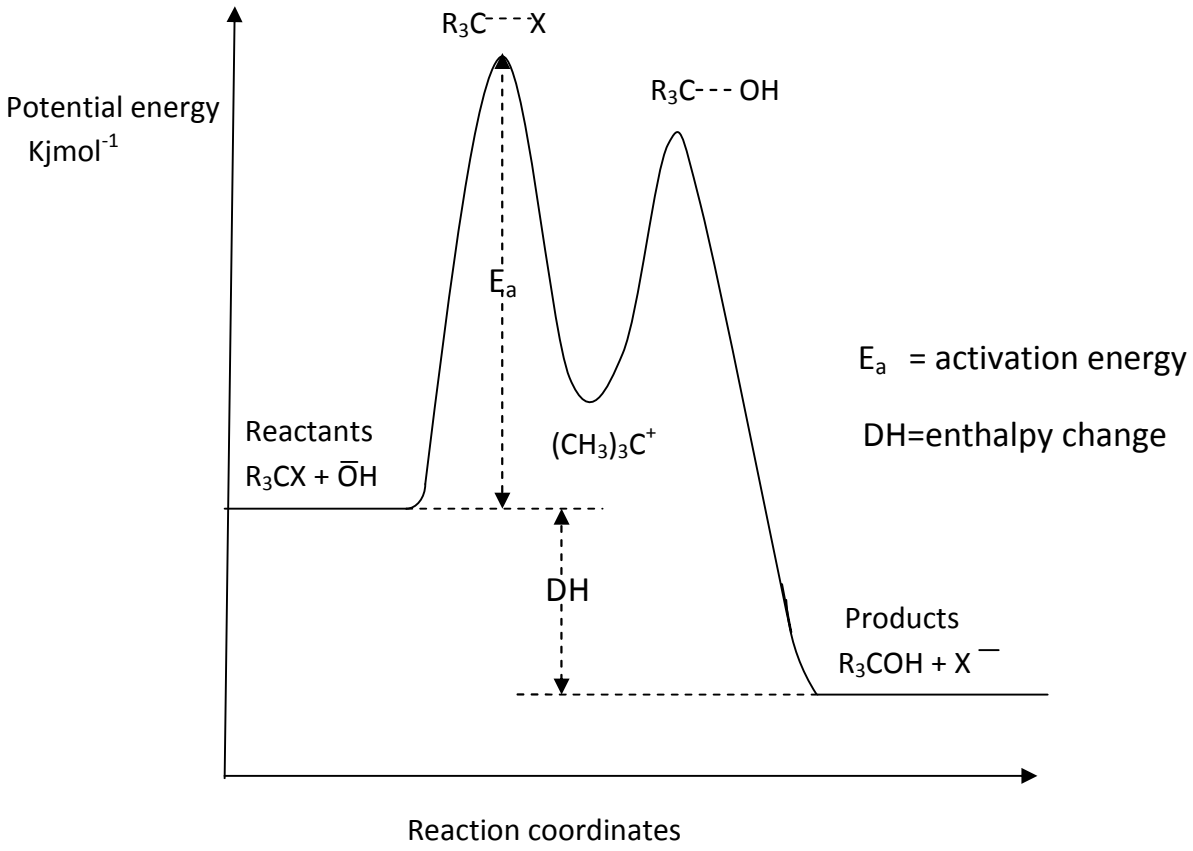
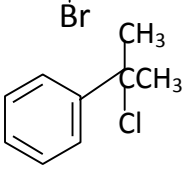
ENERGY PROFILE DIAGRAM FOR S_N1 REACTION



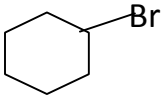
Qn. Complete the following equations and in each case outline the mechanism of the reaction.

1. $CH_3CH_2CH_2Cl \xrightarrow[\text{Heat}]{KOH_{(aq)}}$

2. $CH_3\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow[\text{Heat}]{\bar{O}H_{(aq)}}$

3. 

$\xrightarrow[\text{Heat}]{NaOH_{(aq)}}$

4. 

$\xrightarrow[\text{Heat}]{NaOH_{(aq)}}$

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(b) Reaction of alkyl halides with potassium cyanide

Refluxing an alkyl halide with potassium cyanide in presence of ethanol forms a nitrile.

This reaction is important in organic synthesis since it increases the length of the carbon chain. e.g.

$$CH_3CH_2Br \xrightarrow[\text{Heat}]{KCN / C_2H_5OH} CH_3CH_2CN + KBr$$

(Propanenitrile)

Mechanism

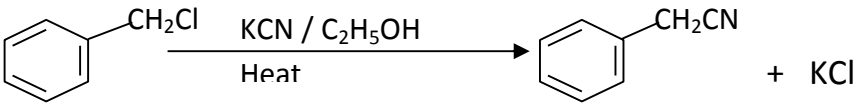
$$KCN \longrightarrow K^+ + \bar{C}N$$

$$CH_3CH_2{-}Br \longrightarrow CH_3CH_2CN + Br^-$$

$$\bar{C}N \qquad K^+ + Br^- \longrightarrow KBr$$

$$(CH_3)_3CBr \xrightarrow[\text{Heat}]{KCN / \text{Ethanol}} (CH_3)_3CCN + KBr$$

(2,2-dimethylpropanenitrile)



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

(i) $CH_2{=}CH_2$ to $CH_3CH_2CH_2OH$

Solution

$$CH_2{=}CH_2 \xrightarrow{HBr} CH_3CH_2Br \xrightarrow[\text{Heat}]{KCN / C_2H_5OH} CH_3CH_2CN$$

$$CH_3CH_2CN \xrightarrow[\text{Heat}]{\text{Conc } H_2SO_4 / H_2O} CH_3CH_2COOH \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2CH_2OH$$

Synthesize

(ii) CH_3CH_2OH to CH_3CH_2COOH

(iii) CH_3CH_2COOH to $CH_3CH_2CH_2COOH$

(iv) CH_3Cl to CH_3COCl

(v) C to CH_3CH_2COOH

(vi) 1,2-dibromoethane to propanoyl chloride

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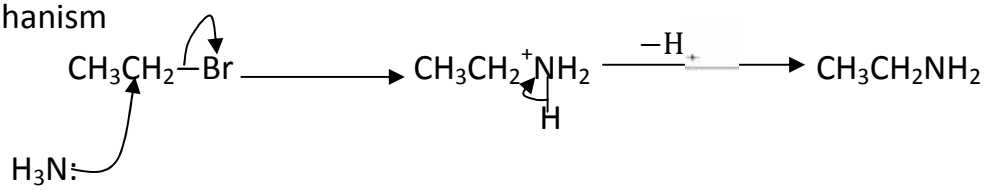
(c) Reaction of alkyl halides with ammonia.

Heating an alkyl halide with concentrated solution of ammonia in a sealed tube forms a primary amine.e.g

$$CH_3CH_2Br \xrightarrow[\text{Sealed tube, heat}]{\text{Conc } NH_3} CH_3CH_2NH_2 + HBr$$

(Ethylamine)

Mechanism



When the alkyl halide is in excess a mixture of amines is formed

$$CH_3CH_2I \xrightarrow[\text{Heat}]{\text{Conc } NH_3} CH_3CH_2NH_2 + HI$$

Ethylamine (a primary amine)

$$CH_3CH_2I + CH_3CH_2NH_2 \xrightarrow{\text{Heat}} (CH_3CH_2)_2NH + HI$$

Diethylamine (secondary amine)

$$CH_3CH_2I + (CH_3CH_2)_2NH \longrightarrow (CH_3CH_2)_3N + HI$$

Triethylamine (tertiary amine)

$$CH_3CH_2I + (CH_3CH_2)_3N \longrightarrow (CH_3CH_2)_4N^+I^-$$

Tetraethylammonium iodide

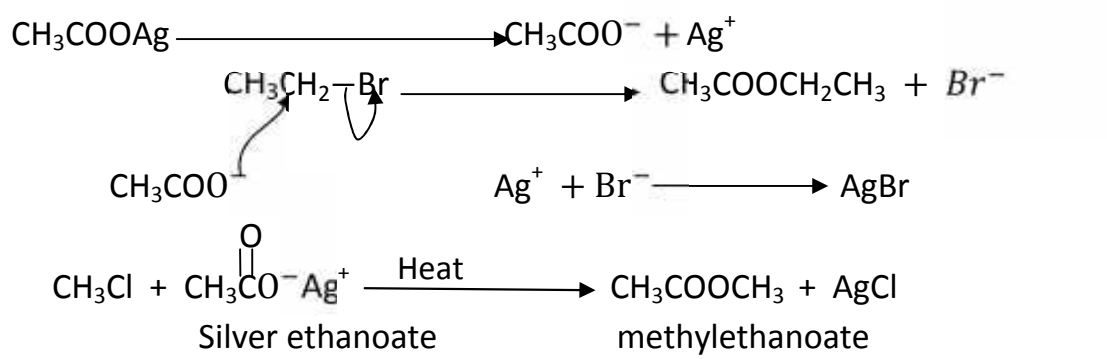
(d) Reaction with a silver salt of carboxylic acid.

Refluxing an alkyl halide with a silver salt of a carboxylic acid forms an ester.e.g

$$CH_3CH_2Br + CH_3COOAg \xrightarrow{\text{Heat}} CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 + AgBr$$

Silver ethanoate — Ethylethanoate

Mechanism



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(e) Reaction of alkyl halides with hot alcoholic solution of potassium or sodium hydroxide

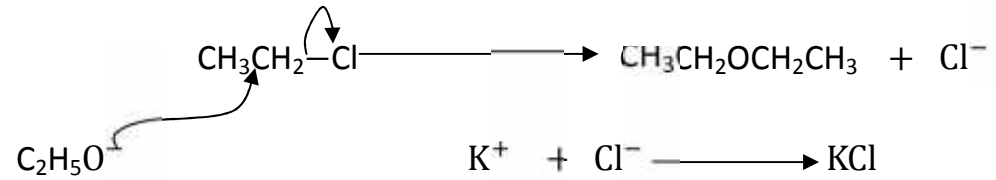
Primary alkyl halides react with hot alcoholic solution of potassium or sodium hydroxide to form ethers.e.g.

$$CH_3CH_2Cl \xrightarrow[\text{Heat}]{KOH / C_2H_5OH} CH_3CH_2OCH_2CH_3 + KCl$$

Mechanism — Ethoxyethane (diethyl ether)

$$C_2H_5OH + KOH \longrightarrow C_2H_5O^- + K^+ + H_2O$$

=



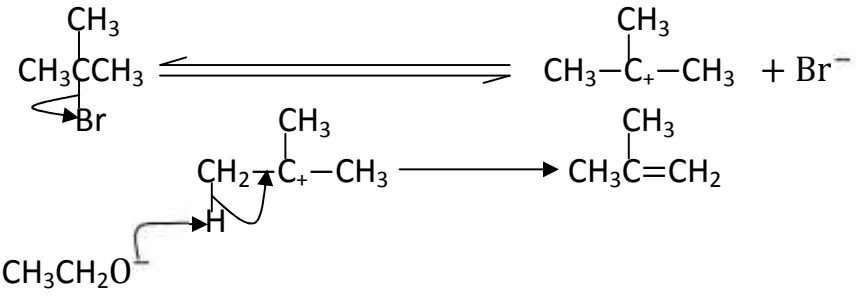
2 .Elimination reactions

(a) Tertiary and secondary alkyl halides react with hot alcoholic solution of potassium or sodium hydroxide to form alkenes. The reaction with tertiary alkyl halides is Unimolecular elimination (E_1 reaction).The reaction with secondary alkyl halide is either E_2 or E_1 e.g

$$CH_3CCH_3(Br) \xrightarrow[\text{Heat}]{KOH / CH_3CH_2OH} CH_3C(CH_3)=CH_2$$

Mechanism

$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2O^- + K^+ + H_2O$$



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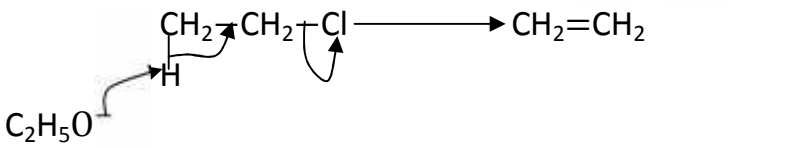
(b) Primary alkyl halide react with hot alcoholic solution of potassium or sodium hydroxide to form an alkene.The reaction is bimolecular elimination (E_2 reaction)

$$CH_3CH_2Cl \xrightarrow[\text{Heat}]{KOH / C_2H_5OH} CH_2{=}CH_2$$

Mechanism

$$C_2H_5OH + KOH \longrightarrow C_2H_5O^- + K^+ + H_2O$$



N.B When primary alkyl halides are reacted with hot alcoholic solution of Potassium or Sodium hydroxide both ether and an alkene are formed.However an ether is formed as the major product and an alkene as the minor product. So during the conversion of a primary alkyl halide to an alcohol, it is advisable to first form an alcohol as an intermediate and then convert an alcohol to an alkene. i.e

Qn. Using equations only show how the following compounds can be converted.

CH_3CH_2Br to $CH_2{=}CH_2$

$$CH_3CH_2Br \xrightarrow[\text{Heat}]{NaOH_{(aq)}} CH_3CH_2OH \xrightarrow[180^oC]{\text{Conc } H_2SO_4} CH_2{=}CH_2$$

Synthesise

1. CH_3CH_2Cl to $CH_3C{\equiv}CH$
2. $CH_3\underset{\underset{Br}{|}}{C}HCH_3$ to $CH_3\underset{\underset{Cl}{|}}{C}H\underset{\underset{Cl}{|}}{C}HCH_3$
3. $CH_3CH_2CH_2Br$ to $CH_3CH_2CH_2CH_2Cl$
4. $CH_3\underset{\underset{Br}{|}}{C}H\underset{\underset{Br}{|}}{C}HCH_3$ to $CH_3\underset{\underset{OH}{|}}{C}HCH_2CH_3$
5. CaC_2 to $CH_3CH_2CH_2OH$

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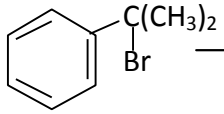
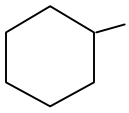
Qn. Complete the following equations and in each case outline the mechanism

1. $CH_3CH_2CH_2Cl \xrightarrow[\text{Heat}]{NaOH / C_2H_5OH}$

2.  $\xrightarrow[\text{Heat}]{EtO^- / EtOH}$

3. $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \xrightarrow[\text{Heat}]{KOH / CH_3OH}$

4. $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[\text{Heat}]{C_2H_5O^-K^+ / CH_3CH_2OH}$

5.  $\xrightarrow[\text{Heat}]{KOH / C_2H_5OH}$

2. Reaction of alkyl halides with metals.

(a) Alkyl halides react with sodium in presence of dry ether in a Wurtz reaction to a higher alkane.

This reaction is important in organic synthesis in reactions involving increase in the length of the carbon chain. e.g

$$2CH_3CH_2I + 2Na \xrightarrow{\text{Dry ether}} CH_3CH_2CH_2CH_3 + 2\,NaI$$

(b) Alkyl halides react with magnesium in presence of dry ether to form Grignard reagents e.g

$$CH_3CH_2Br \xrightarrow[\text{Dry ether}]{Mg} CH_3CH_2MgBr$$

Ethylmagnesium bromide

Qn. Synthesize

1. $CH_3CH_2CH_2CH_3$ from CH_3CH_2OH
2. $CH_3C{\equiv}CH$ to $CH_3CH_2CH_2MgBr$

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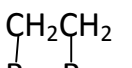
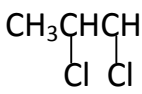
DIHALIDES

These are saturated compounds with two halogen atoms.

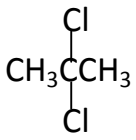
Dihalides are divided into two namely;

(i) **Vicinal dihalide**.These possess two halogen atoms attached on the adjascent carbon atom.e.g


1,2-dibromoethane

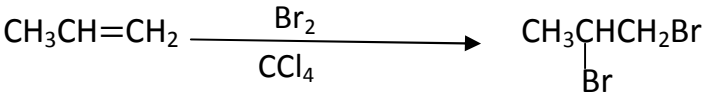

2,3-dichlorobutane

(ii) **Germinal dihalide.** These possess two halogen atoms attached on the same carbon atom.e.g

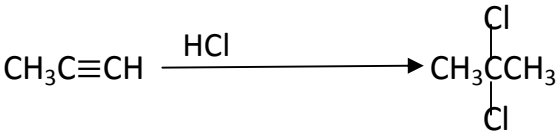

2,2-dichloropropane

Methods of preparation of Dihalides

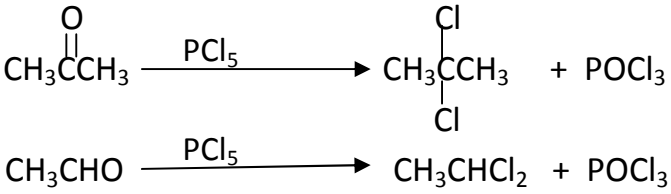
1. Halogenation of alkenes
   This forms vicinal Dihalides e.g



2. Hydrohalogenation of alkynes
   This forms germinal Dihalides e.g



3. Reacting carbonyl compounds with phosphorus pentachloride (PCl_5)
   This forms germinal Dihalides e.g



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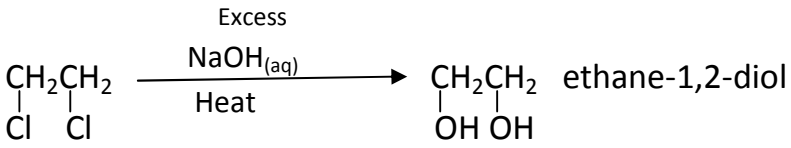
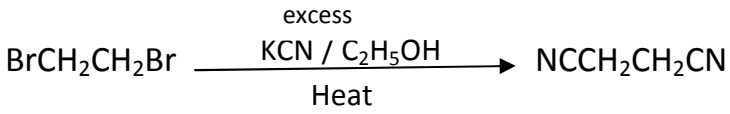
Reactions of Dihalides

1. Reactions with hot sodium hydroxide or potassium hydroxide solution.
   This reaction results into formation of diols. e.g

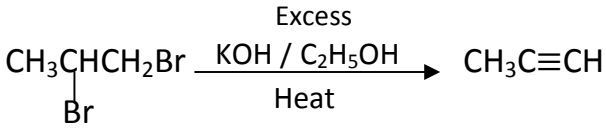


ethane-1,2-diol

2. Reaction with potassium cyanide in presence of ethanol.e.g

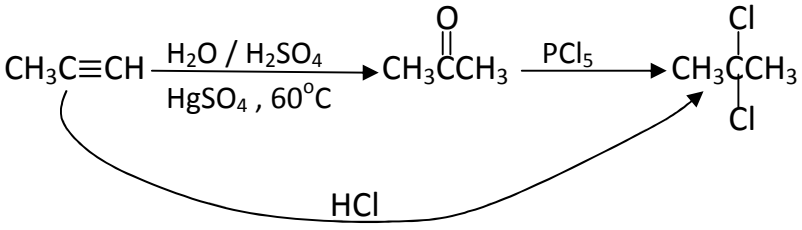


3. Reaction with hot alcoholic solution of potassium or sodium hydroxide.
   This produces alkynes e.g



Qn. Show how the following conversions can be made.

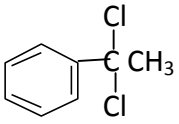
Propyne to 2,2-dichloropropane



Synthesize

(a) $CH_3CH_2CH_2Br$ to $CH_3\overset{Cl}{\overset{|}{C}}CH_3$ (Cl)

(b) CH_3CH_2OH to $HOOCCH_2CH_2COOH$

(C) $HC\equiv CH$ to 

(d) CaO to $ClOCH_2CH_2COCl$

(e) Propan-2-ol to 1,2-dichloropropane.

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AROMATIC HALIDES

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