

AROMATIC COMPOUNDS (ARENES)

The term aromatic is derived from the Greek word Aroma to mean sweet smell. This term has been carried forward by modern Chemists used as aromatic to mean or describe the study of compounds with benzene ring.

Benzene is a parent compound of aromatic compounds.

STRUCTURE AND BONDING OF BENZENE

Structure and bonding of benzene was made clear by analysis made by Chemists. They found out that a clear colourless compound was isolated from distillation of crude oil and on analysis, it was found to contain 92.3% carbon and 7.7% hydrogen only.

When 0.250g of this liquid was vapourized at 100°C, they found out that the liquid occupies 98cm³. The results were subjected to analysis.

| Element | C | H |
|------------------------|---------------------|---------------------|
| Percentage composition | 92.3 | 7.7 |
| Relative atoms | $\frac{92.3}{12}$ | $\frac{7.7}{1}$ |
| Moles | 7.69 | 7.70 |
| Mole ratio | $\frac{7.69}{7.69}$ | $\frac{7.70}{7.69}$ |
| | 1 | 1 |

Empirical formula = CH

$$\begin{aligned}\text{Volume of gas at } 100(373)\text{K} \\ &= \frac{24 \times 373}{293} \\ &= 30.04 \text{ dm}^3\end{aligned}$$

98cm³ of liquid contain 0.25g at 100°C.

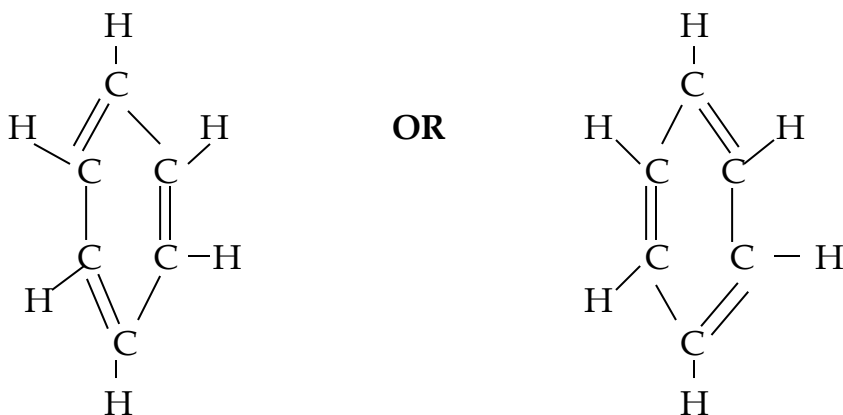
$$\begin{aligned}\text{Mass of 1mol } &\left(\frac{6.25 \times 30040}{98} \right) \text{ g} \\ &= 76.6 \simeq 77\text{g}.\end{aligned}$$

$$\begin{aligned}
 (\text{CH})_n &= 77 \\
 12n + n &= 77 \\
 n &= \frac{77}{13} \\
 n &= 5.9 \simeq 6.
 \end{aligned}$$

Molecular formula is C_6H_6 .

The structure proposed was C_6H_6 with all its isomers.

In 1865, Kekule proposed that the structure of benzene molecule is not a straight chain but an hexagonal ring consisting of alternating double bonds.



But a number of evidences proved out that the above structure, proposed by Kekule was not true. Benzene does not have true double bonds since it does not undergo addition reaction with bromine in darkness.

EVIDENCE PUT TO EXPLAIN BENZENE STRUCTURE.

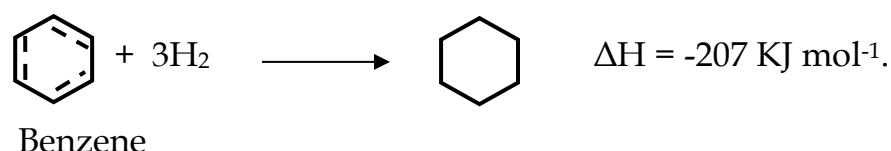
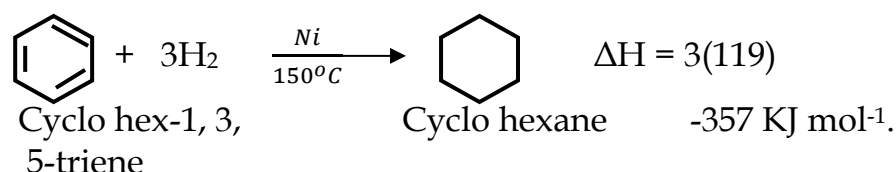
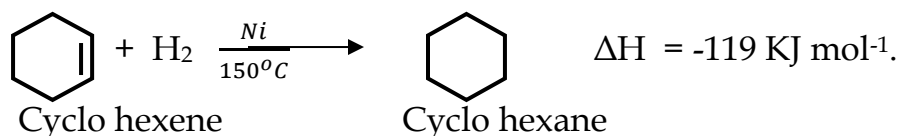
- (i) X-ray structure determination to measure the length of carbon-carbon bonds.

| Compound | Bond | Length/nm |
|--------------|--------------|-----------|
| Cyclo hexane | C – C | 0.154 |
| Cyclo hexene | C = C | 0.134 |
| Benzene | C \equiv C | 0.140 |

The measurements of the bond length showed that, the bond length of benzene are between single and double, therefore are not true double bonds ruling out Kekule's structure of double bonds.

(ii) **Thermodynamic measurements:**

(a) Enthalpy of hydrogenation.



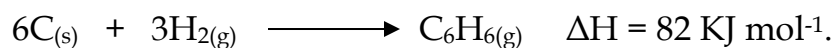
Conclusion:

The double bonds of benzene are not true double bonds.

Benzene is more stable than cyclo hex-1, 3, 5, triene by an extra 150 KJmol⁻¹

(b) **Enthalpy of formation of benzene.**

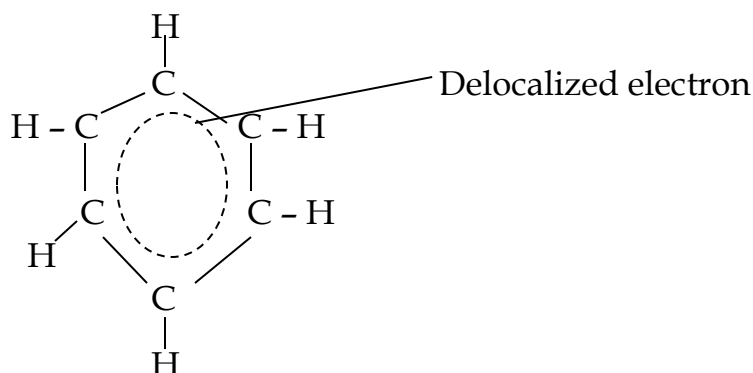
The theoretical/calculated enthalpy of formation of benzene is 252 KJ mol⁻¹ but the practical value of this energy is 82 KJ mol⁻¹. This means benzene is more stable by 170 KJ mol⁻¹ of energy.



(c) **Reactions of benzene**

Benzene does not undergo addition reactions but undergoes substitution reactions implying it does not have double bonds but a system of delocalized electrons or the pie (π system).

DELOCALIZATION OF BENZENE STRUCTURE

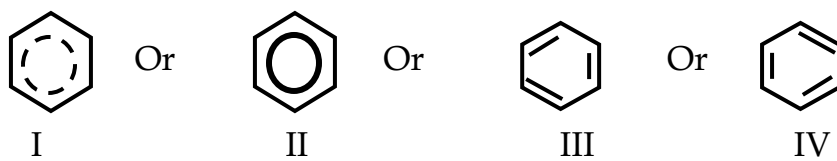


Benzene structure has got six δ carbon - carbon bonds.

It has got 3- π carbon - carbon bonds.

The π bonds are not localized but they are shared by the six carbon atoms giving a π system of electrons and this is called delocalization.

STRUCTURE OF BENZENE.

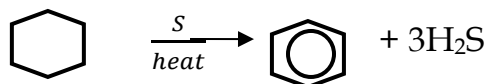
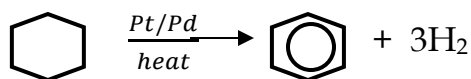


BENZENE

Is the parent aromatic compound with a hexagonal ring of carbon atoms having a π system of electrons.

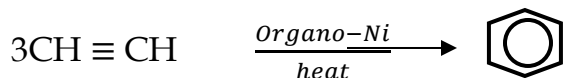
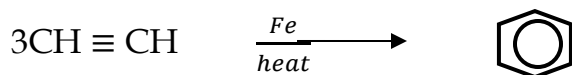
FORMATION OF BENZENE

- (i) From dehydrogenation of cyclo hexane when heated with Pt/Pd or heated with sulphur. Cyclo hexane loses H_2 atoms to form benzene.



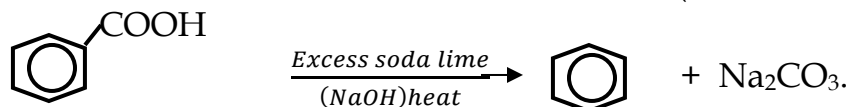
- (ii) **Polymerisation of ethyne**

When ethyne is heated with an organo iron or Nickel, it undergoes cyclisation to form benzene.

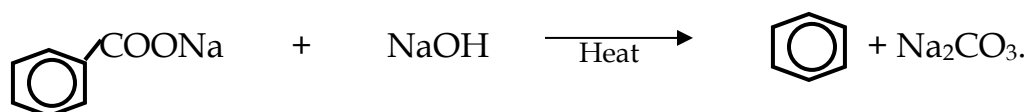
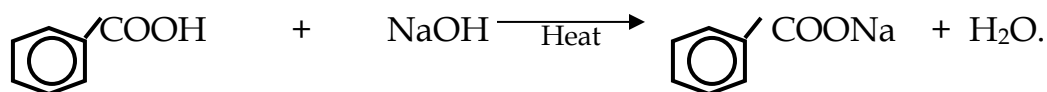


(iii) **Decarboxylation of benzoic acid**

When benzoic acid is heated with soda lime (a mixture of (NaOH and CaO).



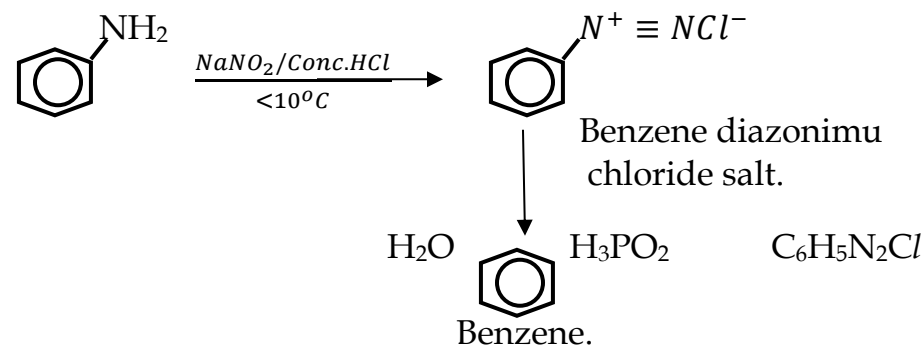
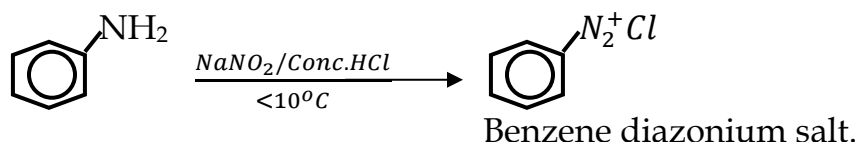
Two step reaction

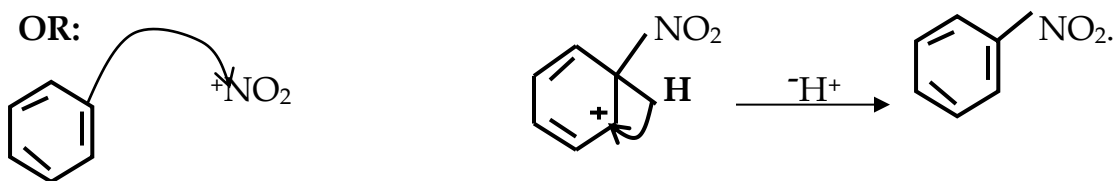
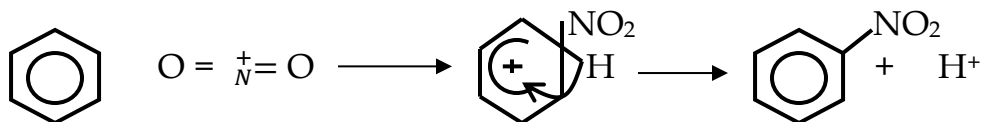
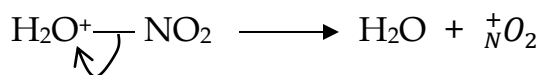
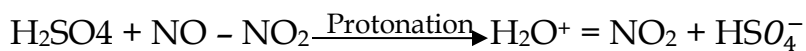


(iv) **From benzene diazonium salt.**

When benzene diazonium salt is reacted with hypophosphorus acid in presence of water, benzene is formed.

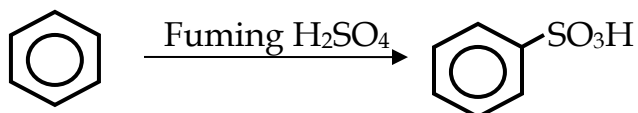
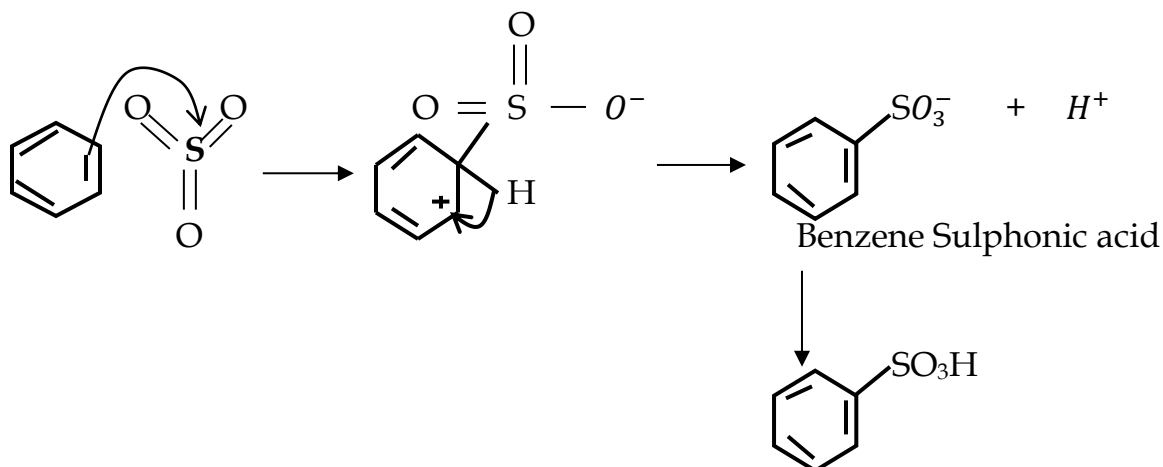
The formation of benzene diazonium salt can be started from phenyl amine which is reacted with a mixture of NaNO_2 and HCl (HNO_2 acid) at a temperature $<10^\circ\text{C}$.



Mechanism:**(ii) Sulphonation:**

This is a reaction where benzene reacts with Conc. Or fuming H_2SO_4 acid to form benzene sulphuric acid.

The electrophille in this reaction is SO_3 which is a neutral electrophille generated from fuming sulphuric acid.

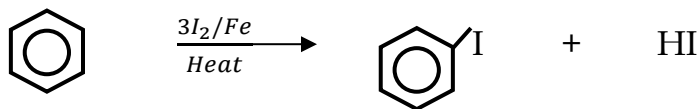
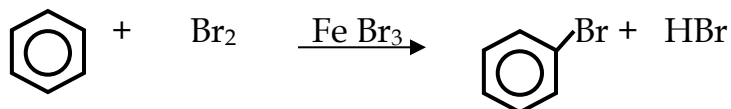
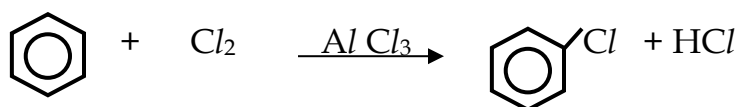
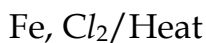
**Mechanism:**

(iii) **Halogenations**

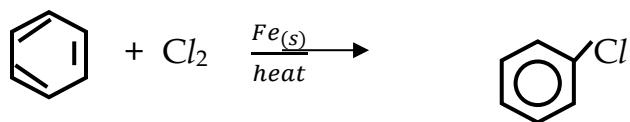
Benzene reacts with halogens like Cl_2 , Br_2 only in the presence of halogen carrier which polarizes the halogen molecule by accepting the lone pair of electrons so that the electrophile is generated.

In the absence of the halogen carrier, benzene does not react with halogens.

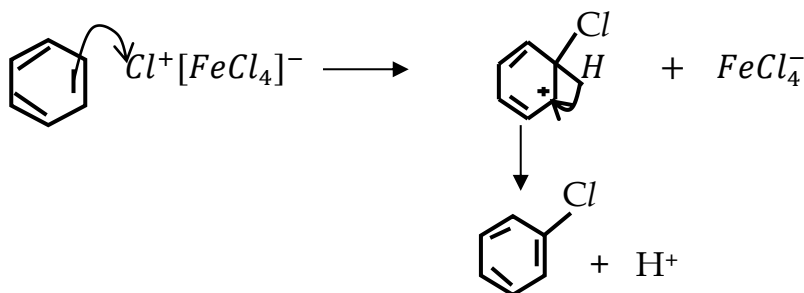
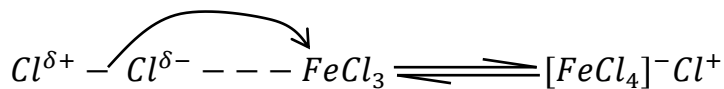
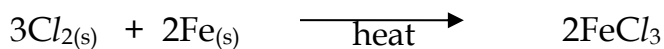
Examples of halogen carriers used are:

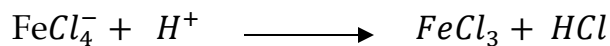


Mechanism:



Mechanism:

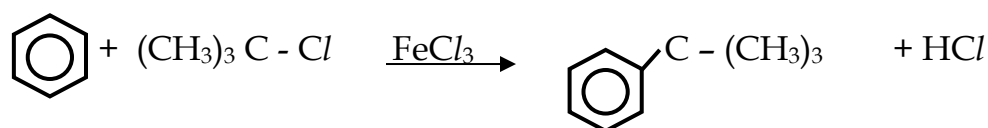
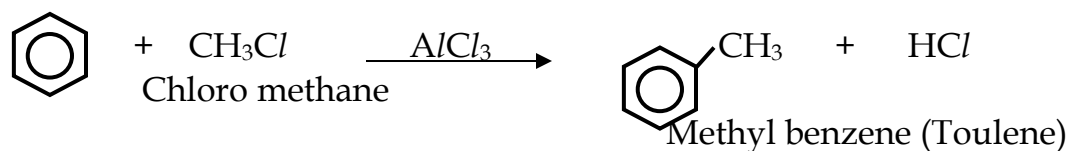




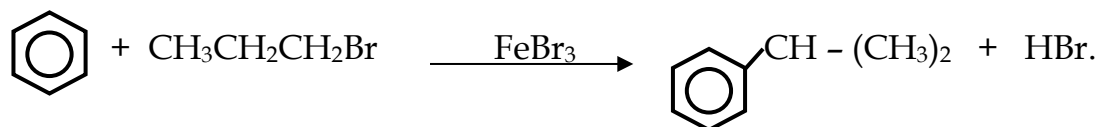
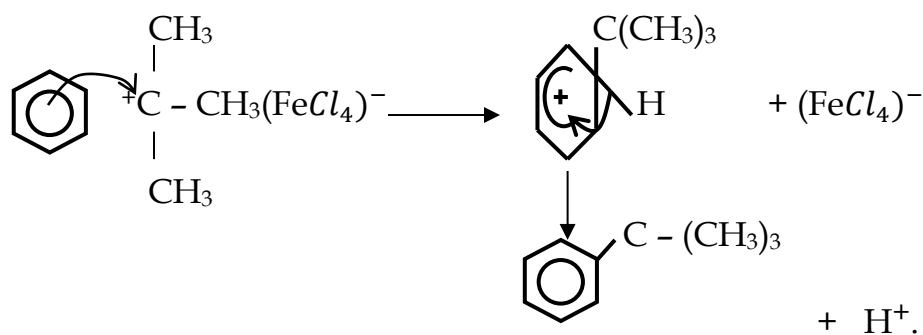
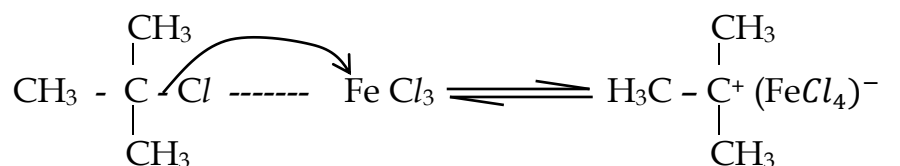
Alkylation of Benzene

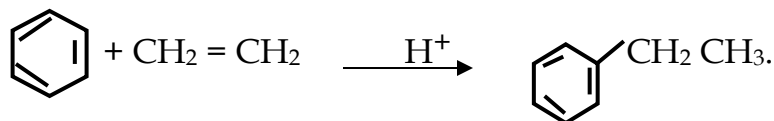
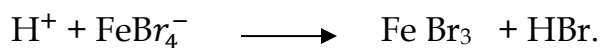
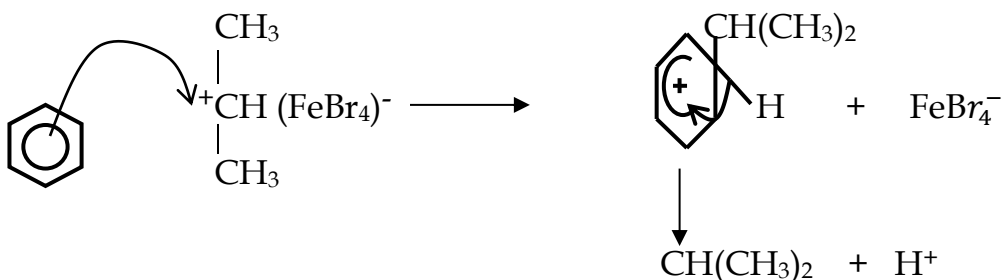
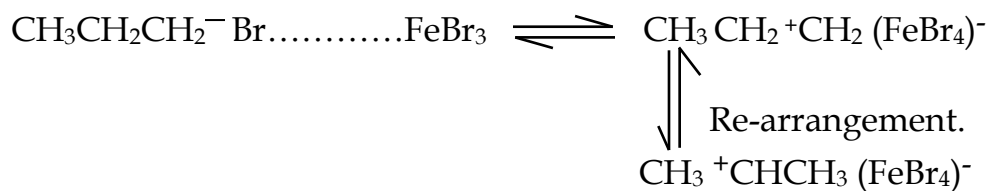
This is the reaction where an aromatic compound reacts with an alkyl halide in the presence of a halogen carrier to form an alkyl aromatic compound.

This reaction was first identified by **Friedel craft**. It is also called Friedel Craft alkylation.

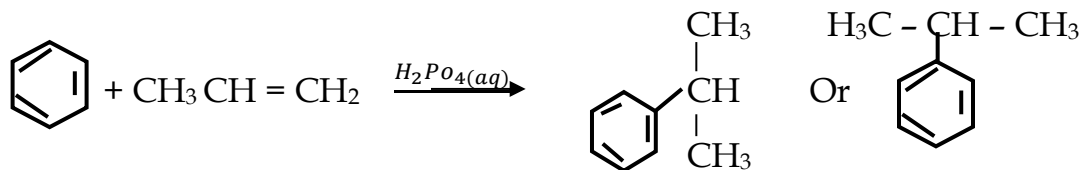
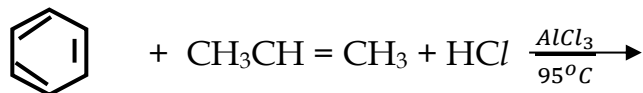
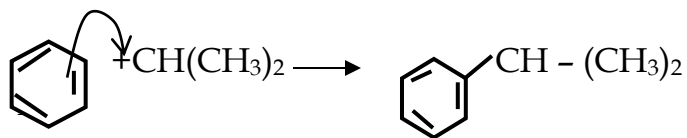
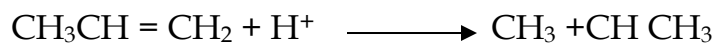


Mechanism



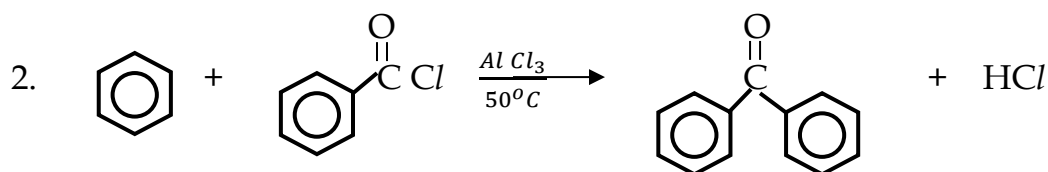
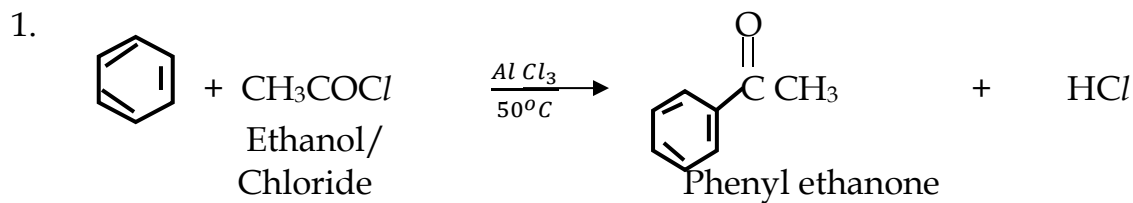
Mechanism:

Benzene reacts with alkenes in presence of a mineral acid.
The mineral acid is necessary to form an electrophile.

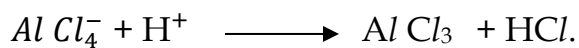
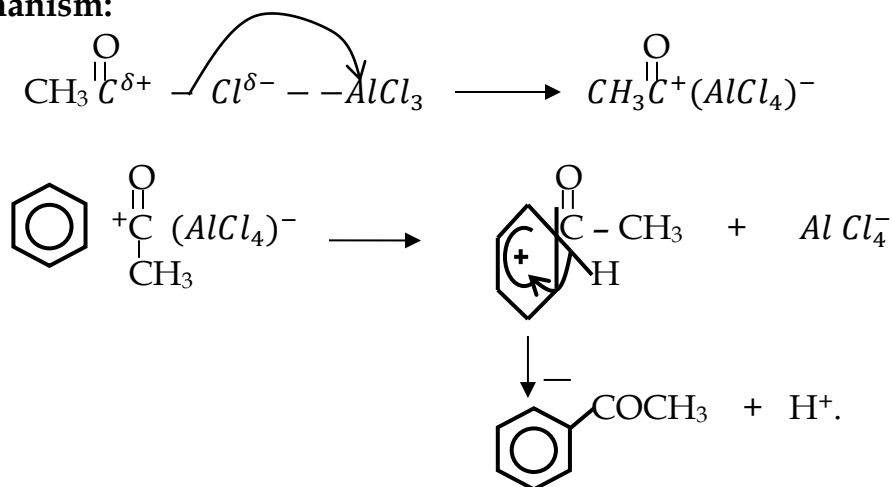
**Mechanism:**

Acylation

Is a reaction of benzene with acid halides in the presence of halogen carriers to form aromatic ketones at a temperature of 50°C.



Mechanism:



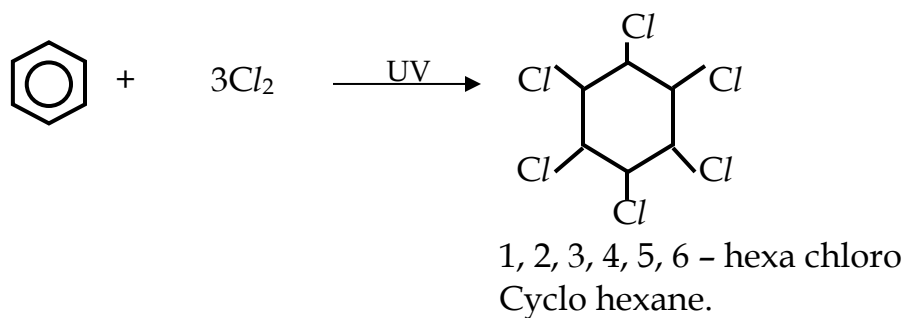
Hydrogenation:

Benzene react with hydrogen in presence of Ni catalyst when heated at 150°C to form cyclo hexane.



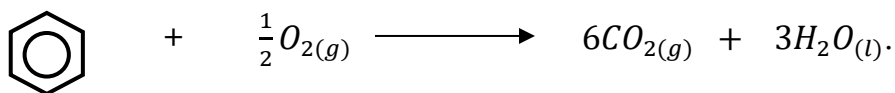
Halogen in presence of light (uv).

When chlorine is mixed with benzene in the presence of sun light or uv rays, the benzene ring becomes highly substituted with chlorine atoms to form 1, 2, 3, 4, 5, 6 hexa chloro benzene.

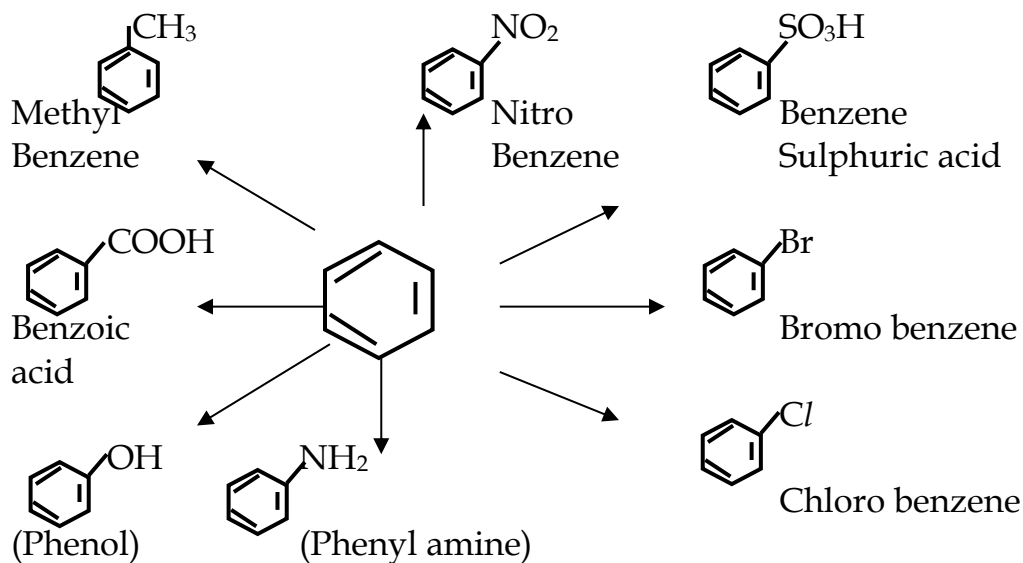


Combustion

Benzene burns in air with a sooty flame to form CO_2 and H_2O .



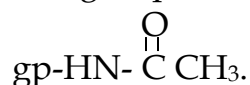
DERIVATIVES OF BENZENE



Derivatives of benzene react differently depending on the behaviour of the group of atom(s). the chemical behaviour of these groups are divided into three groups.

(i) The group which substitutes the benzene ring directing any incoming group 2(ortho) and 4(para) position directors. E.g.

(a) OH-group, ethoxide group OCH_3 , CH_3 -gp, NH_2 -nitro group, amides

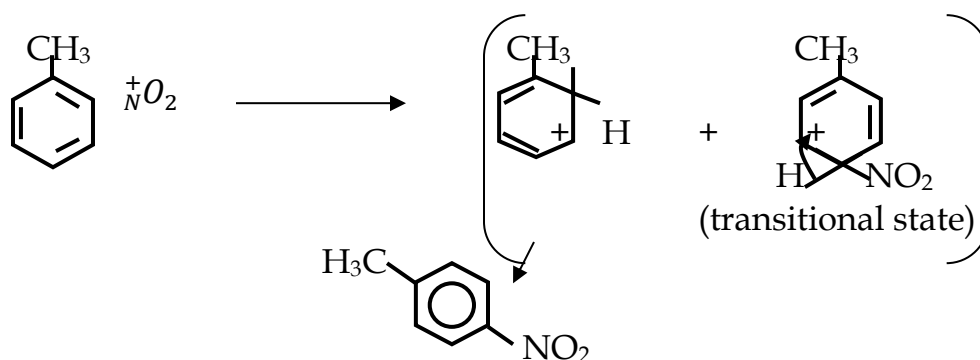
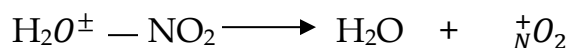
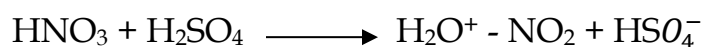
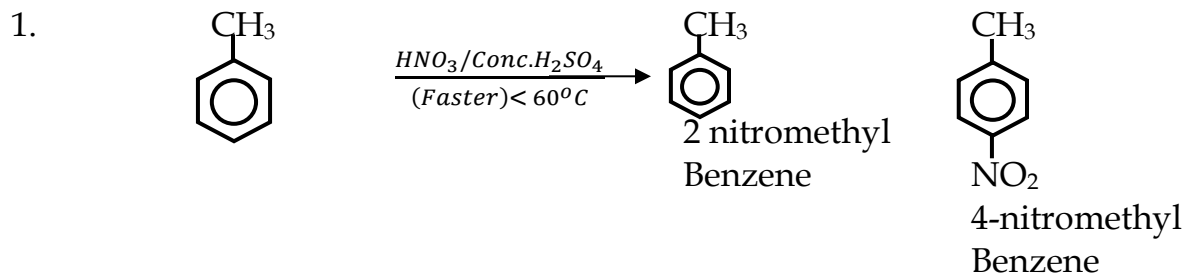


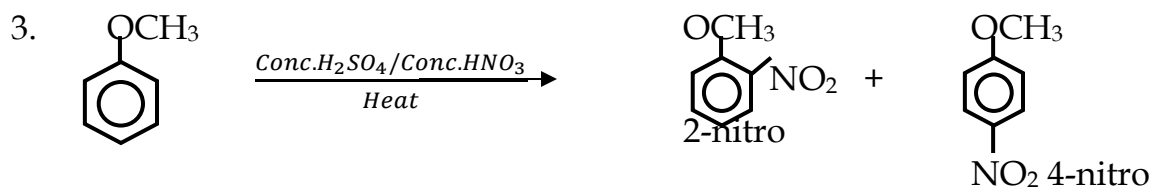
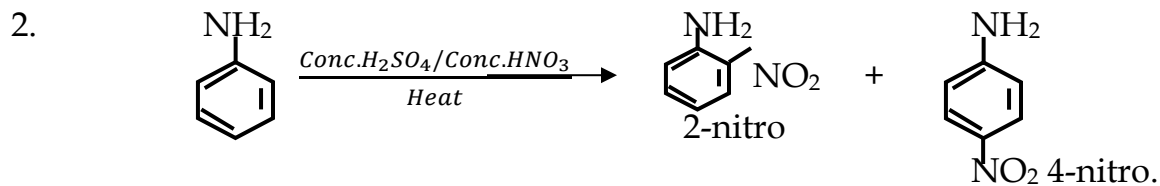
These groups have got positive inductive effect by pushing the electrons towards the ring, activating the benzene ring so that the electrons are available at positions 2, 4, and 6 where the incoming electrophile are added.

By activating the ring, they increase the electron density on the ring so that the electrophilles are added faster.

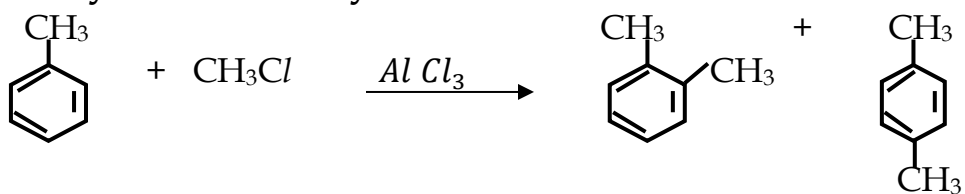
Usually two products are given, i.e. position 2 and position 4 products.

METHYL BENZENE

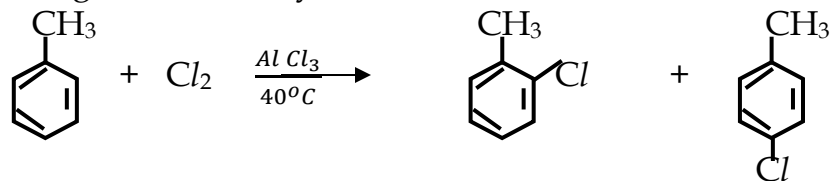




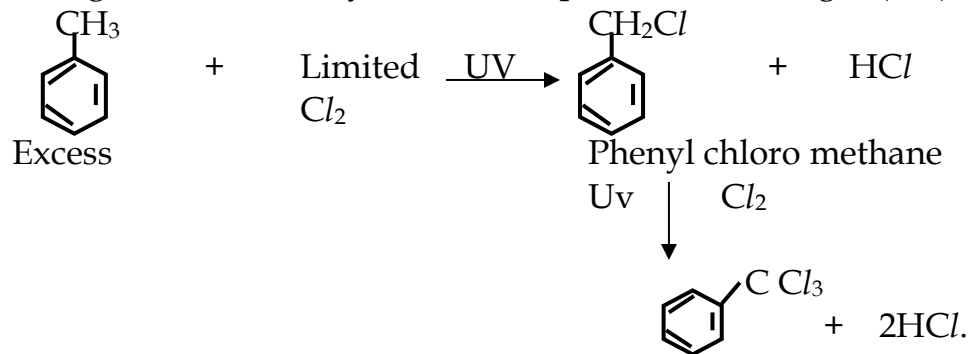
Alkylation of methyl benzene.



(a) Halogenation of methyl benzene.

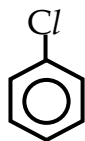


(b) Halogenation of methyl benzene in presence of sunlight (UV).

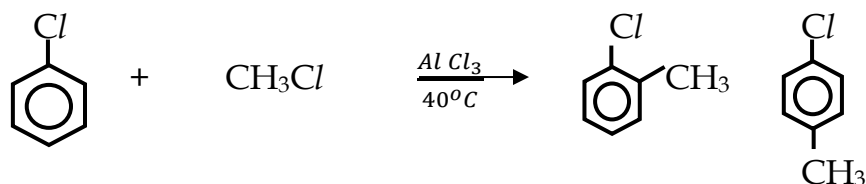
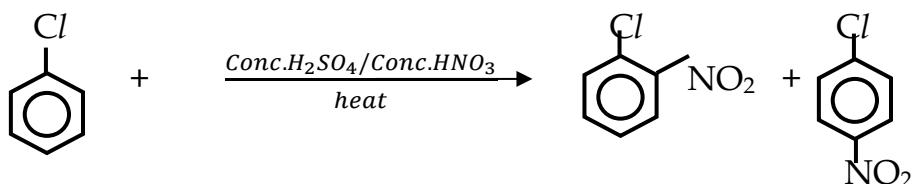


This reaction follows a free radical mechanism.

CHLORO BENZENE



Chloro benzene or other halogeno benzene compounds can substitute the ring at position 2 and 4 but at a much slower rate. This is because halogens have got a negative inductive effect (electronegative) and withdrawal electrons from the ring towards themselves so that the pie electrons on the ring can be availed to electropiles at position 2 or 4 where there is a high electron density.



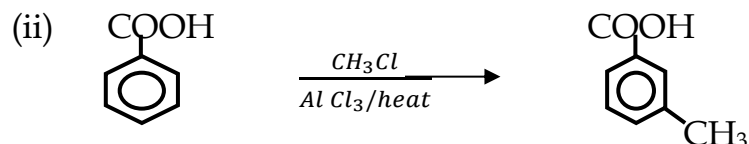
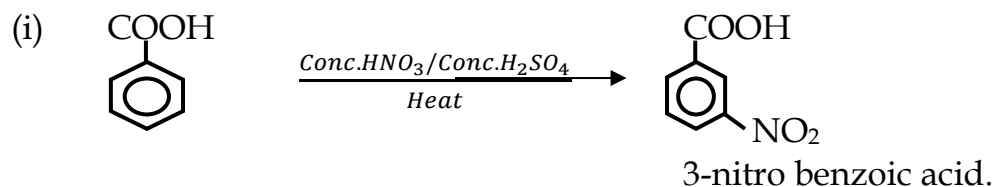
Groups that direct further substitution at position 3 of the ring do so at a much slower rate including COOH, NO₂, CN, SO₃H.

BENZOIC ACID

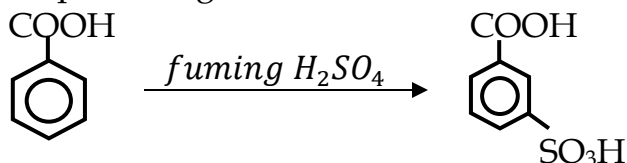


Meta(3) position directors.

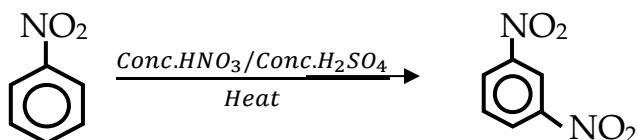
Carboxylic acid on benzoic acid directs the incoming substituents at position 3 so that one major product is formed.



(iii) Sulphonating



(iv)

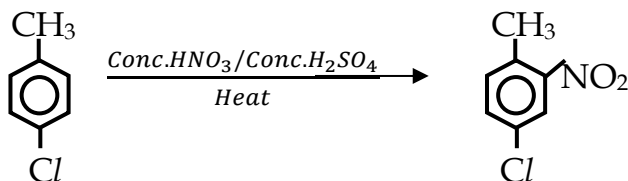
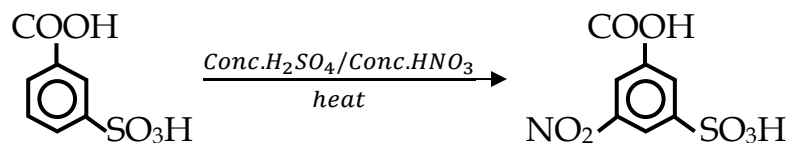
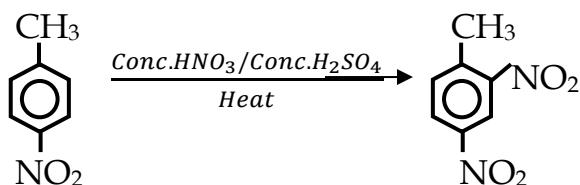


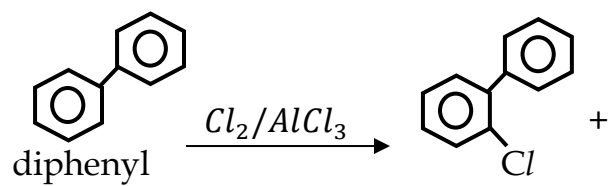
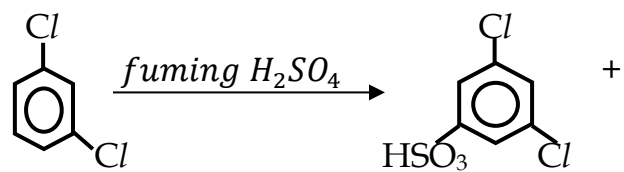
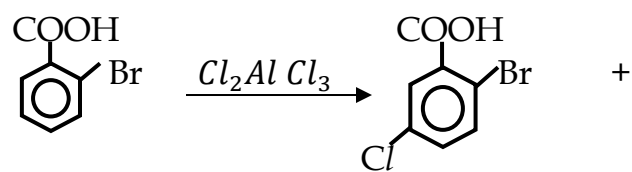
The above are Meta (3) directors because they pull electrons away from the ring and decreasing electron density at position 2 or 4 and the only place where the electrons are available is the Meta position.

DISTRIBUTED COMPOUNDS

When there are two substituents on the benzene ring, the orientation effect of these two will be determined or predicted by their reinforcing effects or the order of their superiority. The following order is normally observed.

- OR > NR₂ > Alkyl group > halogen > Meta directors.





ALKYL HALIDES

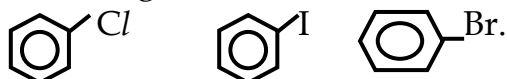
(Halogeno alkanes)

Alkyl halides are compounds in which halogen atoms are directly attached onto the hydro carbon chain or aromatic ring.

R - X where R = Alkyl or Aryl group.

X = Halogen atom (Cl, Br, I, F)

When the halogen is attached to the aromatic ring, it is called aromatic halide. e.g.



When the halogen is directly attached to the hydro carbon, it is called alkyl halide / halogen alkane. E.g.

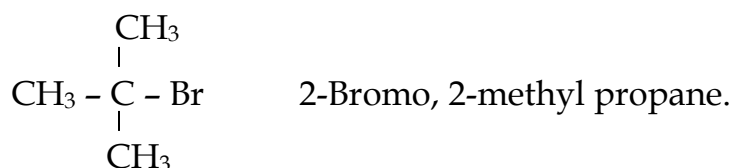
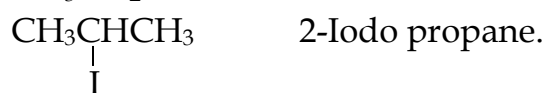


ALKYL OR HALOGENO ALKANES

Nomenclature:

Alkyl halides are named as derivatives of corresponding alkanes by inserting the number and the prefix, chloro, Bromo, Iodo, Fluoro, to the alkane name.

Example:



ISOMERISM

Alkyl halides exhibit two types of isomerism.

- (i) Chain isomerism
- (ii) Positional isomerism

CHAIN ISOMERISM:

These arise as a result of difference in the arrangement of carbon atoms giving different carbon skeleton but the position of the halogen atom remains the same.

C_4H_9Br .

1. $CH_3CH_2CH_2CH_2Br$ 1-Bromo butane.
2. $CH_3\underset{\substack{| \\ CH_3}}{CH}CH_2Br$ 1-Bromo-2-methyl propane.

POSITIONAL ISOMERISM:

These arise as a result of the different positions taken by the halogen atom on the same chain. E.g.

C_4H_9Br .

- $CH_3CH_2CH_2CH_2Br$ 1-Bromo butane
- $CH_3CH_2\underset{\substack{| \\ Br}}{CH}CH_3$ 2-Bromo butane

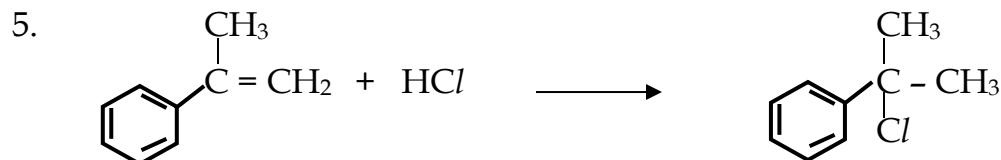
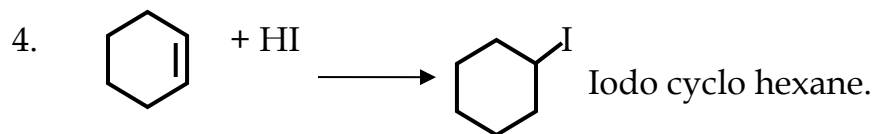
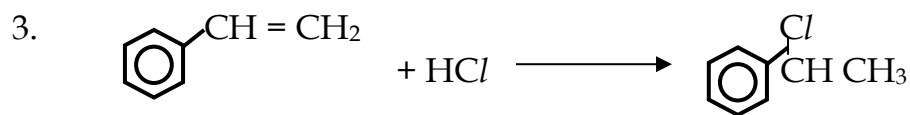
METHODS OF PREPARATION:

Alkyl halides are prepared from the following:

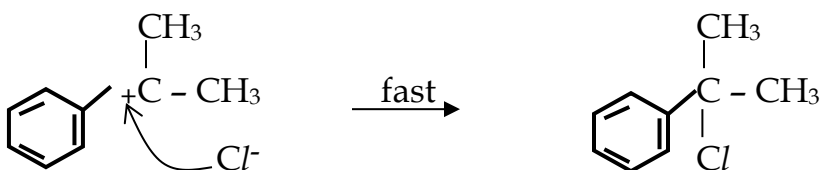
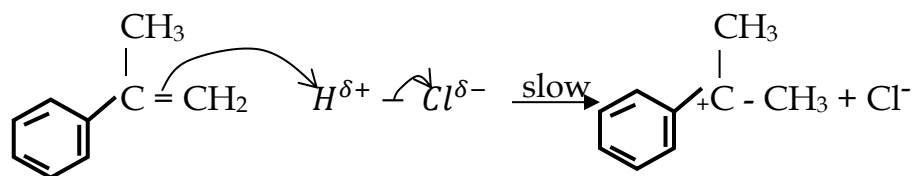
(i) From Alkenes:

Addition of an halogen acid to an alkene at room temperature gives an alkyl halide. When unsymmetrical alkene is used, addition of an halogen acid gives a product predicted by Markovnikov's rule. But if a peroxide used, then the product will be that of anti Markovnikov's rule.

1. $CH_3CH=CH_2 + HBr \xrightarrow{r.t.p} CH_3\overset{\substack{Br \\ |}}{CH}CH_3$
2. $CH_3CH=CH_2 + HBr \xrightarrow[Heat]{ROOR} CH_3CH_2CH_2Br$



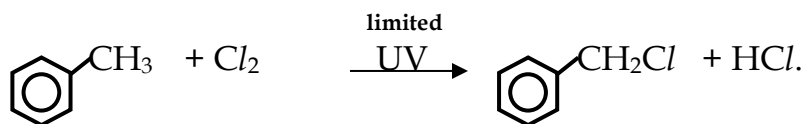
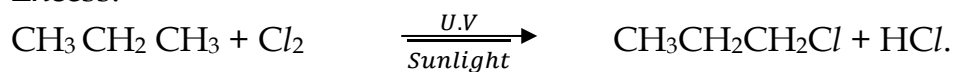
Mechanism:



(ii) **From Alkanes**

When alkanes are reacted with a halogen molecule in presence of UV rays of sunlight. A mixture of alkyl halides are formed but if the reaction conditions are controlled by using excess alkane or limited halogen molecule, then the product formed would be one type of alkyl halide.

Excess:



(iii) From Alcohols:

Alcohols are the most important source of preparing alkyl halides in reaction where hydroxyl groups of alcohol are replaced by halogen atoms which could be derived from:

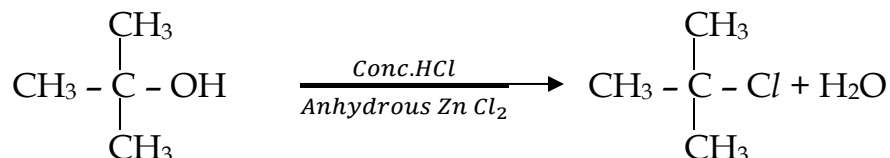
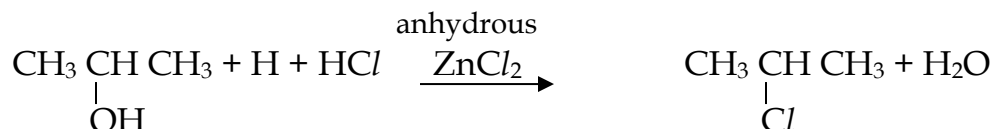
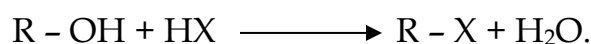
- halogen acids (HX).
- Phosphorus tri or penta halides (PX_3/PX_5)
- Thionyl chloride ($SOCl_2$).

(a) **Action of halogen acid on the alcohol:**

When a halogen acid is heated with an alcohol in presence of a dehydrating agent e.g.

- $ZnCl_2$ (anhydrous)
- Conc. H_2SO_4 .
- Al_2O_3 (Dry)

An alkyl halide is formed. Sometime the halogen acid is generated "insitu."



A solution of anhydrous $ZnCl_2$ in Conc. HCl (Lucas reagent) is an important reagent for distinguishing the three classes of alcohols i.e.

- Primary.
- Secondary and tertiary alcohols.

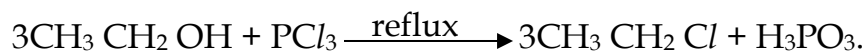
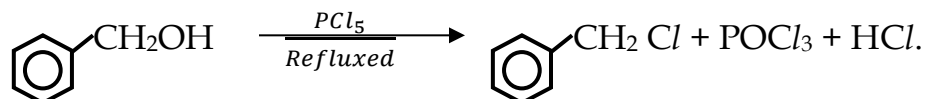
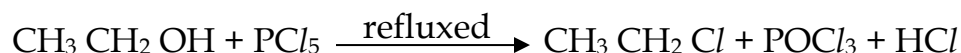
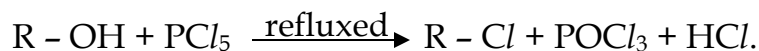
The tertiary alcohol gives an immediate cloudy solution of an alkyl halide. (0.5 minutes).

The secondary alcohol gives cloudy solution between 5 and 10 minutes.

The primary alcohol does not give a cloudy solution at room temperature.

(b) Action of phosphorous halides:

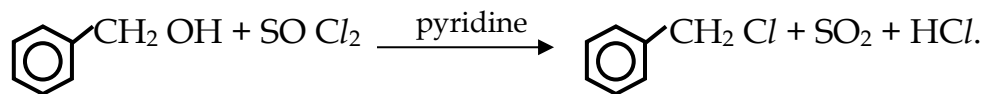
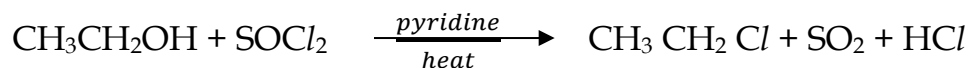
When alcohols are refluxed with phosphorous halide like phosphorous tri chloride or phosphorous penta chloride, the halogeno alkanes or alkyl halides are formed.



(c) Action of thionyl chloride (SOCl₂):

When alcohols are refluxed in presence of thionyl chloride in the presence of an organic base pyridine to neutralize the mixture of toxic gases, an alkyl halide is formed.

This is a very convenient way of preparing alkyl halides.



REACTIONS OF ALKYL HALIDES

CLASSES OF HALOGENO ALKANES

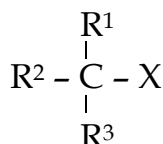
(i) **Primary Alkyl halides** $\text{RCH}_2\text{CH}_2 - \text{X}$.

Here the halogen atom is attached to a carbon which is bonded to only one other.

(ii) Secondary alkyl halide. $\text{R} - \text{CH}^1 - \underset{\text{X}}{\underset{|}{\text{R}^2}}$

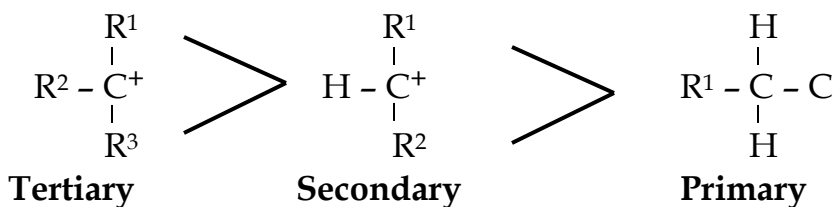
Here the halogen atom is attached to a carbon atom which is bonded to two other carbon atoms.

(iii) Tertiary alkyl halide:



Here the halogen atom is attached to a carbon atom which is bonded to three other carbon atoms.

The three classes of alkyl halides given above react differently due to the stability of the carbo cation ion which is formed as an intermediate during the reaction. The stability is governed by the order that tertiary > secondary > primary.

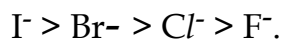


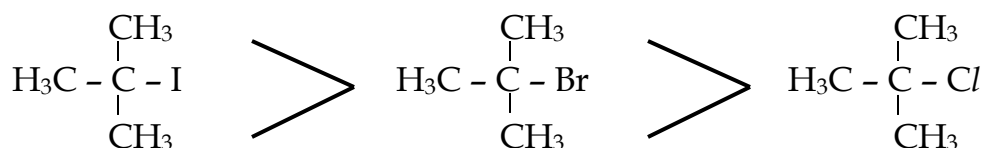
PHYSICAL PROPERTIES:

Lower alkyl halides are gases at room temperature.

The medium ones are liquids and the higher ones are solids.

The boiling points of alkyl halides with the same number of carbon atoms is determined by the atomic size of the halogen which later is as a result of the Van de Waal's forces of attraction.

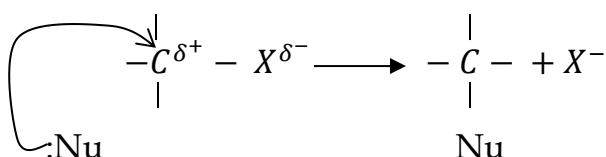




CHEMICAL PROPERTIES:

Halogen atoms being more electronegative than carbon means that the C - X bond is highly polar due to the presence of partial induced charge where the halogen is partially negative and carbon is partially positive.

The polarity of the C - X bond makes alkyl halides to be very reactive to the nucleophile thus nucleophilic substitution.



The type of halogen present also determines the reaction.

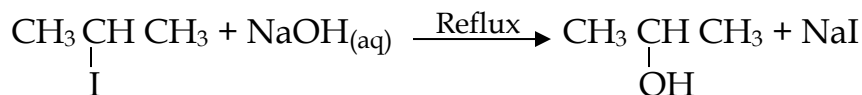
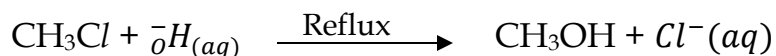
The electronegativity difference between the halogen together with the bond length determines overall the reactivity. Down the group of the halogens there is decrease in electronegativity and at the same time increase in the bond length.

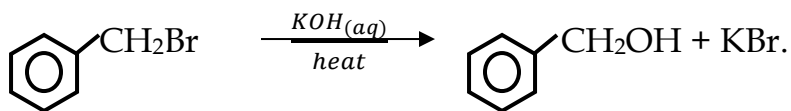
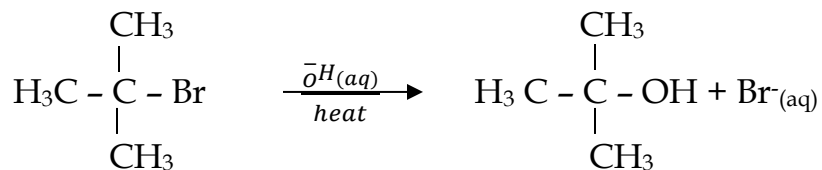
The reaction becomes faster with Iodo-alkanes than Bromo chloro fluoro alkanes because of low electronegativity in the iodides.

NUCLEOPHILIC SUBSTITUTION REACTIONS

(i) Reaction with alkalis:

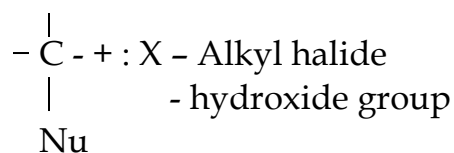
Alkalis react with alkyl halides to form alcohols when they are refluxed.



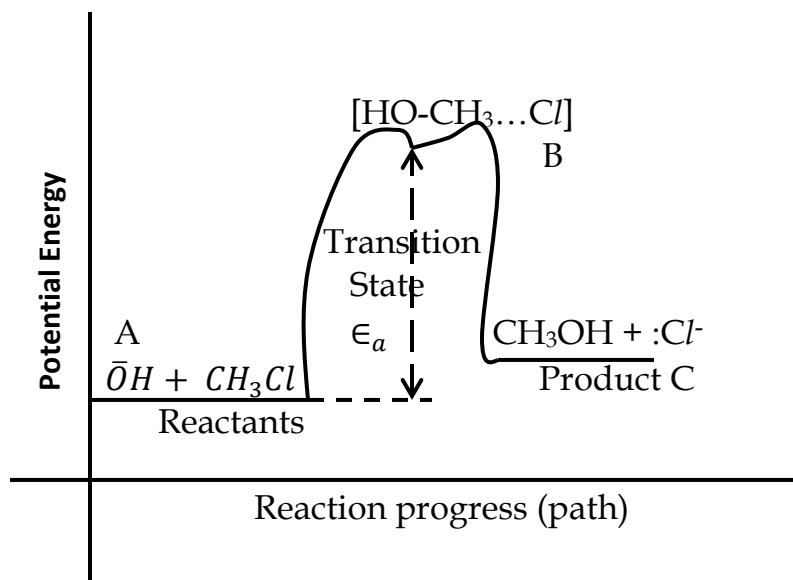
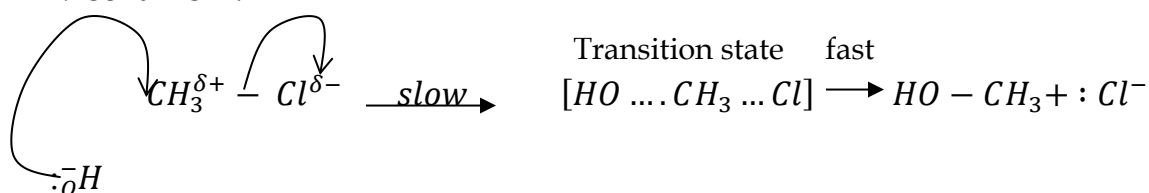


Primary alkyl halides with aqueous alkali.

Primary alkyl halides follow nucleophilic substitution bimolecular (S_N2) mechanism. Is a type of reaction where two molecules involve the rate determining step.



Mechanism:



The nucleophile which is $\bar{O}H$ approaches the carbon atom carrying halogen from the opposite side.

This partially forms a nucleophile carbon bond and at the same time, a carbon halogen bond partly breaks. This leads to the increase in potential energy from A to B.

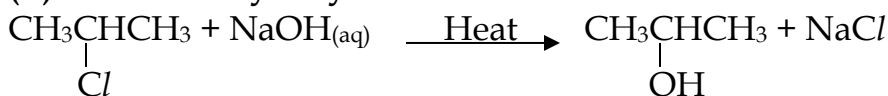
At B, there is partial halogen bond broken and partial nucleophile bond formed. This state is known as **activation complex** or **transition state**.

The energy level between the reactants and the activation complex is called the **activation energy**.

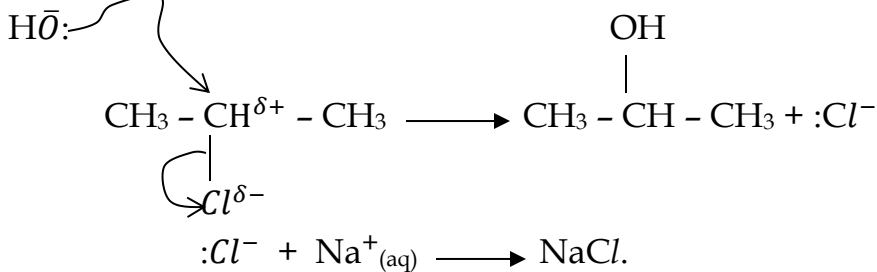
Later, the potential energy of the system increases when all the carbon halogen bonds are broken and the carbon nucleophile bonds are formed.

The energy of the system finally decreases until point C where the product of the alcohol is finally formed. This type of reaction is categorized as SN_2 reactions mechanism because there are two molecules involved at the activated complex.

(ii) Secondary alkyl halide

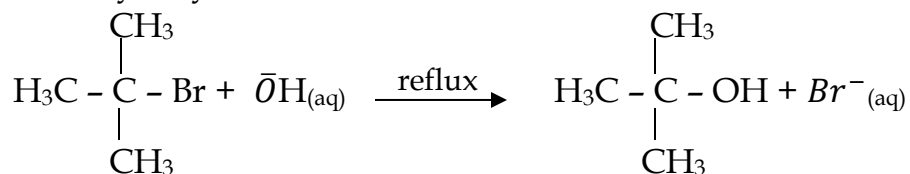


Mechanism:



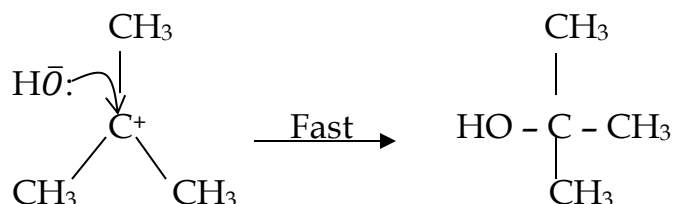
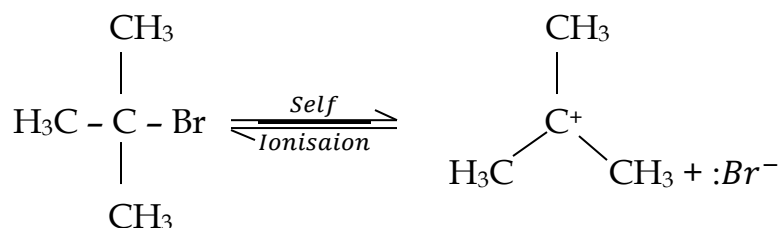
The mechanism followed by secondary alkyl halides is always between SN_1 and SN_2 .

(ii) Tertiary alkyl halides



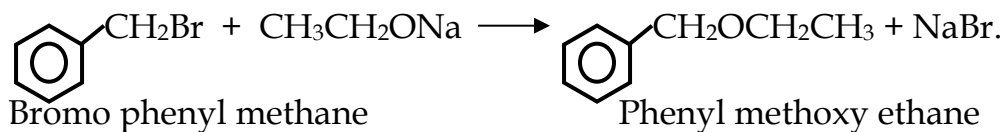
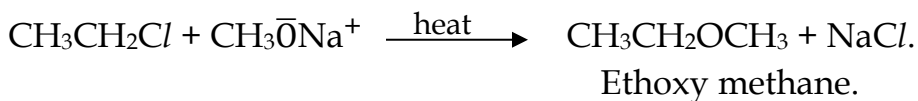
Tertiary alkyl halides follow $\text{S}_{\text{N}}1$ mechanism. Here only the alkyl halide molecule is involved in the activated complex and thus its concentration alone determines the order of reaction.

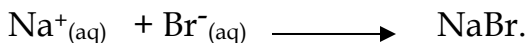
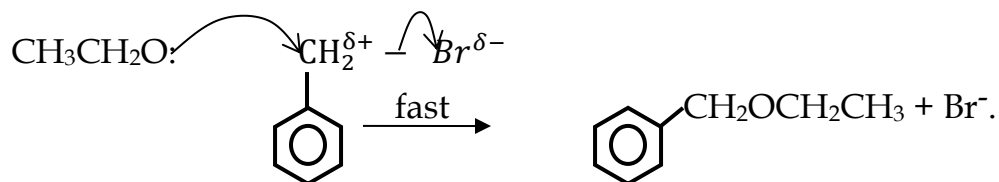
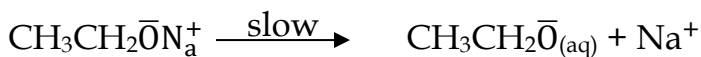
Mechanism:



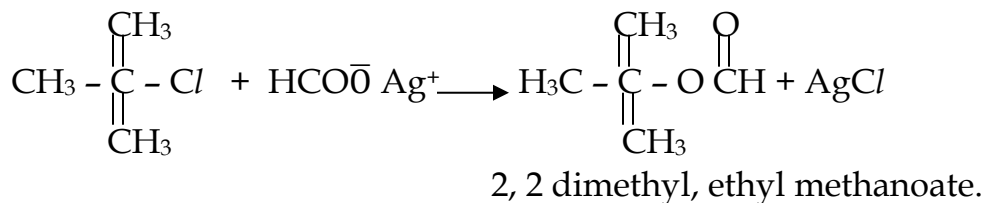
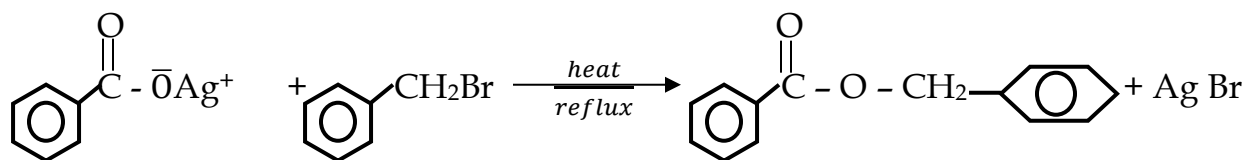
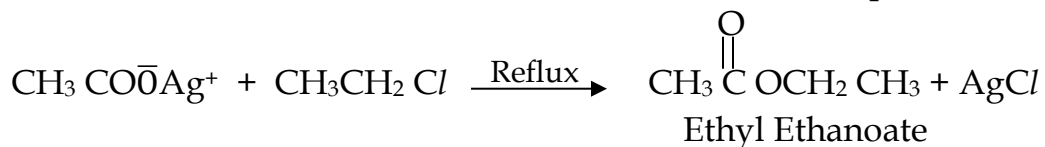
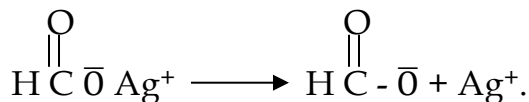
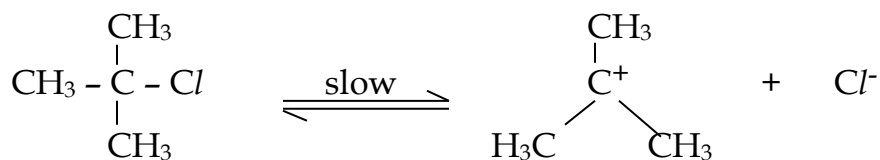
REACTIONS WITH ALKA OXIDES (Na, K)

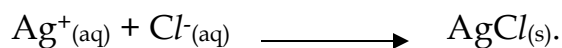
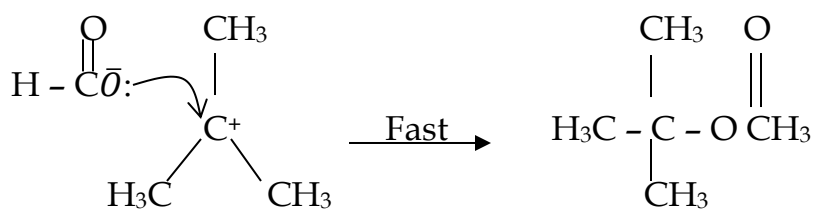
Alkyl halides react with sodium or potassium alkali oxides to form ethers under heat.



Mechanism:**REACTIONS WITH SILVER SALTS OF CARBOXYLIC ACIDS**

Alkyl halides react with silver salts of carboxylic acids when refluxed to form esters. This reaction uses the alkanoate ion as the nucleophile.

**Mechanism:**



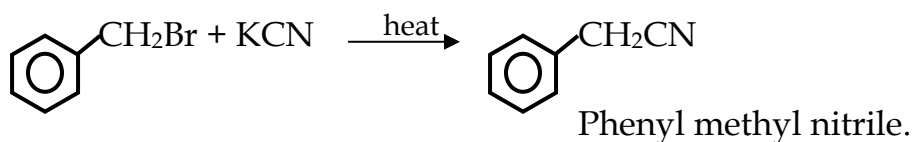
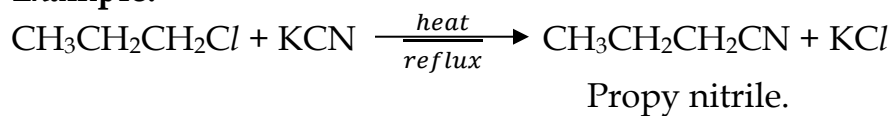
REACTIONS WITH POTASSIUM CYANIDE (KCN)

Alkyl halides react with KCN in presence of an alcohol when refluxed to form alkyl nitriles.

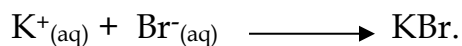
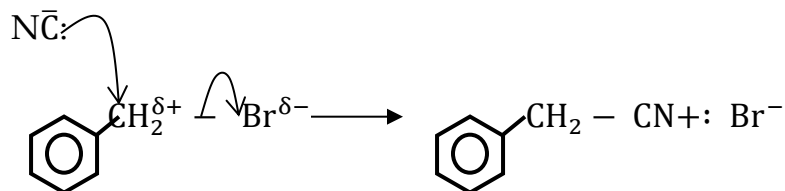
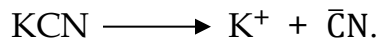
Condition (reflux) – alcohol present.

Nucleophile $\text{C}^- \equiv \text{N}$ or CN^- .

Example:



Mechanism:



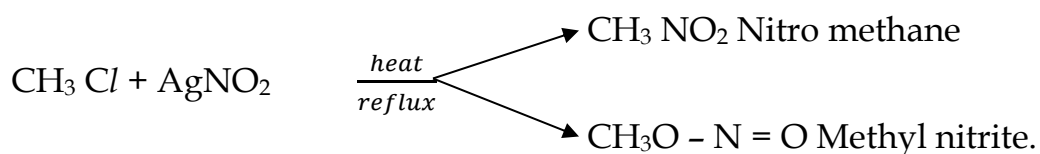
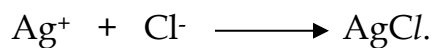
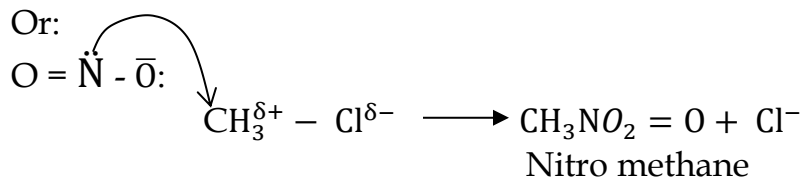
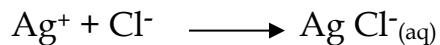
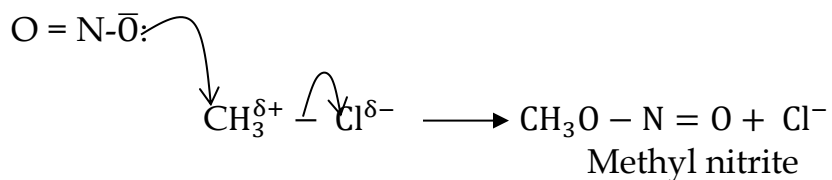
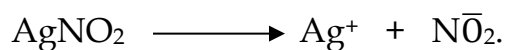
Note:

- (i) The above reaction is important inorganic synthesis, more especially increasing the carbon length (chain) by a single carbon.
- (ii) Silver cyanide can also be used instead of potassium cyanide.

Convert CH_3COOH to $\text{CH}_3\text{CH}_2\text{COOH}$.

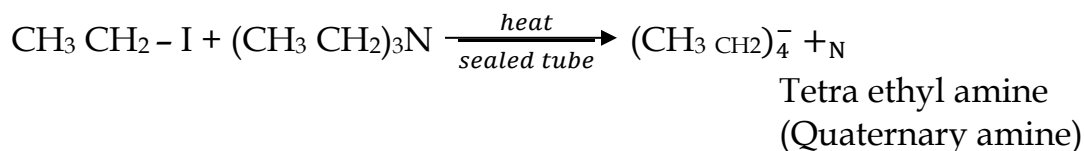
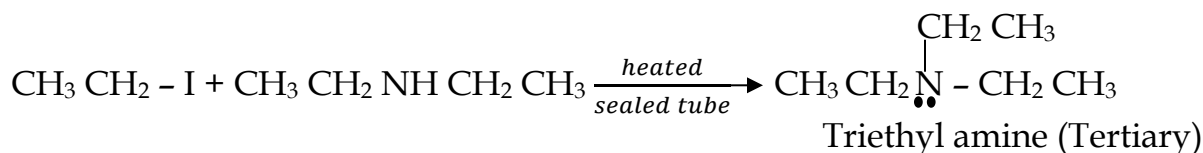
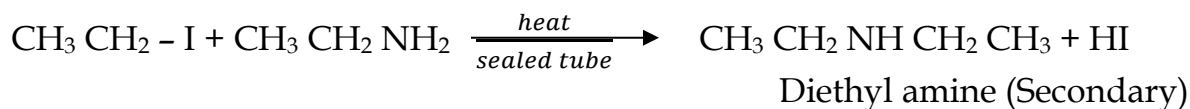
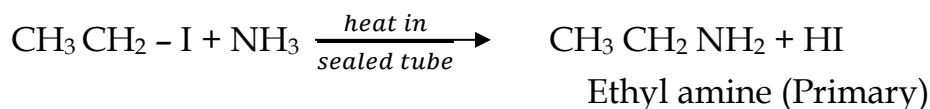
REACTIONS WITH SILVER NITRITE (AgNO_2).

Alkyl halides react with AgNO_2 when refluxed to form a mixture of nitro alkanes and alkyl nitrite. Such types of reactions are not important in synthesis since they yield a mixture of products.

**Mechanism:**

REACTIONS WITH AMMONIA AND AMINES

Alkyl halides react with conc. NH_3 to form a mixture of amines when heated in a sealed tube. A mixture of amines are produced because a product at one stage become a nucleophile for the next stage. The nucleophile is ammonia and the amines.



ELIMINATION REACTIONS OF ALKYL HALIDES

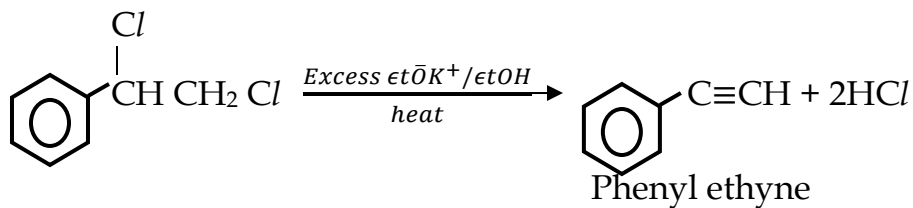
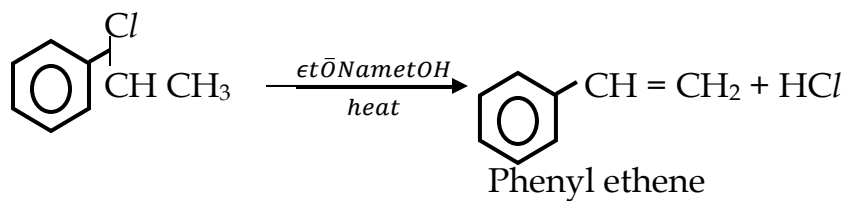
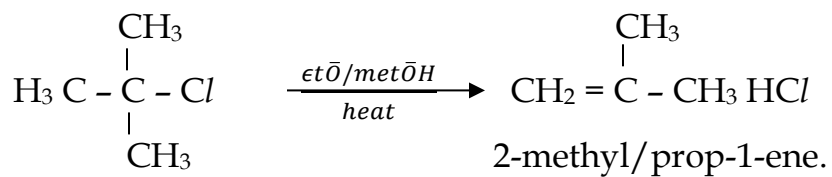
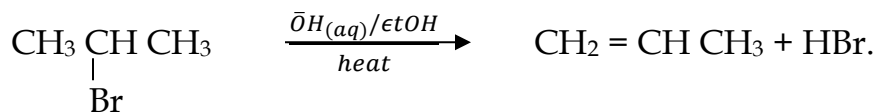
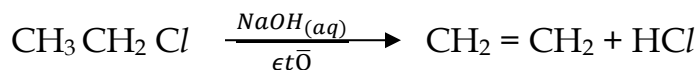
These are reactions that will result into the formation of unsaturated compound with elimination of a water molecule. Alkyl halides when refluxed or heated with an alkali (KOH, NaOH) in the presence of an alcohol, they form alkene. The reaction can also be effected by using a strong base which is an alkoxide.

Strong base (Alkoxide)

Ethoxide / EtO^-

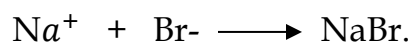
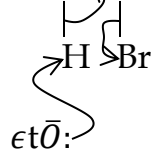
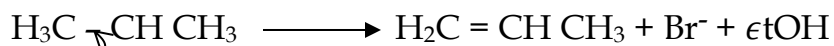
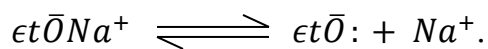
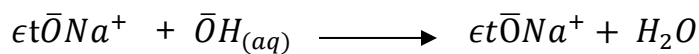
Methoxide / MeO^-

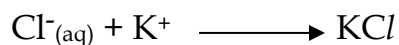
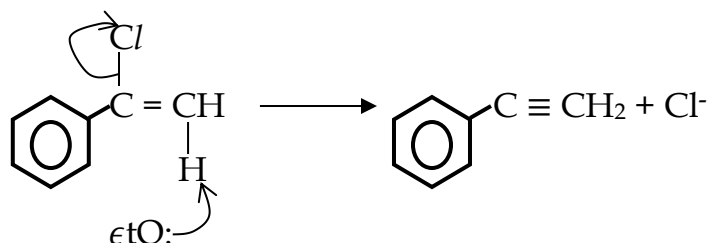
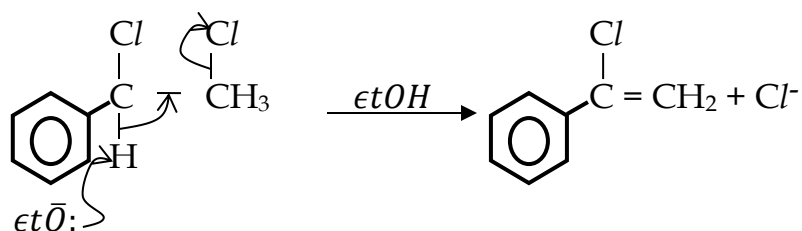
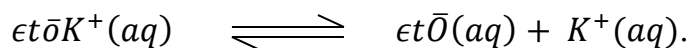
DEHYDROHALOGENATION



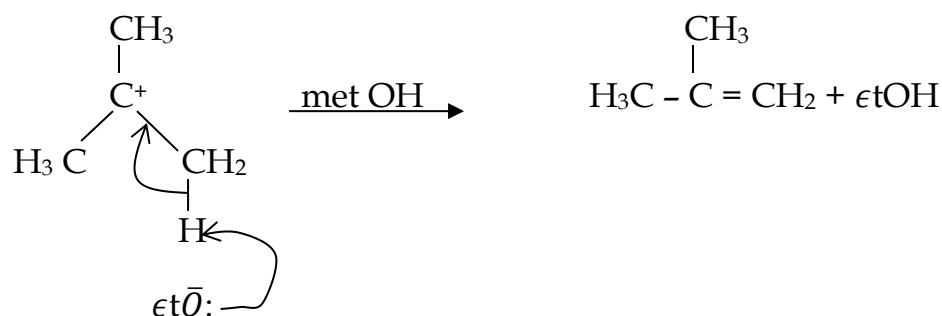
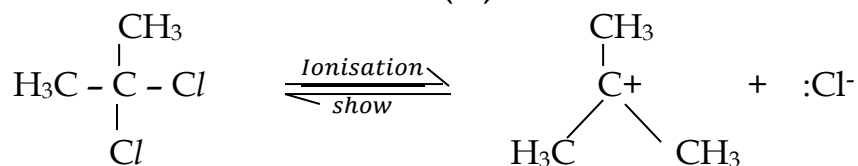
Mechanisms:

Elimination bimolecular (ϵ_2).





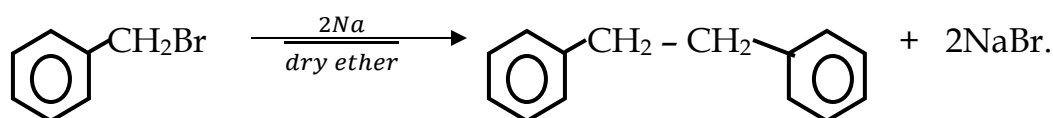
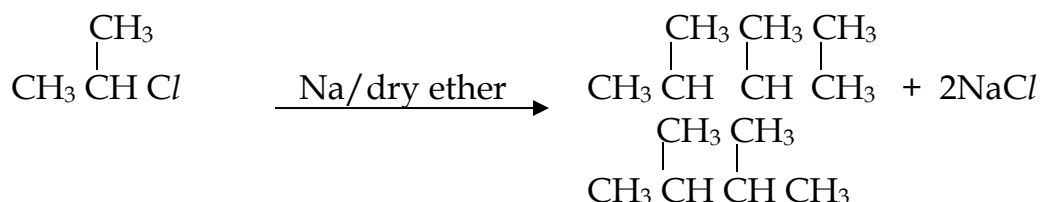
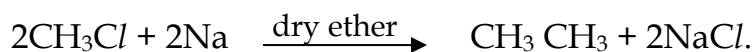
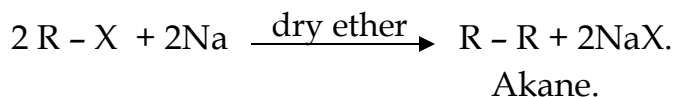
Elimination uimolecular (ϵ_1)



Research: Discuss all the reactions of chloro ethane with NaOH. (25mks)

Wurtz reaction:

When alkyl halides are reacted with Na metal in the presence of ether, alkanes are formed. The product will have an increased carbon atom by 2 i.e. the carbon number doubles.



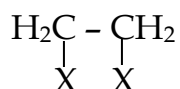
DIHALIDES COMPOUNDS

There are compounds that have got two halogen atoms within the same carbon chain.

There are two types of dihalides;

(i) **Vicinal dihalide**

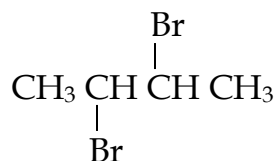
This contains two halogen atoms located on any adjacent carbon atom i.e.



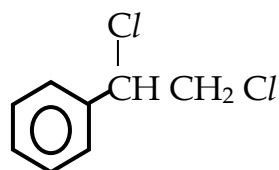
Example:



1, 2-dichloro ethane.



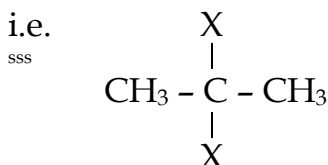
2, 3-dibromo butane.



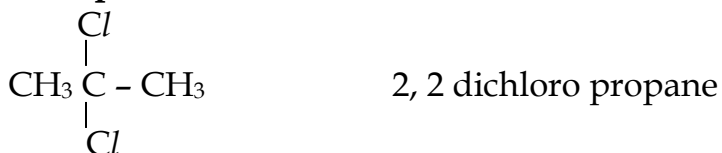
1, 2-dichlorophenyl ethane.

(ii) **Gem dihalides**

These contain the two halogen atoms located on the same carbon atoms.



Example:

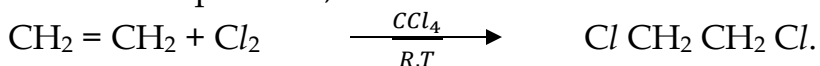


PREPARATION OF DIHALIDES

Dihalides are prepared from the following reactions:

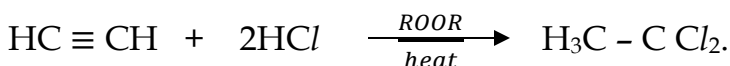
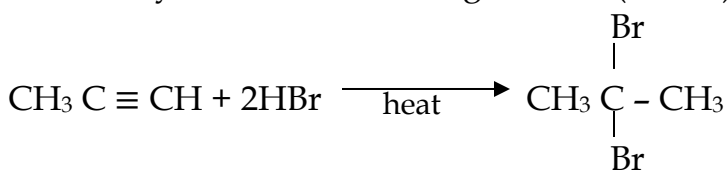
(i) **From Alkenes**

When alkenes are reacted with halogens in presence of CCl_4 (organic base) at room temperature, a vicinal dihalide is formed.



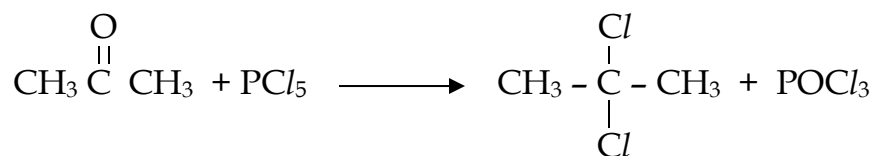
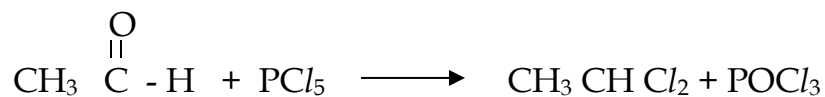
(ii) **From alkynes and halogen acids**

When alkynes react with halogen acids (excess), a gem dihalide is formed.



(iii) **From carbonyl compounds (Aldehydes and Ketones).**

When a carbonyl compound is reacted with phosphorous pentachloride, a dihalide is formed. Using aldehydes, will produce a gem dihalide and ketones also produce gem dihalide.

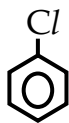
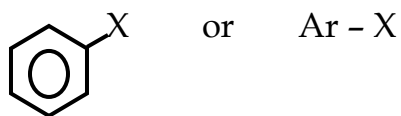


POLYHALIDES

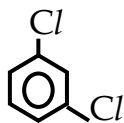
These are halogen compound with more than two halogen atoms on the same carbon chain.

AROMATIC HALIDES

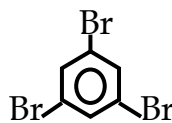
These are compounds with one or more halogen atoms directly attached to the aromatic ring.



Chloro benzene

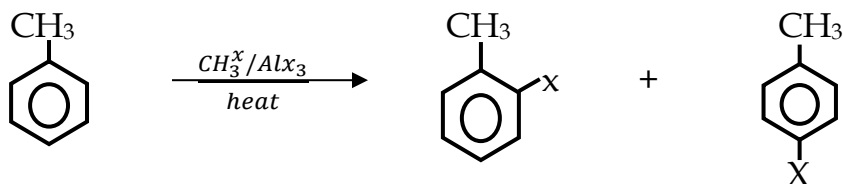
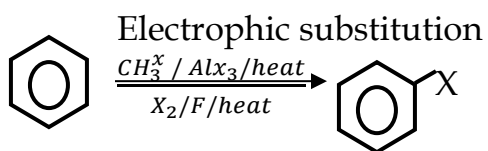


1, 3-dichloro benzene

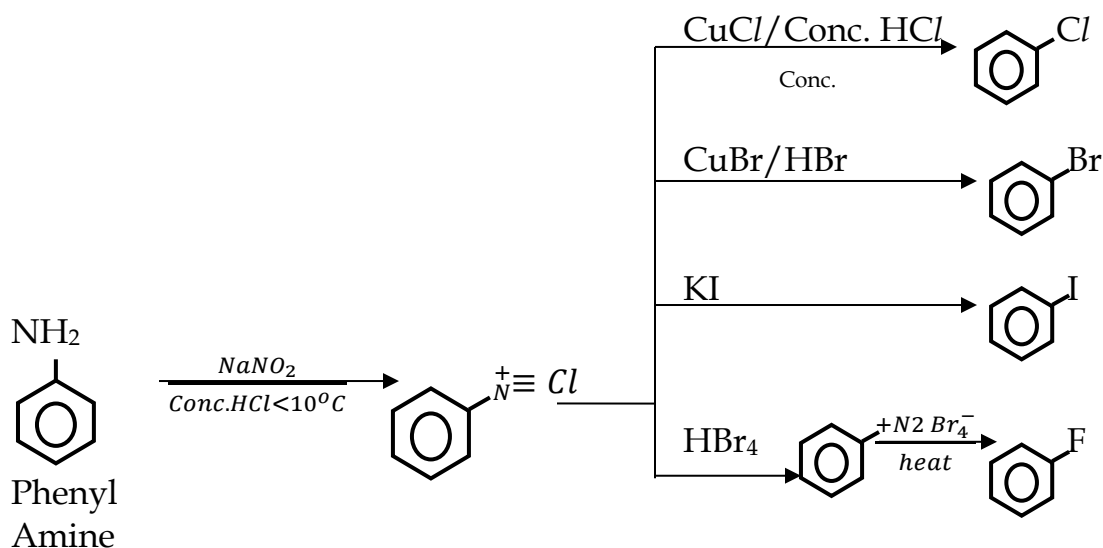


1, 3, 5-tribromo benzene.

PREPARATION



From benzene diazonium salt



PHYSICAL PROPERTIES OF AROMATICS

They are colourless liquids or solids with characteristic flame.

They are insoluble in H_2O but soluble in organic solvents like CCl_4 .

NOTE:

They do not easily undergo nucleophilic substitution unlike alkyl halide.

Distinguish between Clc1ccccc1 and ClCC1=CC=CC=C1

Reagent: Hot aqueous NaOH in dil HNO_3 and AgNO_3 .

Observations:

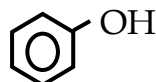
- A white precipitate forms with ClCC1=CC=CC=C1.
- No observable change with Clc1ccccc1.

ALCOHOLS AND PHENOLS:

These are compounds that contain hydroxyl group. Therefore the functional group is hydroxyl group. The difference between alcohol or alkanols and phenol is that the hydroxyl group is directly attached to the aromatic ring in phenols.

Alkanol
 $R - OH$

Phenol
 $Ar - OH$



ALKANOLS OR ALCOHOLS

Alcohols are organic compounds derived from hydro carbons but where one or more hydrogens is/are replaced by hydroxyl group. The general formula is $R - OH$ where R is an alkyl group or simply represented as $C_nH_{2n+1}OH$. Where n = simple number.

They are also called alkanols simply because a hydroxyl group replaces a hydrogen.

TYPES OF ALCOHOLS

There are basically three types of alcohols:

(i) Monohydric alcohol

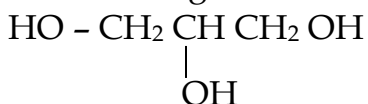
This is one that has got one hydroxyl group.

(ii) Dihydric alcohol

This is one that has got two hydroxyl groups.

(iii) Polyhydric alcohol

These have got more than two hydroxyl groups e.g.



NOMENCLATURE

Alcohols are named as alkanols according to the IUPAC. This is done by replacing the last "e" in alkane name with suffix "ol" (functional group name).

The position of the functional group has to be indicated just before the suffix "ol".

If the stem name has got a vowel, then a consonant letter must be added just before the position of the functional group.

E.g. $\text{CH}_3\text{CH}_2\text{OH}$ Ethano-1-ol

$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ | \\ \text{OH} \end{array}$ Propan-2-ol

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$ 2-methyl butan-2-ol.

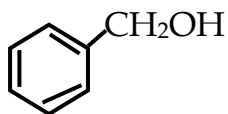
$\text{HO}-\text{CH}_2\text{CH}_2\text{OH}$ Ethane-1, 2 - diol

$\text{HO}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ Propane - 1, 2, 3 - triol.

 Cyclohexan-1-ol

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{C}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$ 2-methyl propan-2-ol

 Cyclohexan-1, 3-diol
Xyclohexane-1, 3-diol



Phenyl methan-1-ol.

NOTE: Look at isomerism in alcohols.

Types - structural:

(i) Chain

(ii) Position

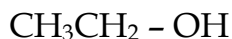
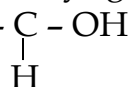
- Functional (alcohol and others are isomeric).

CLASSES OF ALCOHOLS

Monohydric alcohols are classified into three classes.

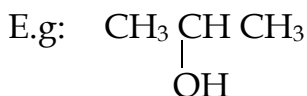
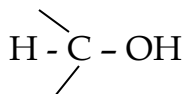
(i) **Primary alcohol**

This has one alkyl group attached to the carbon atom carrying the -OH group. E.g.



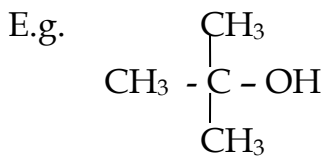
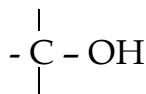
(ii) **Secondary alcohol**

This has got two alkyl groups attached to the carbon atom carrying the OH group.



(iii) **Tertiary alcohol**

This has three alkyl groups attached to the carbon atom carrying the OH group.

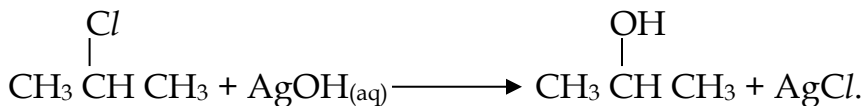
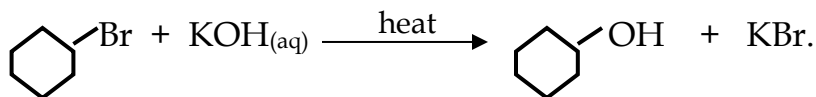
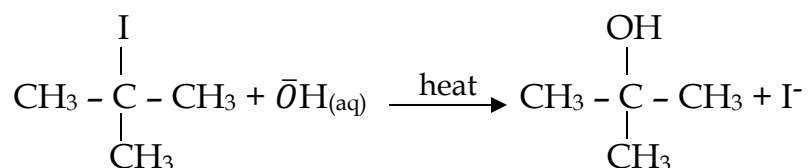
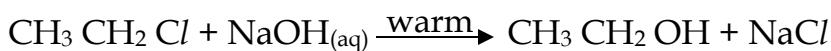


METHODS OF PREPARATION

(i) From alkyl halide (SN reaction)

When alkyl halides are refluxed with aqueous alkali (KOH or NaOH) or with moist silver oxide, alcohols are formed.

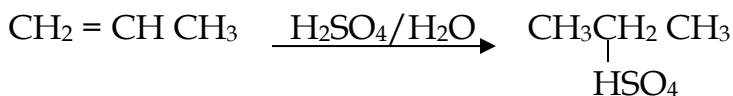
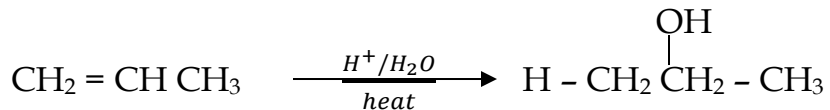
This is a hydrolysis reaction that occurs by nucleophilic substitution reaction.



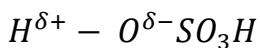
(ii) From alkenes

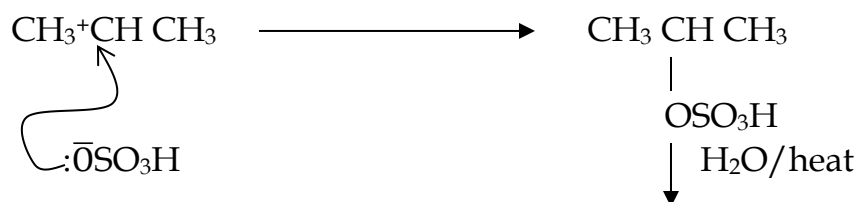
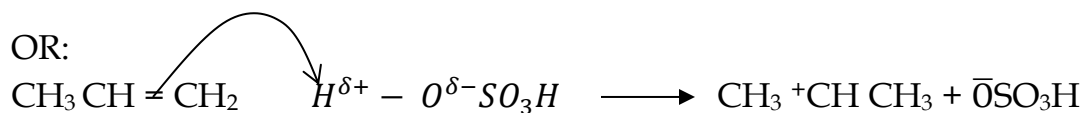
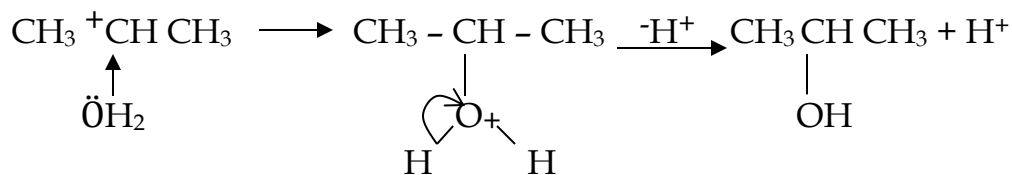
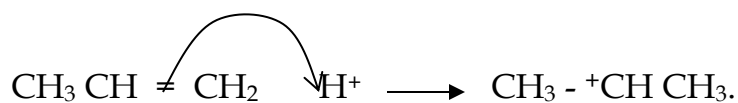
When alkenes are reacted with dilute mineral acid water and heated, an alcohol is formed. They usually used acid is H_2SO_4 acid.

If the mixture is not heated, then an alkyl hydrogen sulphate is formed.



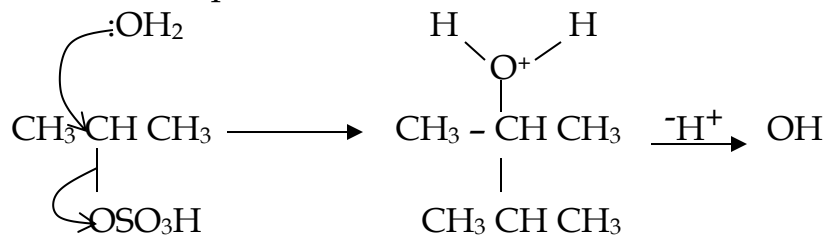
Mechanism:



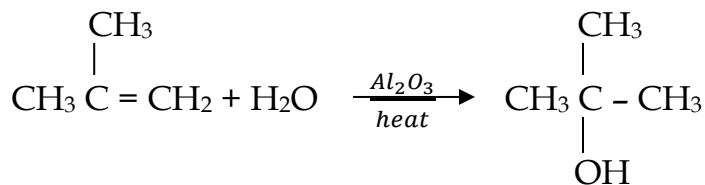
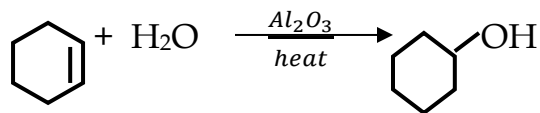
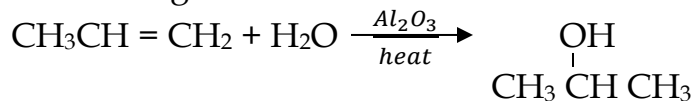


NOTE:

H₂O acts as a nucleophile that will react with the alkyl hydrogen sulphate in the last step to form an alcohol. i.e.



When alkenes are reacted with H₂O in presence of Al₂O₃, an alcohol is formed. E.g.



(iii) **From carbonyl compounds (Aldehydes and ketones)**

Carbonyl compounds are reduced in the presence of a suitable reducing agent to alcohols.

Aldehydes $\xrightarrow{[H]}$ Primary alcohols

Ketones $\xrightarrow{[H]}$ Secondary alcohols

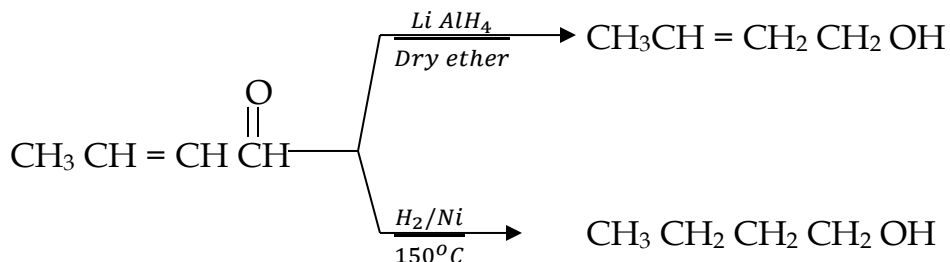
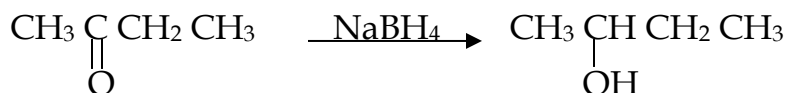
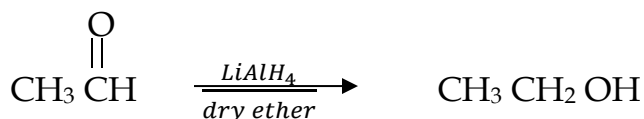
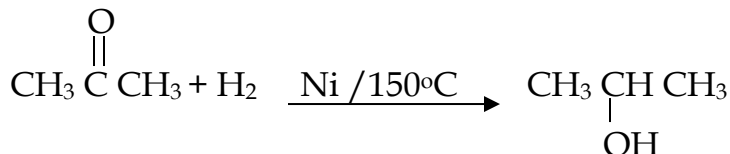
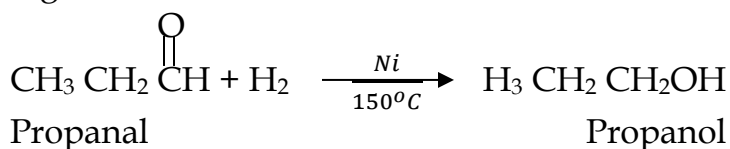
Reducing agents normally used:

Hydrogen in presence of catalyst, Ni/150, Pt/pd, r.t.p.

Using Li Al H₄ (Lithium, Aluminium, Tetra hydride) in presence of dry ether.

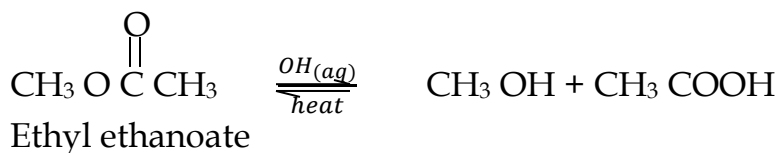
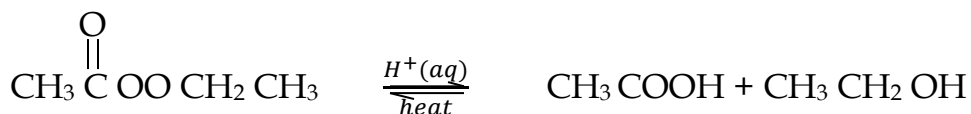
Sodium boron tetrahydride (NaBH₄)

E.g.



(iv) **Hydrolysis of esters**

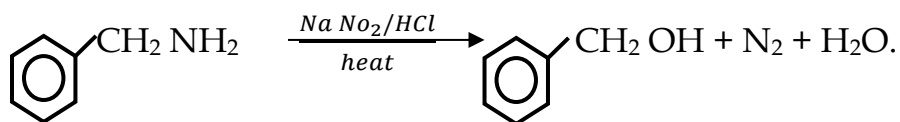
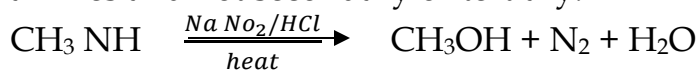
Esters are hydrolyzed in presence of mineral acids or alkalis to form corresponding alcohols and carboxylic acids. This reaction is not very useful for synthesizing alcohols because of the mixture of alcohol and acid.



Mechanism: (look for acid/base hydrolysis of esters).

(v) **From primary amines**

They react with HNO_2 acid which is generated “insitu” by reacting sodium nitrite and conc. HCl to form alcohols. This reaction is only for primary amines and not secondary or tertiary.



(vi) **From fermentation of carbohydrates.**

PROPERTIES OF ALCOHOLS

PHYSICAL PROPERTIES

Lower members are liquids, higher members are solids at r.t.p with x-tic smell.

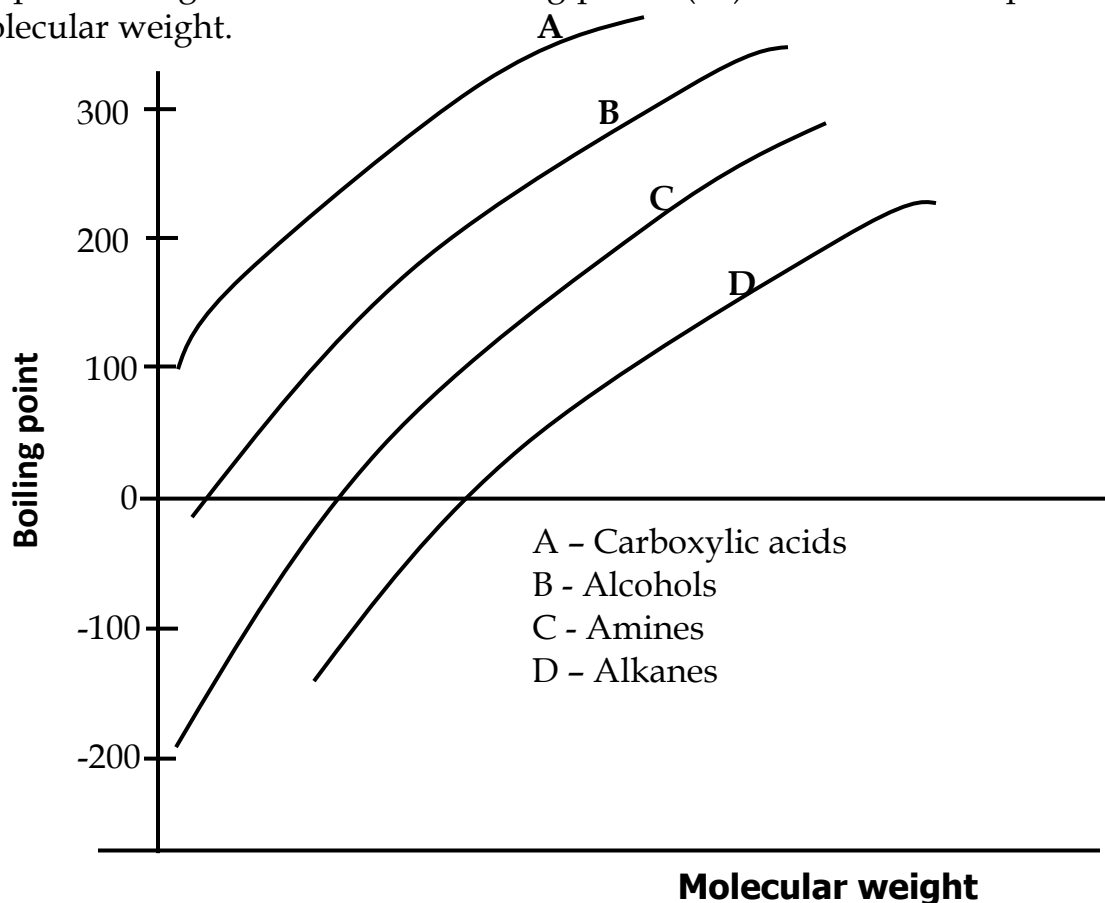
The lower members are very soluble in H₂O but the solubility decreases with the molecular mass.

Alcohols have got relatively higher boiling points compared to similar hydrocarbons of approximately the same molecular mass.

Examples:

| | Molecular weight | Boiling points |
|-----------|------------------|----------------|
| Ethane | 30 | -42 |
| Methanol | 32 | 46 |
| Butane | 58 | -0.5 |
| Propan-ol | 60 | 98 |

Graph showing the variation of boiling points (°C) of different compounds with molecular weight.



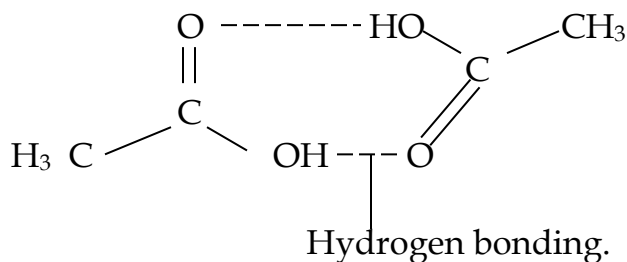
Note:

The boiling points increase generally with increase in molecular weight. Increase in molecular weight increases the Van Der Waal's forces of attraction. This makes the compound stronger hence high boiling points.

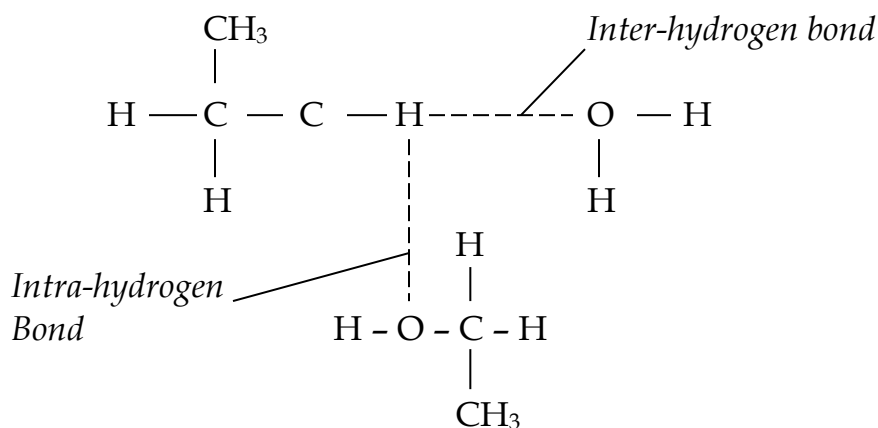
Explanation:

The boiling points of the compounds above on the graph are determined by hydrogen bonding.

Carboxylic acids have got the highest boiling points due to extensive hydrogen bonds which makes molecules to dimerise in a liquid hence difficult to separate them during boiling so that they escape to vapour.



Alcohols' boiling point is higher than that of alkanes but lower than that of carboxylic acid because of inter and intramolecular hydrogen bonding. Molecules will interact in liquids and aqueous phases and high boiling point.



Amines boil at a lower temperature than alcohols of the corresponding molecular weight because nitrogen is less electronegative than oxygen so the hydrogen bonds formed in amines are weaker than in alcohols thus amines boil at a lower temperature.

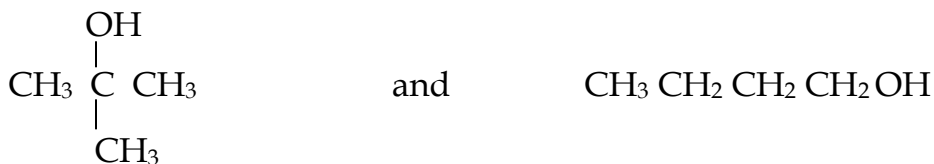
Alkanes have the least boiling point because of the absence of hydrogen with only Van der Waal's forces of attraction which are weaker and easily broken during boiling.

In summary:

The solubility in water and the boiling points of alcohols are due to hydrogen bonding.

Questions:

1. Methyl amine (mm = 31) boils at -6.3°C while methanol (mm = 32) boils at 46°C . Explain.
2. 2-methyl propan-2-ol boils at a lower temperature than butan-1-ol yet they all have the same molecular weight.



2 methyl propan-2-ol is highly branched giving it a spherical shape which decreases on the size and weakens the Van der Waal's forces of attraction existing between the molecules.

Butan-1-ol is a straight chain molecule which gives it an extended structure resulting in relatively stronger Van der Waal's forces.

CHEMICAL PROPERTIES OF ALCOHOLS

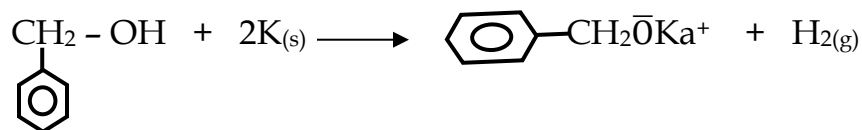
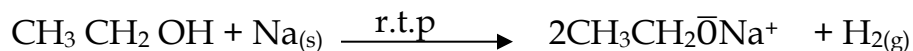
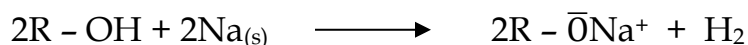
Alcohols consists of three major bonds that are involved in a chemical reaction.

- (i) Functional group - OH group.
Where the O - H bond is involved in the reaction.
- (ii) Oxygen-carbon bond which is highly polarized.
- (iii) Alkyl groups - R group.

REACTION INVOLVING CLEAVAGE OF THE O - H BOND

Reactions with electropositive metals:

When an alcohol is reacted with a metal like sodium or potassium, an alkoxide and H₂ gas are formed.

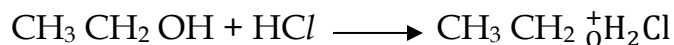
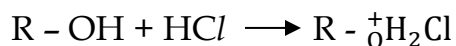


Observation:

Effervescence of a colourless gas that burns with a pop sound.

Reactions with mineral acids:

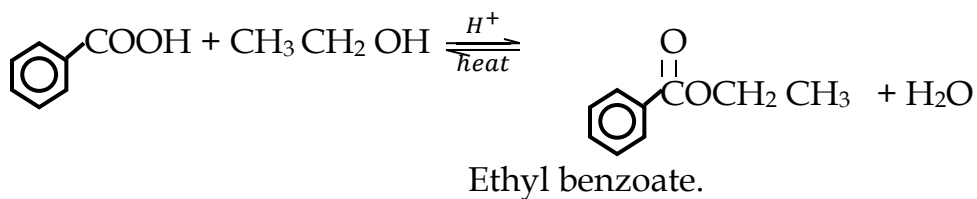
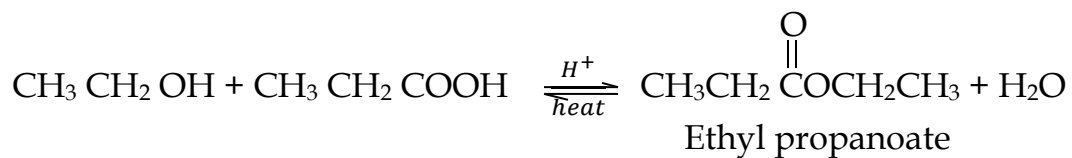
When an alcohol is reacted with a mineral acid, a salt is formed.



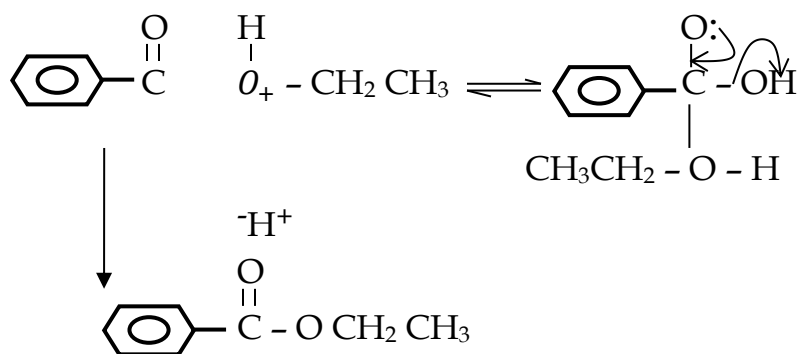
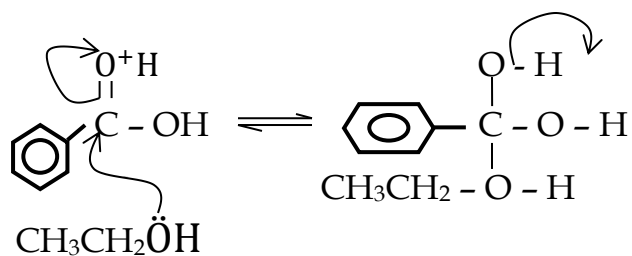
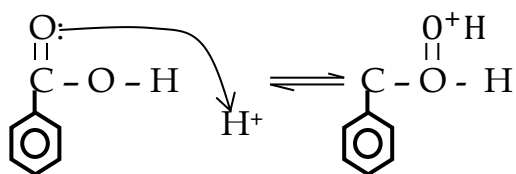
From the two reactions above, alcohols are regarded as amphoteric because they react with acids and bases to show both acidic and basic.

Esterification

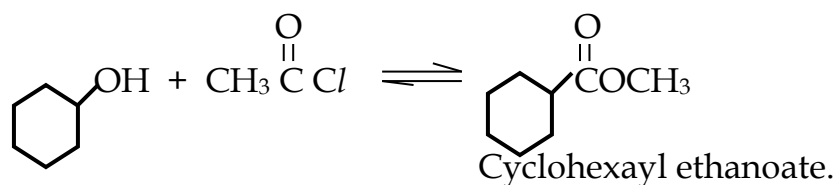
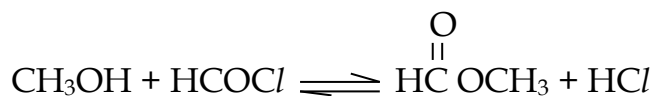
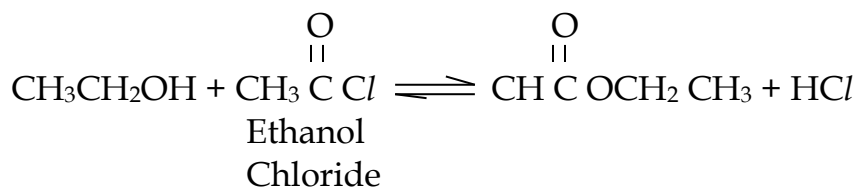
Alcohols react with carboxylic acids in presence of mineral acids to form esters. This reaction is known as esterification.



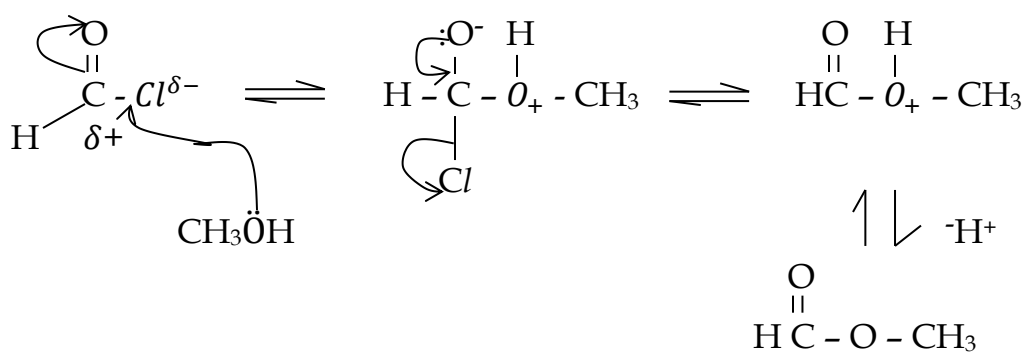
Mechanism:



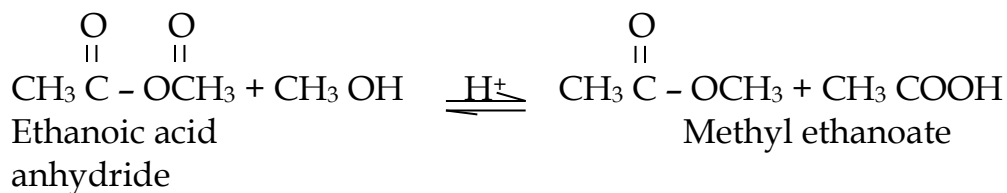
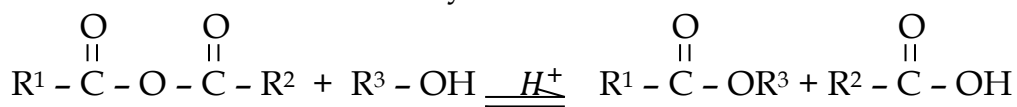
Alcohols react with acid chlorides to form esters.



Mechanism:

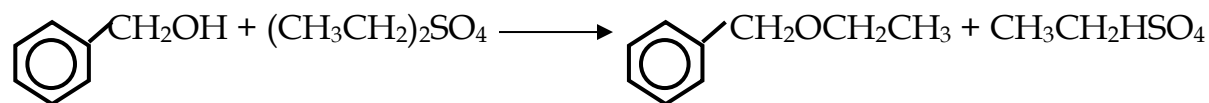
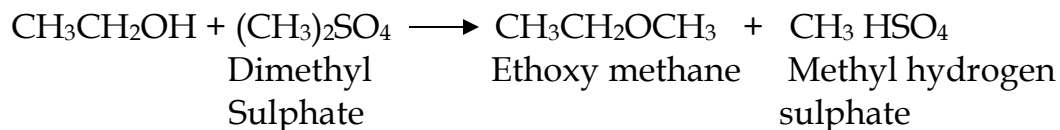


Alcohols react with acid anhydrides to form esters.



Alkylation of alcohols

Alcohols react with dialkyl sulphates to form ethers and alkyl derivatives. This reaction involves replacement of hydrogen in the alcohol with alkyl group.

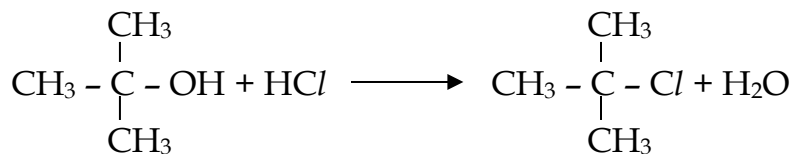
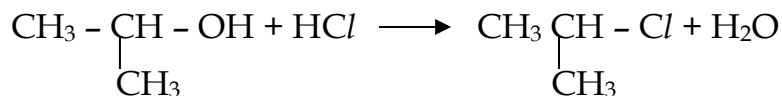
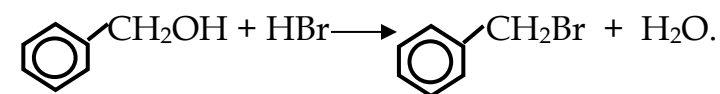
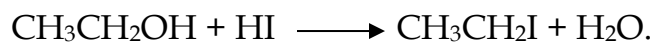
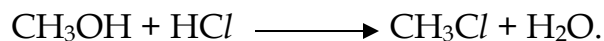


REACTIONS INVOLVING CLEAVAGE OF A CARBON OXYGEN BOND

In these reactions, we are removing both oxygen and hydrogen atoms from the alcohol.

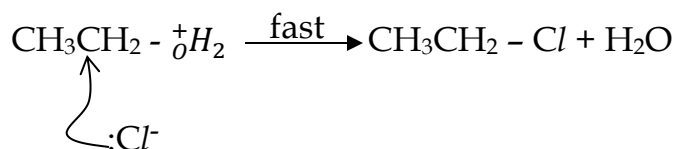
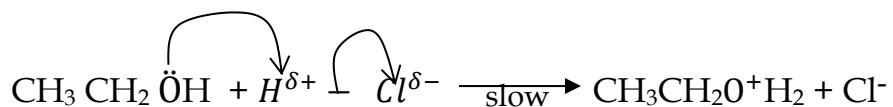
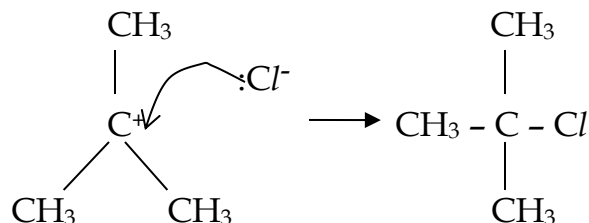
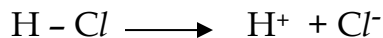
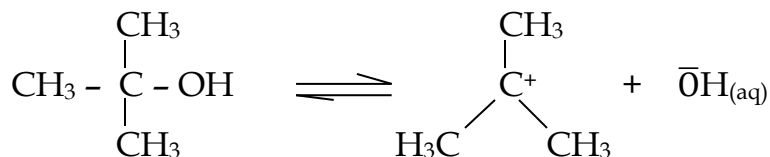
Reactions with halogen acids (Hx)

Alcohols react with halogen acids to form alkyl halides.



Mechanism:

Primary and secondary alcohols follow $\text{S}_{\text{N}}2$ mechanism because of the fairly unstable carbon cation ion, while the tertiary alcohols follow $\text{S}_{\text{N}}1$ because of the stability of the carbon cation ion formed.

 $\text{S}_{\text{N}}2$: **$\text{S}_{\text{N}}1$:**

PRACTICAL IMPORTANCE OF THE REACTION

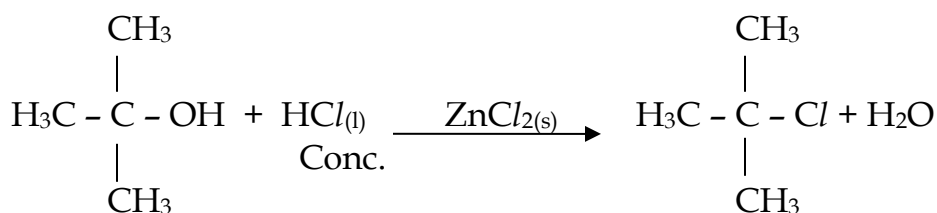
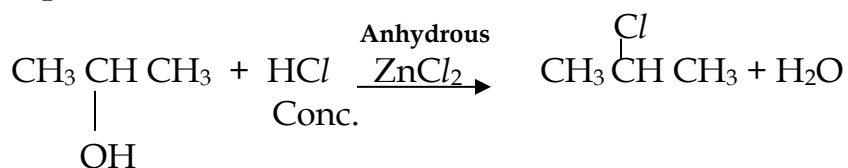
The practical importance of the above reaction is to distinguish between the three classes of alcohol.

Reagent: Anhydrous zinc chloride in concentrated hydrochloric acid.

Observation:

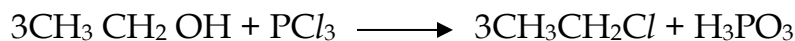
- An immediate cloudy solution at room temperature forms with a tertiary alcohol.
- Within 5 minutes at room temperature, a cloudy solution is formed with a secondary alcohol.
- No cloudy solution forms at room temperature with primary alcohol.

Equations:



REACTIONS WITH PHOSPHORUS HALIDES

Alcohols react with PX_5 and PX_3 to form alkyl halides where X is a halogen.



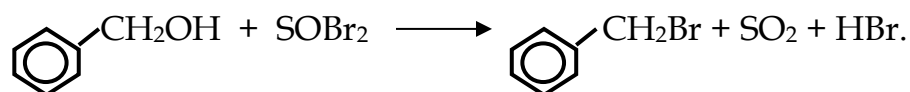
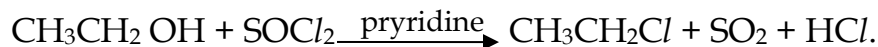
Others: PI_3/PI_5
 $\text{PBr}_3/\text{PBr}_5$.

NOTE:

Evolution of HCl or fuming when PCl_5 is added to a compound suggests the presence of OH group in that compound.

REACTION WITH THINLY CHLORINE

Alcohols react with SOCl_2 or SOBr_2 to form alkyl halides. An organic base like pyridine must be included to neutralize toxic and poisonous gases liberated.



Mechanism:

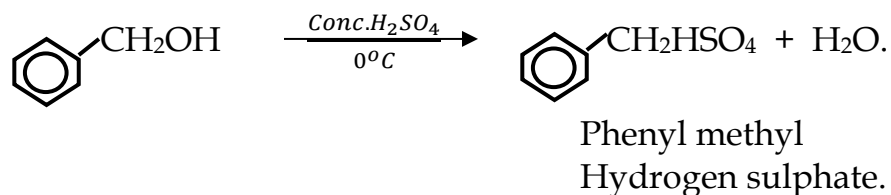
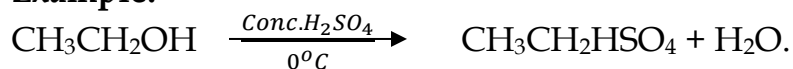
REACTION WITH H_2SO_4 ACID

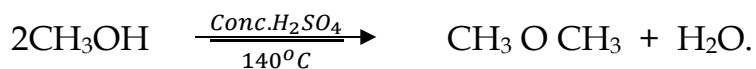
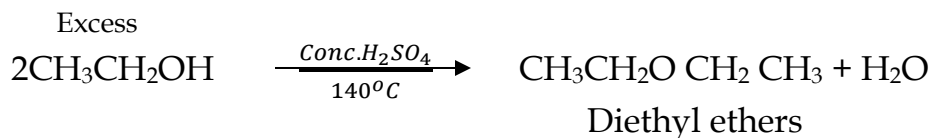
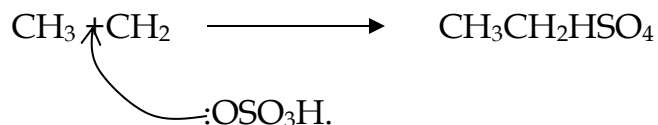
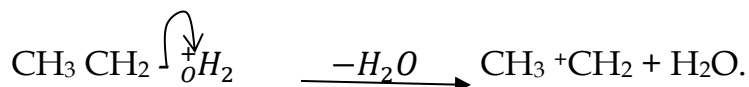
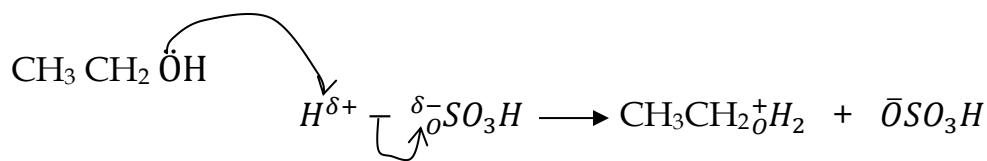
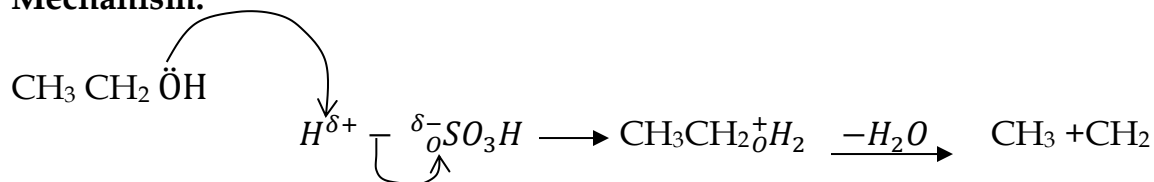
Alcohols react with H_2SO_4 giving different products depending on the conditions of reaction.

Conditions:

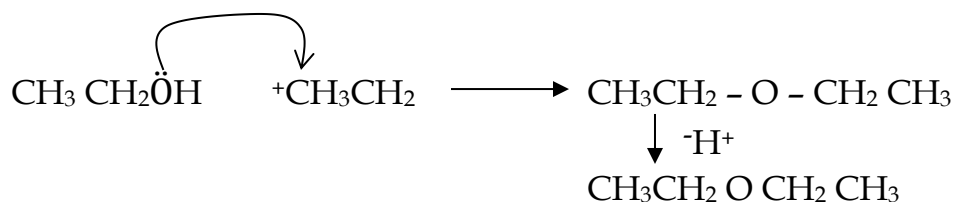
- A. (i) Conc. H_2SO_4 Products got are substituted products.
(ii) Excess alcohol
(iii) Low temperatures.
Substituted products.
Alky hydrogen sulphate – 0°C .
Ether – warm (140°C)
- B. (i) Conc. H_2SO_4 .
(ii) High temperatures (heat) - Elimination product.
(iii) Limited alcohol.

Example:



Mechanism:**Mechanism:**

$[\text{CH}_3\text{CH}_2\text{OH}] \gg [\bar{\text{O}}\text{SO}_3]$ therefore $\text{CH}_3\text{CH}_2\text{OH}$ is a better nucleophile.



Alcohols are dehydrated when heated with conc. H_2SO_4 and H_3PO_4 acid to form alkenes in a liquid phase or when the alcohol is passed over heated Al_2O_3 at 300° in a vapour phase.

Water molecule is eliminated and therefore this type of reaction is known as elimination or dehydration.

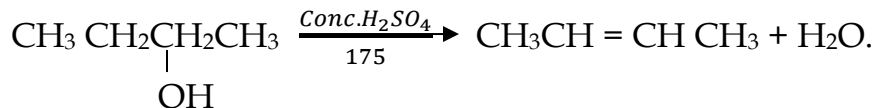
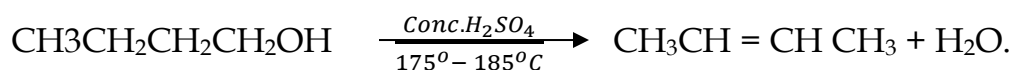
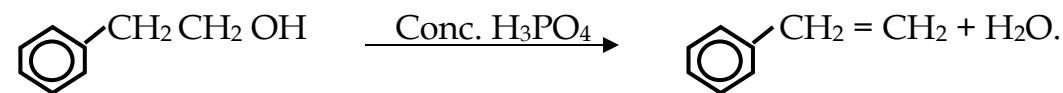
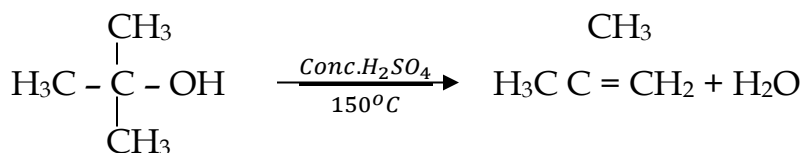
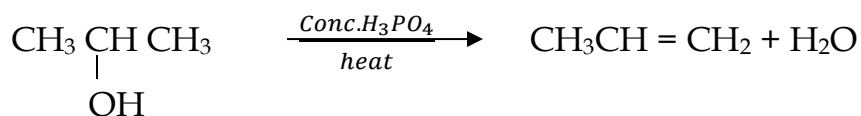
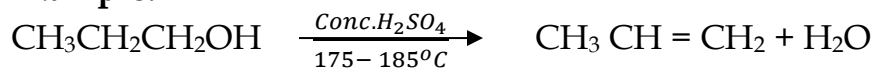
The reactivity in the liquid phase is determined by the type of carbon cation ion formed.

Elimination reactions occur under the following conditions:

- (i) Heat: [170 – 185°C] Primary alcohol
 [150 – 180°C] Secondary alcohol
 [90 – 150°C] Tertiary alcohol.

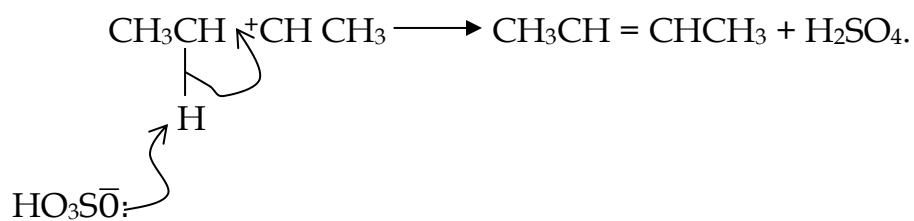
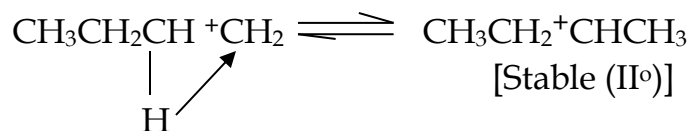
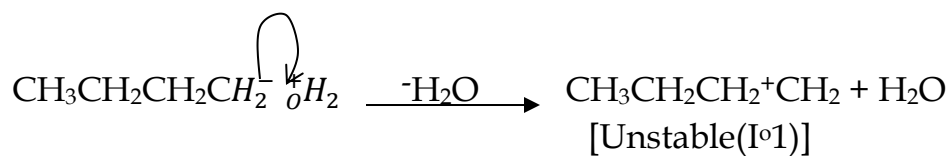
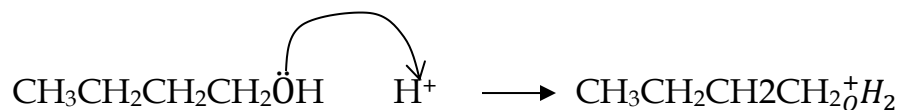
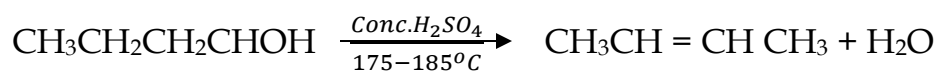
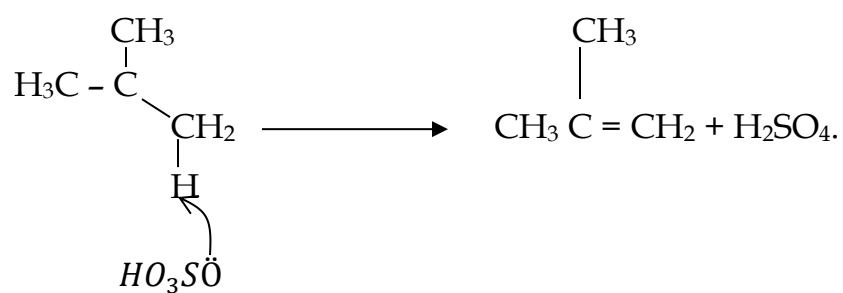
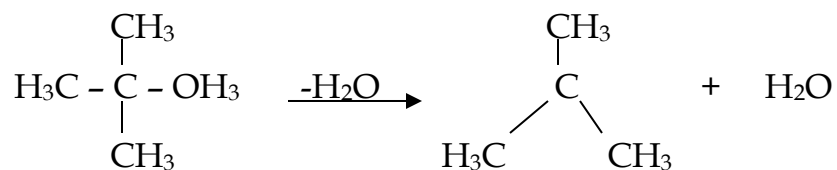
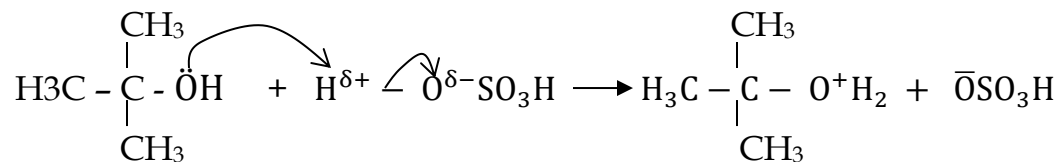
- (ii) Conc. H₂SO₄: [>60%].

Example:



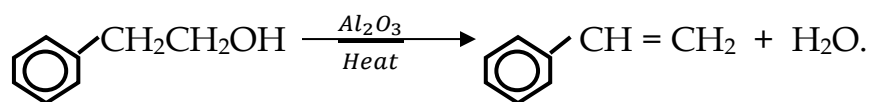
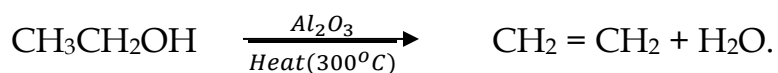
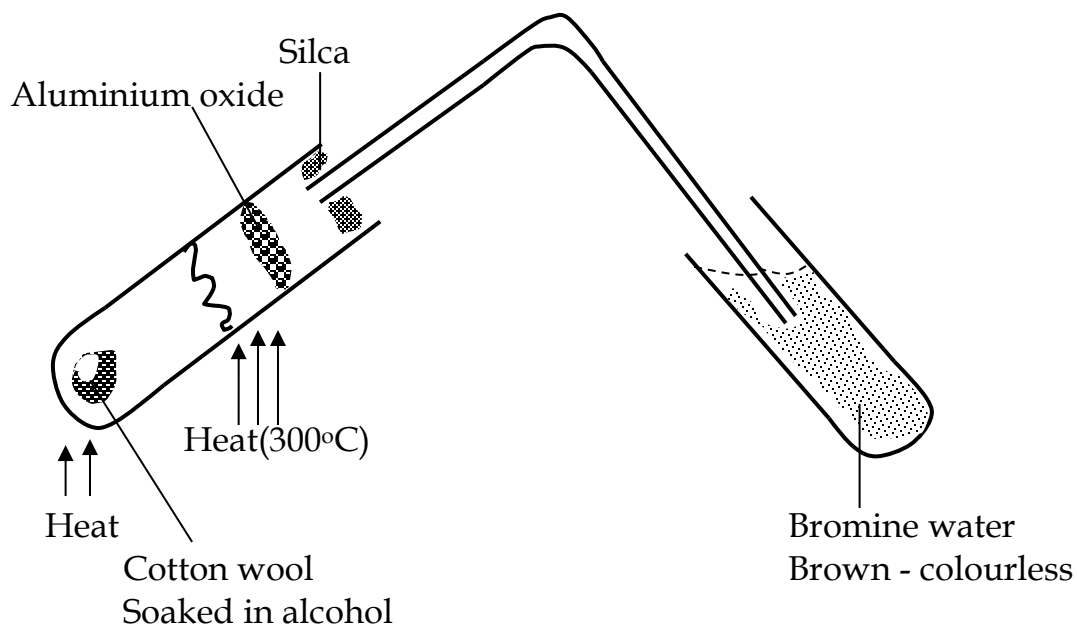
Mechanism:

1. Protonation of alcohol
2. Loss of H₂O to form carbo cation ion.
3. Re-arrangement of the carbo cation to a more stable form.
4. Loss of the proton to form alkene.

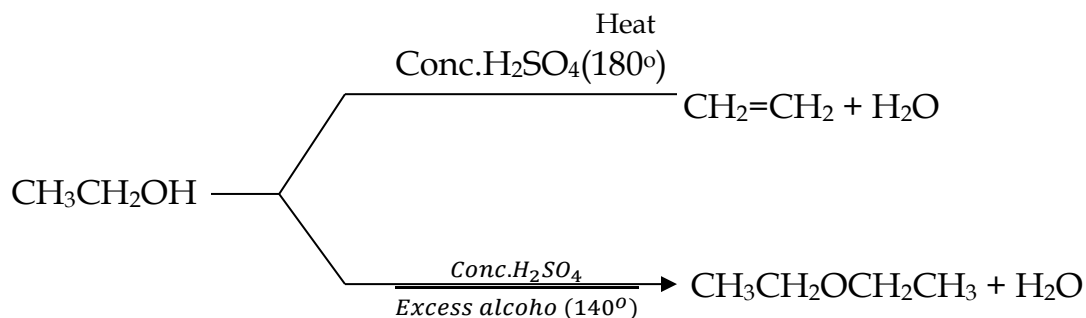


DEHYDRATION IN VAPOUR PHASE

When an alcohol is heated and its vapour is passed over heated Al_2O_3 at 300° , an alkene is formed which is detected by turning bromine water colourless.



N.B: Elimination reactions in alcohols compete with substitution reactions. The difference is due to the conditions provided.



OXIDATION REACTIONS

Primary alcohol $\xrightarrow{[O]}$ Aldehyde $\xrightarrow{[O]}$ Carboxylic acid.

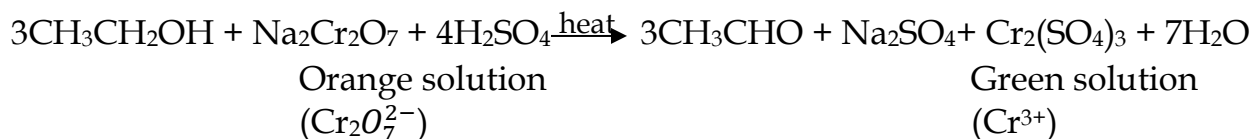
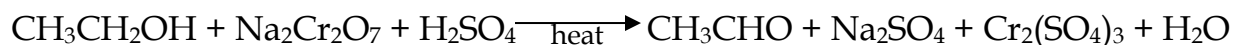
Secondary alcohol $\xrightarrow{[O]}$ Ketones $\xrightarrow{[O]}$ No product

Tertiary alcohols $\xrightarrow{[O]}$ No product.

Oxidation of alcohols is effected by oxidizing agents such as:

- (i) Acidified $K_2Cr_2O_7 / H^+_{(aq)}$
- (ii) Acidified $Na_2Cr_2O_7 / H^+_{(aq)} / Cr_2O_7^{2-}_{(aq)}$
- (iii) Chromic acid, CrO_3 .

Acidification is done by use of sulphuric acid.

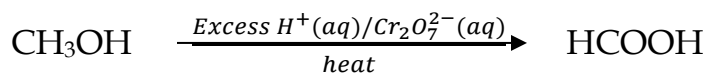
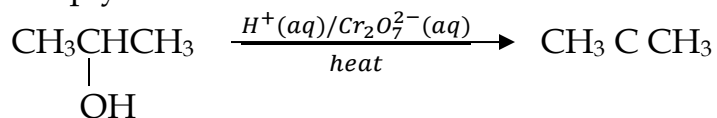


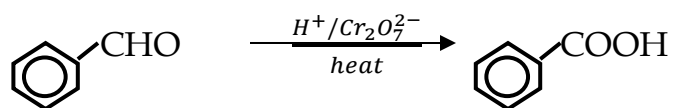
During the process, the solution mixture turns from orange to green indicating the conversion of the dichromate to chromium(III) ion.

Excess oxidizing agent.



Simply:

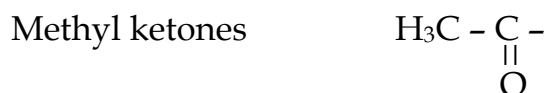
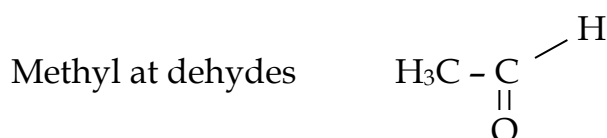




iodo form/ halo form test

This test is usually performed to confirm for the presence of compounds that have got a methyl group.

Example:

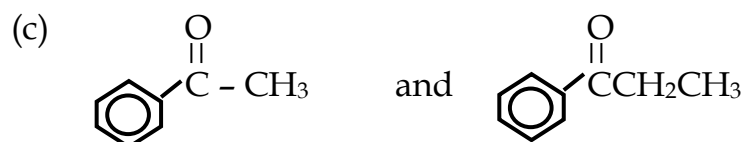
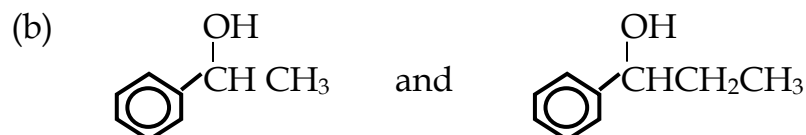


Product formed CHI_3 - Tri iodo methane (Yellow ppt)

This test confirms / differentiates methyl / alcohols from the rest. Methyl alcohols form tri iodo methane when oxidized which is observed as a yellow ppt, while the rest of the alcohols no observable change.

Reagent: Hot NaOH in Iodine solution.

Question: Give a reagent that can be used to distinguish between pairs of the compounds below and state what is observed in each case. Write the equation for the reaction(s) that take place.



Solutions:

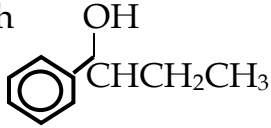
(a) Hot sodium hydroxide solution.

With $\text{CH}_3\text{CH}_2\text{OH}$ - A yellow precipitate is observed.

With $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ - No observable change.

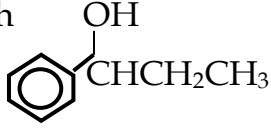
(b) Reagent: Hot sodium hydroxide in iodine solution.

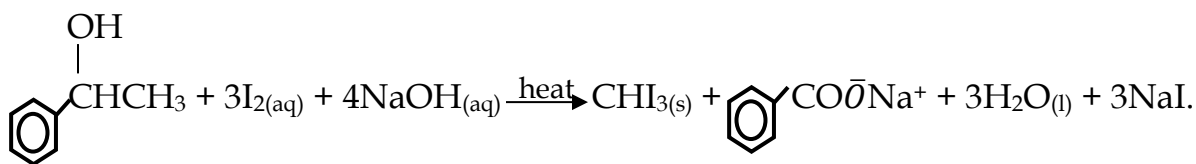
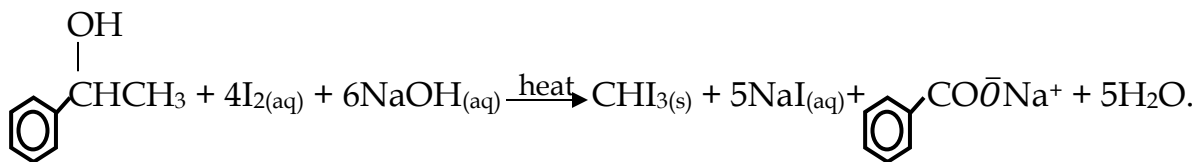
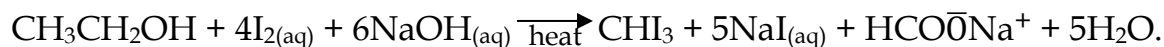
With  - A yellow precipitate is observed.

With  - No observable change.

(c) Reagent: Hot sodium hydroxide in iodine solution.

With  - A yellow precipitate is observed.

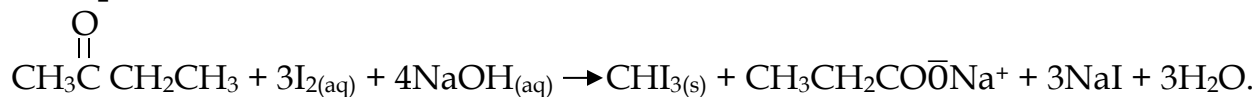
With  - No observable change.

Equations:

Rule: Alcohols; 4I_2 ; 6NaOH

Aldehydes/ketones, 3I_2 ; 4NaOH .

Example:

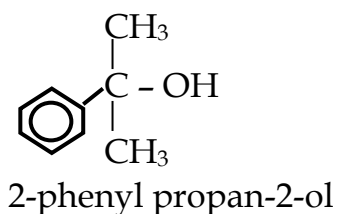
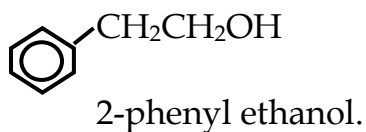
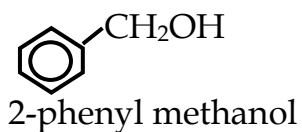


AROMATIC ALCOHOLS

These are aromatic compounds with hydroxyl groups. They are divided into two: Aromatic alcohols and phenols.

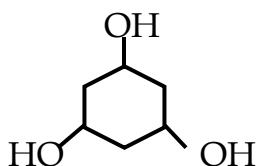
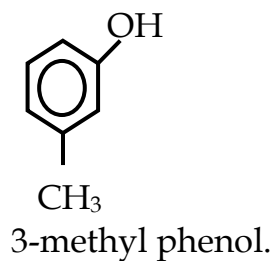
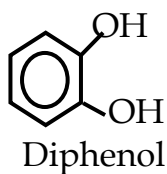
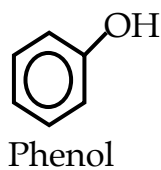
(i) **Aromatic Alcohols:**

These contain an aromatic ring and then the hydroxyl group which is not directly attached to a ring but attached via the chain on the ring.



(ii) **Phenols:**

These contain an aromatic ring with one or more OH group directly attached to the ring.

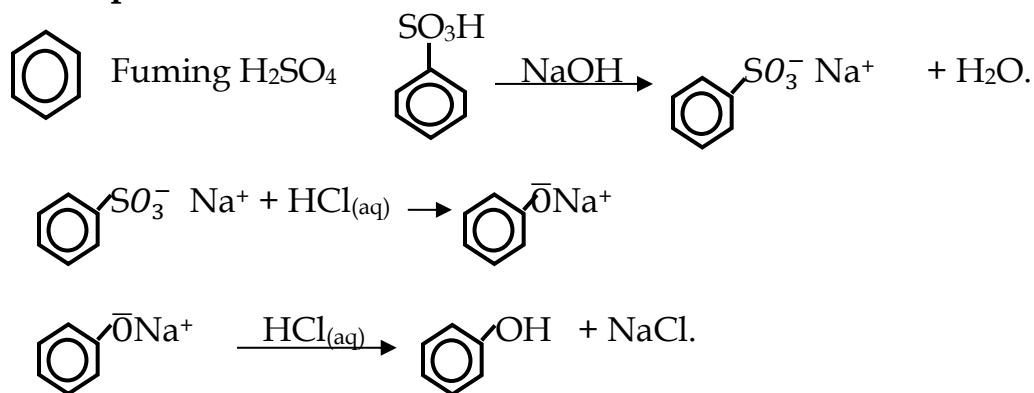


PHENOLS

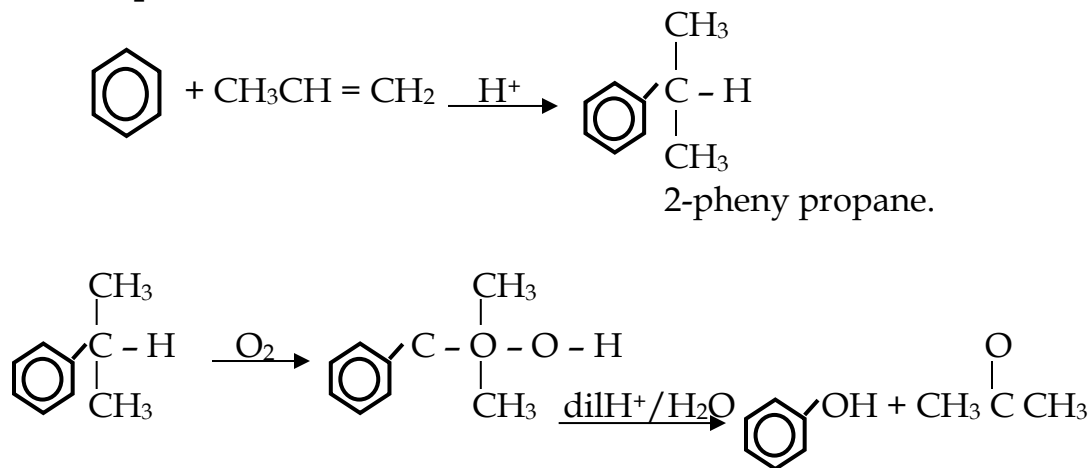
Is a class of compounds named as phenols and one or more OH groups are directly attached to the ring.

METHODS OF PREPARATION

1. Benzene sulphonic acid



2. Cumene process



3. Aromatic halides

In cumene process, Benzene is reacted with propene in presence of an acid or halogen carrier like AlCl_3 to form two phenyl propane.

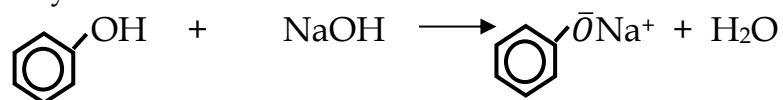
Molecular O_2 is blown into this product and the intermediate is acid hydrolysed to give a phenol.

When an aromatic halide is treated with alkali at extremely harsh conditions like 300°C , 200 atm of pressure and copper, a phenol is formed.

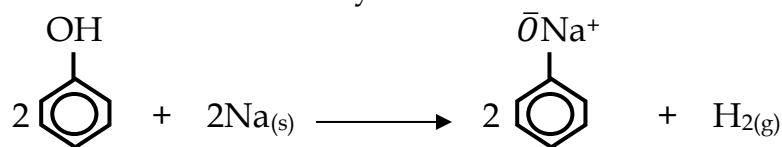
This subsequently strengthens the C - O bond by developing a partial double bond between C and O and at the same time weakening the O - H bond by decreasing the electron density and releases a proton easily. This does not occur in aliphatic aromatic alcohols as ordinary alcohols.

Subsequently, phenols being slightly acidic, under the following:

(i) Very soluble in NaOH or KOH

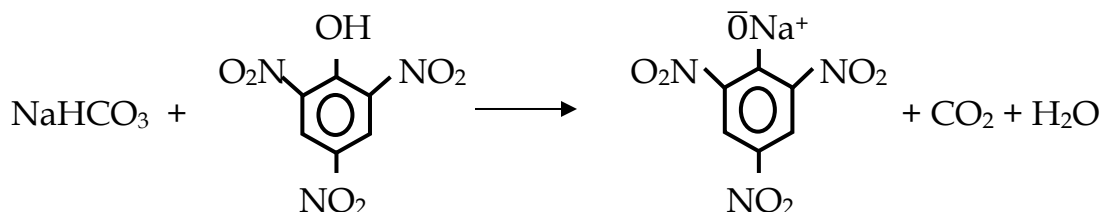


(ii) Phenols react with very reactive metals like Na to form salt and H₂.



Acid properties of phenols can be improved by;

Adding electrons with a.....which de-active the ring. Such groups include the Nitro groups. 2, 4, 6-trinitrophenol is more acidic than phenol. It liberates CO₂ from saturated NaHCO₃.



Carboxylic acids are more acidic than phenols. [Give the reactions that distinguish acidic character of phenols and carboxylic acids.]

COMPLEX FORMATION WITH NEUTRAL FeCl₃.

Phenols form a complex with aqueous neutral FeCl₃ and the colour of the complex product is violet colouration (purple). This reaction is important in confirming the presence of a phenolic group and it is also useful in distinguishing between phenol and aromatic alcohols.

Question: Distinguish between HCOOH and CH₃COOH.
(We use the Iodo form test).

OR:

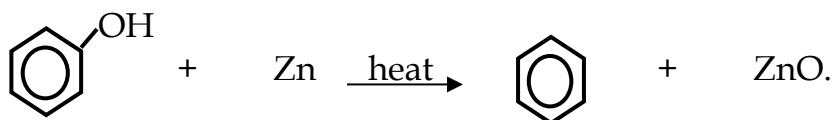
Using neutral (iron III) chloride) solution.

A purple colouration with HCOOH.

No observable change with CH₃COOH.

REACTION WITH ZINC DUST:

Phenol when heated with Zinc dust forms benzene.



ALCOHOL REACTIONS OF PHENOLS RESEMBLING

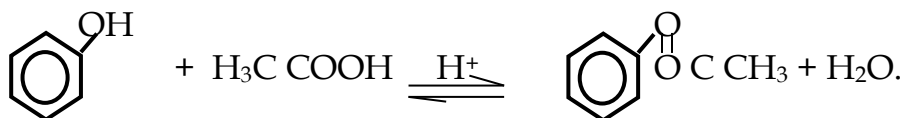
This involves cleavage of C - O bond.

Phenols undergo some reactions resembling alcohol where the C - O bond is involved.

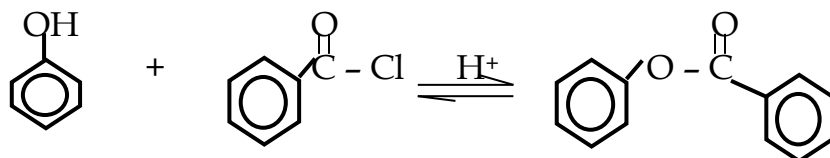
Esterification:

Phenols react with carboxylic acids, halides and acid anhydrides to form an ester.

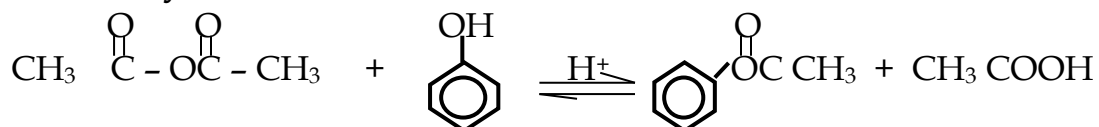
Carboxylic acids:



Acid halides:

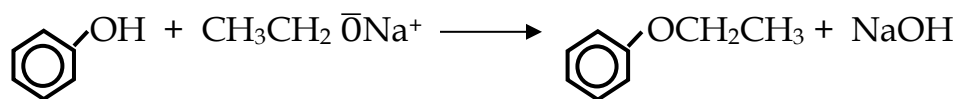


Acid anhydride:



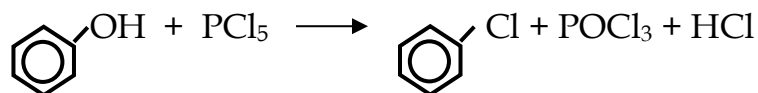
Ether formation:

Phenols react with alkali oxides to form ethers.



Phosphorous penta halides:

Phenols react with PCl_5 liberating HCl gas which fumes in air.



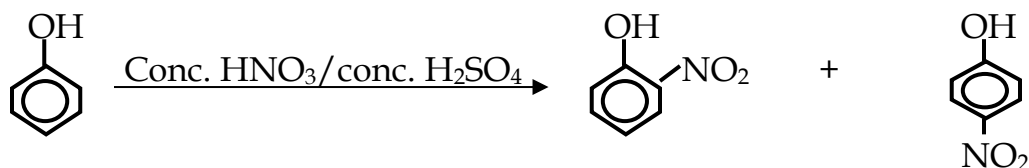
Reactions with liquid NH_3 .

REACTIONS OF THE RING IN PHENOL

Due to the presence of the OH group in phenol, phenol undergoes a number of reactions where delocalized electrons on the ring are involved.

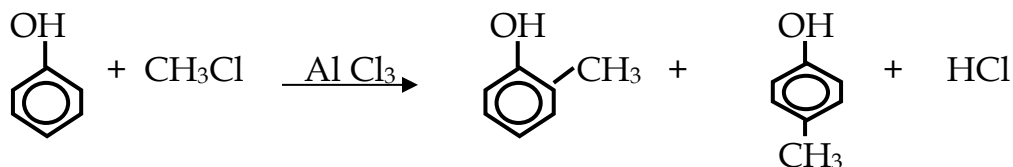
Nitration:

Phenol reacts with conc. H_2SO_4 and conc. HNO_3 acids to form 2-nitro phenol and 4-nitrophenol.



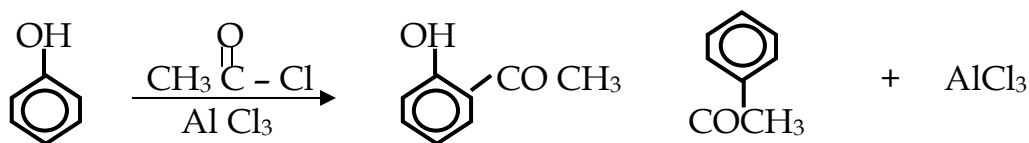
Alkylation:

Phenol reacts with alkyl halides in presence of a halogen carrier to form alkylated product phenol.



Acylation $\left(\text{C}_6\text{H}_5\text{CO} \right)$

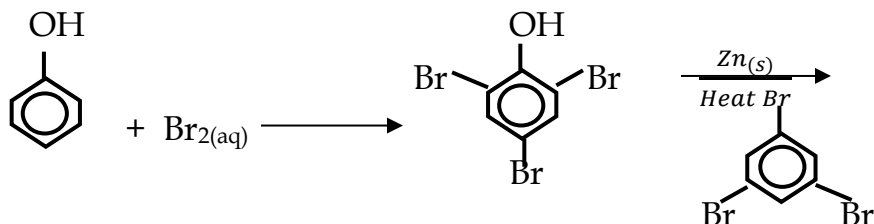
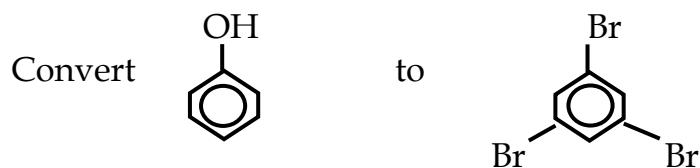
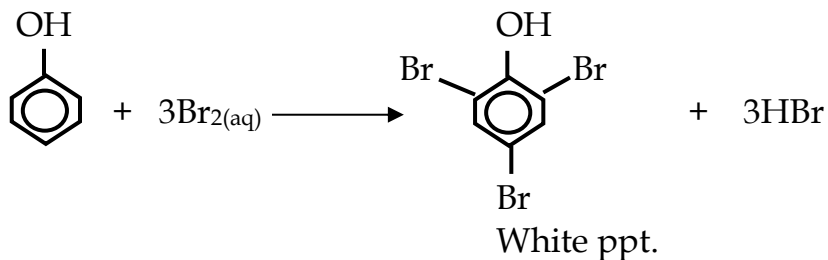
C



Bromine H₂O.

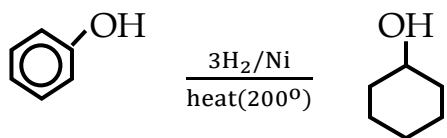
When reacted with bromine, H₂O phenol forms a substituted poly product of 2, 4, 6 tri bromo phenol which is a white precipitate.

The presence of OH makes phenol to be very reactive. This reaction is very important in confirming the presence of phenol together with the neutral iron (III) chloride test.



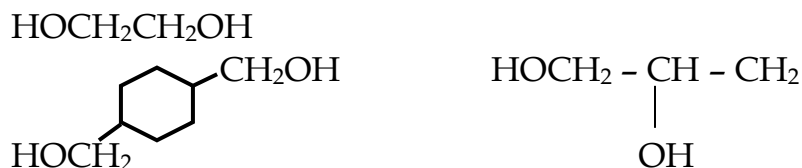
Hydrogen in presence of heated Ni catalyst.

Phenol can be hydrogenated into cyclohexanol when reacted with H_2 in the presence of a heated catalyst.



POLYHYDRIC ALCOHOLS

These are alcohols with more than one OH group attached to the same carbon chain as:



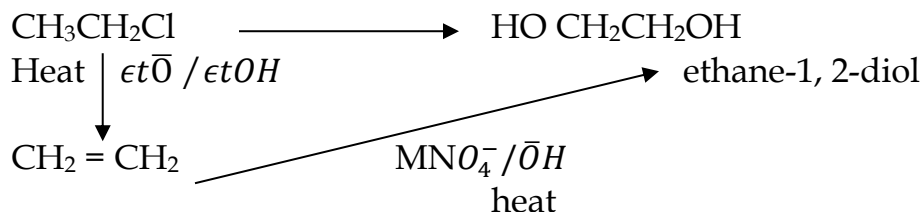
The chemical and physical properties of these types of alcohols are slightly the same; however, there are slight differences.

Ethane-1, 2-diol boils at a higher temperature.

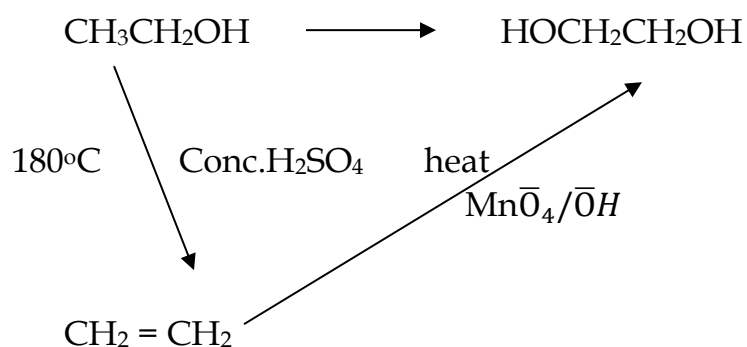
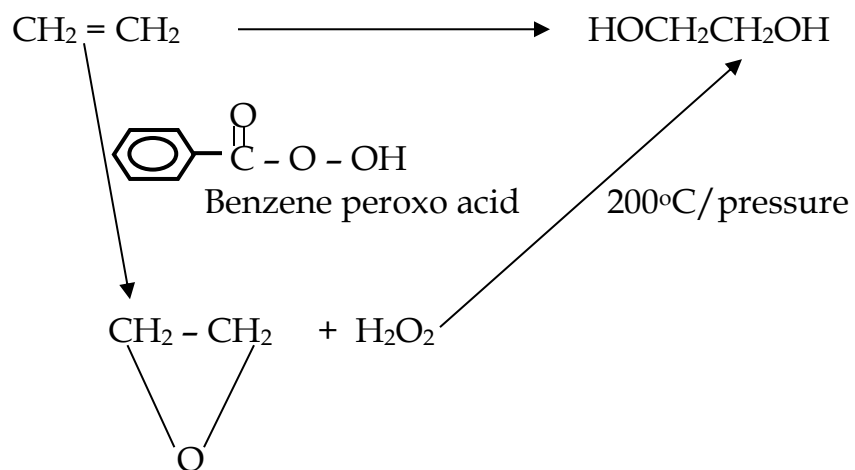
Ethane-1, 2-diol has two OH group which results into formation of extensive hydrogen bonds which is difficult to break hence high boiling point.

PREPARATION OF DIOLS

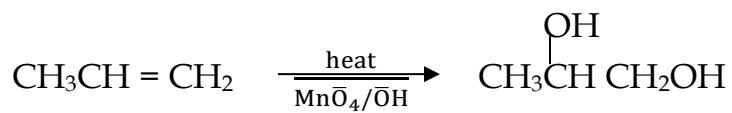
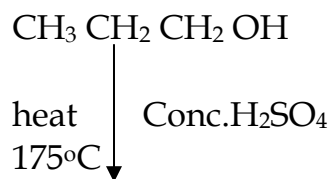
They can be prepared from alkyl halides.



Alkenes



Reactions of diols are the same as those of monohydric alcohols.
The difference is that excess of the reagent is used.



CARBONYL COMPOUNDS

These are compounds containing a carbonyl functional group. They are alkanal (Aldehydes) and alkanones (Ketones).

These two belong to a group of organic compounds known as carbonyl compounds with a general formula $C_nH_{2n}O$.

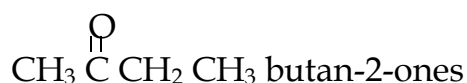
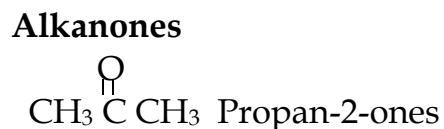
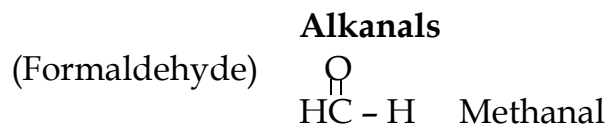


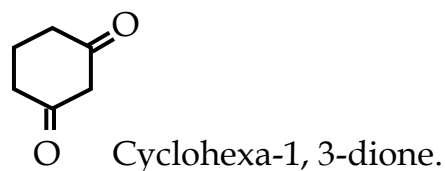
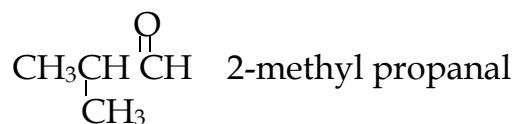
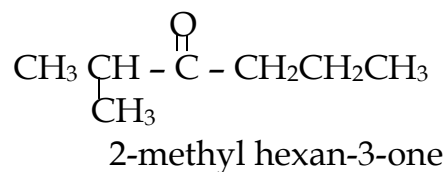
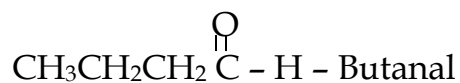
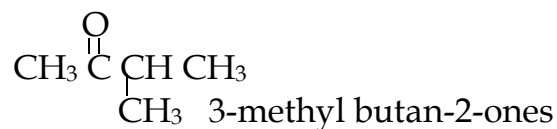
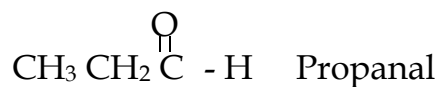
The major difference between aldehyde and ketone is in the presence or absence of H_2 attached onto the carbonyl carbon.

In aldehydes, "H" is to the carbonyl carbon while in a ketone, similar or different alkyl groups are attached to the carbonyl carbon as shown above.

NOMENCLATURE

IUPAC system is used in the naming of both aldehydes and ketones. Generally, aldehydes are named as alkanals by replacing "e" in the alkane name with "-als" while ketones are named as alkanones by replacing "-e" with "-ones".





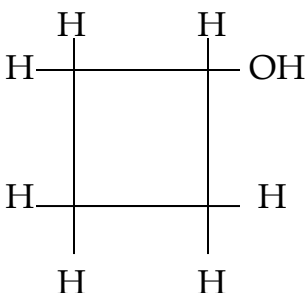
ISOMERISM

Both aldehydes and ketones exhibit structural and functional isomerism.

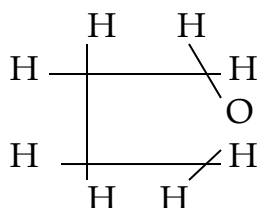
In structural isomerism, they show position and chain isomers.

In functional isomerism, both aldehydes and ketones are isomeric within themselves and with other classes of organic compounds like alcohols and cyclic ethers.





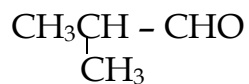
Cyclic butanol (cyclic alcohol)



Cyclic ether (Tetacfuran)



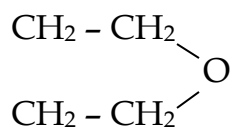
Butanal



2-methyl propanal (Aldehyde)



Butan-2-one (Ketone)



Tetrahydrofuran (furan)

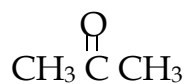


But-en-4-ol

Write all the isomers of the compounds with the molecular formula C_3H_6O .



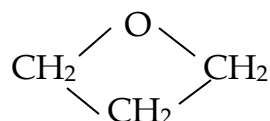
Propanal (Aldehyde)



Propanone (Ketone)



Prop-1-en-3-ol.



Trihydrofuran

PREPARATION OF CARBONYL COMPOUNDS

They can be prepared from the following:

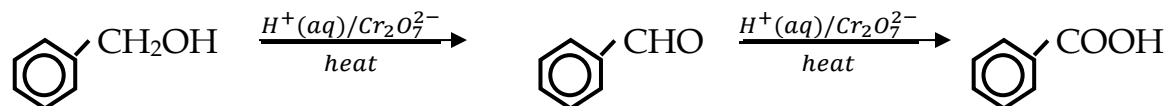
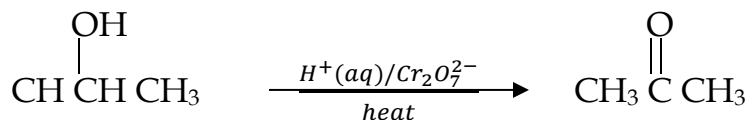
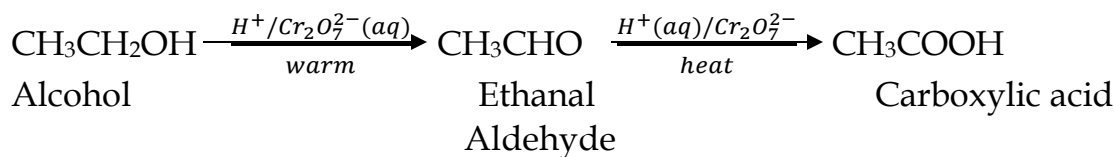
- i) Mild oxidation of alkanol (alcohols)
- ii) Carboxylic acids or their salts.
- iii) Ozonolysis of alkenes followed by hydrolysis.
- iv) Acid hydrolysis of alkynes.
- v) Hydrogenation of acid chlorides.
- vi) Acylation (aromatic ketones)

OXIDATION OF ALCOHOLS

Primary and secondary alcohols are oxidized in liquid phase using $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$ or $\text{Na}_2\text{Cr}_2\text{O}_7 / \text{H}^+$, $\text{CrO}_3 / \text{H}^+$ to form aldehydes and ketones respectively.

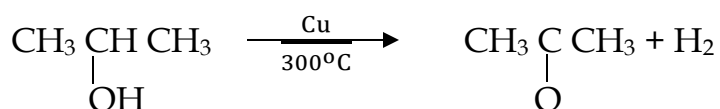
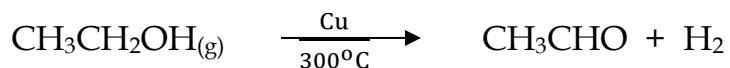
During oxidation process, a colourless solution turns to green solution.

Examples:

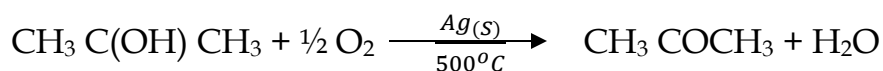
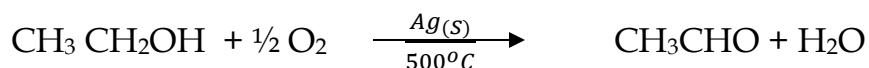


During the oxidation process, especially for primary alcohols, there will be further oxidation to carboxylic acid which renders this method ineffective but this further oxidation can be avoided by carrying out a reaction under low heat (temperatures) or limiting the amount of the oxidant used.

Oxidation can also be effected under vapour phase. When an alcohol vapour is passed over heated Cu at 300°C, it is oxidized to an aldehyde or ketone.

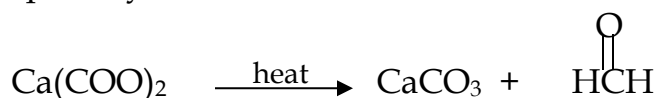


Oxidation under vapour phase can also be brought about when an alcohol together with limited O₂ is passed over heated Ag at 500°C.



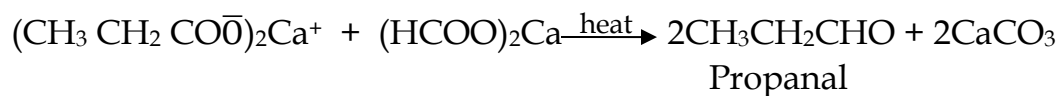
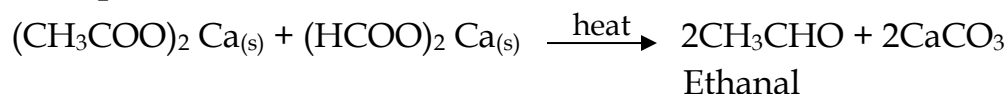
CARBOXYLIC ACIDS

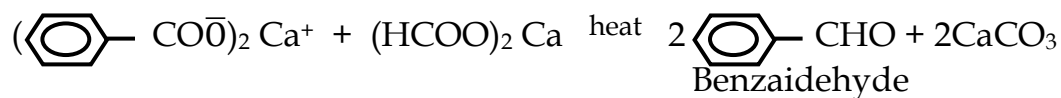
When a carboxylic acid salt of calcium is heated, an aldehyde is formed. More specially methanol is formed.



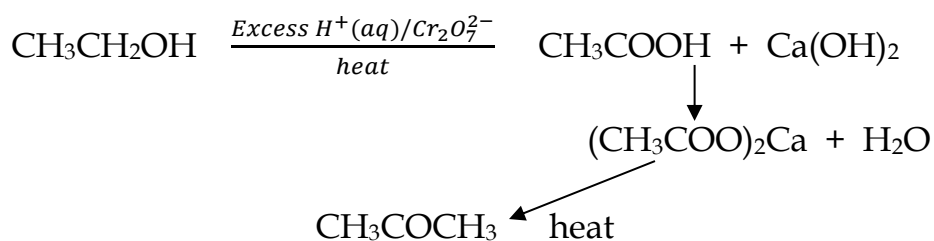
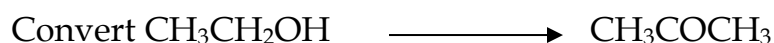
With other higher aldehydes, Ca salt of a carboxylic acid is heated with calcium methanoate.

Examples:





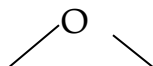
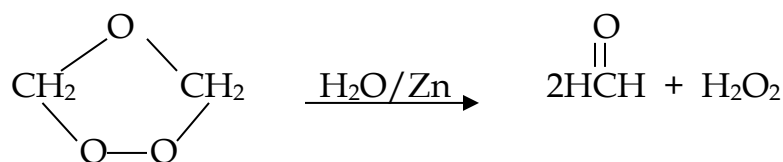
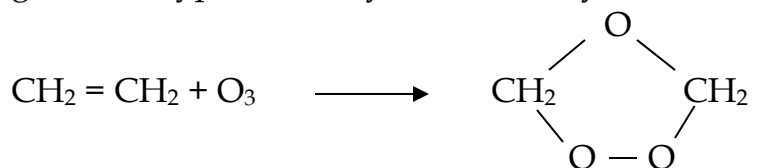
Ketones can be prepared by heating Ca salts of higher carboxylic acids.

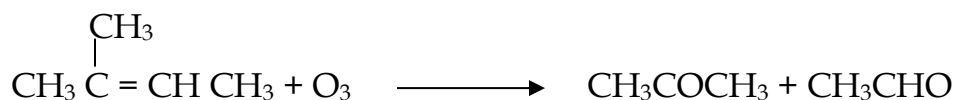
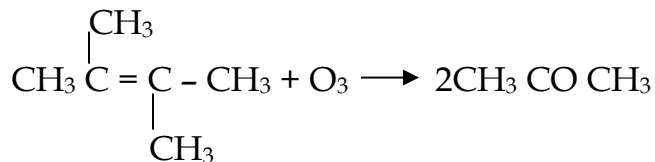
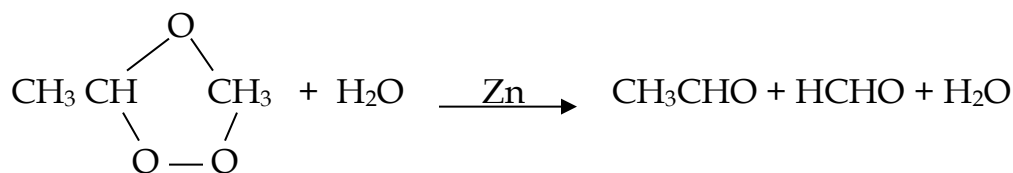
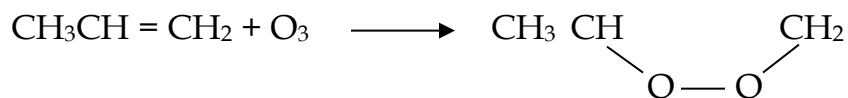


OZONOLYSIS

When an alkene is reacted with ozone, an ozonide is formed. When the ozonide is diluted in H_2O in presence of some zinc, a carbonyl compound is formed. Zinc dust is used to decompose H_2O_2 .

Note: Aldehydes formed depends on the types of alkene used. Symmetrical alkene gives one type of aldehyde while unsymmetrical will give you both carbonyls.

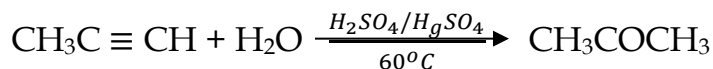
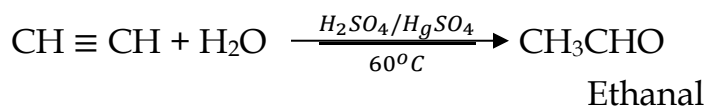




The above method has the disadvantage of yielding a mixture of products which may not be good in organic synthesis.

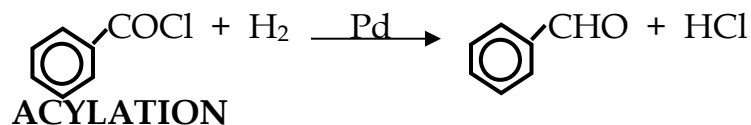
HYDROLYSIS (ACID) OF ALKYNES

When an alkyne is passed through hot H_2SO_4 in presence of mercury sulphate, the carbonyl carbon is formed.

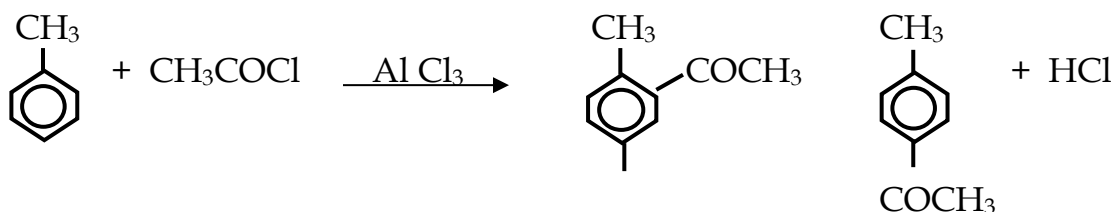
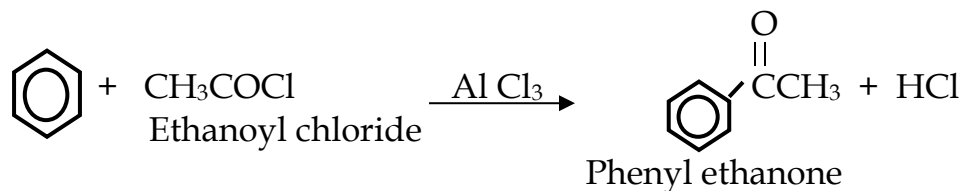


HYDROGENATION OF ACID CHLORIDES

Acid chlorides are reduced by hydrogen in presence of catalysts like Pd to form aldehydes.



Alkyl acylation is a reaction between acid halides with a benzene ring compound. This reaction produces aromatic ketones when it is carried out in presence of a halogen carrier (AlCl_3 , FeCl_3)



PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS

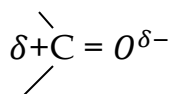
Lower members of aldehydes and ketones are liquids and are miscible with H_2O forming neutral solutions. The miscibility in H_2O is due to the polar carbonyl carbon.

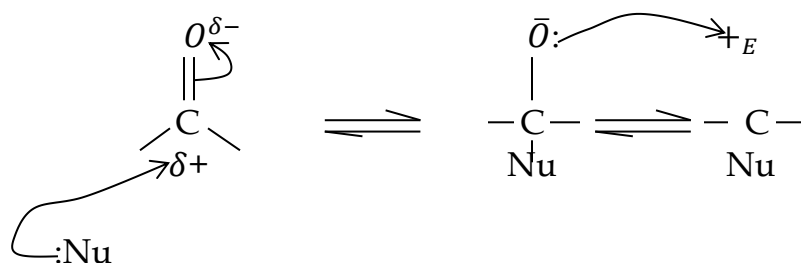
They have higher boiling points than their hydrocarbon counterparts. This is because of the polar nature of the carbonyl carbon that results into the intermolecular attractions but their boiling points are lower than those of alcohols and carboxylic acids due to the lack of H_2 bonding.

CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

Carbonyl compounds chemically react because of the property of the carbonyl carbon which is a common functional group present in both aldehydes and ketones.

A carbonyl carbon contains more electronegative oxygen bonded to carbon which pulls electrons towards itself and attains a δ^- charge while the carbon remains δ^+ . Therefore, the carbon oxygen bond is polarised creating a good condition for nucleophilic reagents to be added across the carbonyl carbon. The intermediate formed with a negative on oxygen reacts with an electrophile to form the final end product.

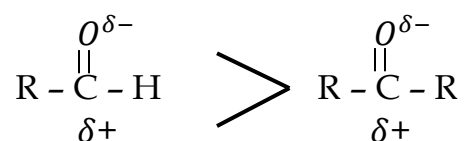




Carbonyl group in aldehyde is more reactive than in ketones.

Explanation:

In ketones, the presence of two alkyl groups having a positive inductive effect highly neutralizes the positive charge in the carbon resulting into a less attraction of a nucleophile.



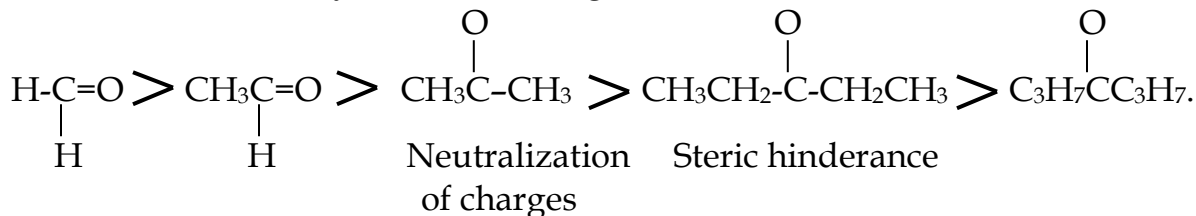
Methanol is more reactive than other aldehydes. Explain.

In methanol only hydrogen is bonded to the carbonyl carbon that the partial positive charge formed is not neutralized making methanol more reactive.

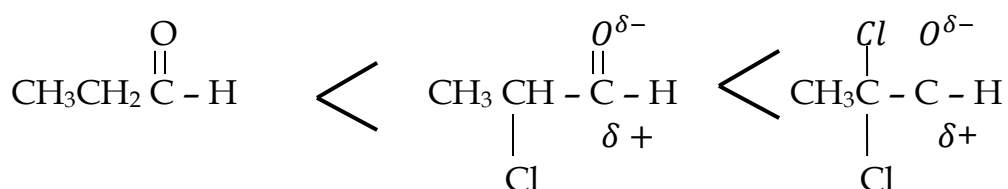
Therefore, the more number of alkyl groups added to a carbonyl carbon, the less the reaction due to the following reasons:

- (i) The alkyl groups have got electron pushing (positive inductive) effect which neutralizes the partial positive charge on the carbon.
- (ii) Several alkyl groups will have a crowding effect preventing a nucleophile from being attached to the carbon.

Order of the reactivity of the following:



When other atoms of a more electronegative effect are added next to the carbonyl group, the reactivity of the carbonyl carbon compound increases. E.g. if a hydrogen on the carbon atom next to the carbonyl group is replaced with a halogen, the reactivity increases.

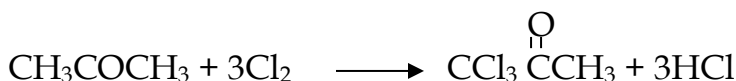
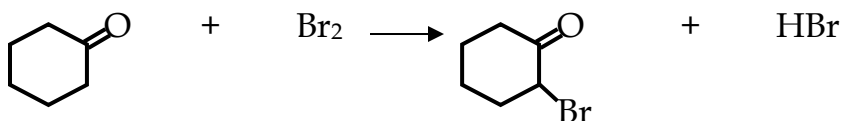
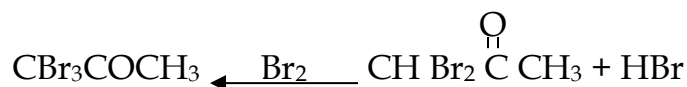
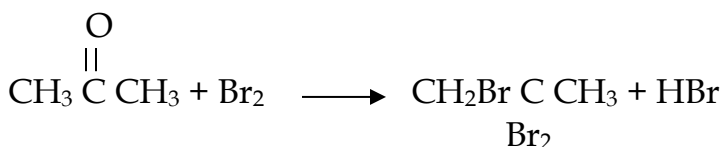
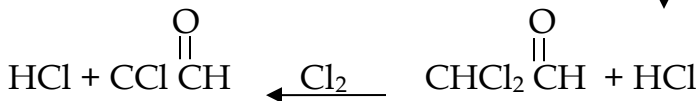
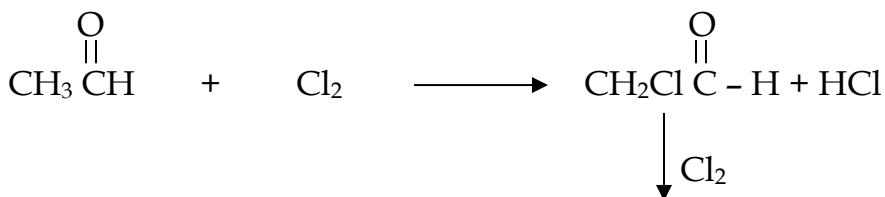


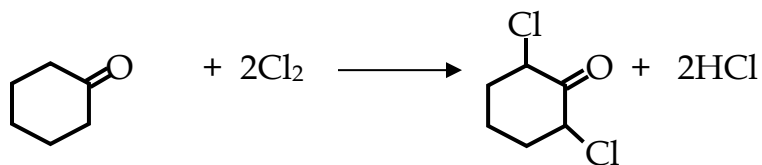
REACTION OF CARBONYL COMPOUNDS

GENERAL REACTION (BOTH KETONES AND ALDEHYDES)

(i) Reactions of alkyl groups:

Both aldehydes and ketones containing alpha hydrogen i.e. hydrogens on the carbons next to the carbonyl group undergo halogenations reaction, when reacted with a halogen to form substituted products. Substitution proceeds until the alpha hydrogens are replaced.



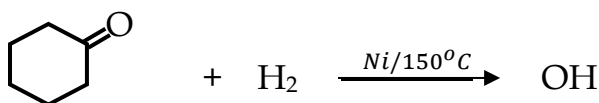
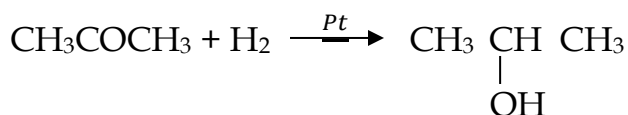
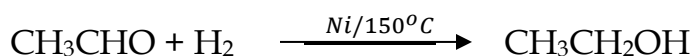


(ii) **Reactions due to carbonyl group:**

Both aldehydes and ketones containing a carbonyl group undergo the following reactions:

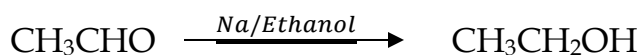
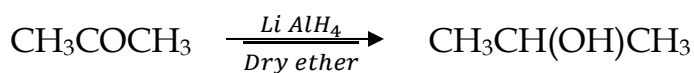
Reduction (Reaction with H₂)

Aldehydes and ketones are reduced by H₂ in presence of a suitable catalyst e.g. Ni/150°C, pt/pd into primary and secondary alcohols respectively.

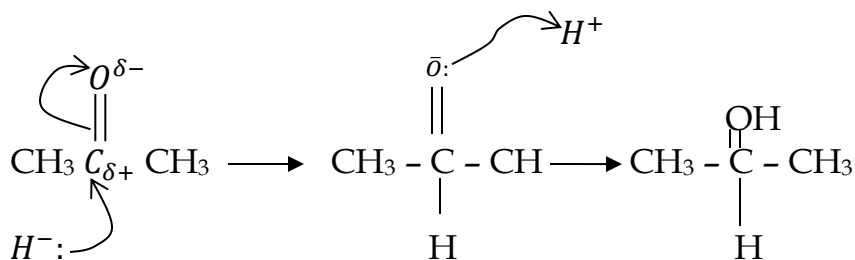
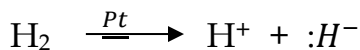


Using reducing agents:

Similarly strong reducing agents such as Aluminium, Na, Lithium tetrahydride, Na/Ethanol can also be used to effect reduction.

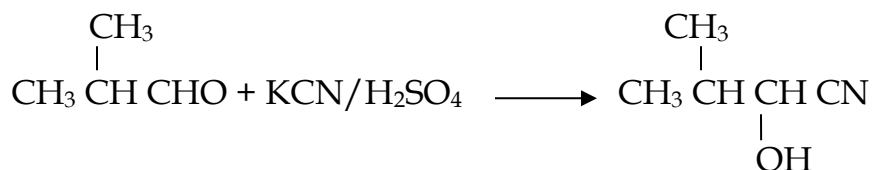
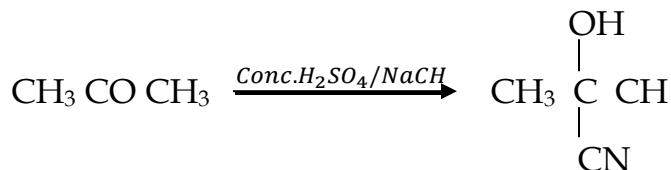
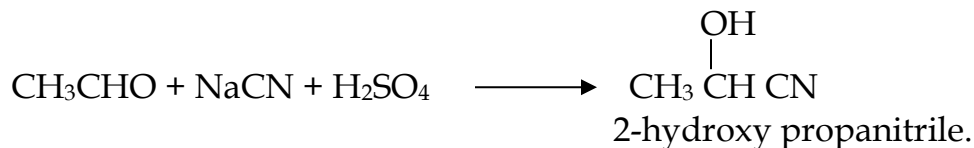


Mechanism of reduction:

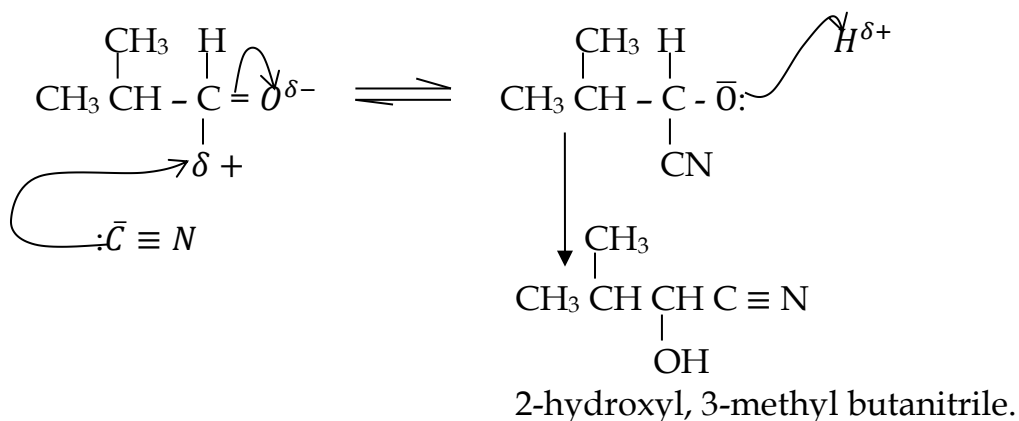
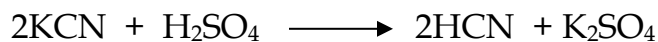


Addition of HCN (hydrogen cyanide)

Both carbonyl compounds react with HCNs to form 2 hydroxyl nitrates or cyanohydrins. The HCN is generated insitu from the reaction between NaCN and Conc. H_2SO_4 .

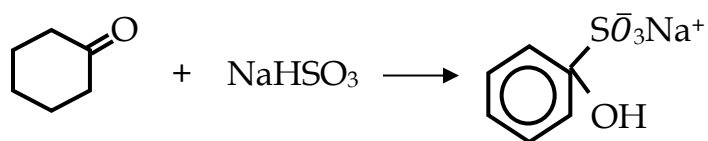
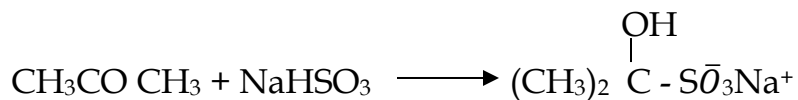
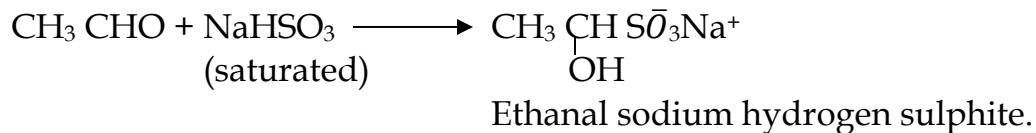


Mechanism:

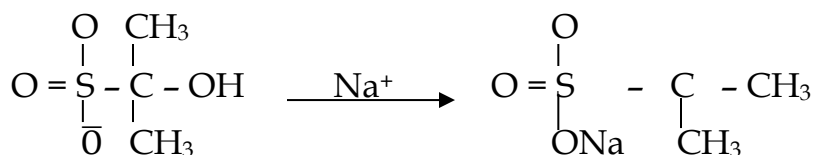
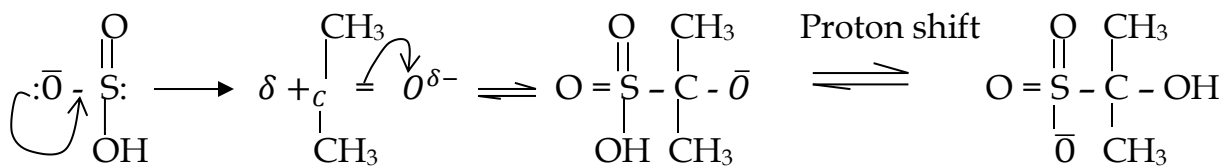


REACTION WITH NaHSO₃

Both carbonyl compounds react with a saturated solution of NaHSO₃ to give crystalline solids of NaHSO₃ derivatives.

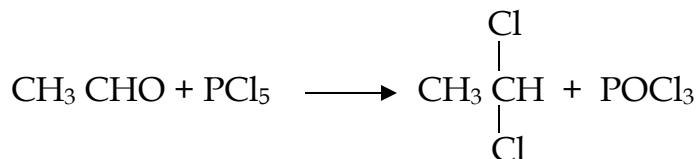


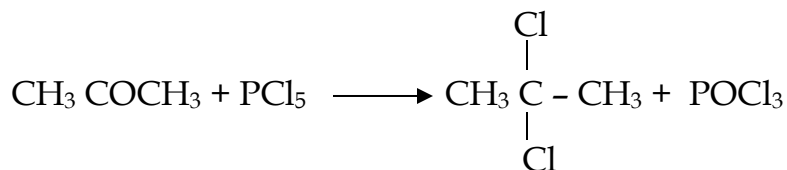
Mechanism:



ADDITION REACTION WITH PCl₅.

Both carbonyl compounds react with PCl₅ to give gem-dihalides with no steaming in moist air i.e. (No hydrogen halide formed) which distinguishes between alcohols and carbonyl compounds.

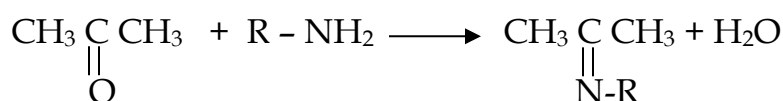
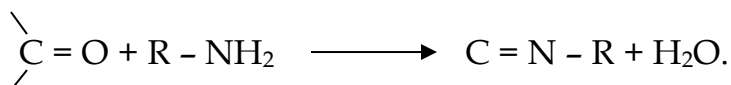


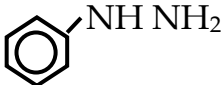

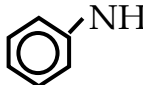
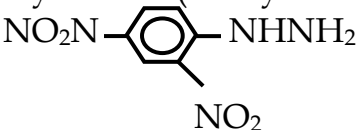
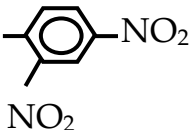
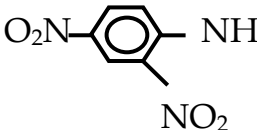


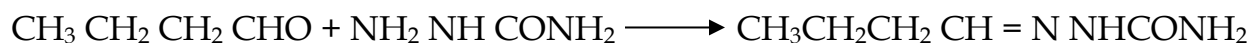
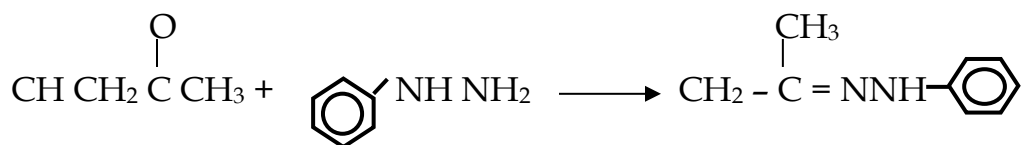
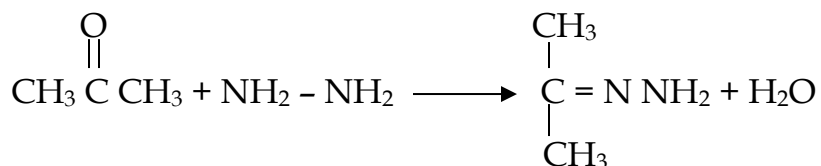
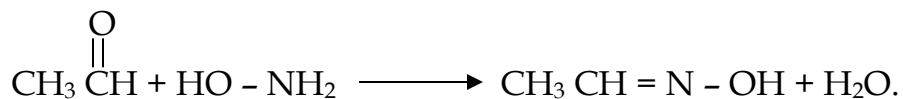
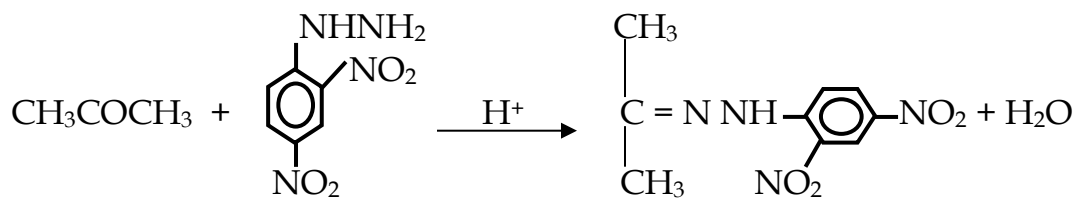
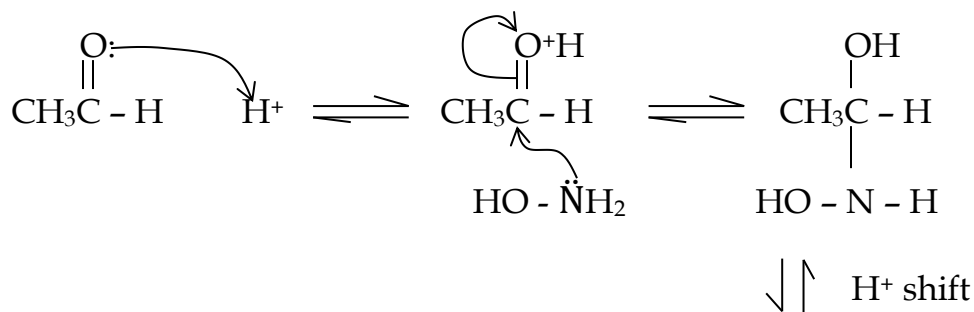
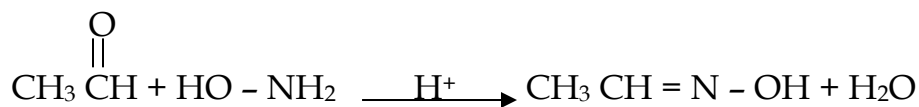
CONDENSATION REACTIONS

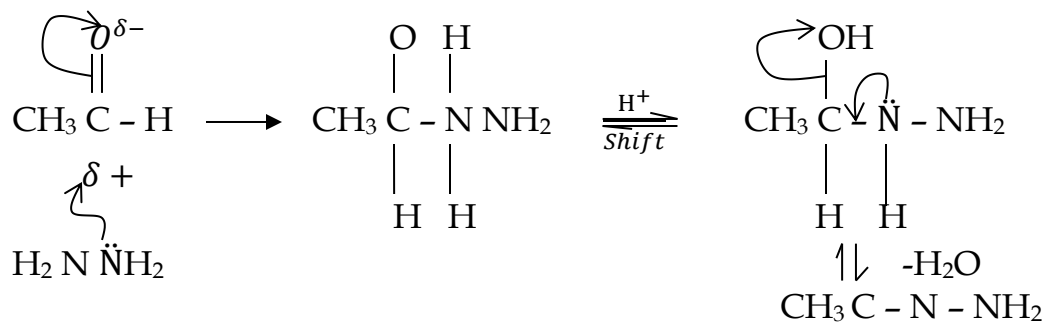
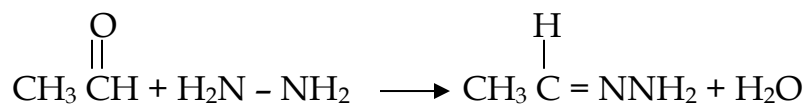
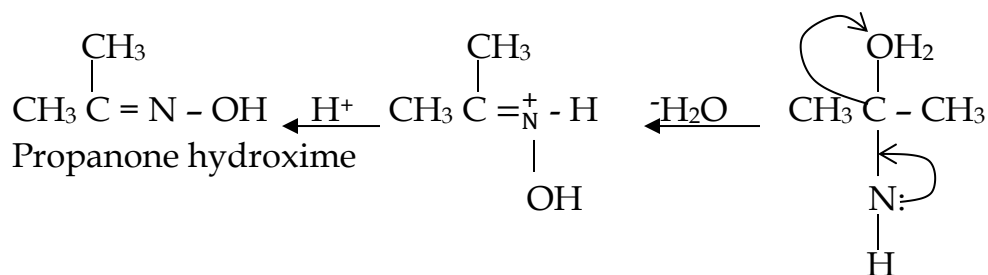
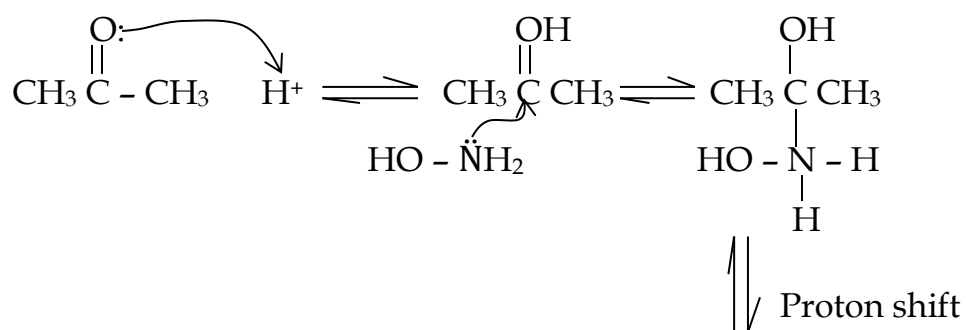
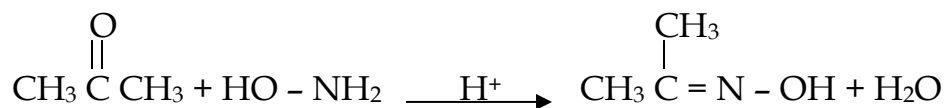
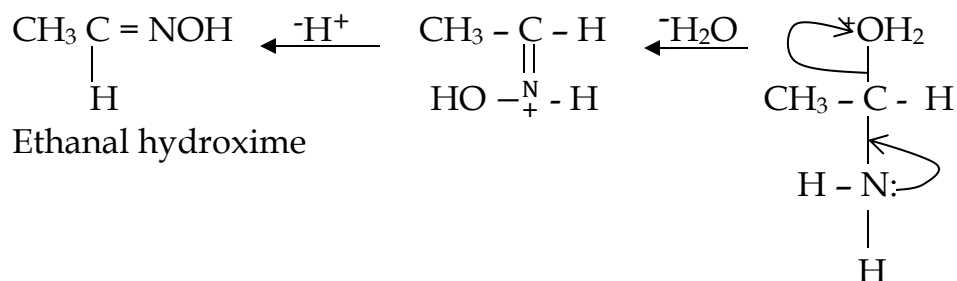
Aldehydes and ketones react with compound containing amino groups to form condensations products and loss of H_2O molecule. These products formed have got sharp melting points which are used in identification of the original compounds.

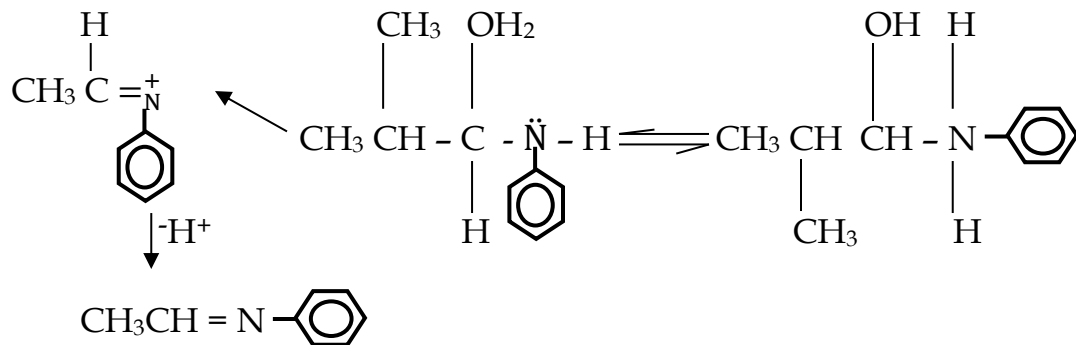
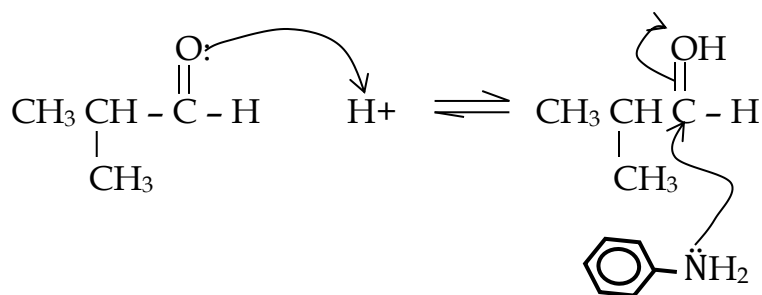
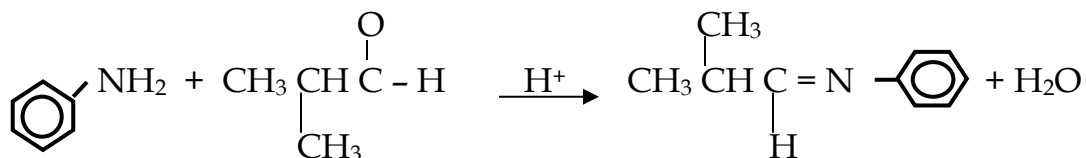
These types of reactions are condensation because there is elimination of a H_2O molecule.



| | Reagents | Product | R - group |
|----|--|---|---|
| 1. | Hydroxyl amine HO-NH_2 | Oxime >C=N-OH | $-\text{OH}$ |
| 2. | Hydrazine NH_2-NH_2 | Hydra zone >C=N-NH_2 | $-\text{NH}_2$ |
| 3. | Phenyl hydrazine  | Phenyl hydra zone >C=N-NH-  |  |
| 4. | Semi carbazine $\text{NH}_2\text{NHCONH}_2$ | Semi carbazone >C=N-NHCONH_2 | NH-CONH_2 |
| 5. | 2, 4 dinitrophenyl Hydrazine (Brady's reagent)  | 2, 4 dinitrophenyl hydrazone >C=N-NH-  |  |

Mechanism:**Mechanisms of condensation reactions of carbonyl compounds**

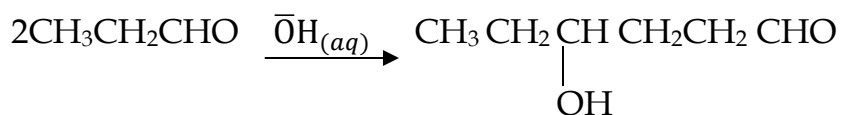
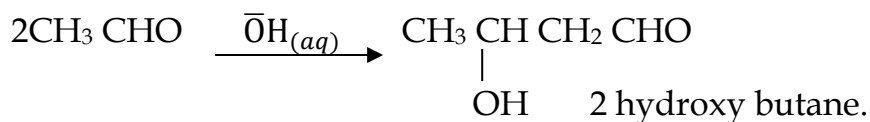


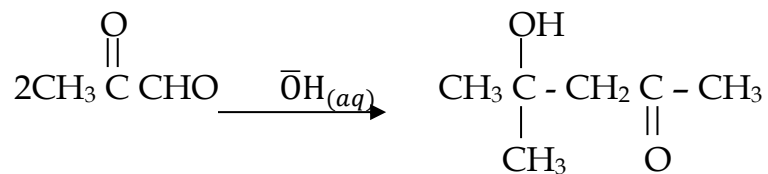


Reactions with dilute NaOH

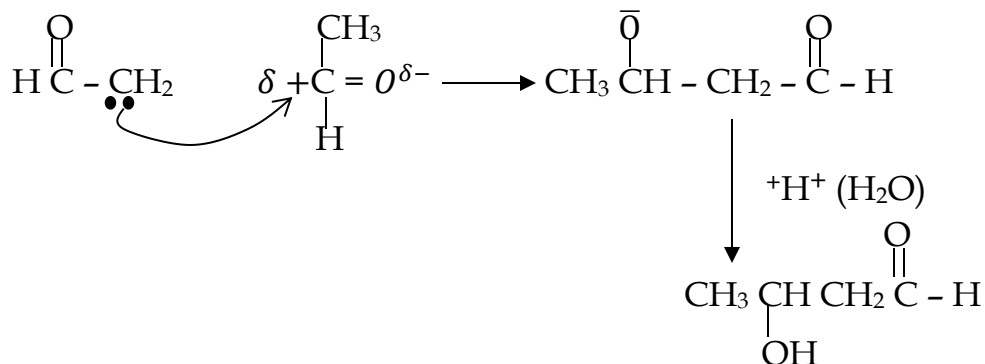
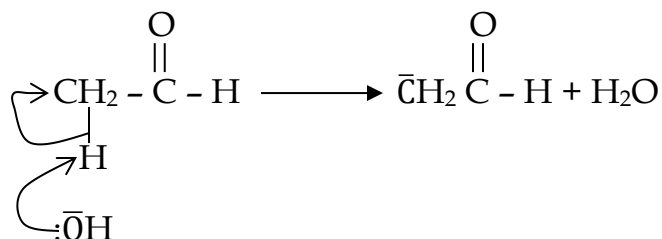
Aldehydes containing α -hydrogens and ketones react with dilute NaOH to form hydroxyl alkanals or alkanones which are compounds containing both hydroxyl group and carbonyl carbon but with doubling of the chain.

When these compounds are heated, H_2O is lost and a double bond is formed.



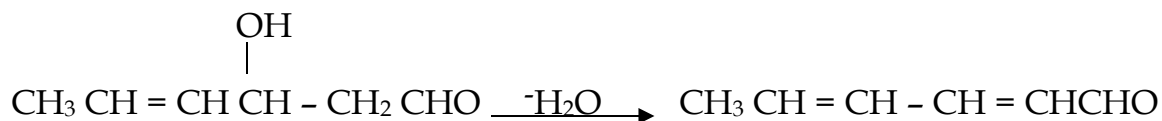
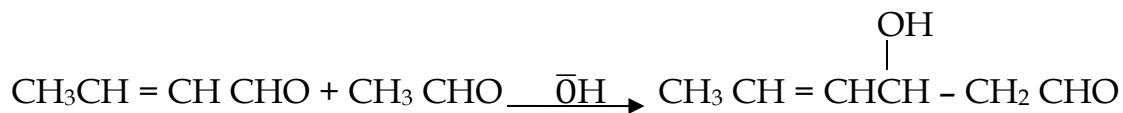
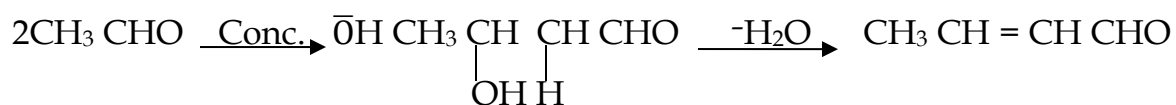


Mechanism:



Reactions with conc. NaOH

This reaction is possible only with aldehydes having α -hydrogens and not with ketones to give brown resinous compounds formed by a series of condensation.



Polymerization:

i.e. $n\text{CH}_3\text{CHO} \xrightarrow{\text{Conc. } \bar{\text{O}}\text{H}} \text{CH}_3(\text{CH}=\text{CH})_n\text{CHO}$.

Reaction that distinguish between aldehydes and ketones.**Oxidation:**

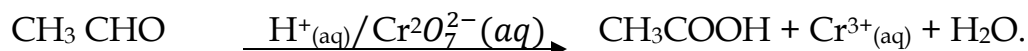
Aldehydes are oxidized by oxidizing agents e.g. $\text{H}^+_{(\text{aq})}/\text{K}_2\text{Cr}_2\text{O}_{7(\text{aq})}$ H^+/CrO_3 to carboxylic acid.

Ketones are resistant to oxidation and therefore they never yield any product with the same reagents.

Test:

Add 2 drops of an aldehyde into 2cm^3 of $\text{H}^+_{(\text{aq})}/\text{K}_2\text{Cr}_2\text{O}_{7(\text{aq})}$ and warm.

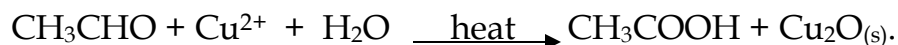
An orange solution turns to green, the resultant solution becomes acidic.

**Benedicts or Fehling's solution:**

Increases a solution containing Cu^{2+} ions. This solution is blue in colour but when reacted with an aldehyde under heat, the aldehyde decreases Cu^{2+} to Cu^+ resultant into a red-brown precipitate of $\text{Cu}_2\text{O}_{(\text{s})}$.

This property of aldehyde is reduction.

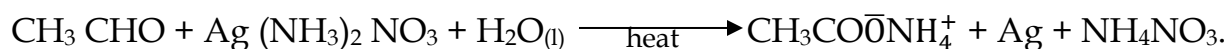
Ketones do not give a red-brown precipitate.

**Ammoniacal silver nitrate (Tollens reagents)**

Ammoniacal silver nitrate solution is a solution of silver nitrate in NH_3 .

Aldehydes unlike ketones are oxidized by this mild oxidizing agent to a carboxylic acid.

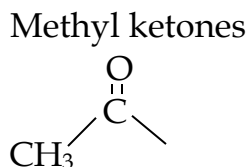
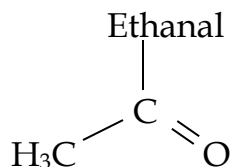
The Ag^+ in the AgNO_3 is reduced to Ag metals. Therefore, the observation made in practicals is; a grey deposit or silvery coating on the sides of the test tube.



Note that atmospheric O₂ can also oxidize aldehydes. This is why samples of aldehydes are normally contaminated when exposed to the atmosphere.

Iodoform / haloform reaction:

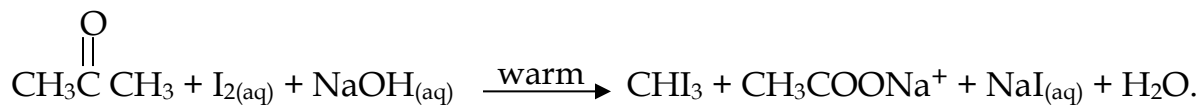
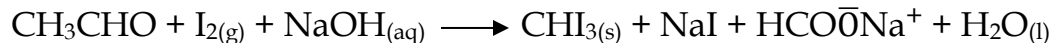
This reaction is only possible for methyl aldehydes and ketones. Since we have only one methyl aldehyde, ethanal, the reaction is strictly positive for ethanol and methyl ketones with the following structure.



The reaction is useful in practicals in determining the structure of carbonyl compounds.

Test:


When iodine and NaOH is added to ethanol or a methyl ketone and warmed, a yellow precipitate of tri iodo methane is formed.

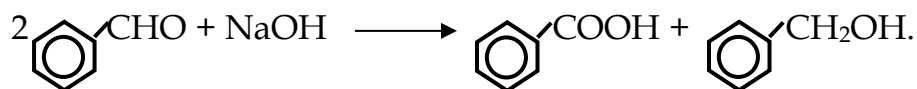


CANNIZZO REACTIONS:

This reaction is only possible for aldehydes without α -hydrogen ketones.

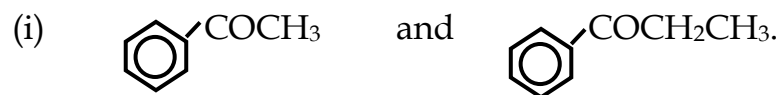
When NaOH is reacted with an aldehyde without an α -hydrogen of general formula.

HCHO, CHO, the aldehyde is oxidized to carboxylic acid and the other half is decreased to the alcohol.







Name the reagent that can be used to distinguish between the following pairs of compounds and in each case, state what would be observed when the reagent is separately treated with each compound.



Reagent: Hot iodine solution in aqueous sodium hydroxide.

With -COCH₃ : A yellow precipitate.

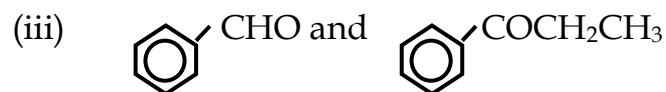
With -COCH₂CH₃ : No observable change.



Reagent:

With CH₃COCH₃

With HCHO



Reagent:

With -CHO

With -COCH₂CH₃



Reagent:

With CH₃CH₂COCH₂CH₃

With HCHO