

ORGANIC CHEMISTRY

Is about structural formulae, naming [nomenclature], preparation [synthesis], and properties of Compounds formed by carbon excluding carbon monoxide [CO], carbon dioxide [CO₂], metal carbonates, carbon disulphide [CS₂] and hydrogen carbonates which are classified as inorganic compounds.

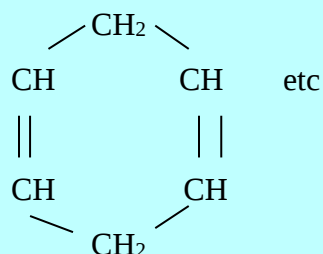
UNIQUE NATURE OF CARBON

The Carbon atom possesses the unique ability to form multiple bonds between itself and other Carbon atoms i.e. $\text{H}_2\text{C} = \text{CH}_2$ and $\text{HC} \equiv \text{CH}$ and also with the atoms of certain other elements such as Oxygen $\text{H}_2\text{C} = \text{O}$, $\text{H}_2\text{C} = \text{S}$, and Nitrogen $\text{HC} \equiv \text{N}$.

It also has the ability to form chains of identical atoms (CATENATION) which is an essential feature of its chemistry. These chains may exist as short or long open systems, where several modes of branching are possible or as closed ring systems

e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

or



NB: To catenate, an element must have a valency of at least two and be able to form fairly strong covalent bonds with itself. Carbon has a valency of four, permitting the existence of multiple bonds in chains of carbon atoms in certain compounds.

It should also show a valency of +4 in all stable compounds it forms.

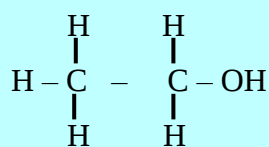
CHARACTERISTICS/ PROPERTIES OF ORGANIC COMPOUNDS

Organic compounds are generally gases, volatile liquids or low melting point solids, they tend to be insoluble in water unless they contain polar groups such as -OH, -COOH, -SO₃H etc, but are usually soluble in organic, non-polar solvents such as tetra chloromethane/carbon tetrachloride, ethoxyethane/ diethyl ether, benzene etc.

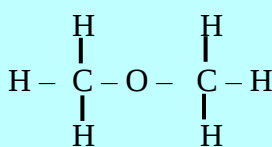
On burning in excess oxygen, they yield carbon dioxide and water (except when the compound contains no hydrogen, which is comparatively rare). Organic reactions are generally slow in and often require energy. Some has the ability of possessing the same molecular formula to exist in different forms on account of their having different structural arrangements of atoms.

Example;

C₂H₆O applies to two entirely different compounds that is ethanol and methoxymethane which posses distinctly different properties



Ethanol



methoxymethane/dimethylether

In organic chemistry we can concentrate on a relatively small group of commonly encountered elements i.e. carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus and the halogens.

NAMING ORGANIC COMPOUNDS

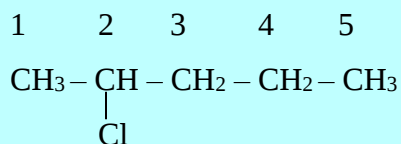
The most universal and systematic method of naming these compounds is that devised by a commission appointed by the International Union of Pure and Applied Chemistry (IUPAC). It provides a convenient and relatively straightforward method for naming even the most complicated molecules and the advantage is that the same basic principles are employed for each series of compounds i.e. it defines the structures more clearly

The following provides an outline of the systematic principles adopted.

- i) The largest continuous chain of carbon atoms containing the functional group is selected and named according to the parent alkane.

NB. All organic compounds are considered as derivatives of alkanes.

- ii) The carbon atoms of the chain are numbered in order to indicate the positions of any substituents in the chain. The end of the chain from which the numbering starts is chosen so as to use the lowest values

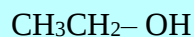
Example

2-chloropentane

- iii) The names of the substituents prefix, the name of the parent alkane alphabetically and the positions of substituent precede the whole.
- iv) The numbers assigned to the functional groups are chosen so as to be as small as possible. These are usually placed between the stem and the ending of the name. The functional group numbers are given precedence over those assigned to other substituents.

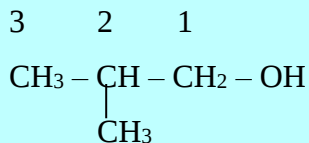
Example:

Simple alcohols are named by dropping the “e” from the end of the name of the parent alkane and adding the suffix “ol”



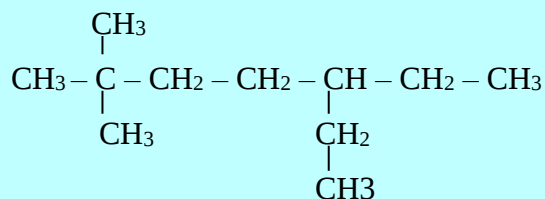
Ethanol

(Parent alkane; ethane)

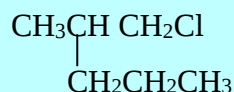


2 methyl propane – 1 – ol

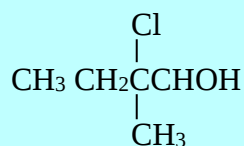
(Parent alkane; propane)



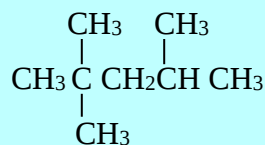
4 – ethyl – 2,2 – dimethyl heptane



1 – chloro – 2 - methyl pentane

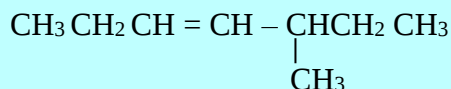


2 – chloro – 2 - methyl butan – 1 – ol



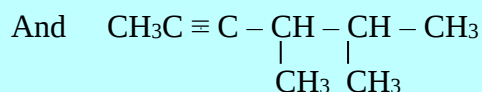
2, 2, 4 – trimethyl pentane

In alkenes the suffix “ene” replaces “ane” of the corresponding alkane, then;



5 – methyl – 3- heptene or

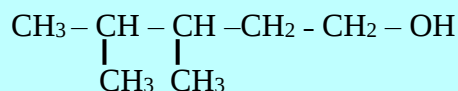
5 – methyl hept – 3- ene



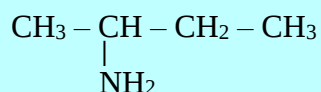
4, 5 – dimethyl –2- hexyne

NB: Naming mono functional compound, the longest chain should include the functional group and the carbon are numbered so that the position of the functional group gets the smaller value. The last “e” of the corresponding alkane is then dropped and replaced by the suffix representing the functional group. And the position of the functional group written before the name of the hydrocarbon separated on either side by hyphens.

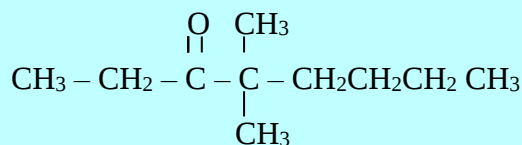
i.e.



3, 4 dimethyl – 1 – pentanol

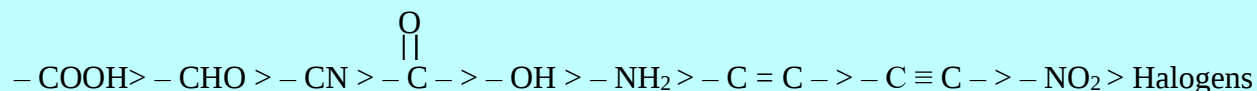


2 – amino butane

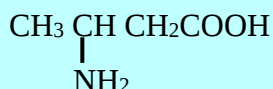


4, 4 dimethyl – 3 – octanone

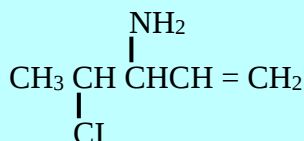
NB: The order of seniority is



i.e.

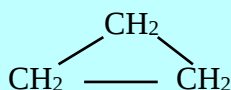


2 – amino butanoic acid



4 chloro – 3 – amino – 1 pentene

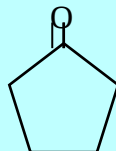
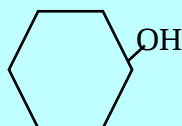
NB: For cyclic compounds, the prefix cyclo must be put before the name of the parent hydrocarbon i.e.



or



cyclopropane



cyclopentanone

etc

ISOMERISM

Is the phenomenon whereby certain compounds possessing the same molecular formula exist in different forms because they have different arrangements of atoms. Hence is the existence of compounds with same molecular formula but different structural formulae and the compounds are called **Isomers**.

This concept illustrates the fundamental importance of molecular structure in organic chemistry.

There are two main types of isomerism.

- Structural isomerism, in which the atoms are linked together in different ways.
- Stereo Isomerism, in which the atoms have different spatial arrangements. Stereo Isomerism will be seen at higher levels.

STRUCTURAL ISOMERISM

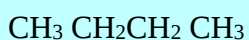
Arises from the differences in the arrangement of atoms within the molecule resulting in two or more different structural formulae. Hence structural Isomers have same molecular formula but different structures.

Types of structural Isomerism

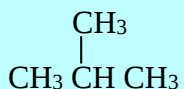
1. CHAIN ISOMERISM: Is due to the difference in the structure of carbon chain or the arrangement of carbon atoms in the molecule.

Example:

a) C_4H_{10}



Straight chain Isomer

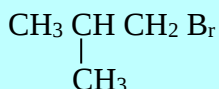


Branched chain Isomer

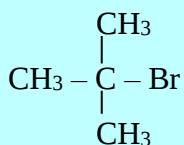
b) C_4H_9Br



1 – bromo - butane

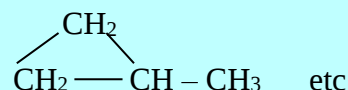
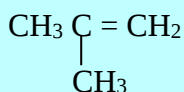
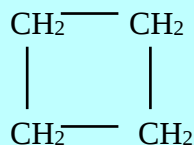
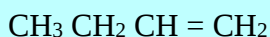


1 – bromo – 2 – methyl propane



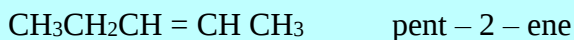
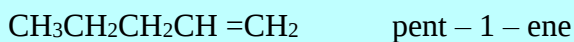
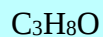
2 – bromo – 2 – methyl propane

c) C_4H_8



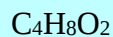
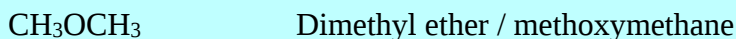
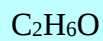
2. **POSITION ISOMERISM:** Is a type of structural isomerism in which the compounds have the same carbon skeleton or chain and the same functional group but the positions on to which the functional groups are attached differ.

e.g.



3. **FUNCTIONAL GROUP ISOMERISM:** Is a type of isomerism in which the compounds have different carbon skeletons and also have different functional groups.

Example:



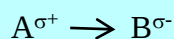
STRUCTURE AND PHYSICAL PROPERTIES

Physical properties of a compound depend primarily upon the nature of the bonds holding the atoms in the molecules together and also upon the size and shape of the molecules themselves.

POLARIZATION OF A COVALENT BOND

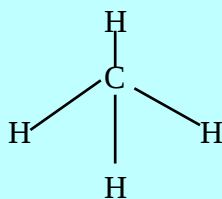
A covalent bond is formed by the sharing of two electrons, one being contributed by each of the constituent atoms, these electrons are not distributed exactly between the two atoms unless they happen to be identical or possess exactly equal electronegativity values.

NB: Small atoms attract electrons more readily than do larger ones. And those which have nearly filled shells tend to have higher electronegativity values than those with only partly filled shells. The electrons in a bond joining two atoms A and B are displaced towards the more electronegative atom, which acquires a relatively negative charge (σ^-) and the other relatively positive (σ^+). Then the bond is said to be POLARIZED



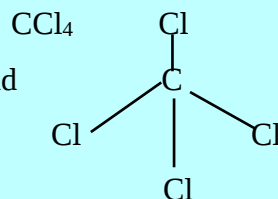
A molecule that has an asymmetrical distribution of electrons is said to pose a DIPOLEMOMENT which is the product of the size of the charge and the distance of separation in the molecule.

In methane



Methane

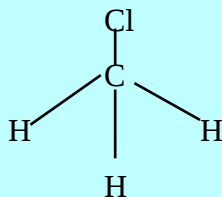
and



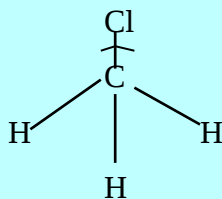
Tetra chloromethane

Dipole moment is zero, because the electron distribution within the molecules is completely symmetrical.

But CH_3Cl



Dipole moment is not zero, because chlorine is more electronegative and the distribution of electrons within the molecule is not symmetrical i.e.



Hence;

The dipole – dipole interaction; Is an attractive force between the relatively positive end of one polar molecule and the relatively negative end of another i.e. $A^{\sigma+} - B^{\sigma-} / B^{\sigma-} - A^{\sigma+}$

MELTING POINT

Organic solids are composed of molecules which are predominantly covalent and are held together by attractive forces between non-bonded atoms (Vanderwaal's forces) which can exist between atoms within a molecule which are not attached to each other or between the atoms of different molecules. These attractions are weak and function only over a short range. So as these non-bonded atoms approach each other more closely the attractive forces vanish and a repulsive force emerges.

And are also held by dipole-dipole interactions which are also weak. Hence these solids have correspondingly lower melting point.

NB: The size and shape of the molecules of a solid are closely related to its melting point, Compounds composed of large molecules tend to have higher melting points than those composed of small ones. And the more symmetrical the molecule the higher the melting point.

Examples:

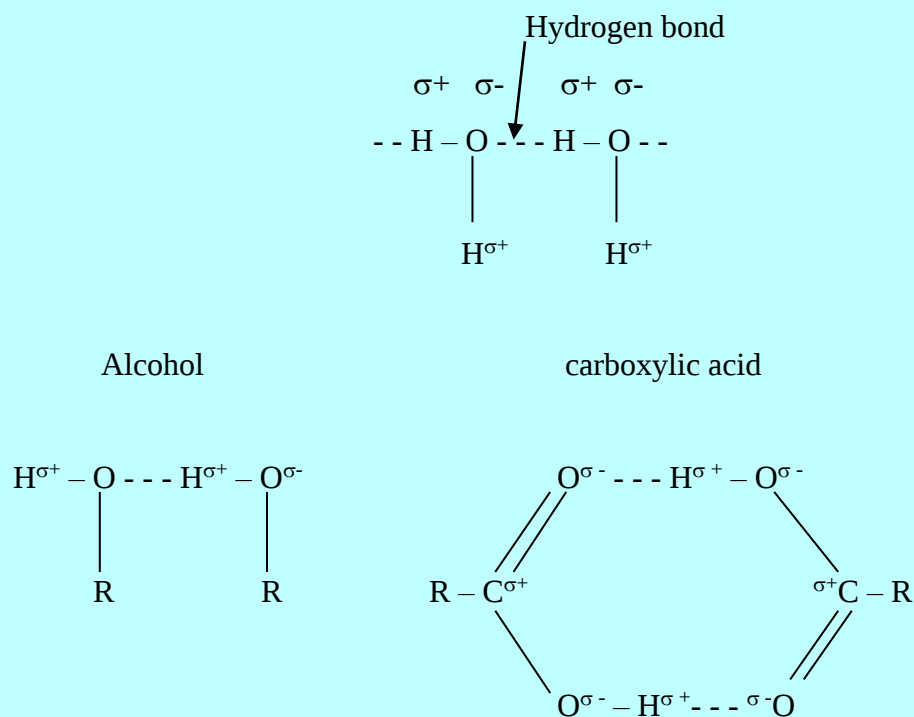
Carboxylic acids with an “even” member of the series has higher melting point than the “odd”

BOILING POINTS

Organic liquids whose molecules contain –OH group tend to have abnormally high boiling points, this is because of hydrogen bonding which limits the formation of a covalent bond with one and holding the other solely by electrostatic forces resulting into a very strong dipole-dipole interaction.

NB: Hydrogen bonding is the bond formed between hydrogen atom and an electronegative atom. Hydrogen bonding has two different forms.

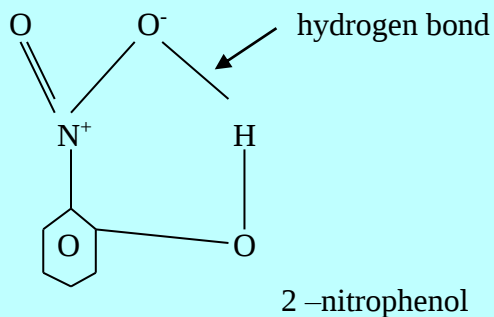
- a) **Intermolecular hydrogen bonding** which occurs between separate molecules giving rise to association in the liquid and solid phases. It causes an elevation in the boiling point. Water forms a series of hydrogen bonds which have to be broken down in order to convert the liquid into steam.



The greater polarity of carboxylic acid molecules and the formation of two intermolecular hydrogen bonds give rise to boiling point higher than for the corresponding alcohols.

- b) **Intra molecular hydrogen bonding** which occurs between different atoms within the same molecule.

In 2-nitrophenol, the intramolecular hydrogen bond is formed between one of the oxygen atoms of the nitro group and the hydrogen atom of the hydroxyl group. Hence having a greater volatility than either 3-nitrophenol or 4-nitrophenol



Explain the following

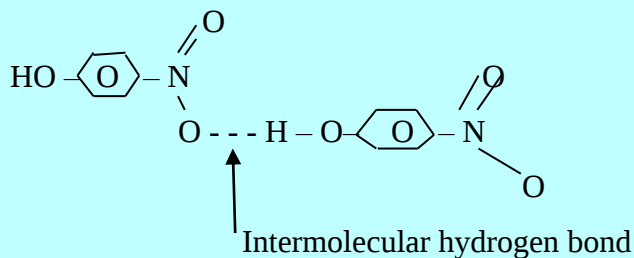
- a) Ammonia boils at -33°C whereas Phosphine PH_3 boils at -88°C .

Solution: Ammonia has a higher boiling point than Phosphine because the nitrogen atom in ammonia has a high electronegativity power than phosphorus. This allows formation of hydrogen bonding between ammonia molecules and Vanderwaals bonding in phosphine molecules.

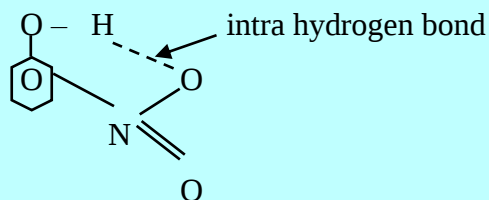
However, the hydrogen bonding is stronger and hence need a lot of energy to break compared to one need for weak Vanderwaals.

- b) The melting point of 4 – nitro phenol is higher than that of 2 – nitrophenol.

Solution: In 4 – nitrophenol molecule, the two functional groups are further apart and thus able to associate via intermolecular hydrogen bonding i.e.



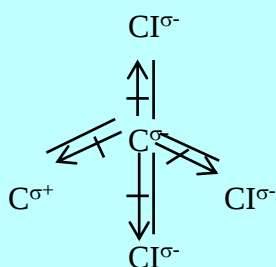
Whereas in a 2 – nitro phenol molecule, the functional groups are closer and this causes an intra hydrogen bond to be formed by interaction of the hydrogen on the hydroxyl group with the oxygen atom on the nitro functional group i.e.



This leads to the molecules in 2 – nitrophenol to associate with a much weaker vanderwaals forces of attraction which are in fact much easier to break than the intermolecular hydrogen bonds in 4 – nitrophenol. Therefore, the melting point of 4 – nitrophenol is higher than 2 – nitro phenol

- c) Carbon tetra chloride molecule is non-polar yet the bonds in carbon tetra chloride are polar.

Solution: Chlorine atom is more electronegative than carbon therefore; it tends to attract the bonding electrons between C – Cl more towards itself so that it acquires partial negative charge while carbon acquires a partial positive charge. This un-equal distribution of electrons establishes a dipole moment in the direction of the more electronegative chlorine atom thus making the C – Cl bond in CCl_4 polar. However, the whole molecule of tetra chloromethane is non -polar because the C – Cl bonds are symmetrical and tetrahedrally arranged around the central carbon atom. Therefore, the effect of bond polarity in the opposite directions cancel out with each other so that the net dipole moment in the whole molecule of tetra chloromethane is zero and thus non -polar



Solubility

This depends upon the intermolecular forces between the dissolved substance, irrespective of whether it is a solid or a liquid and the solvent. The solubility of a non-electrolyte in water depends on whether the compound can form hydrogen bonds with water for compounds containing –OH group. The best solvents are those which also contain –OH group. The size of a substance also determines its solubility alkanes are all virtually insoluble in water but the smallest member of the series (methane) is more soluble than any of the larger members. **NB:** Any possibility of hydrogen bonding in this instance is deemed unlikely.

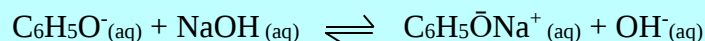
Explain the following

1. Phenol (hydroxybenzene) is sparingly soluble in water but very soluble in dilute sodium hydroxide.

Solution: Hydroxybenzene is slightly acidic, therefore it poorly ionizes in water to form a phenoxide ion and a hydrogen ion. i.e.



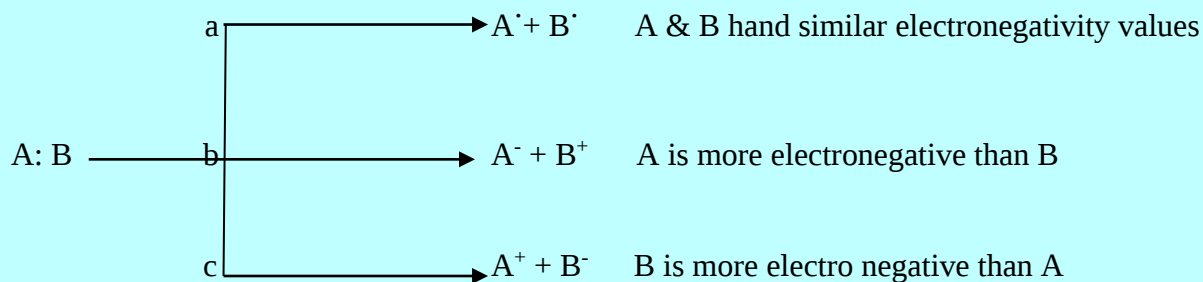
In addition, the phenoxide ion so formed readily combines with sodium ions from sodium hydroxide to form sodium phenoxide (sodium salt of phenol) which is highly soluble. Therefore, phenol is more soluble in dilute sodium hydroxide



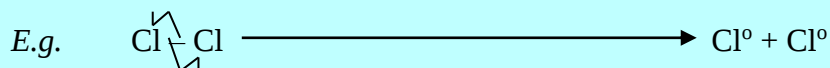
REACTANTS AND REACTIONS

In a chemical reaction the reactant molecules undergoing attack is referred to as the SUBSTRATE and the attacking species is the REAGENT these two interact to yield the products of the reaction.

During the process; chemical bonds have to be broken in order that new compounds may be formed. This breaking (fission) of bonds can happen in any of the different ways depending upon the electronegativity values of the two atoms formed by the bond
i.e.



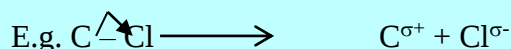
Where the difference in electronegativity between bonded atoms is small, as in a rupturing the bond between them results in the formation of very reactive FREE RADICALS with each atom acquiring one of the bonding electrons. The process is known as HOMOLYTIC FISSION. The movement of a single electron during homolytic fission is depicted by a half arrow.



Where one atom is distinctly more electronegative than the other, there is a tendency for both bonding electrons to remain with the more electronegative atom after rupture of the bond.

The process is HETEROLYTIC FISSION. The more electronegative atom gains a single negative charge owing to the acquisition of an extra electron and the less electronegative atom becomes positively charged.

The shift of a pair of electrons is indicated by a curly arrow



NB. Heterolytic fission is the type most frequently encountered in organic chemistry.

ELECTROPHILES AND NUCLEOPHILES

- | | |
|--|---|
| <ul style="list-style-type: none"> Electrophiles are electron loving example H^+, Cl^+, I^+, N^+O_2, RN_2^+, R_3C^+. Hence electrophiles are donors of protons or acceptors of electron pairs. Thus are oxidizing agents. | <ul style="list-style-type: none"> Nucleophiles are nucleus loving example; H_2O, ROH, OH^-, RO^-, Cl^-, Br^-, I^-, NH_3, RNH_2, CN^-. Nucleophiles are acceptors of protons or donors of electrons pairs Thus are reducing agents. |
|--|---|

FUNCTIONAL GROUP AND HOMOLOGOUS SERIES

Organic compounds are categorized according to their functional groups. These are groups of atoms or bonds common to a series or family of compounds and which govern the principal chemical properties of the series.

Each series follows a regular structural pattern in which each member differs from the next by a constant amount and such a series is called a HOMOLOGOUS SERIES and the individual members of it are referred to as HOMOLOGUES.

Alkanes are series of hydrocarbons; they contain only carbon and hydrogen.

General structural formula $\text{C}_n\text{H}_{2n+2}$, $n = 1, 2, \dots$ each homologue differs by the increment $-\text{CH}_2-$ and the first member is methane, formula, $n = 1$, CH_4 followed by $n = 2$, C_2H_6 , ethane, $n = 3$, C_3H_8 propane and so on.

The table below gives the general structural formulae of the aliphatic homologous series and their functional groups.

Homologous series	General structural formula	Functional group
✓ Alkanes	$\text{C}_n\text{H}_{2n+2}$	– single bond

✓ Alkenes	C_nH_{2n} for $n \geq 2$	$>C = C<$ double bond
✓ Alkynes	C_nH_{2n-2} for $n \geq 2$	$-C \equiv C-$ tripple bond
✓ Alcohols	$C_nH_{2n+1}OH$	$-OH$
Ethers	$C_nH_{2n+1}O$ for $n \geq 2$	$-O-$
Aldehydes	$C_nH_{2n+1}CHO$ for $n \geq 2$	$H \diagup C = O$
Ketones	$C_nH_{2n+2}CO$ for $n \geq 2$	$>C = O$
✓ Carboxylic acids	$C_nH_{2n+1}COOH$	$\begin{array}{c} -C = O \\ \\ OH \end{array}$
Primary amines	$C_nH_{2n+1}NH_2$	$-NH_2$

“R” is the conventional means of representing the general formula of an alkyl group as the formulae RH, ROH, RCHO etc represents the alkanes, alcohol and aldehydes respectively.

NB: Each alkyl group named from the parent alkane by dropping the ending “-ane” and replacing it with “-yl” e.g.

That derived from methane is the methyl group ($-CH_3$).

Ethane is the ethyl group ($-CH_2CH_3$)

Propane is the propyl group etc.

SATURATED AND UNSATURATED HYDROCARBONS

All carbon valences of alkanes are saturated with hydrogen. Alkanes contain only carbon hydrogen and carbon – carbon single bonds, they are said to be SATURATED and are described as saturated hydrocarbons.

Compound possessing carbon-carbon multiple bonds are said to be UNSATURATED and those possessing one set of carbon-carbon double bonds $>C=C<$ are called ALKENES and those possessing a set of carbon-carbon tripple bonds $-C \equiv C-$ are called ALKYNES and these carbon-carbon multiple bond represents the functional group

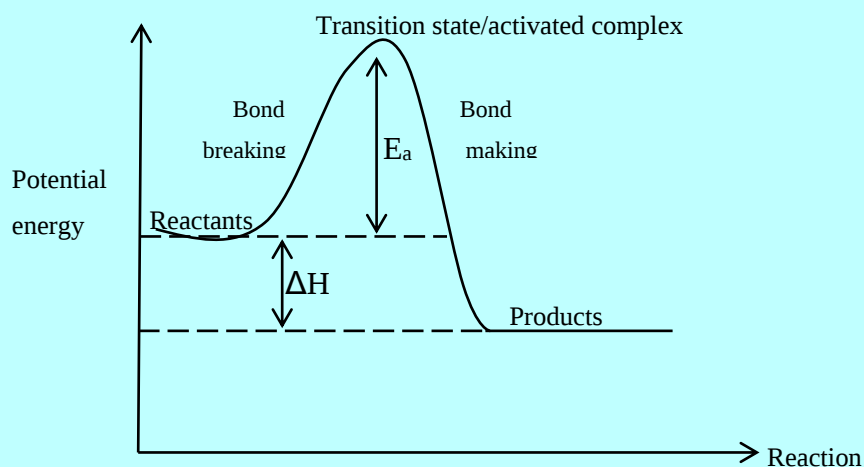
Energetics and Kinetics of a reaction

A detailed description of a chemical reaction outlining each separate stage is called a MECHANISM.

NB: Nucleophiles always attack and the electrophiles are always attacked

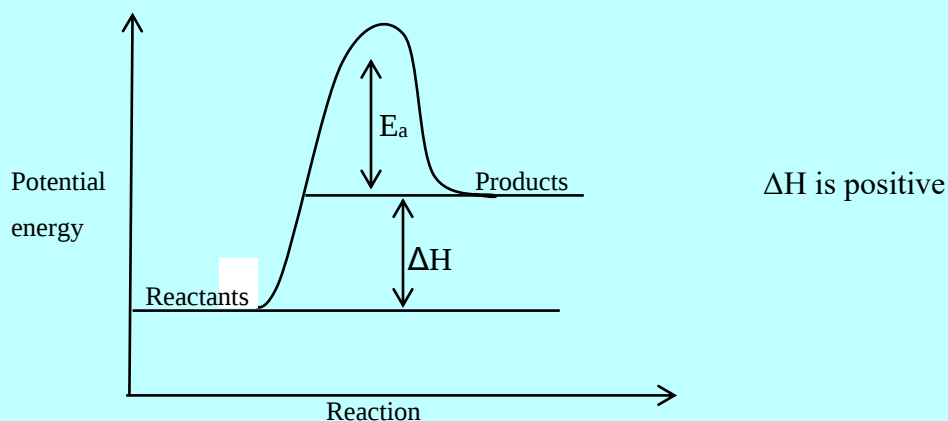
The reactant molecules become activated owing to their greater energy content and are referred to as the TRANSITION STATE or ACTIVATED COMPLEX. The complex is the least stable state through which the reactants pass before forming the products. The quantity of energy required to raise the reactant molecules to this state is referred to as the ACTIVATION ENERGY (E_a) for the reaction. It is in fact, this energy which is the most influential in determining the rate which a reaction precedes.

Exothermic

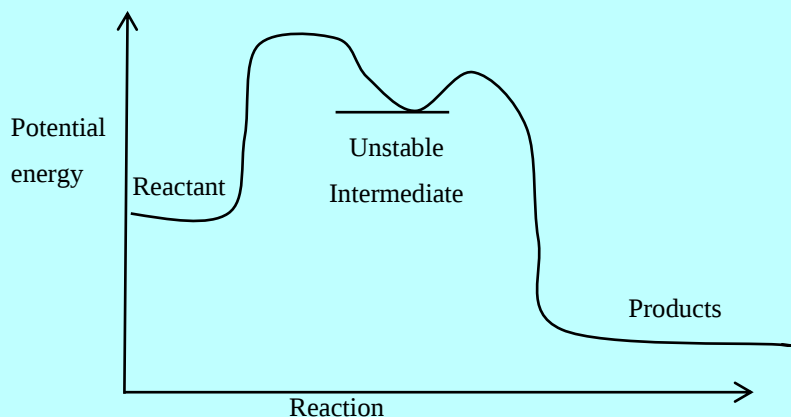


NOTE: Products formed via an exothermic process have lower energy content than the reactants from which they are formed and ΔH is negative.

Endothermic



If the activated complex exists as an UNSTABLE INTERMEDIATE which in many instances may actually be isolated, thus observed in a reaction profile as a trough in the activated peak of the curve resulting in a double hump i.e.



As the intermediate becomes more stable, the greater the likelihood of being able to separate the intermediate from the reaction mixture during the course of the reaction.

NB: The majority of organic reactions are complex and processed via the formation of intermediate which corresponds to a trough in the activated part of the reaction profile.

Since the reaction cannot proceed more rapidly than its slowest stage it is this RATE – DETERMINING STEP that governs the rate of the overall reaction.

The molecularity of the reaction describes the number of species involved in bond cleavage in the rate determining step. Reactions in which only one molecule is involved in bond cleavage during this step i.e.

$AB \longrightarrow A + B$ are described as UNIMOLECULAR and those in which two molecules are involved i.e.

$AB + C \longrightarrow A + BC$ are described as BIMOLECULAR and the molecularity must be a whole number

Example: The hydrolysis of a tertiary haloalkane is Unimolecular and the hydrolysis of a primary haloalkane is bimolecular.

Determination of Relative Molecular mass of a compound.

Method:

- a) Vapour density measurements example gas syringe

$$\text{Relative molecular mass} = \text{Vapour Density} \times 2$$

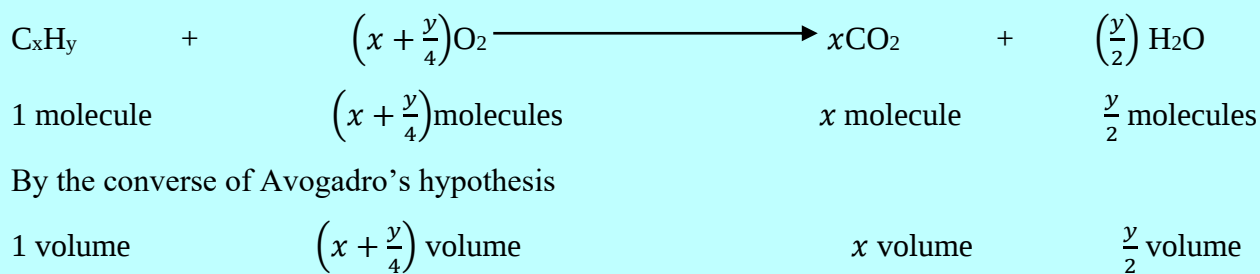
Having determined the relative molecular mass and empirical formula, the molecular formula of the compound can be found

$$\text{Molecular formula} = (\text{Empirical formula}) n$$

- b) The molecular formula of gaseous hydrocarbons can usually be determined by gas explosion reactions (eudiometry). A known volume of the gas is repeatedly sparked in excess oxygen in a eudiometer until no further change in volume is observed. After cooling to the ambient temperature, the volume is noted and the amount of carbon dioxide determined by dissolving in potassium hydroxide. The remaining gas is excess oxygen.

Example:

30cm³ of a gaseous hydrocarbon C_xH_y were mixed with 140cm³ of oxygen (in excess) and exploded. After cooling to room temperature, the residue gases occupied 95cm³. By absorption with potassium hydroxide solution a diminution of 60cm³ was produced and the remaining gas was shown to be oxygen. Determining the formula of the hydrocarbon.

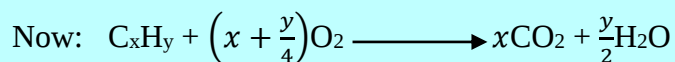


Assume that the steam will condense to water and occupy negligible volume

The potassium hydroxide solution absorbs the volume of carbon-dioxide produced i.e. 60cm³

$$\therefore \text{Volume of excess oxygen is } (95 - 60) \text{ cm}^3 = 35 \text{ cm}^3$$

$\therefore$ 30cm³ of C_xH_y combines with (140 – 35) = 105cm³ of oxygen to give 60cm³ of carbon dioxide



$$\begin{array}{ccc} 30\text{cm}^3 & : 105\text{cm}^3 & : 60\text{cm}^3 \\ 1 & : 3.5 & : 2 \end{array} \quad (\text{simplest ratio})$$

$$x = 2$$

$$\text{And } \left(x + \frac{y}{4}\right) = 3.5$$

$$y = 6$$

Giving the molecular formula of the hydrocarbon as C_2H_6 (Ethane)

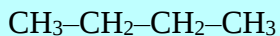
ALKANES (Paraffin)

General formula C_nH_{2n+2} , forms a series of saturated hydrocarbons and successive members differ in composition by $-CH_2$; they are tetrahedrally surrounded by hydrogen and other carbon atoms, they are very stable and relatively unreactive.

NOMENCLATURE

With exception of methane CH_4 , ethane C_2H_6 , propane C_3H_8 , and butane C_4H_{10} straight chain alkanes are named by taking the Greek prefix appropriate to the number of carbon atoms and adding the ending “-ane”. For branched alkanes, the largest un branched chain of carbon atom is

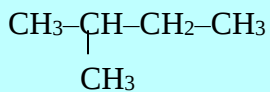
selected and named accordingly and the name of the alkyl substituents prefix the name of the main chain.



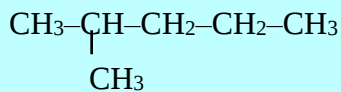
Butane



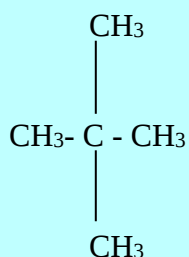
Pentane



2 – Methyl butane



2 – methyl pentane

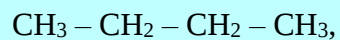


2, 2 Dimethyl propane

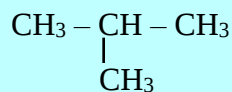
Structural Isomerism in Alkanes

Methane, ethane and propane have no isomers, butane has two, pentane has three and the following higher homologous of the series have a progressively greater number. All isomers are due to branching of the hydrocarbon chain and are referred to as CHAIN/ Branched chain isomers.

Butane C₄H₁₀



Butane

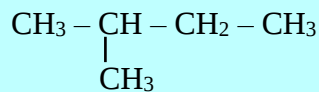


2 – methyl propane

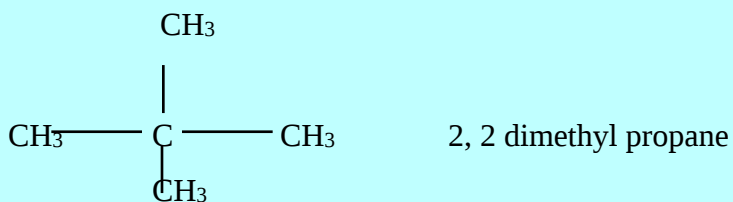
Pentane C₅H₁₂



Pentane



2 – methyl butane



Classification of Carbon

A primary (1^0) carbon is one which is attached to not more than one other carbon atom.

i.e. $-\text{CH}_3$

A secondary (2^0) carbon is one which is attached to two other carbon atoms i.e. $-\text{CH}_2-$

A tertiary (3^0) carbon is one which is attached to three other carbon atoms i.e. $-\text{CH}$

i.e. $1^0\text{CH}_3 - 2^0\text{CH}_2 - 2^0\text{CH}_2 - 1^0\text{CH}_3$

$1^0\text{CH}_3 - 3^0\text{CH} - 1^0\text{CH}_3$
 1^0CH_3

Physical Properties

- ❖ The first forms are gases but the C_5 to C_{17} are liquids and the rest are solids at 20°C .
- ❖ The Boiling point and melting point of alkanes increases with increasing relative molecular mass but the branched – chain isomers are more volatile than their straight isomers. Hence the greater the degree of branching in an isomer, the greater is to volatility.
- ❖ They are non-polar and immiscible with water but soluble in non-polar organic solvents such as trichloro methane, ether, benzene etc. Methane shows a light tendency to dissolve in water but this is due to its small size of its molecules.

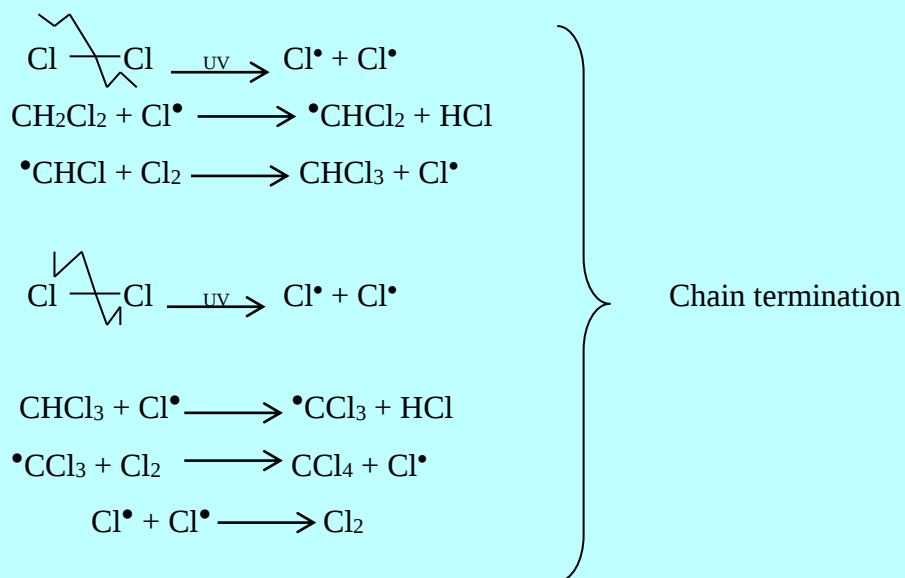
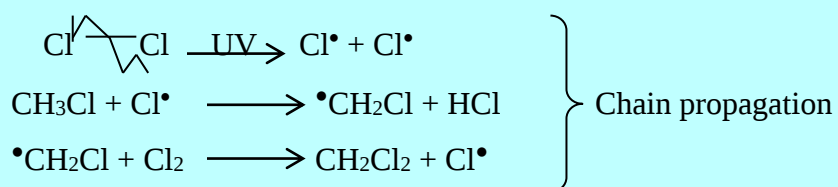
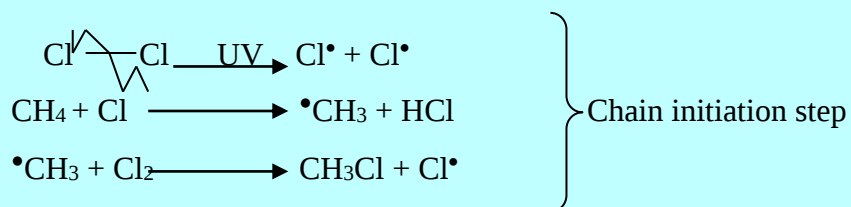
REACTIONS

a) Chlorination

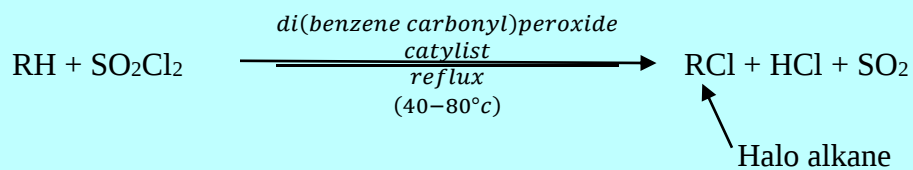
Alkanes undergo chlorination in presence of ultra-violet light ($250 - 400^\circ\text{C}$) yielding a mixture of chloromethane CH_3Cl , dichloromethane CH_2Cl_2 , trichloro methane (chloroform) CHCl_3 and tetra chloromethane (carbon tetra chloride) CCl_4



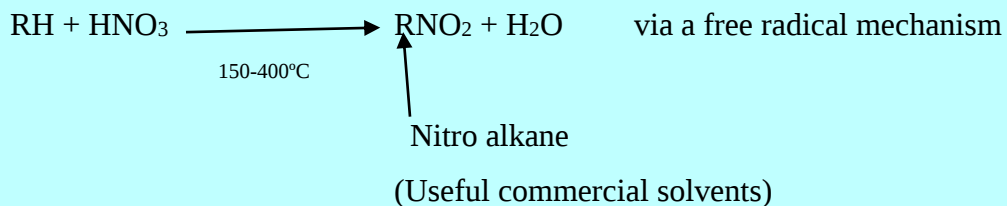
Mechanism



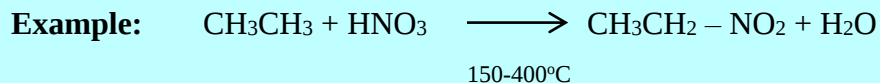
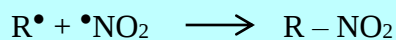
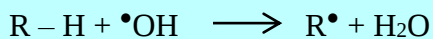
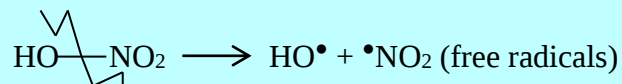
b) Halogenation using sulphur dichloride dioxide (SO₂Cl₂)



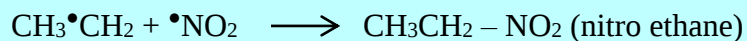
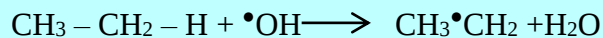
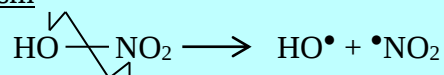
c) Nitration



Mechanism



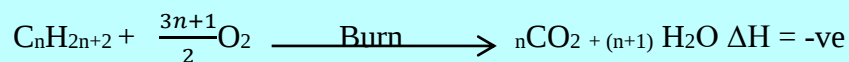
Mechanism



Note: Is a substitution reaction because a hydrogen atom of the alkane is substituted by NO₂-group producing nitro alkane.

d) Combustion

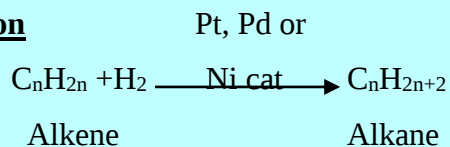
Burn exothermically in excess oxygen with non-smoky flame to give CO₂ and steam.



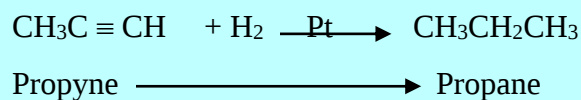
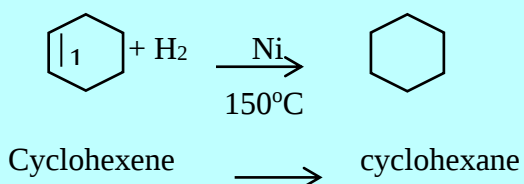
It's via a high temperature free radical mechanism.

Preparations

1. Hydrogenation

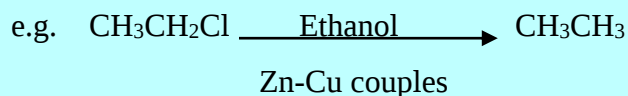
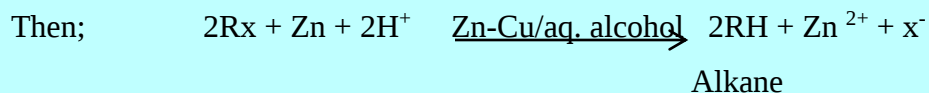
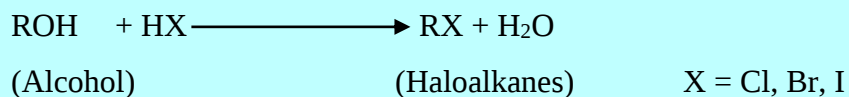


Example;

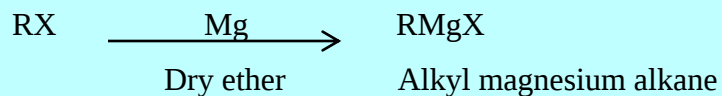


NB. Reduction with Pt (platinum) and Pd (palladium) occurs at room temperature while these with Ni (Nickel) requires a temperature of about 150°C

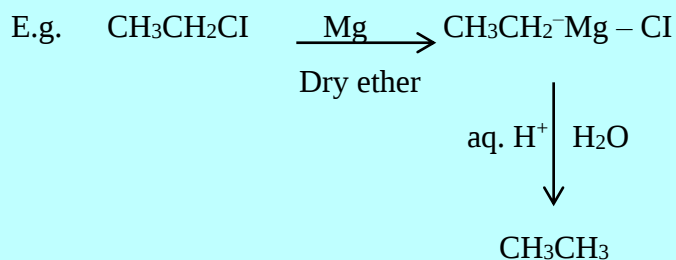
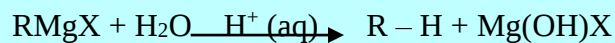
2. Reduction of Haloalkanes



3. Grignard reaction

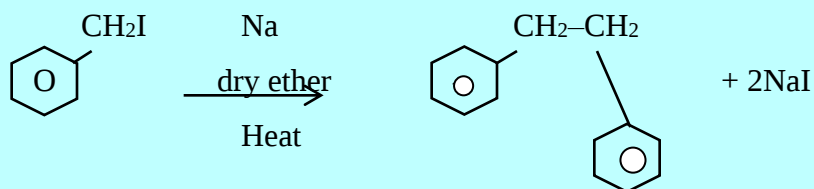
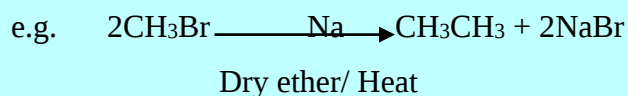
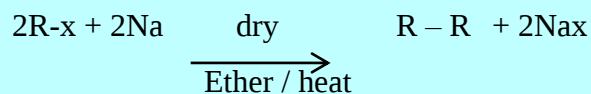


And on treatment with aqueous H^+ liberate the alkane



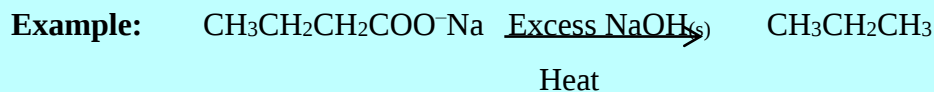
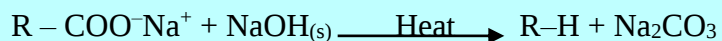
4. Wurtz synthesis

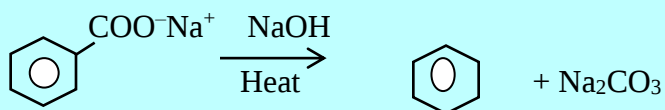
(Alkyl acids when heated with sodium metal in dry ether)



5. From carboxylic acids

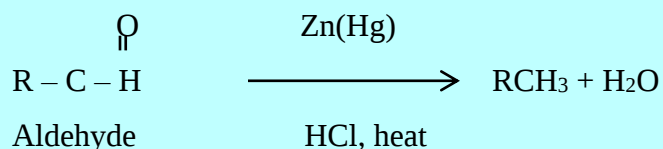
When sodium salts of carboxylic acids are heated with soda limes they eliminate a molecule of carbon dioxide to form alkane



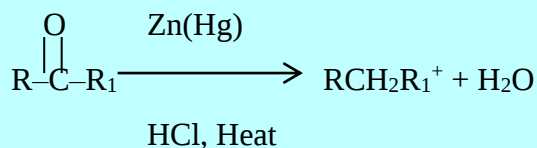
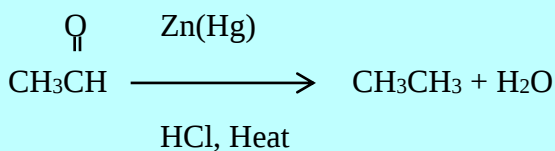


6. From Carbonyl compound

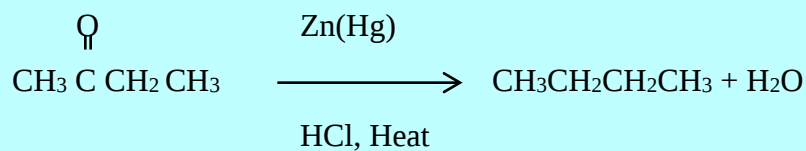
Reduction of carbonyl compounds with amalgamated zinc (Zn (Hg)) and hydrochloric acid



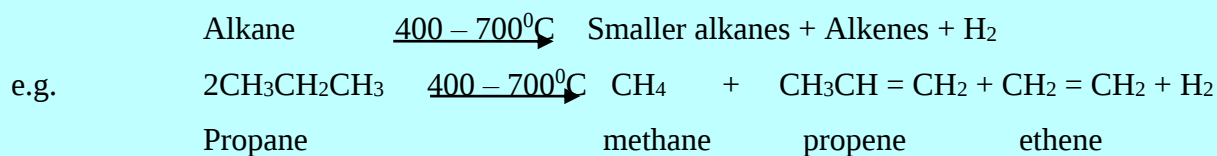
Example:



e.g.



NB: Pyrolysis of alkanes is referred to as CRACKING, particularly where petroleum is involved. Paraffin fraction in the Vapour state are passed through a metal chamber heated to $400 - 700^\circ\text{C}$ using various metallic oxides as catalyst. The starting alkanes are broken down into a mixture of smaller alkanes, alkenes and some hydrogen i.e.



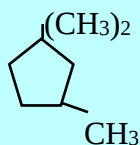
Therefore, CRACKING

Is a process in which less volatile higher hydrocarbons are converted to more volatile hydrocarbons by application of heat / a catalyst and the products formed will depend on

- structure of the hydrocarbon
- Temperature and pressure applied.

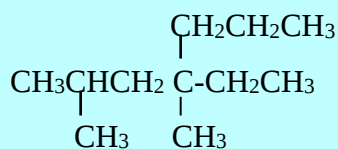
Example: 1. Give the IUPAC name for

a).



1, 1, 3 – trimethyl cyclo pentane

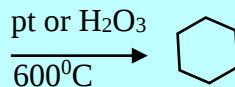
(b)



4 – ethyl – 2, 4 – dimethyl heptane

NB: During cracking the following changes may occur.

- Formation of a mixture of hydrocarbon of lower chains
- Saturated hydrocarbon may be converted to unsaturated hydrocarbons
- Cyclisation may occur e.g. $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$



Types of Cracking

- Thermal cracking, here cracking takes place by heating by either liquid or gases hydrocarbon.
- Catalyst cracking; Here cracking takes place by heating in the presence of a mixture of Silica and Aluminum silicate as catalyst

ALKENES (OLEFINS)

General formulae C_nH_{2n}

They possess a double bond; $\text{>C}=\text{C}<$ which makes them generally much more reactive than the alkanes.

NOMENCLATURE

“-ane” of the alkane is replaced by “-ene” and the position of the double bond is specified by placing the appropriate number between the stem of the name and the “-ene”.

Example $\text{CH}_2 = \text{CH}_2$ ethene
 $\text{CH}_3 - \text{CH} = \text{CH}_2$ propene

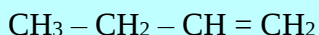
(4) (3) (2) (1) (4) (3) (2) (1)
 $\text{CH}_3 \text{ CH}_2 - \text{CH} = \text{CH}_2$ But -1 -ene $\text{CH}_3 \text{CH} = \text{CH} - \text{CH}_3$ But - 2 - ene

$\text{CH}_3 - \text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} - \text{CH} = \text{CH}_2$ 3 - phenylpent - 1- ene etc

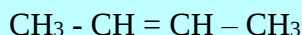
STRUCTURAL ISOMERISM IN ALKENES

Ethene and propene have no structural Isomers but

C_4H_8



But - 1 - ene



But - 2 -ene

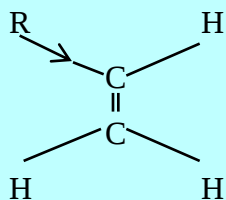
These are straight - chain structures with the difference being in the position of the double bond, hence are positional isomers.

$\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2$
 2 - methyl propane is branched -chain

PHYSICAL PROPERTIES

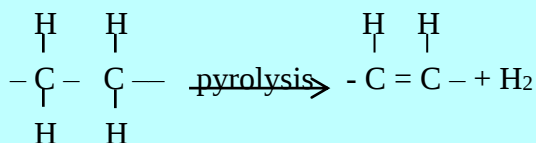
Ethene propene and But-1-ene are gases and the rest are liquids with the exception of higher members with more than fifteen Carbons which are solids. Branching enhances the volatility and their boiling points are generally marginally lower than corresponding alkanes. They are virtually insoluble in water but soluble in non-polar organic solvents such as chloroform, ether, benzene etc.

Unsymmetrical alkene is slightly polar due to the electron donating properties of the alkyl group(s) i.e.



Industrial source

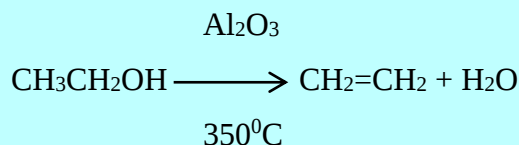
Large alkenes are obtained by the cracking of petroleum



And then separated by fractional distillation

Ethane

By passing ethanol Vapour over an aluminium oxide catalyst at 350°C

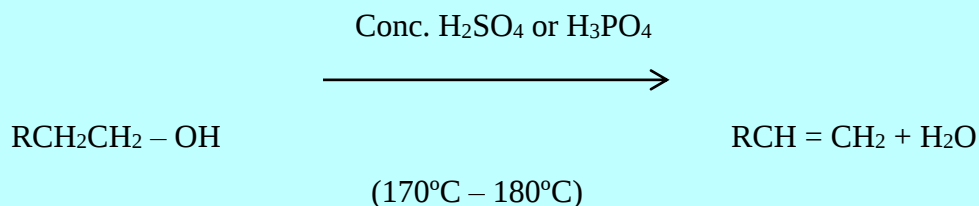


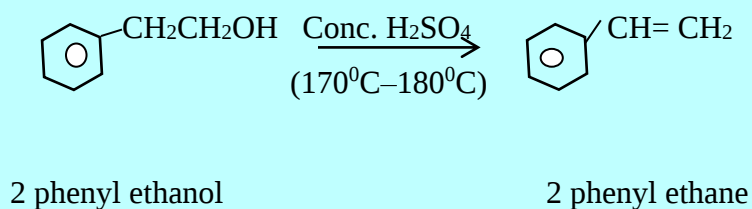
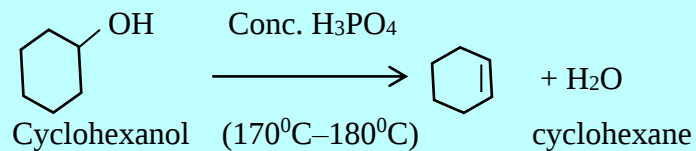
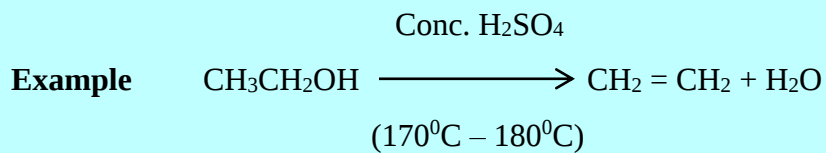
Synthetic preparations

This mainly involves elimination of atoms l groups from two adjacent carbon atoms, mainly from alcohols and halo alkanes.

Dehydration of alcohol using a concentrated sulphuric acid and phosphoric acid

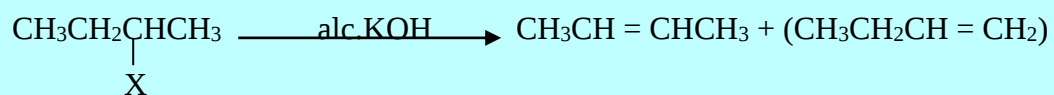
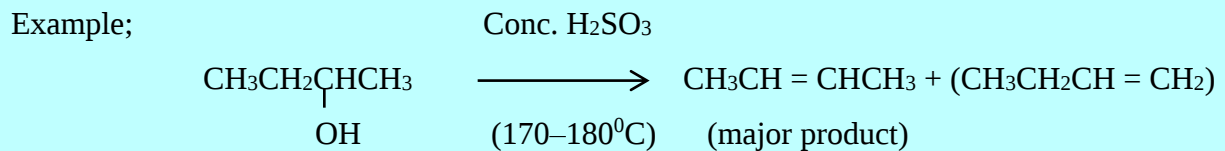
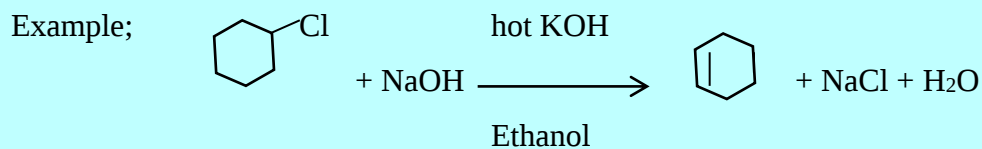
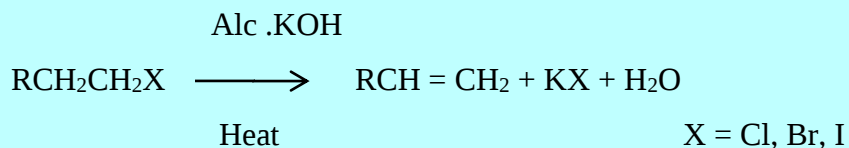
Heating is required and acid must be in excess, temperature required 170 – 180°C.



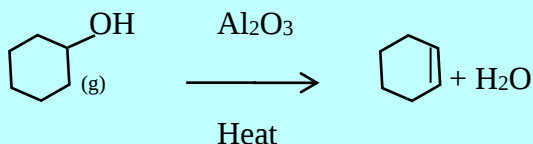
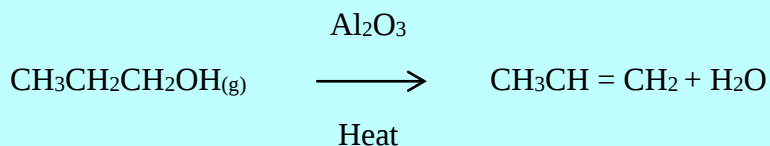


Dehydrohalogenation

Carried out by heating them in an alcoholic solution of potassium hydroxide



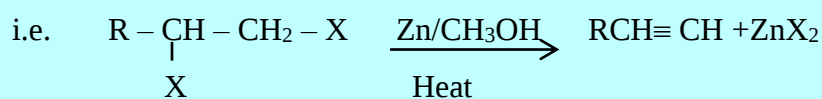
By passing alcohol vapours over heated Aluminium oxide as catalyst



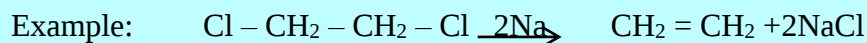
By dehalogenation of Vicinal – dihalides

Vicinal dihalides, Are halogen compounds with two halogen atoms on adjacent carbon atoms.

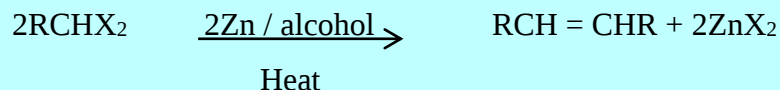
Germ-dihalides, have two halogen atoms on the same carbon atom. This is carried by heating out vicinal-dihalides with zinc in alcohol



Metallic sodium is also used



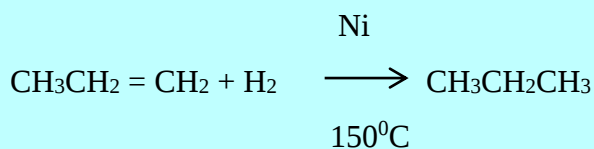
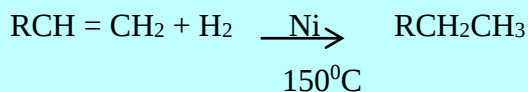
Note: With germ halides higher alkanes are produced by increasing the length of the carbon chain e.g.

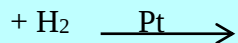


REACTIONS

- Addition of hydrogen / Hydrogenation**

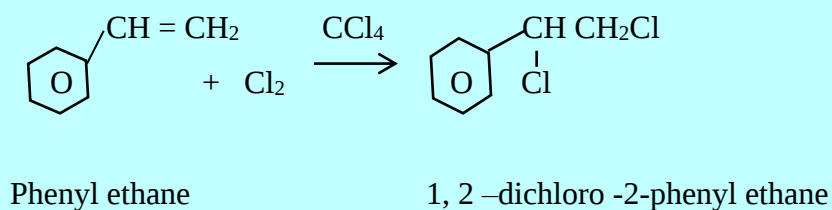
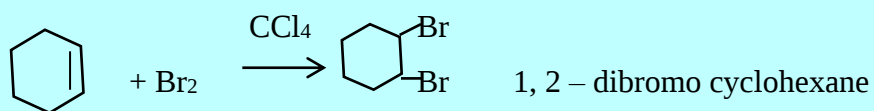
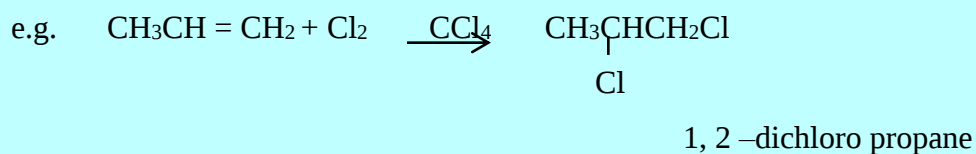
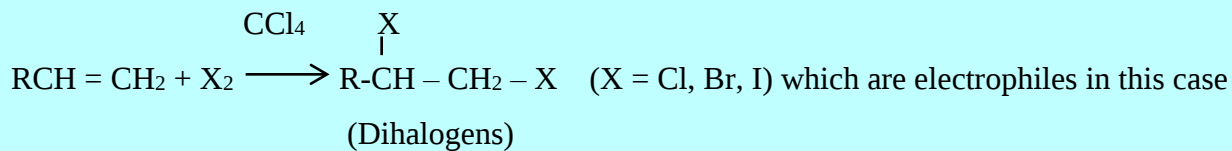
Occurs in the presence of Pt, Pd or (Ni at 150°C) catalyst.



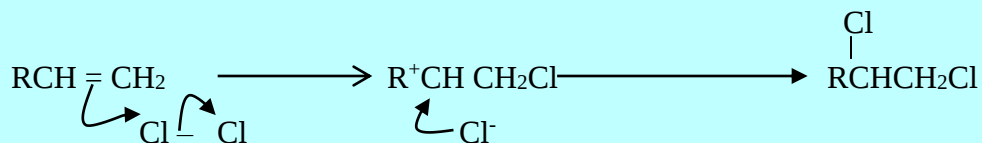
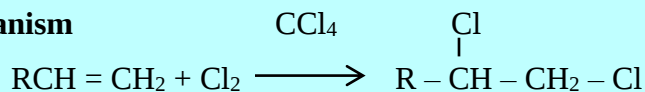


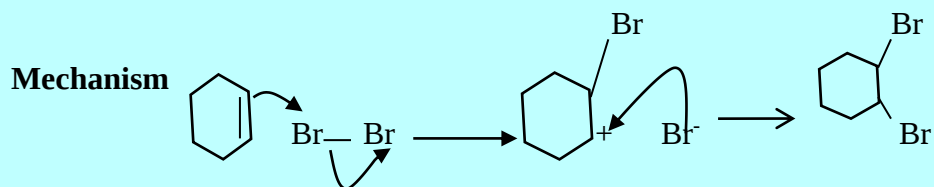
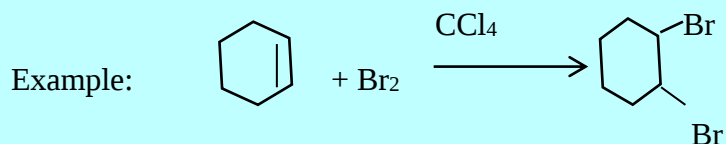
This reaction is used in the synthesis of saturated compounds like in the manufacture of margarine.

- **Addition of halogens**

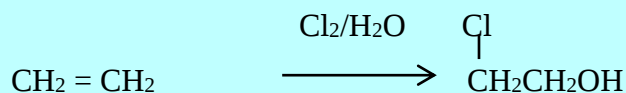


Mechanism

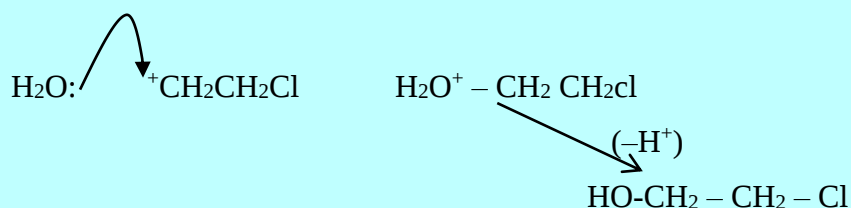
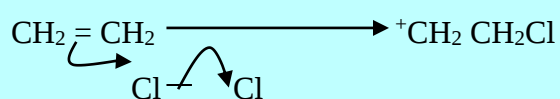




NB: Halogenation may be carried out in presence of water. Then example

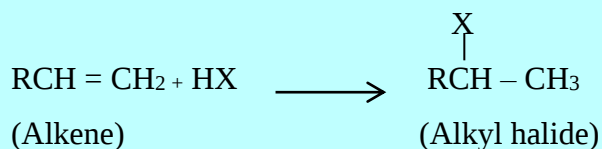


Mechanism

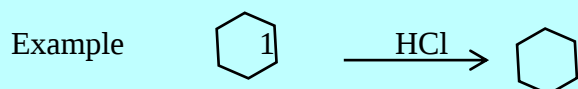
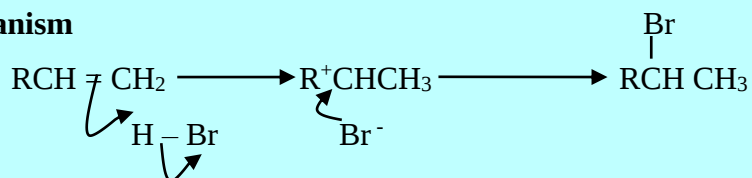


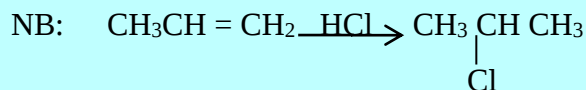
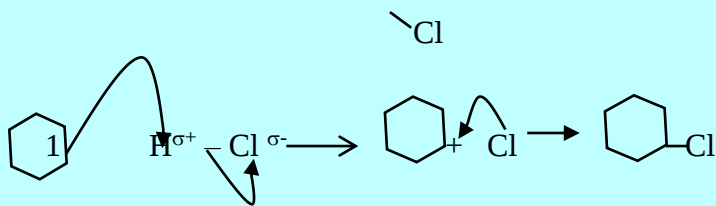
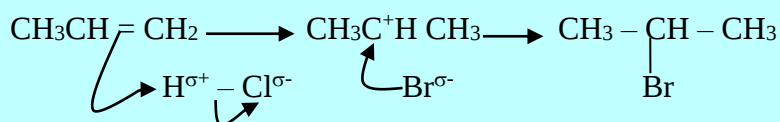
NB: Reaction of Bromine is used to test the presence of multiple bonds where Bromine gets decolourised.

- Addition of halogen acids (HX) for X = Cl, Br, I**



Mechanism

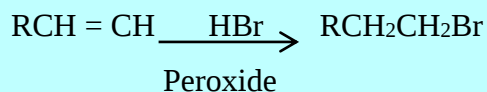


Mechanism**Mechanism**

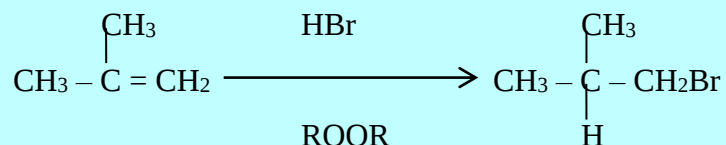
$\text{CH}_3\text{CH}_2-\text{CH}_2^+$; This carbonium ion (1°) is also possible but it is not very stable. Instead we consider the carbonium ion (2°) which is more stable $\text{CH}_3-\text{CH}^+-\text{CH}_3$. This is according to Markchoniokoff's rule.

In addition, reactions involving a symmetrical alkene (Alkenes with carbon atoms carrying double bond having different number of hydrogens), the hydrogen of the halogen acid adds to the carbon which carries the greater number of hydrogen atoms while the halide atom adds to one with the lesser.

- **Addition of halogeno-acids in presence of a peroxide (RO-OR)**

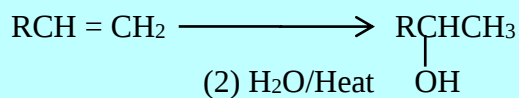


Example:

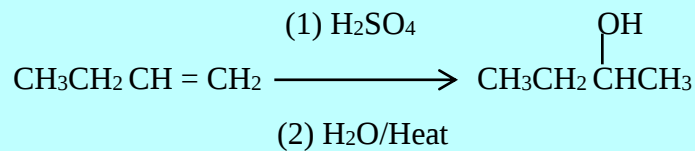


- **Hydration of alkenes (Preparation of alcohols)**

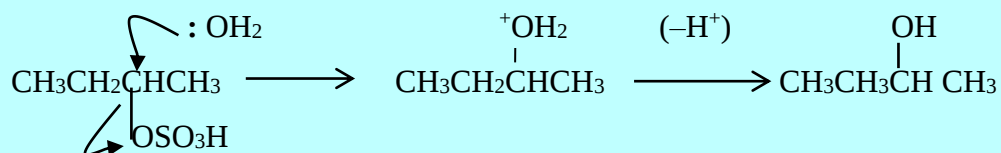
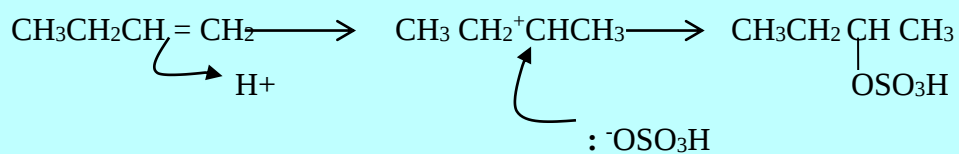
(1) H_2SO_4



Example;

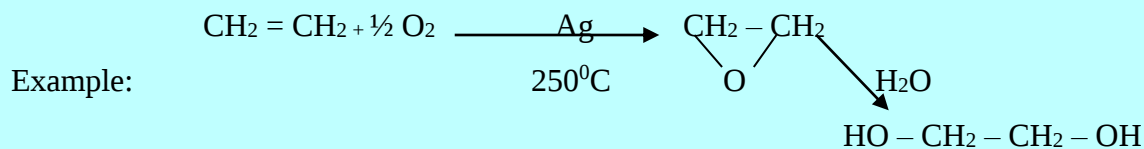


Mechanism; $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + ^-\text{OSO}_3\text{H}$

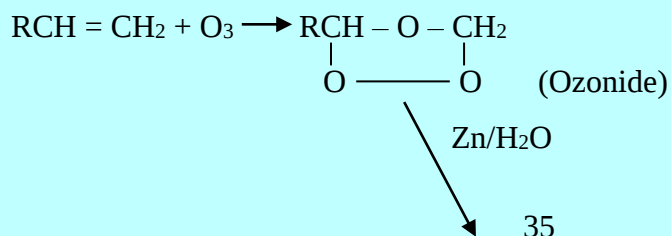


- Reaction with Oxygen**

Over heated silver catalyst, they form epoxides. And Diols are produced on hydrolysis of the epoxide.

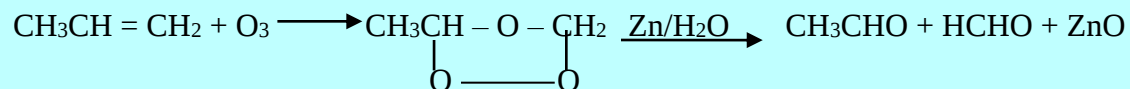


- Reaction with Ozone / Ozonized Oxygen (O₃)**





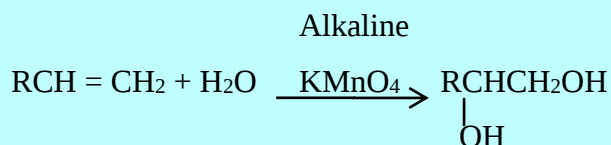
Example;



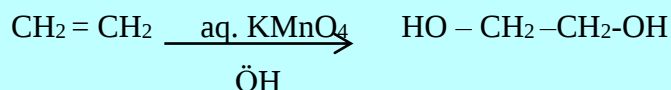
This reaction is important in conversion of an alkene to aldehyde or ketone. It is also used to investigate the position of the double bond for symmetrical alkenes one product is formed and for unsymmetrical alkenes; two different products are formed.

- **Oxidation Reaction**

Undergo oxidation reaction using potassium permanganate to form diols.



Example;



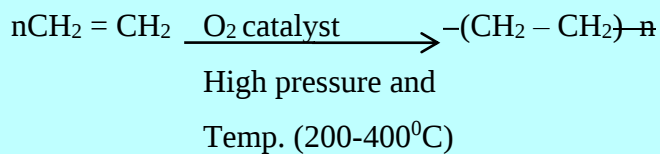
NB: Purple potassium manganate (VII) gets decolourised.

POLYMERIZATION

Polymerization is a process by which many simple molecules join together to form very large molecules.

Simple alkenes polymerize to form a family of long chain addition polymers.

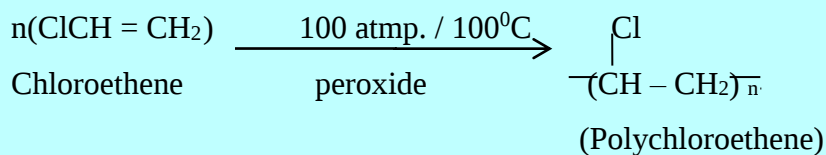
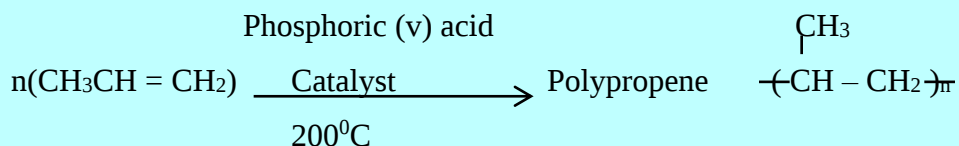
Ethene polymerizes to form polyethene (polythene)



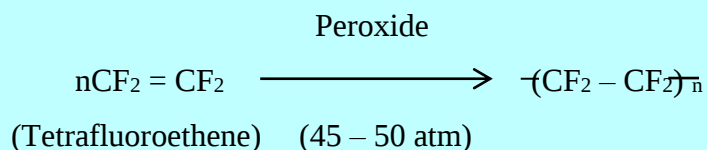
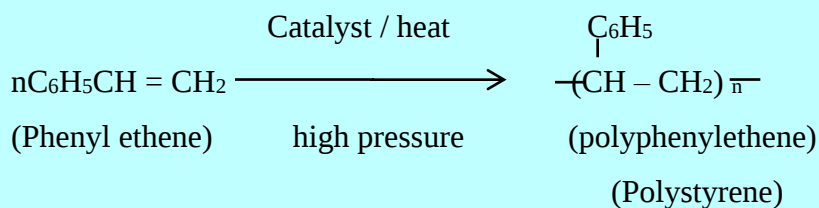
Uses: Making polyethene bags

In a similar way;

Propene forms Polypropene (polypropylene)



Uses; Used in making plastic rain coats, curtains, furniture coverings, records, water piping and guttering (polyvinyl chloride).



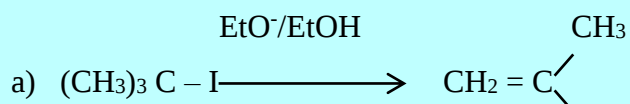
Teylon (PTFE)

Uses; Used in making non-stick cooking utensils and low friction bearings.

NOTE: They burn with a luminous, smoky flame.

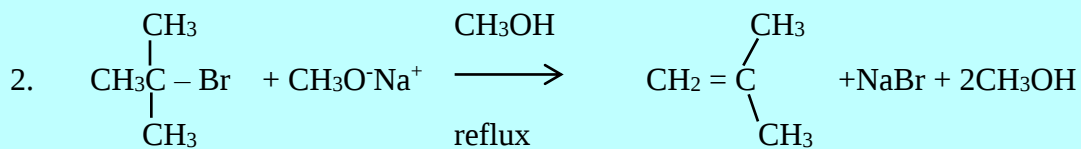
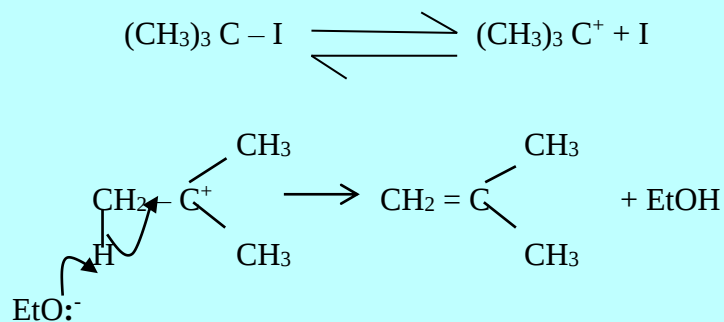
Examples

1. Complete the following and write a mechanism

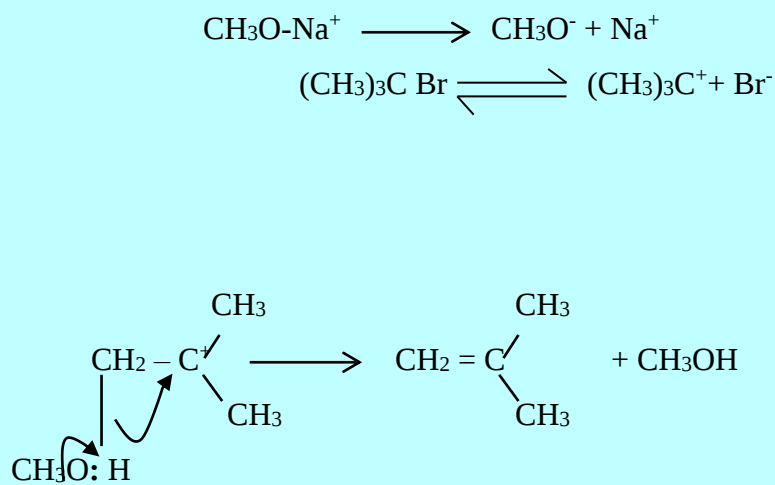




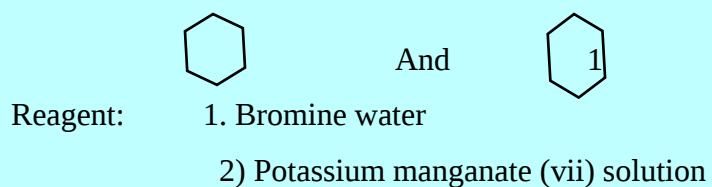
Mechanism



Mechanism



2. Name the reagent that can be used to distinguish between the following pairs of compounds.



Observation

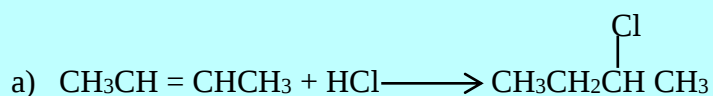
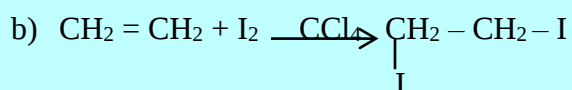
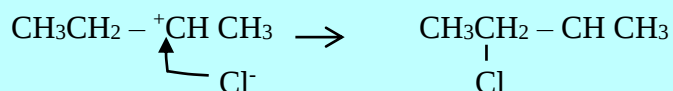
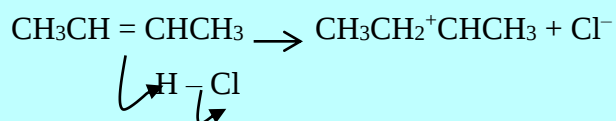
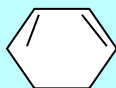
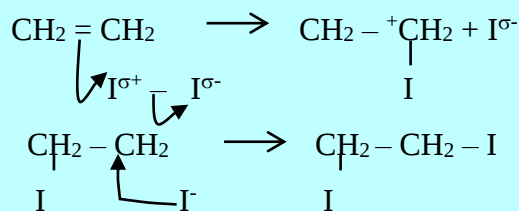
- 1) Gives no observable change
- 2) Gives no observable change



- 1) decolourises bromine water
- 2) The solution turns from purple to colourless

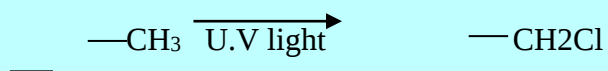
3. Write equations to show the reactions that can take place between the following pairs of compounds and indicate the mechanism for the reaction

- a) But-2-ene and hydrogen chloride
- b) Ethane and iodine
- c) Methyl benzene and chlorine in the presence of sunlight

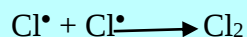
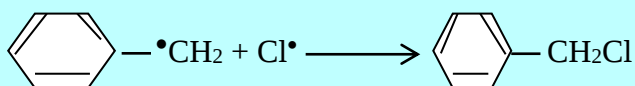
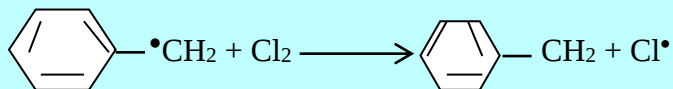
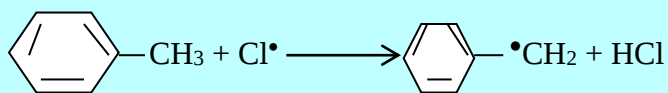
Solution**Mechanism****Mechanism**

Cl_2





Mechanism



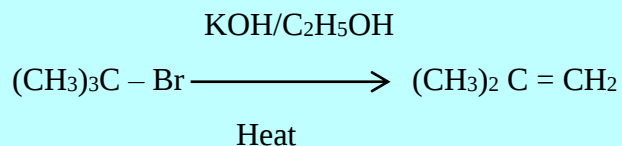
Note that the sequence of reaction is eventually stopped when two of the free radicals collide and form a stable molecule

And if it was excess Cl_2 , the phenyltrichloromethane is formed

4. Write equation to show how each of the following compounds can be synthesized

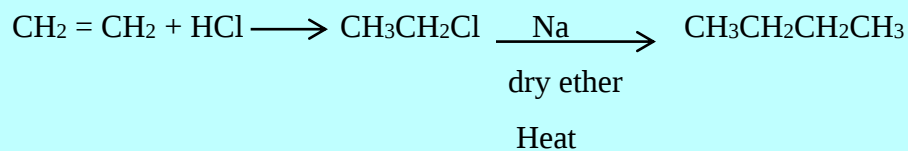
a) $(\text{CH}_3)_2\text{C}=\text{CH}_2$ from 2-bromo-2-methyl propane

Solution

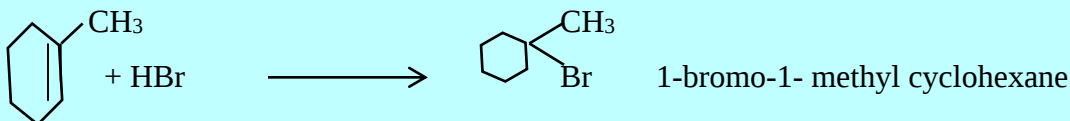
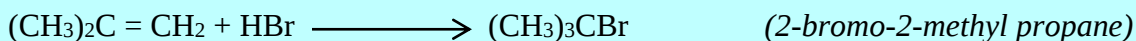
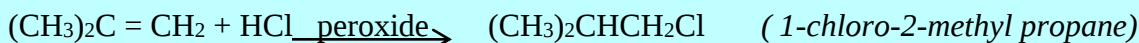
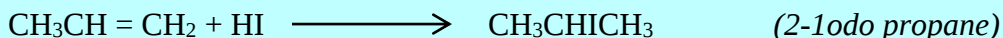


b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ from $\text{CH}_2=\text{CH}_2$

Solution



1. Give the structural formulae and IUPAC name of the product of each of the following reactions



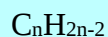
2. Write the mechanism for the addition of the following reagents to propene and name the products.



ALKYNES (ACETYLENES)

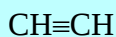
Form a homologous series of unsaturated hydrocarbons containing a carbon-carbon triple bond.

General molecular formula

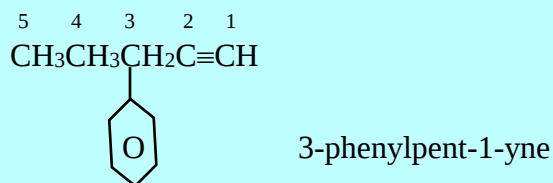
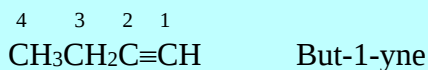


Nomenclature

The stem of the name of the corresponding alkane is taken and replacing the ending “-ane” of the alkane with the suffix “-yne”. The position of the triple bond is indicated by inserting the appropriate number between the stem and the ending e.g.



Ethyne



The first three members are gases, and the rest are liquids at 20°C.

NB: When the triple bond is at the end of the chain e.g. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$, it is called **Terminal triple bond**.

When the triple bond is in the middle of the chain e.g. $\text{CH}_3\text{C}\equiv\text{CCH}_3$, it is called **Internal triple bond**.

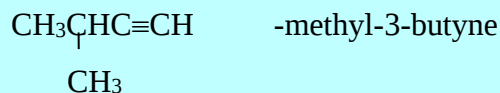
ISOMERISM

Ethyne and propyne do not form isomers but the rest exhibit three types of isomerism.

a) Chain isomerism

The triple bond position does not change, but the chain structure differs.

e.g. C_3H_8 $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ – pentyne



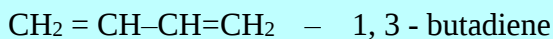
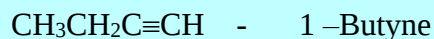
b) Position Isomerism

It is due to different positions of the triple bond in the same chain e.g.



c) Function Isomerism

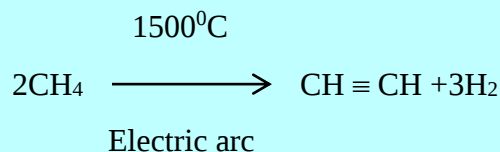
Due to the formation of dienes i.e. alkenes with two double bonds



Alkynes do not show **geometrical isomerism** because the molecule around the triple bond is linear.

Industrial sources

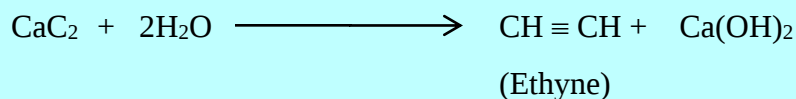
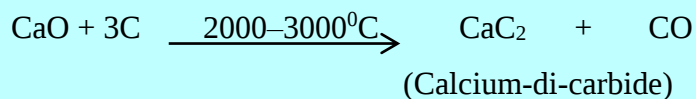
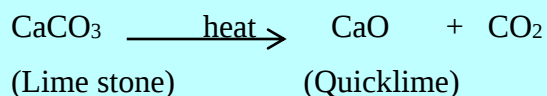
Ethyne is manufactured primarily from natural gas and higher alkanes obtained from petroleum.



Also can be obtained by treating calcium dicarbide with water.

1st stage

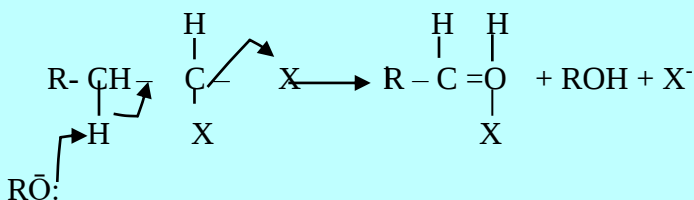
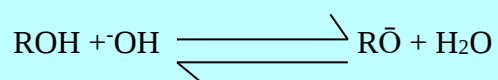
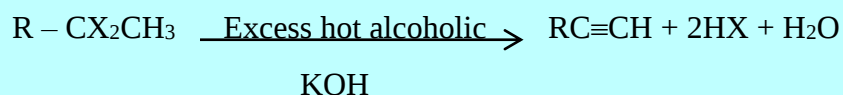
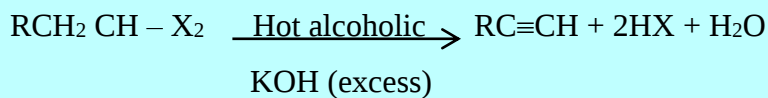
Calcium dicarbide is obtained by reducing quicklime, obtained from lime stone, with coke in an electric furnace at 2000 – 3000°C



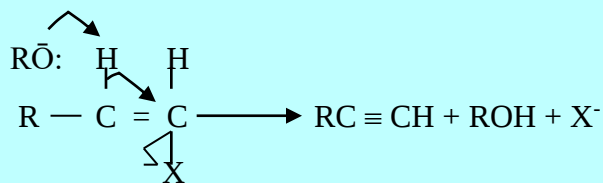
This method is now obsolete owing to high electrical costs involved in maintaining the high temperatures in the furnace.

Synthetic preparations

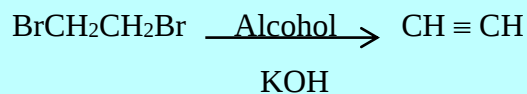
a) From dihalogen compounds.



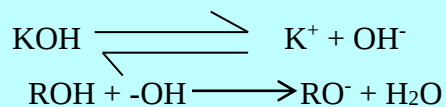
Another RO^- then removes the remaining hydrogen atom

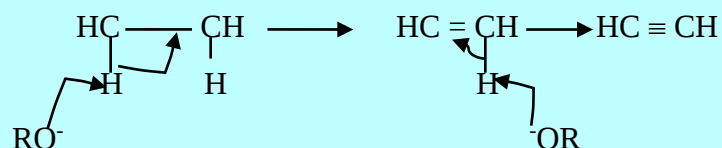


Example.



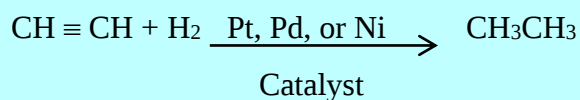
Mechanism





REACTIONS

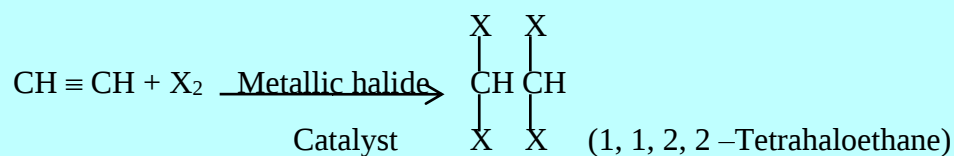
a) Addition of hydrogen



Note: - Applies to the rest of Alkynes

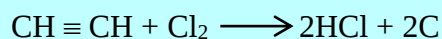
- Nickel (Ni) requires heating about (125°C-250°C)

b) Addition of Halogens

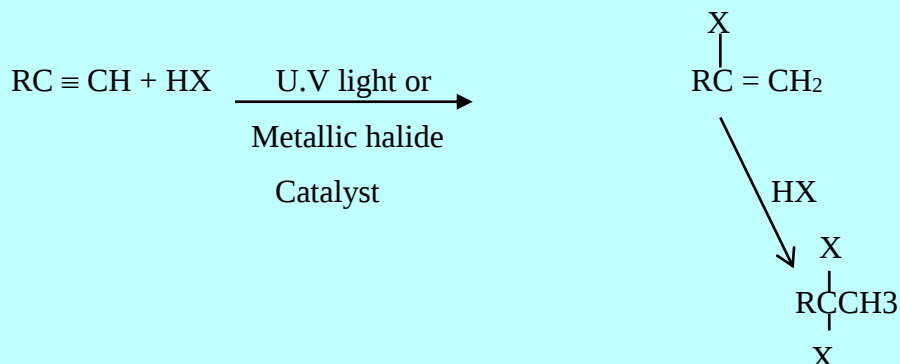


Note: - Applies to the rest of Alkynes

- In the absence of a catalyst, chlorine reacts explosively with ethyne yielding hydrogen chloride and carbon



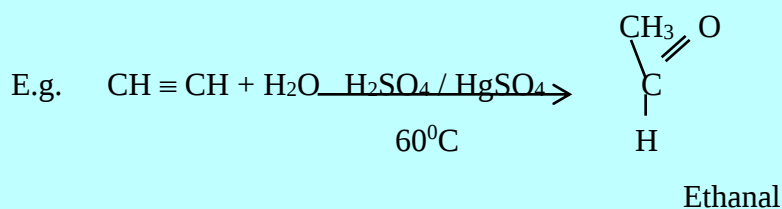
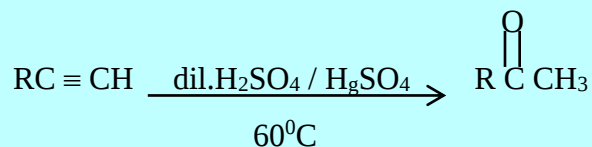
c) Addition of Hydrogen Halides



1, 1 dihalo (Alkene)

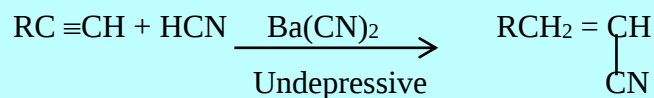
Note: Rate of reaction $\text{HI} > \text{HBr} > \text{HCl}$.

d) Addition of water



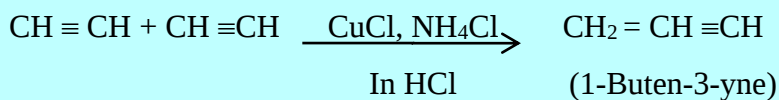
The reaction is initiated by nucleophilic attack.

e) Addition of Hydrogen cyanide

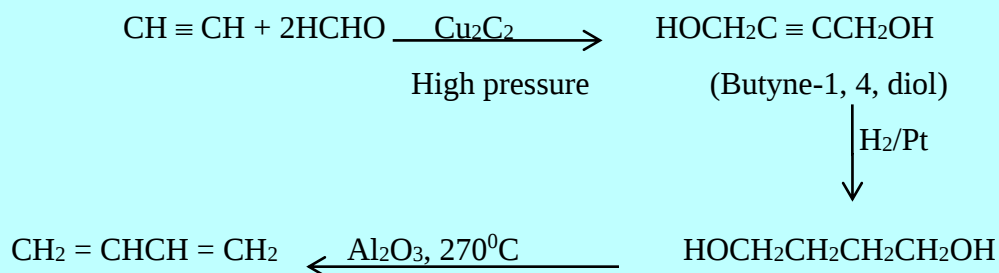


f) Dimerization of Ethyne

Ethyne dimerizes in a solution of copper (I) chloride and ammonium chloride in hydrochloric acid



g) Additional of methanol



(Buta – 1, 3 – diene)

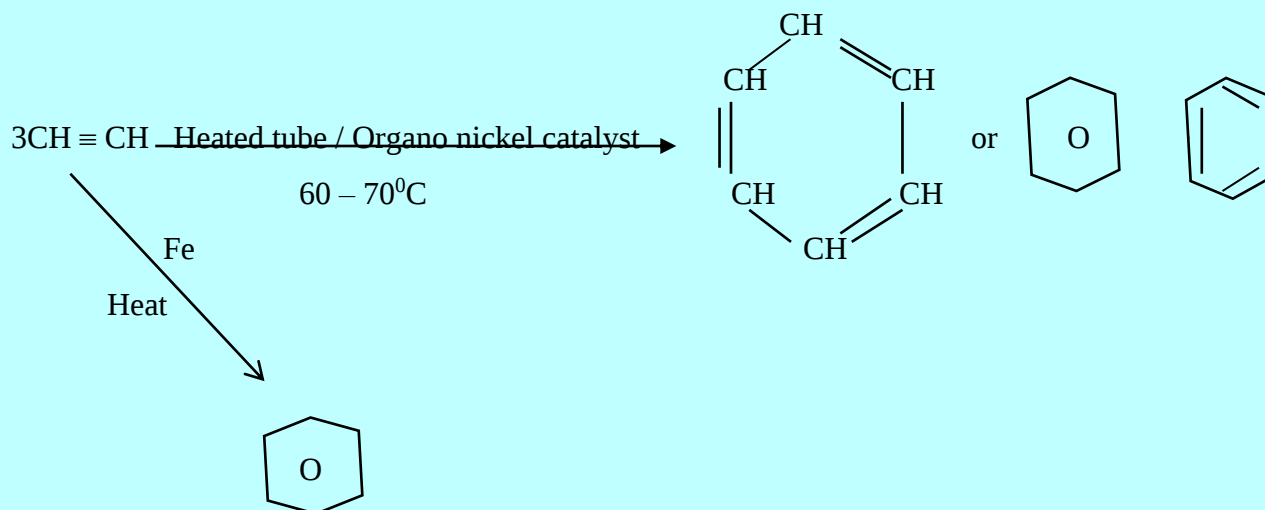
-2H₂O

(Butane 1, 4, diol)

This is an important reagent in the preparation of synthetic rubbers.

Polymerization of Ethyne.

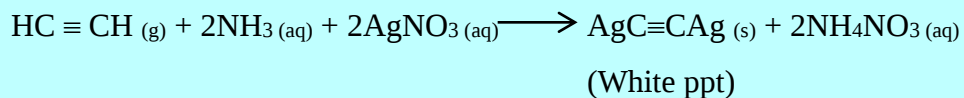
Polymerizes to benzene when passed through a heated tube containing a complex organo-nickel catalyst.



Note:

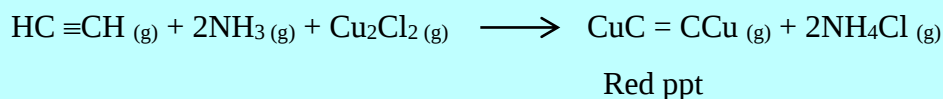
Alkynes with terminal triple bonds when passed through a solution of ammoniacal silver nitrate, deposits a white precipitate of silver dicarbide

E.g. Ethyne



And; When passed through a solution of ammoniacal copper (1) chloride, deposits a red ppt of copper (1) dicarbide

E.g. Ethyne

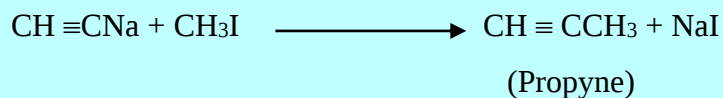
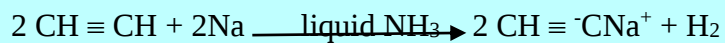


Alkynes of the type $\text{RC} \equiv \text{CR}$ (with internal triple bond) do not react and therefore these reactions can be used to test for the terminal triple bond.

These heavy metal dicarbides are dangerously sensitive explosives

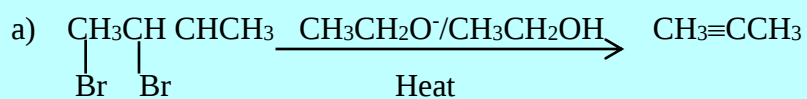
Formation of Ethenyl sodium

Ethyne reacts with sodium in liquid ammonia to form ethenyl sodium

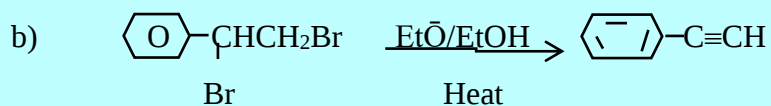
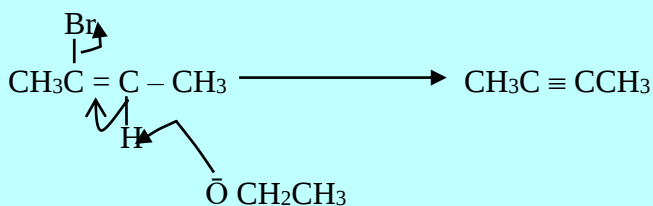
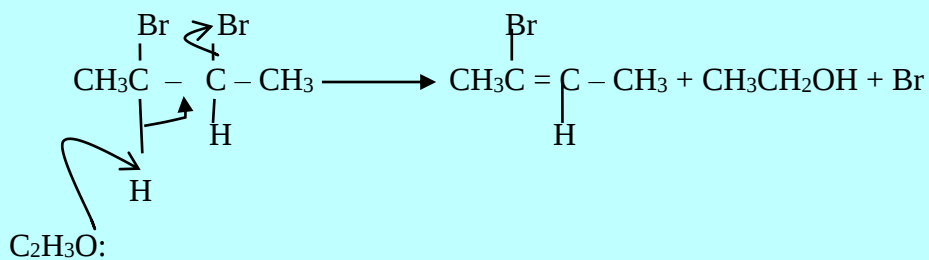


Examples

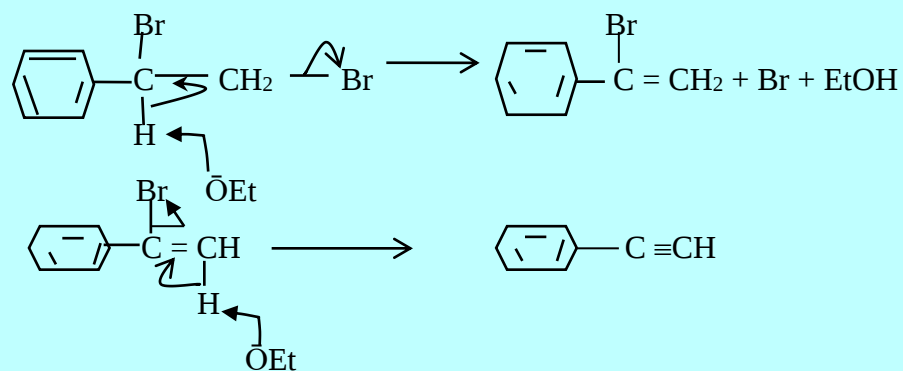
Complete the following and in each case outline a mechanism for the reaction.



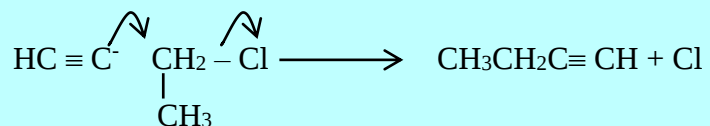
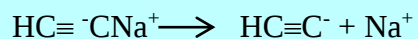
Mechanism



Mechanism

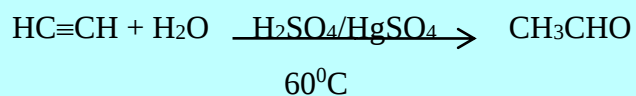
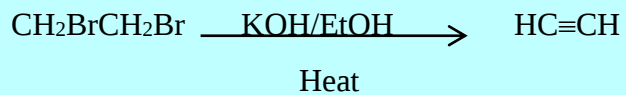


Mechanism

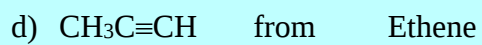
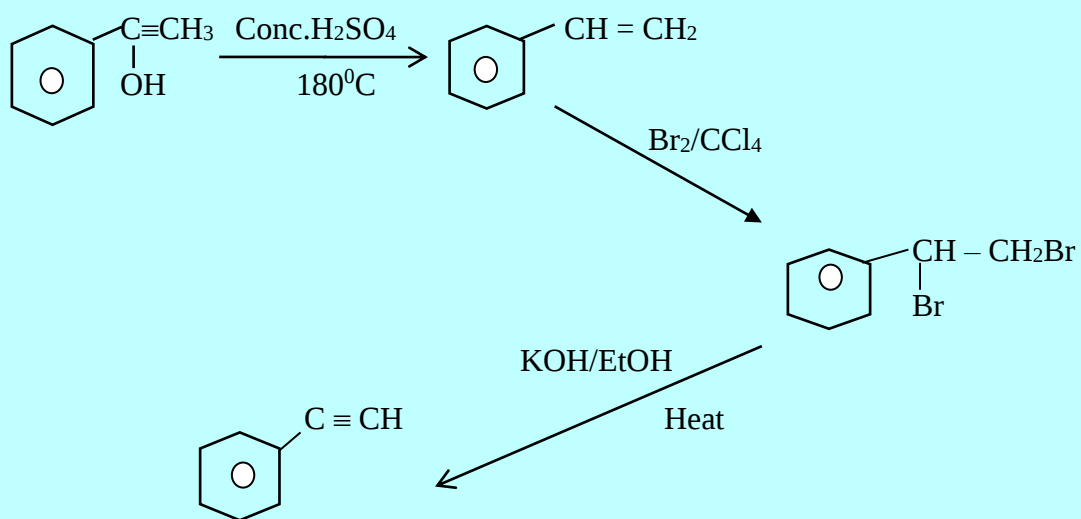
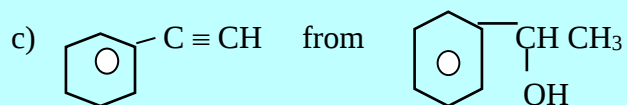
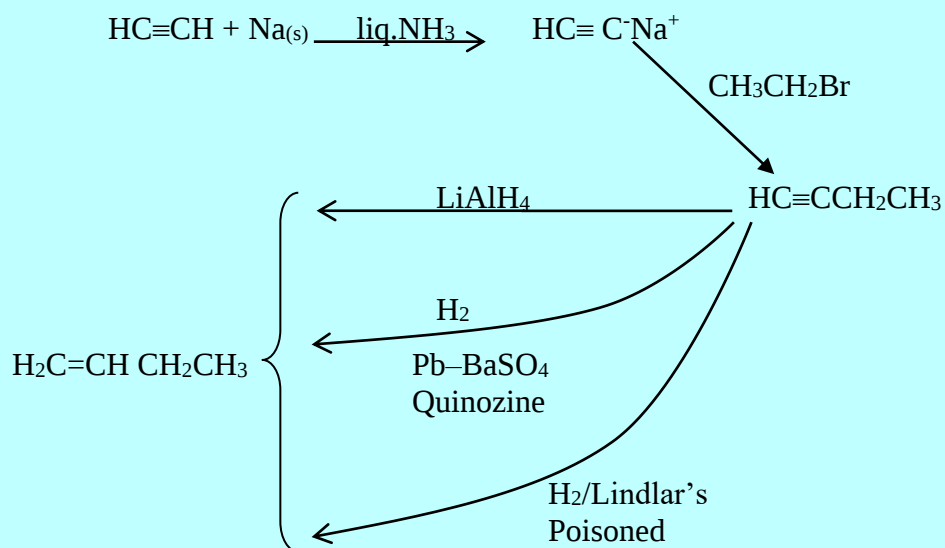


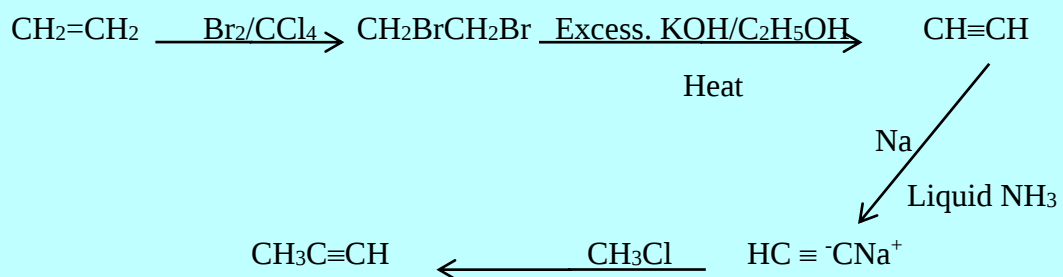
QN: Write equations to show how the following compounds can be synthesized

a) CH_3CHO from 1, 2, - dibromoethene



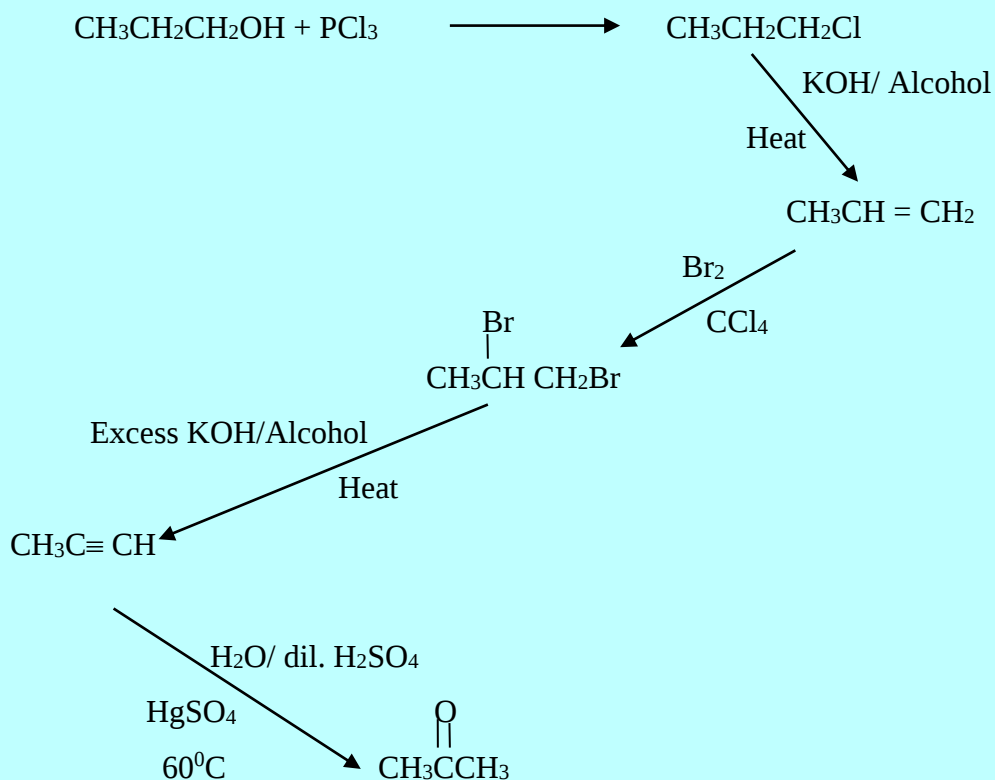
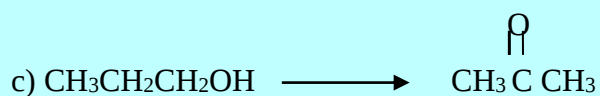
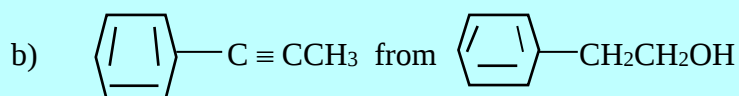
b) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ from Ethyne





Exercise

a) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ from Ethanol



NB: $\text{CH}_3\text{C}\equiv\text{CCH}_3$ and $\text{CH}\equiv\text{CCH}_2\text{CH}_3$ (Distinguishing them)

(i) Reagent

Tollen's reagent (silver nitrate solution in ammonia solution)

Observation.

$\text{CH}_3\equiv\text{CCH}_3$	No observable change
$\text{CH}\equiv\text{CCH}_2\text{CH}_3$	White precipitate forms

Reagent

Fehling's reagent (copper (1) chloride solution in ammonia solution)

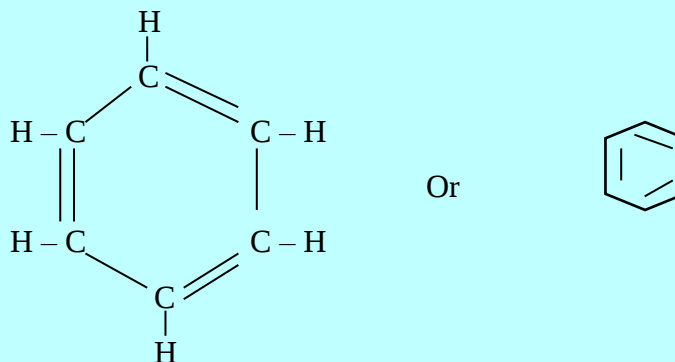
Observation

$\text{CH}_3\equiv\text{CCH}_3$	No observable change
$\text{CH}\equiv\text{CCH}_2\text{CH}_3$	Red precipitate forms

AROMATICITY AND BENZENE

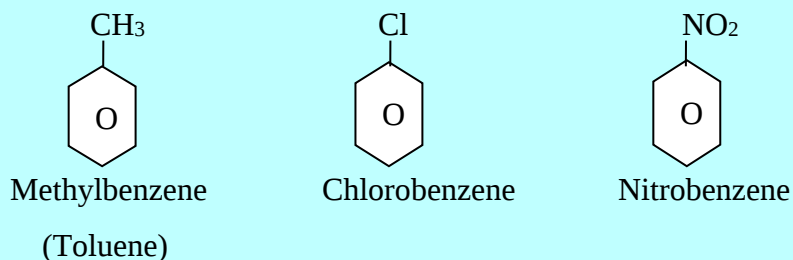
Aromatic compounds are those possessing the ring structures of benzene or other molecular structures that resemble benzene in electronic configuration and chemical behavior.

Benzene



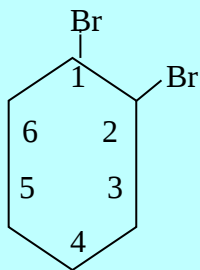
Naming substituted Benzene derivatives

A benzene molecule in which one hydrogen atom has been replaced by an atom / group is referred to as a **Mono-substituted derivative**



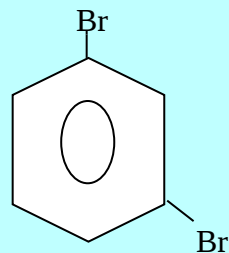
For each di-substituted derivative there are three different Isomers depending upon the position of substitution in the ring

Example



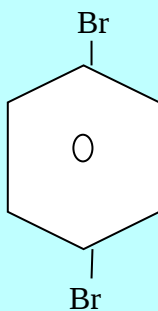
1, 2 – Dibromo benzene

It is **ortho derivative**, because two substituents are attached to adjacent carbon in the ring



1, 3 Dibromo benzene

It is **meta derivative**, because the substituents are in the next –but-one position



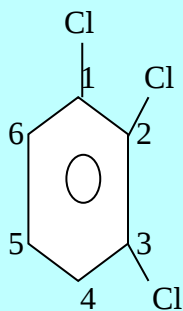
1, 4 – Dibromo benzene

It is **Para derivative** because

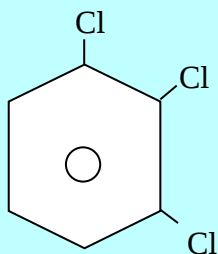
the two substituents are diametrically opposite

NB: The positions of substitution are indicated by numbering the carbon atoms in the ring and choosing unity so as to give the lowest combination of numbers.

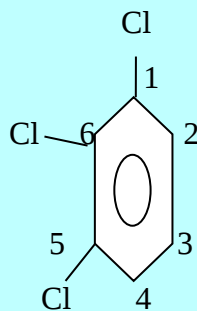
Example



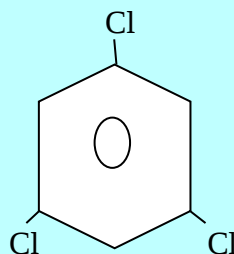
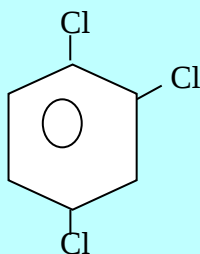
1, 2, 3, Trichlorobenzene



not

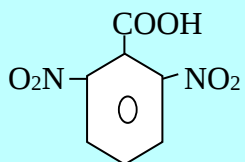


1,5,6 Trichlorobenzene



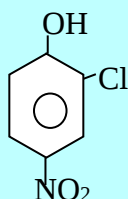
1, 2, 3 – Trichlorobenzene 1, 2, 4 – Trichlorobenzene 1, 3, 5 – Trichlorobenzene

- If one of the groups present gives rise to a compound with a special name, then only two positions of substitution are mentioned.



2, 6- Dinitrobenzene carboxylic acid

2,6 -Dinitro benzoic acid



2 – chloro-4-nitrophenol

NB: For convenience especially when writing complicated structural formulae, the phenyl group is often abbreviated to “ph”.

i.e. $\text{C}_6\text{H}_5\text{—}$ phenyl group “ph”

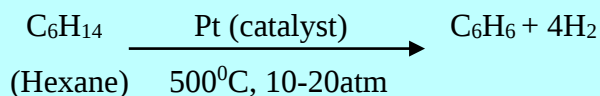
PHYSICAL PROPERTIES

Benzene is a colourless liquid (b.p 80°C , m.p 5.5°C) with a characteristic aromatic smell. It is immiscible with water, (forms upper layer) but it is soluble in organic solvents. It burns with a yellow smoky and luminous flame like other aromatic compounds. It is highly toxic

INDUSTRIAL SOURCE

Benzene can be obtained from coal tar and petroleum.

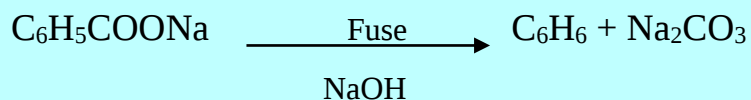
Petroleum vapour containing hexane and other hydrocarbons is passed over a finely divided platinum catalyst at 500°C and under 10–20 atmospheric pressure. This process is known as “reforming”



SYNTHETIC PREPARATIONS

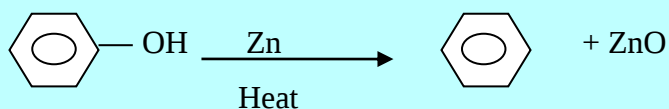
- Decarboxylation of a sodium salt

Sodium benzoate is fused with soda lime ($\text{NaOH}_{(s)}$)

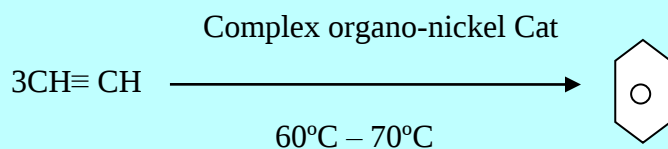


- **From phenol**

Phenol vapour is passed over heated zinc dust



- **Polymerization of Ethyne**

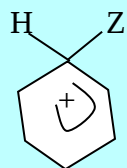


REACTIONS

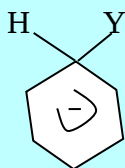
The availability of π - electrons in benzene serves as a source of electrons (a nucleophilic reagent) and its reactions are characterized by electrophilic substitution in the ring.

An unstable intermediate is formed in which the entering atom/group and the leaving hydrogen atom are both momentarily bonded to the ring. This causes a disruption in the symmetry of the delocalized π – electrons and may be illustrated by an incomplete circle inside the ring.

If the attacking species is an electrophile, which is most common, then the reaction intermediate will carry a positive charge which is distributed over the bulk of the molecule



Electrophilic
attack

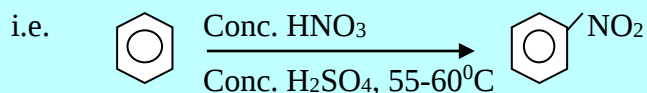
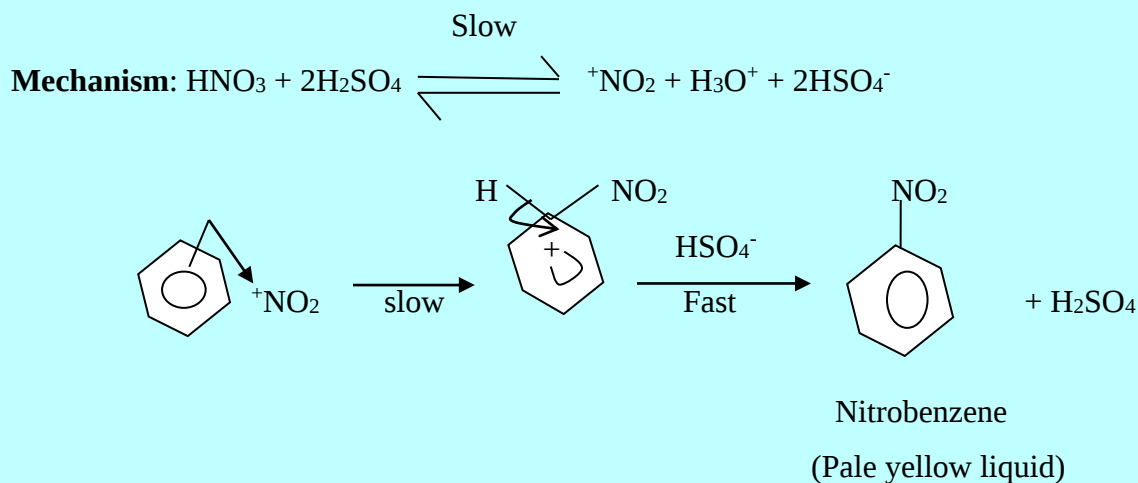


Nucleophilic
attack

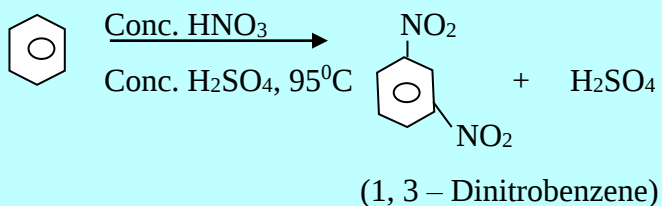
In the case of nucleophilic substitution, a negative charge is distributed over the molecule.

- **Nitration**

A nitrating mixture (equal molar quantities of concentrated nitric and sulphuric acids) is carefully added to the benzene and the mixture is then refluxed in a water bath maintained at 55°C – 60°C. Weaker nitric acid functions as a base in highly acidic sulphuric acid medium releasing the Nitronium cation ($^+\text{NO}_2$) which then undergoes substitution in the ring.



But at 95°C, 1, 3 – dinitrobenzene is obtained

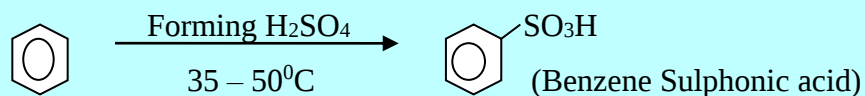


- **Sulphonation**

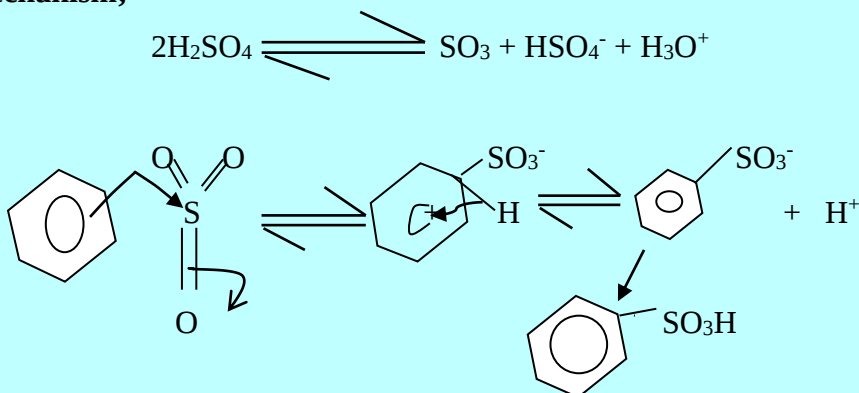
Sulphonation of benzene to form benzene Sulphonic acid is best carried out using fuming sulphuric acid. The reaction takes place on gently warming to 35 – 50°C.

N.B Ordinary concentrated sulphuric acid may be used, but the mixture then requires refluxing for several hours.

The most probable mode of attack seems to be electrophilic substitution by the electron-deficient sulphur (iv) oxide, SO_3 , although the SO_3H^+ ion has been considered as a possibility.



Mechanism;

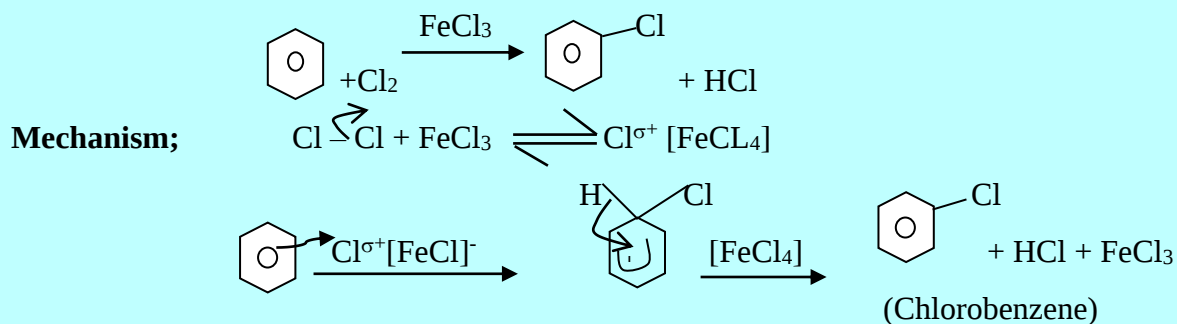


The reaction is reversible with equilibrium tending towards the left.

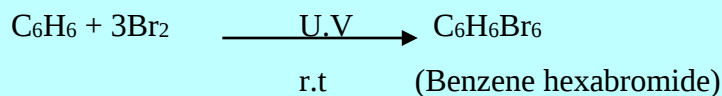
- **Halogenation**

Substitution by chlorine / bromine in benzene takes place readily at room temperature in the presence of a halogen carrier catalyst

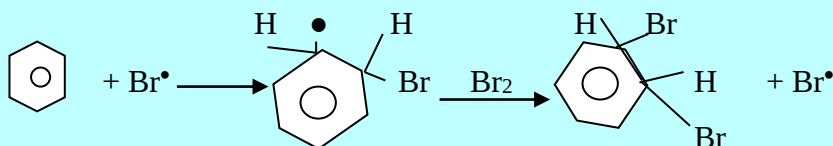
E.g. Fe, Al



In the presence of direct sunlight or ultra-violet radiation benzene reacts with chlorine or bromine at room temperature to form white crystals of 1, 2, 3, 4, 5, 6- hexachlorocyclohexane or hexabromocyclohexane respectively



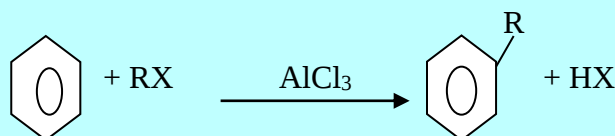
It is an addition reaction and proceeds via a free-radical mechanism.



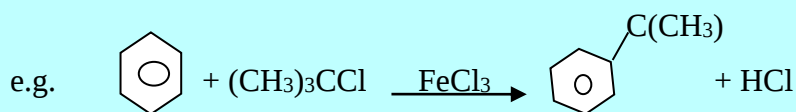
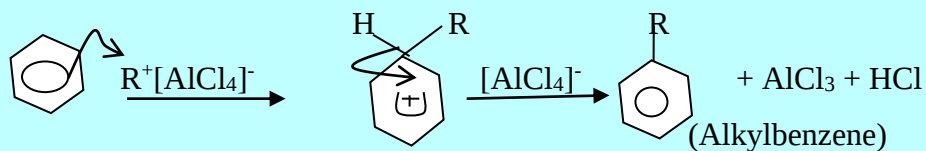
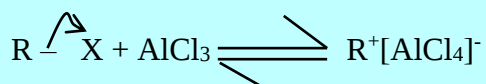
The propagation stages are repeated until $\text{C}_6\text{H}_6\text{Br}_6$ is formed as the major product. The final product has several stereo isomers and in the case of the hexachloride, one of these is a powerful insecticide.

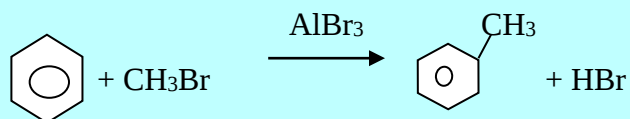
- **Friedel-crafts Alkylation**

Alkylation is a reaction of aromatic compounds with alkyl halides (R-X) in the presence of a halogen carrier to produce alkyl aromatic compound



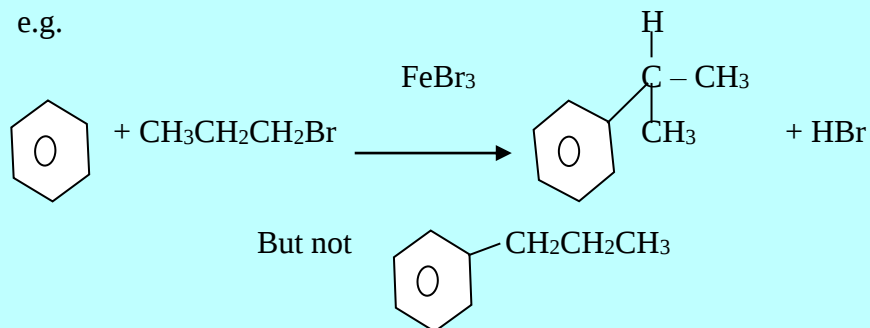
Mechanism



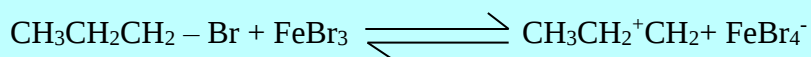


Rearrangement can take place

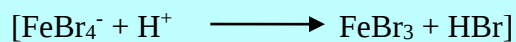
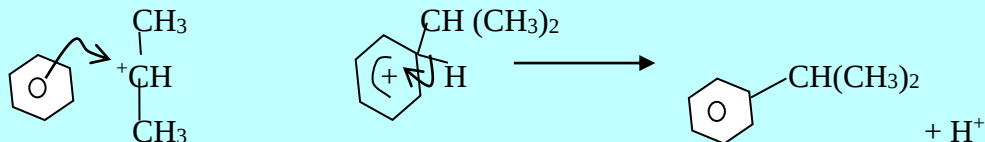
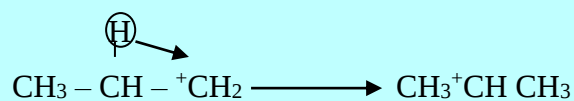
e.g.



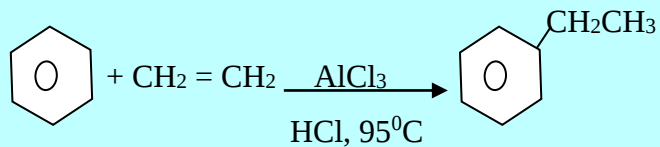
Mechanism



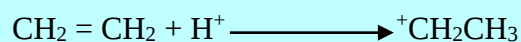
The primary carbonium ion formed undergoes rearrangement to give a more stable secondary carbonium ion

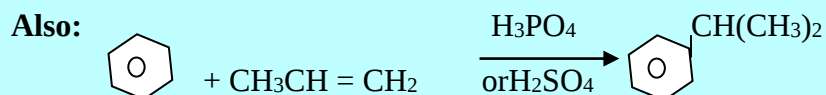
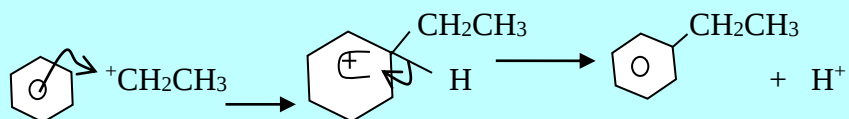


N.B: Alkyl aromatic compound can also be produced using alkenes.

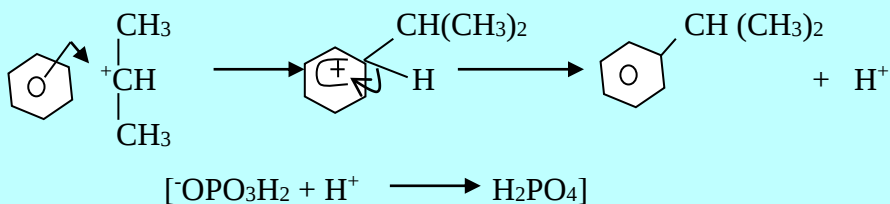
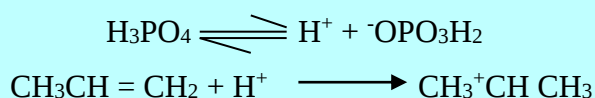


Mechanism;



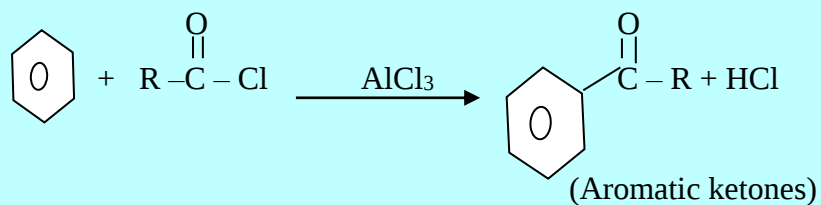


Mechanism;

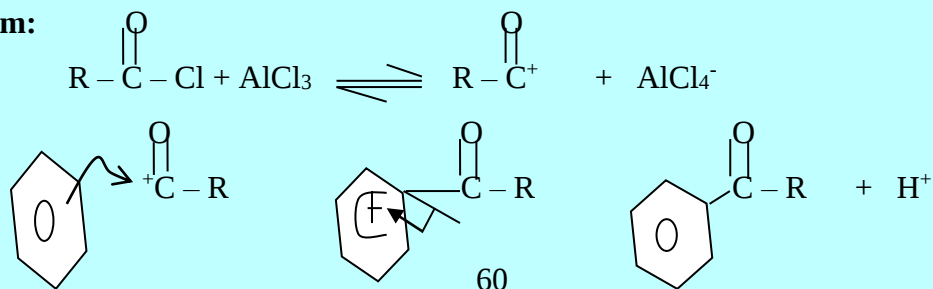


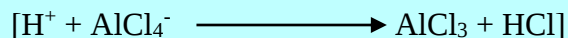
- **Friedel – crafts Acylation.**

Is a reaction where aromatic compounds react with acid chlorides in the presence of a halogen carrier to give aromatic ketones as the products. The mixture is refluxed on a water bath at 50°C (It is a condensation reaction)



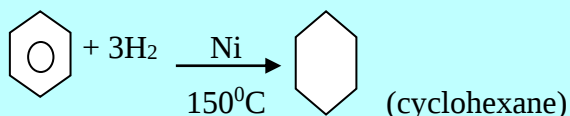
Mechanism:



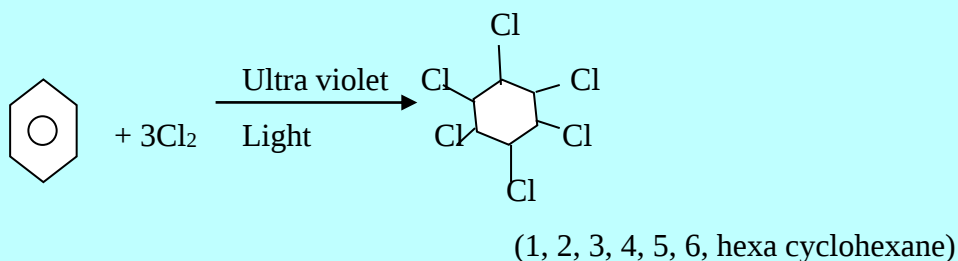


NB: A condensation reaction is one in which a new compound is formed from two or more reactants together with the elimination of a simple molecule such as water, ammonia, hydrogen chloride etc.

- **Reaction with Hydrogen**



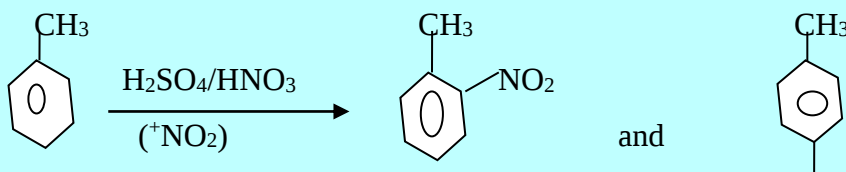
- **Reaction with chlorine in the presence of ultra violet light**

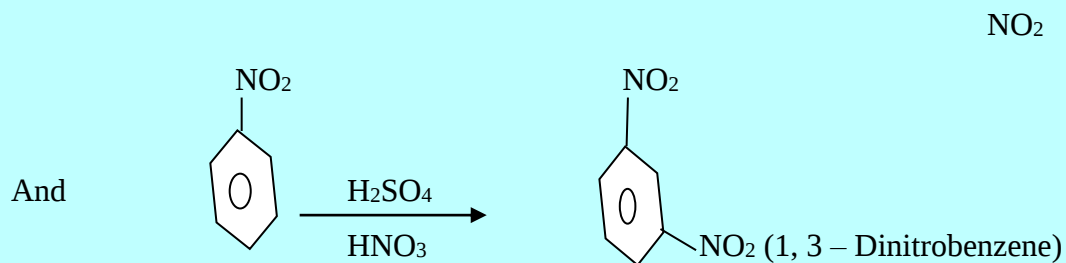


- **Orientation of substitution in a mono substituted benzene nucleus.**

When a second atom / group of atoms is attached to a monosubstituted benzene ring, the position of substitution is determined by the nature of the substituent already attached to the ring and is not dependent upon the attacking atom or group of atoms

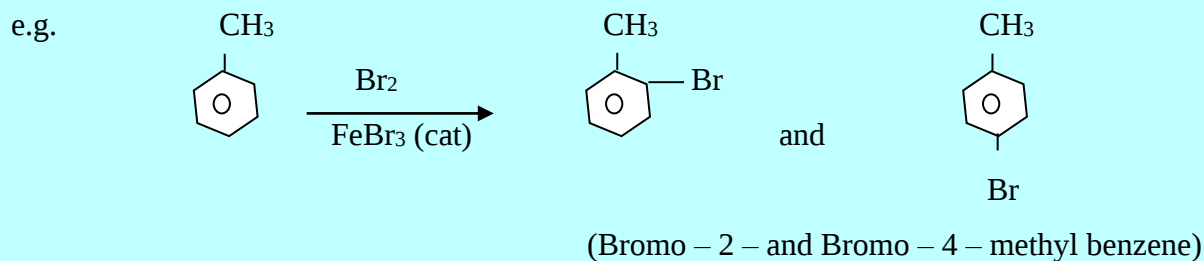
E.g. the Nitration and Bromination of methylbenzene (toluene) and nitrobenzene.



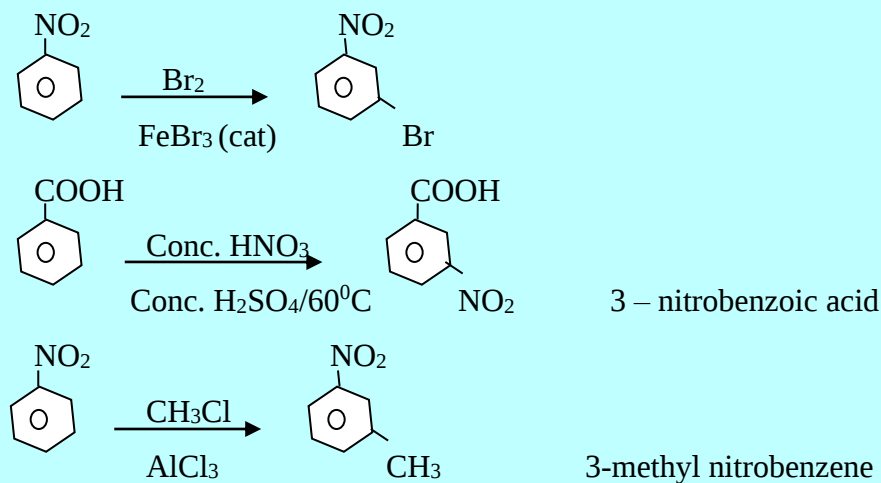


It's the methyl or nitro group which actually determines the position of a secondary substitution. And the position of substitution of the second substituent is governed largely by whether or not the atom or group already present is donating electrons to the ring or withdrawing electrons from it.

Electron donating substituents enhance the availability of electrons about the ring which is said to be activated. The 2 – and 4 – positions are the sites predominantly affected by the increase in electron density, rendering them more vulnerable to attack by an electrophilic reagent.



Electron withdrawing substituents reduce the availability of electrons about the ring, which is said to be deactivated; electrons are withdrawn mainly from the 2 – and 4 positions rendering the 3 – position relatively richer in electrons. And any subsequent attack by an electrophile takes place preferentially in the 3 - position

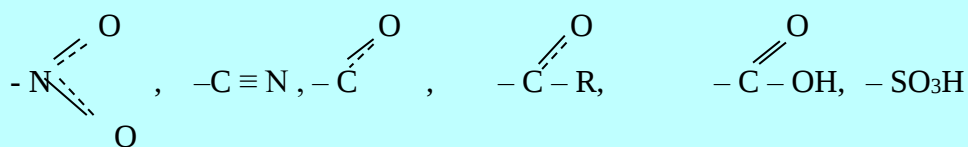


NOTE: Examples

Ring activating directing to 2- and 4 – positions

–R, –OH, –OR, –NH₂, –NHR, –NR₂

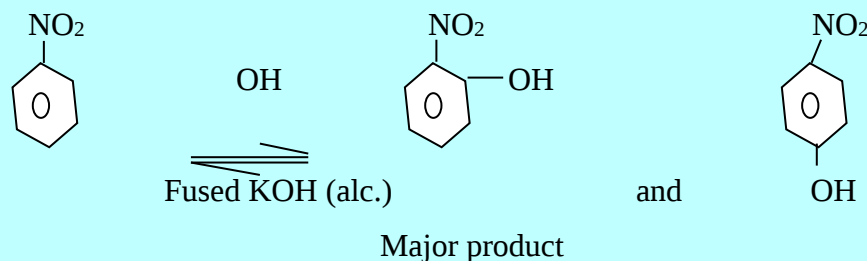
Ring deactivating, directing to 3 – position



But Halogens prove an exception to those general rules and direct to the 2 – and 4 – positions despite withdrawing electrons from the ring.

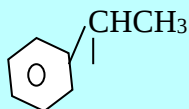
NB:

- Saturated group direct predominantly to the 2-and 4- position
- Unsaturated groups direct predominantly to the 3-positions hence halogens are saturated group
- If a strong electron withdrawing substituent is already attached to the ring, then the relative decrease in the availability of the electrons in the 2- and 4- positions may render these sites sufficiently deficient in electrons as to undergo attack by a nucleophile. E.g. If nitro benzene is fused with potassium hydroxide in the presence of air 2- nitrophenol is formed as the major product, because the electrons withdrawing inductive effect of the nitro group makes the 2- position more deficient in electrons than the more distant 4-



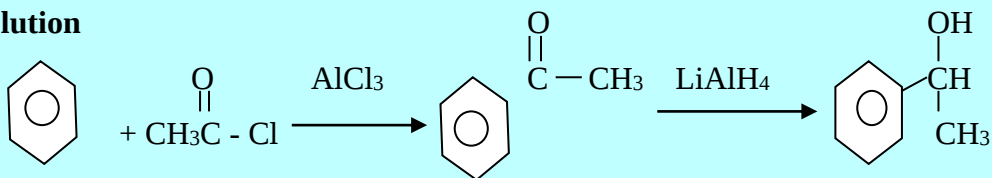
Example;

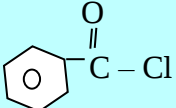
Write equation to show how the following conversions can be carried out



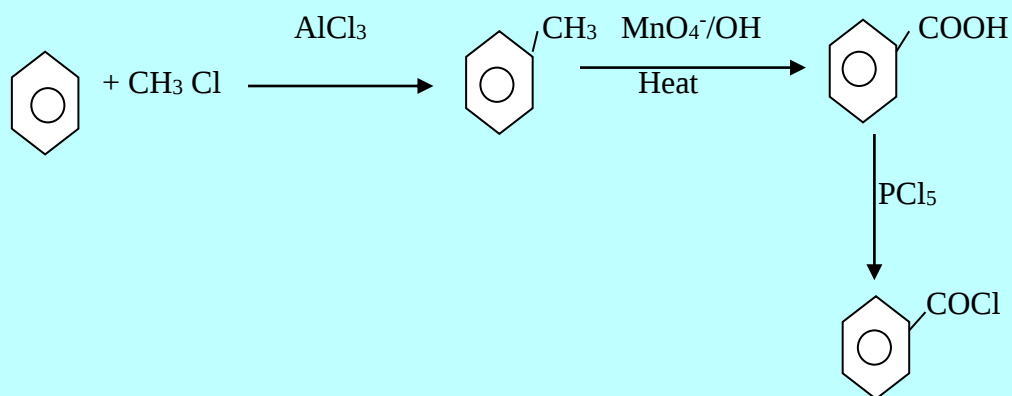
1. Benzene to  OH

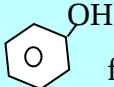
Solution

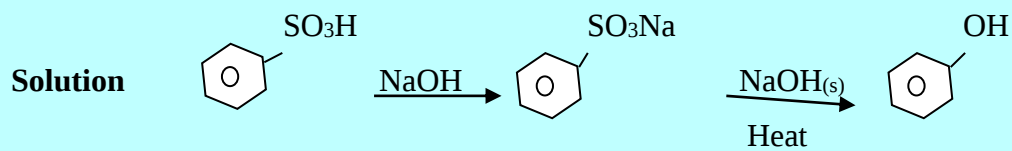


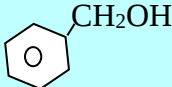
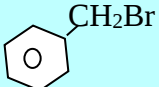
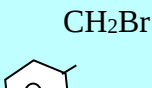
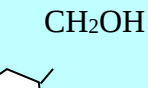
2.  to 

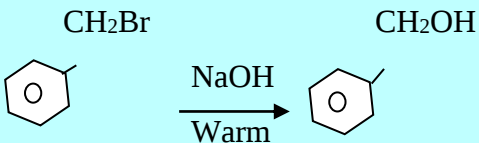
Solution



3.  from benzene sulphonic acid



4.  from 
 

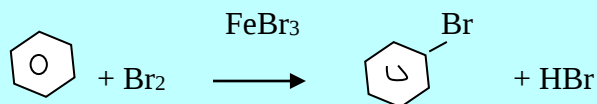

c1ccccc1CBr.[NaOH]>Warm>c1ccccc1CO

Write notes on the following

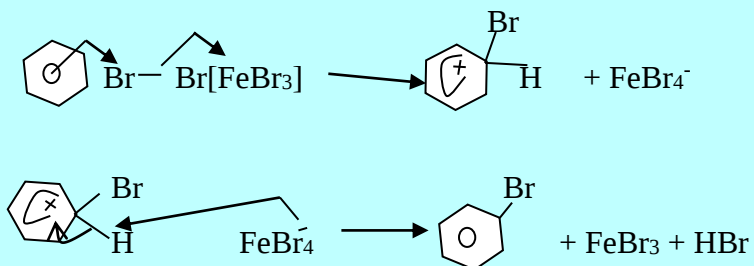
a) Electrophilic substitution reaction

Solution: This is a reaction in which a hydrogen atom in the benzene ring is replaced by another atom or group of atoms.

E.g. Benzene reacts with bromine in the presence of Iron (iii) bromide

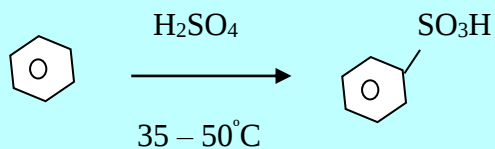


Mechanism

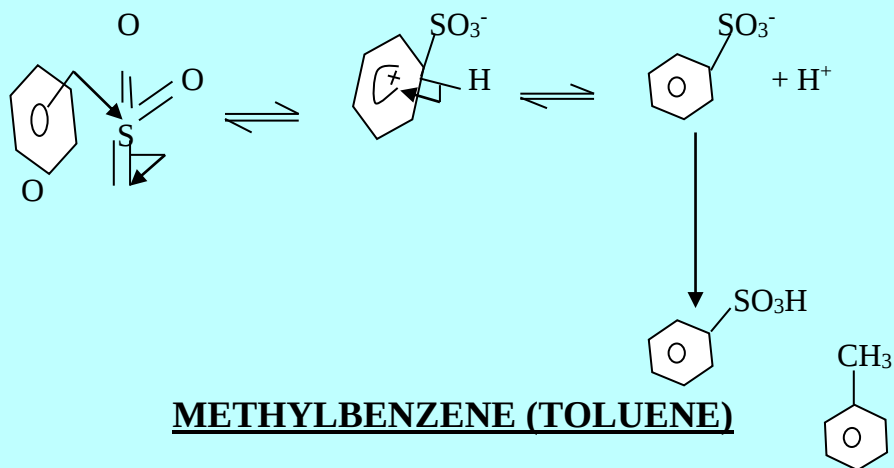


b) **Sulphonation** is the reaction in which aromatic compounds react with forming sulphuric acid

Example: Benzene react with fuming sulphuric acid at a temperature of about $35^\circ\text{C} - 50^\circ\text{C}$ to form Benzene Sulphonic acid



Mechanism

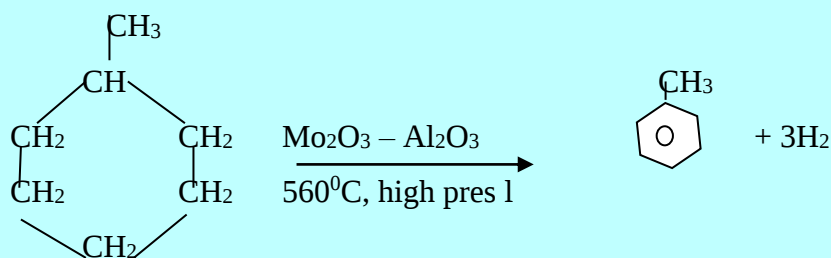


Is a higher homologue of benzene, colourless liquid, insoluble in water but soluble in organic solvents.

It's a better solvent than benzene since its fumes are less toxic than those of benzene.

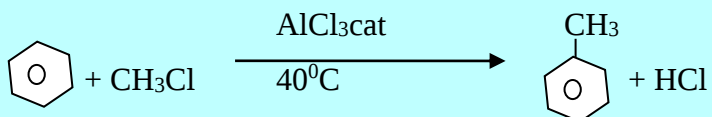
Industrial Source

Methyl cyclohexane is heated under pressure in the presence of molybdenum (III) oxide and Aluminium oxide catalysts where dehydrogenation occurs.



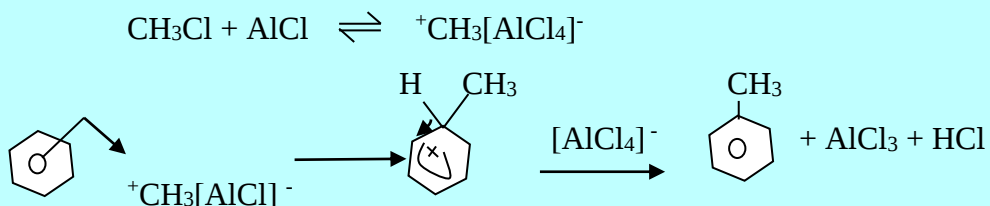
Synthetic preparations

- a) **Chloromethane** is bubbled through dry benzene in the presence of an anhydrous aluminium chloride catalyst at a temperature of 40°C .



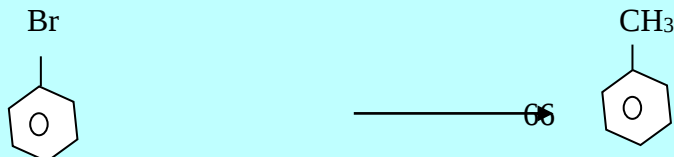
A better yield is obtained if the mass of catalyst used is about $1/3$ that of benzene

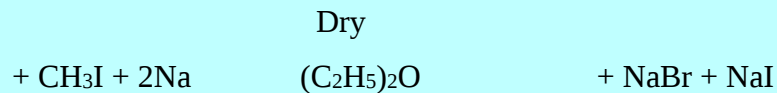
Mechanism



- b) **Wurtz synthesis of alkanes**

Sodium is slowly added to a dry ethereal solution of bromobenzene and iodomethane

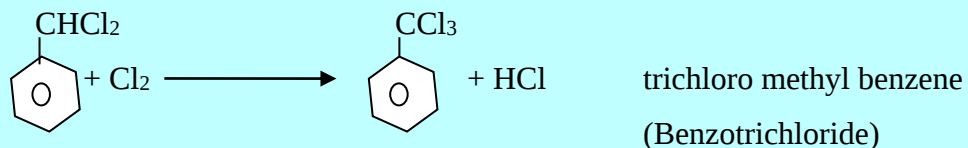
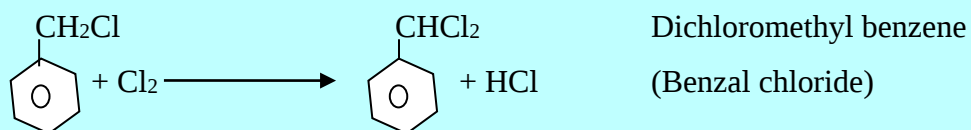
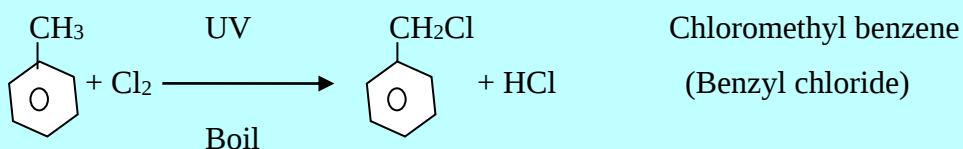




Then methyl benzene is separated by fractional distillation

REACTIONS

- a) Side chain substitution, which proceeds via a free radical mechanism chlorine is bubbled through boiling methylbenzene in the presence of ultra-violet light, substitution occurs in the side chain yielding successively chloromethyl benzene, dichloromethyl benzene and trichloromethyl benzene.



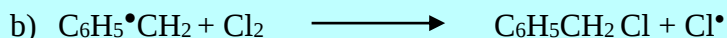
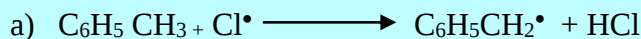
Also Bromination of methylbenzene takes place under similar conditions

Mechanism

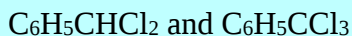
Step 1: Chain initiation



Step 2: Chain propagation

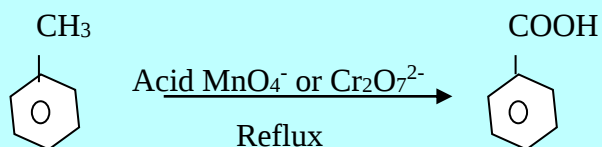


Step 2 (a) and (b) are repeated to give the further product i.e.



Oxidation (side chain reaction)

Using acidified potassium manganate (vii), potassium dichromate (vi) or dilute nitric acid

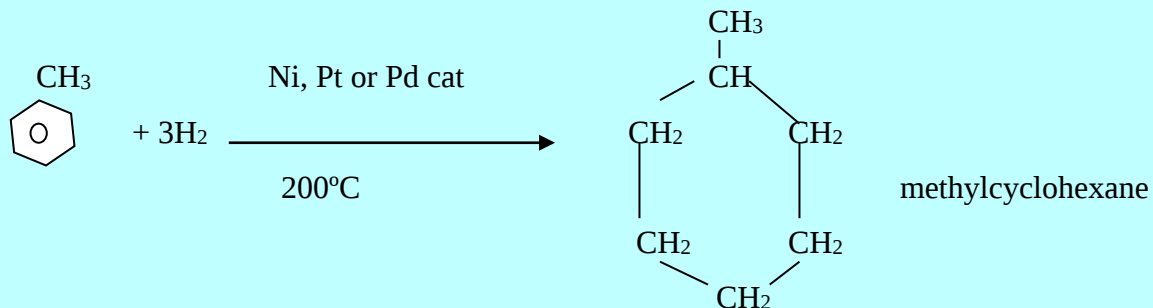


Benzoic acid (benzoic acid)

NB: If a milder oxidizing agent is used e.g. Manganese (IV) oxide or chromium (VI) dichloride dioxide (chromyl chloride), Methylbenzene is only oxidized as far as benzene carbaldehyde (Benzaldehyde).

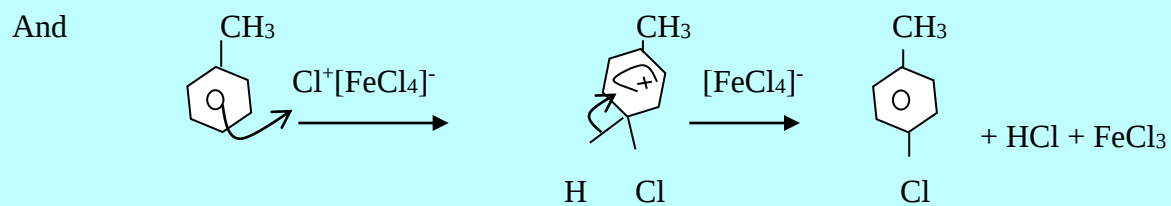
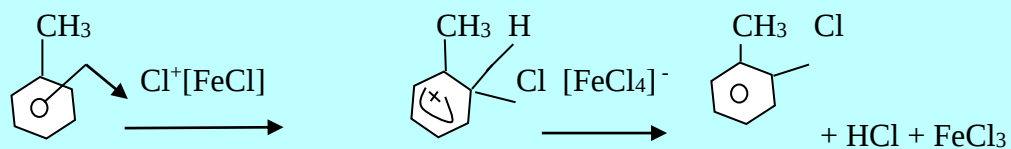
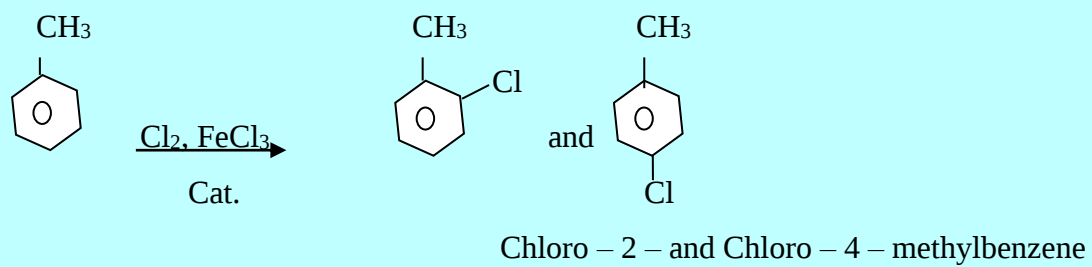
Hydrogenation (addition in the ring)

Methylbenzene Vapour is passed over finely divided Nickel, Platinum or Palladium catalyst at 200°C , addition occurs giving methylcyclohexane.

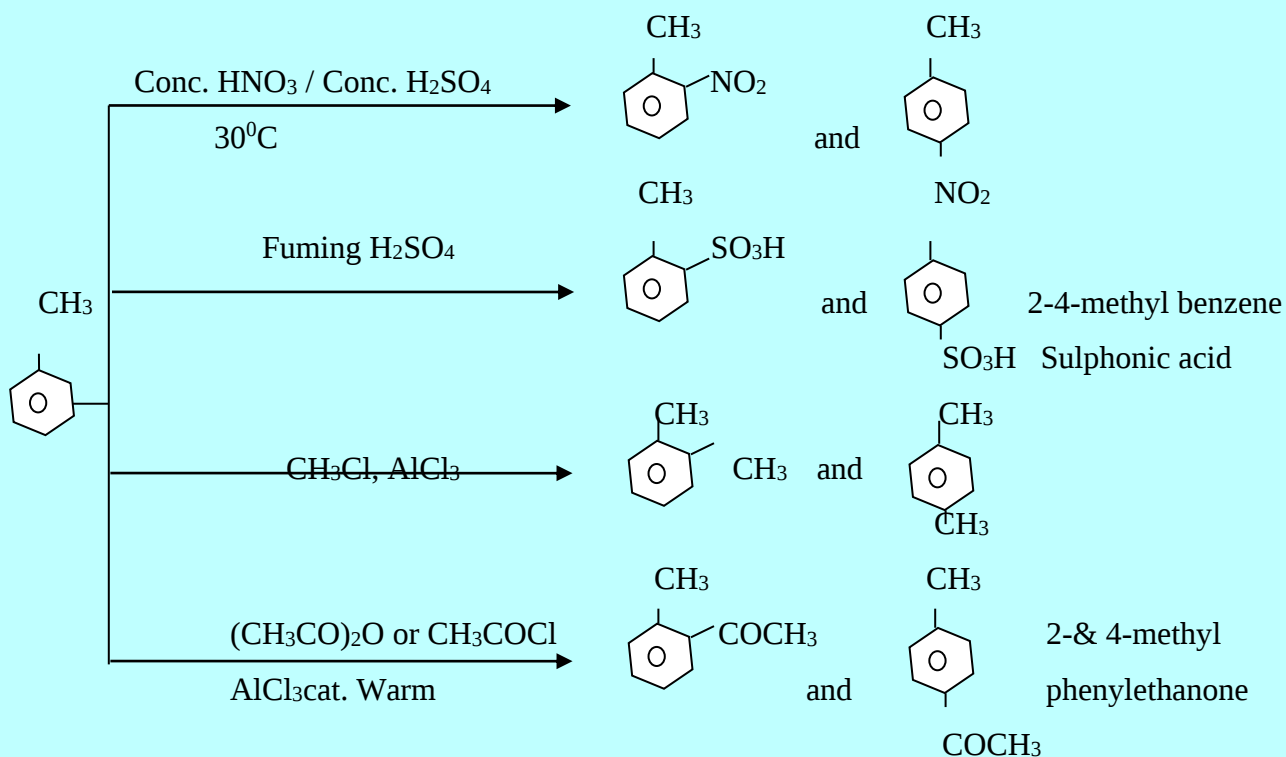


Ring substitution

If methylbenzene is treated with chlorine /bromine in the presence of a suitable halogen carrier at room temperature and in absence of sunlight

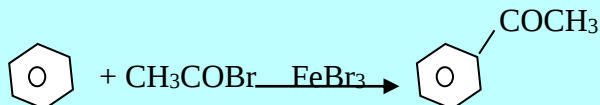


Other ring substitution reactions

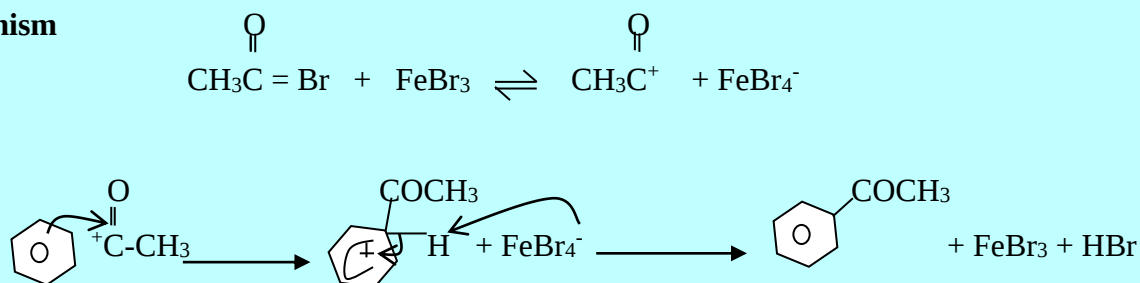


Example 1:

Complete the following and outline a mechanism



Mechanism

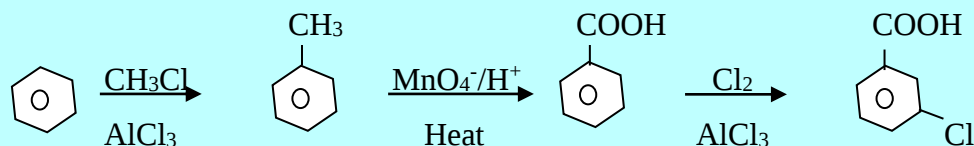


Example 2.

Give a reaction scheme to show how the following conversions can be effected.

2-Chloro benzoic acid from benzene

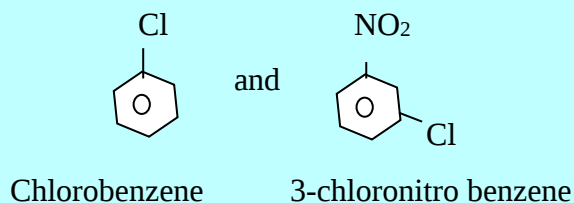
Solution:



HALOHYDROCARBONS

Are derivatives of alkanes with formula R-X where R is an alkyl group e.g. $\text{CH}_3\text{CH}_2\text{Br}$ and X an halogen such as Cl^- , I^- , Br^- , Fe^-

Alkyl halides are compounds in which the halogen atom is attached directly to an aromatic ring. Formula ArX e.g.



Vinyl halides (halo ethenes) are compounds in which the halogen is attached directly to a doubly bonded carbon e.g.

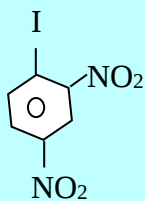
Chloroethene (vinyl chloride) $\text{CH}_2 = \text{CHCl}$

Unsaturated halogen compounds of the type $\text{CH}_2 = \text{CHCH}_2\text{X}$ are called Alkyl halides.

If two halogen atoms are attached to adjacent carbons, the compound is referred to as a VICINAL (VIC) DIHALIDE and if both are attached to the same carbon, then it is known as a GERMINAL (GEM) DIHALIDE

Nomenclature

CH_3Cl	Chloromethane	(Methyl chloride)
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ \\ \text{I} \end{array} \text{CH}_3$	2- Iodopropane	(Isopropyl iodide)
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	Chloromethyl benzene	(Benzl chloride)
	4-Iodomethyl benzene	



Iodo – 2, 4 –dinitro benzene

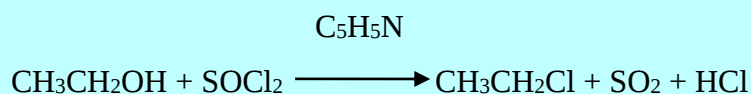
Synthetic preparation of halo alkenes

Substitution in Alcohols

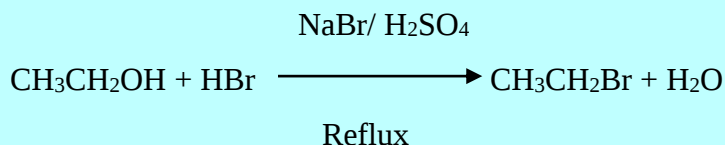


Note that in the case of the more reactive tertiary alcohols, the reaction proceeds in the cold.

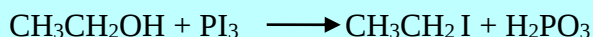
Chlorination can also be brought about by refluxing with sulphur dichloride oxide (thionyl chloride) SOCl_2 in the presence of small amounts of pyridine $\text{C}_5\text{H}_5\text{N}$ which absorbs the hydrogen chloride.



Bromination of tertiary alcohols can be brought about in the cold by treating them with either Hydrogen bromide ($\text{NaBr}/\text{Conc. H}_2\text{SO}_4$) or red phosphorus and bromine but primary alcohols are less susceptible and require refluxing



Iodoalkane is prepared by adding iodine to a mixture of the alcohol and red phosphorous and then refluxing on a water bath

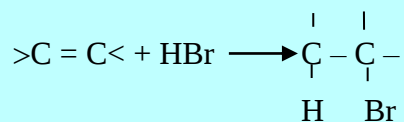


NB: An iodine and sulphuric acid cannot be used as the hydrogen Iodide produced, being a powerful reducing agent, would be oxidized to Iodine by the acid.

Therefore, ease of substitution of alcohols

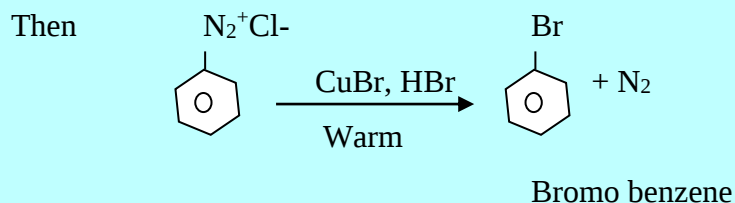
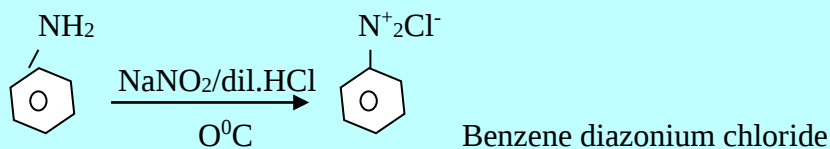
3° alcohol > 2° alcohol > 1° alcohol and is dependent upon the order of stability of the intermediate carbonium ion.

Addition of hydrogen halides to Alkenes

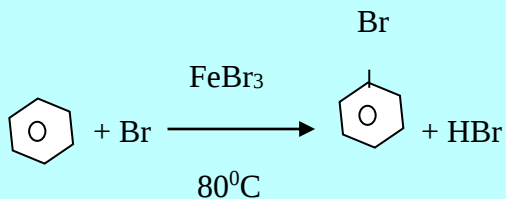


Replacement of a Diazonium salt (Sandmeyer Reaction)

Diazonium salt is obtained by treating a primary aromatic amine such as phenyl amine with $NaNO_2$ /dil. HCl at $0^\circ C$ (dilute nitrous acid at $0^\circ C$)



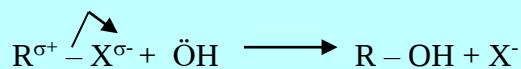
Direct halogenations



Note that the bromine molecule is polarized during the reaction, forming complex $Br^+ [FeBr_4]^-$

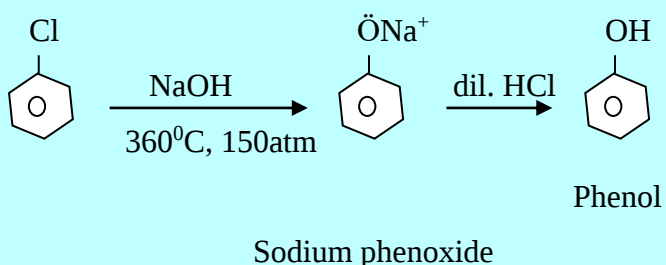
REACTIONS

Alcohol formation



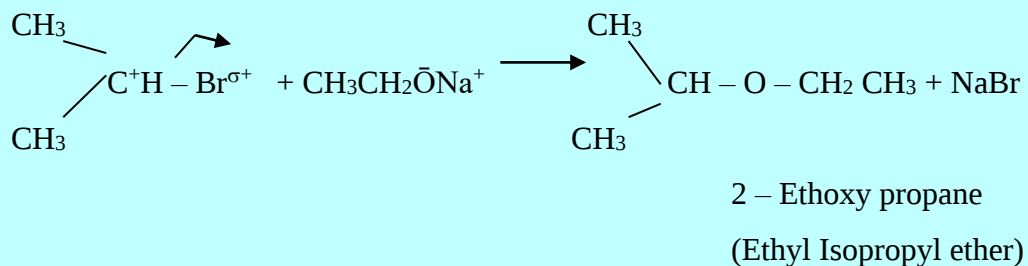
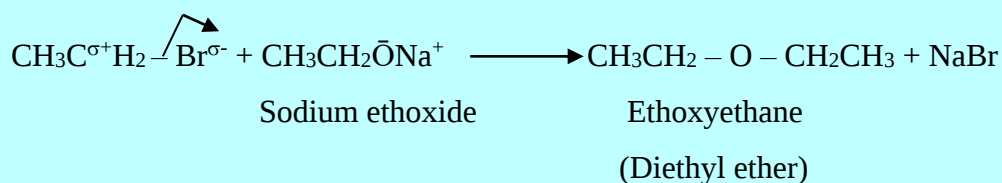
Primary and secondary Haloalkanes undergo alkaline hydrolysis to the alcohol.

Aryl halides are not sufficiently reactive to undergo hydrolysis to phenols except under severe conditions; phenol can be obtained by heating Chlorobenzene with aqueous sodium hydroxide at 360°C at a high pressure and then hydrolyzing the phenoxide formed with hydrochloric acid

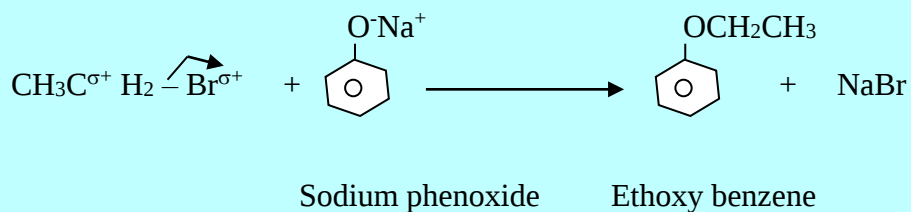


Ether formation (Williamson's synthesis)

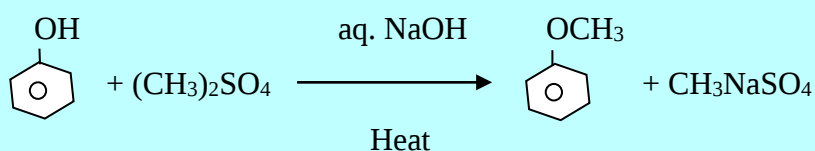
This reaction is suitable for both symmetrical and unsymmetrical ethers as well as alkoxy aromatics and alkoxy alkanes. Sodium or potassium alkoxide (Alkylate) is prepared by dissolving the alkali metal in excess of the appropriate alcohol which reacts with the halo alkane to form the ether



The reaction may also be performed using the phenoxide

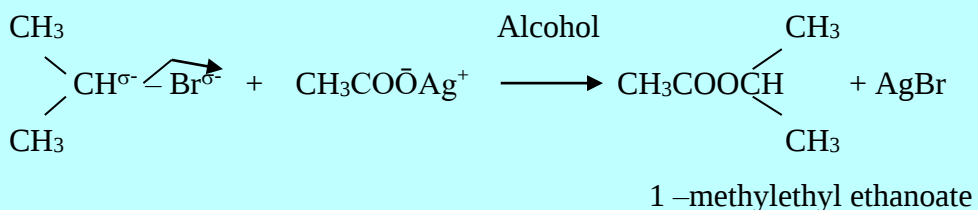
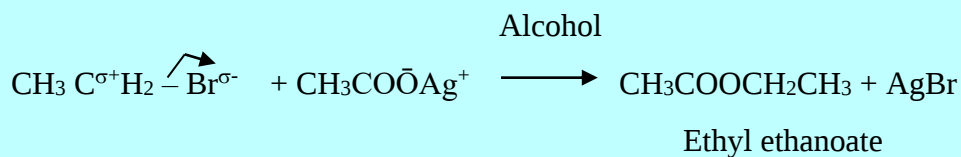


NB: For methoxy aromatics, it is more usual to use dimethylsulphate
(CH₃)₂SO₄ and a phenol in aqueous sodium hydroxide



Ester formation

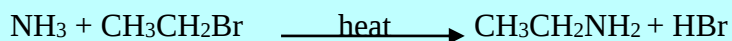
An alcoholic solution of silver (I) salt of a carboxylic acid is warmed with an halo alkane.



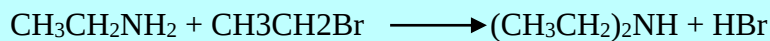
NB: Phenyl esters cannot be obtained by the direct interaction of the aryl halide and the carboxylate ion.

Amine formation

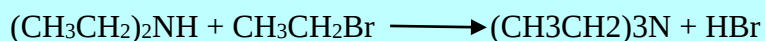
Alkylation of ammonia takes place if an alcoholic solution of ammonia is heated with a haloalkane



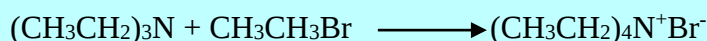
1° amine



2° amine



3° amine



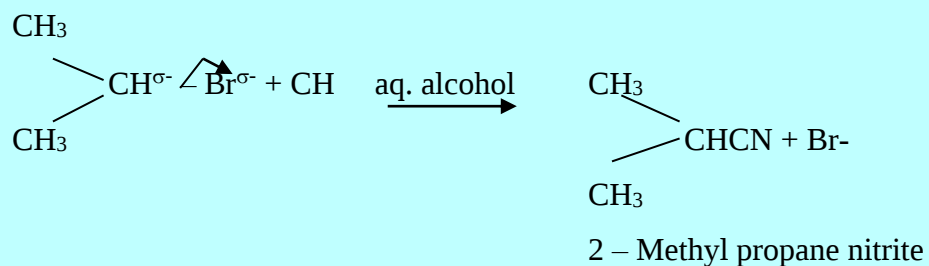
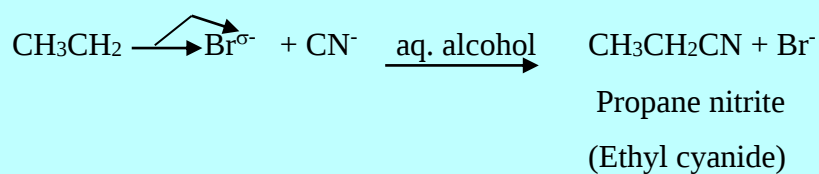
4° quaternary ammonium salt

The reaction has the disadvantage that a mixture of different classes of amines results since the alkyl amines are more reactive than the ammonia.

NB: The reaction tends to be limited to the aliphatic series, although aryl halides will react if electron withdrawing substituents are present in the 2 – or 4 positions.

Cyanide formation

These are prepared by heating the haloalkane with sodium cyanide in a suitable solvent (aqueous alcohol)

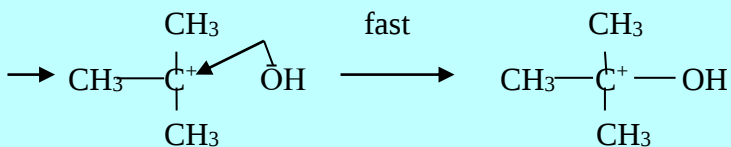
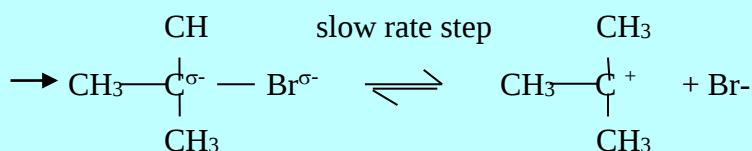


NB: Aromatic nitrites are not prepared from the un-reactive aryl halides but from diazonium salts.

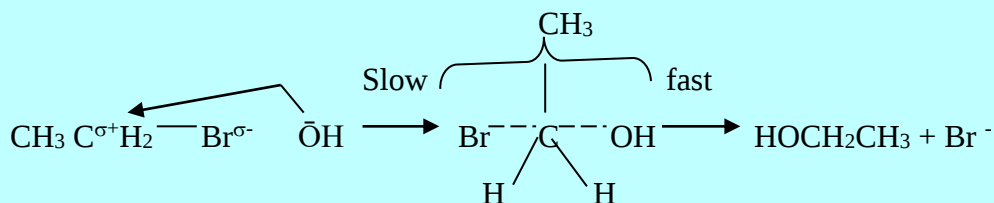
NB: The molecularity of the reaction describes the number of species involved in bond cleavage in the rate-determining step i.e.

The substitution Nucleophilic unimolecular (SN1) reaction has a molecularity of one.

I.e. Rate = K [RX]

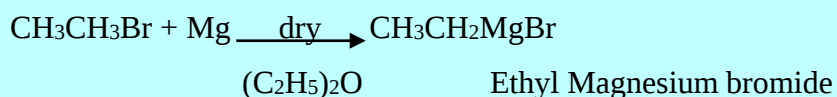


The substitution Nucleophilic bimolecular (SN²) reaction has a molecularity of two
i.e. Rate = K[R X] [OH⁻]



The Grignard reagent

Turnings or granules of Magnesium are treated with a dry ethereal solution of a haloalkane. The formula is usually represented as simply ALKYL MAGNESIUM HALIDE RMgX e.g.

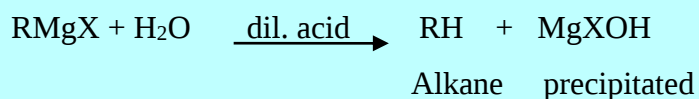
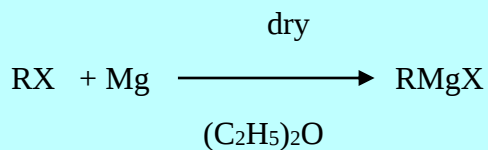


The Magnesium – carbon bond is covalent, but the magnesium-Halogen bond is ionic. The Grignard reagent may be employed for preparing alkanes, alkenes, alkynes, alcohols, aldehyde, ketones and carboxylic acids.

NB: Aromatic Grignard reagents are made in the same way and perform exactly similar reactions

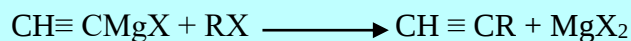
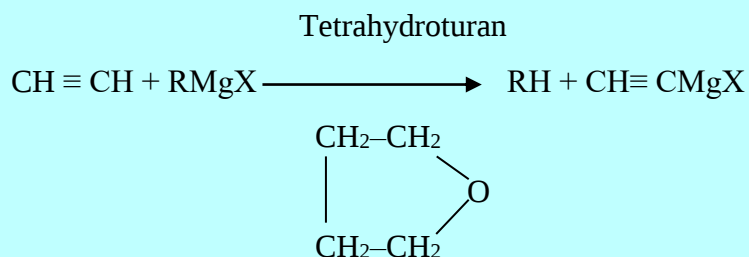
Synthetic applications of Grignard reagents

Preparation of alkanes



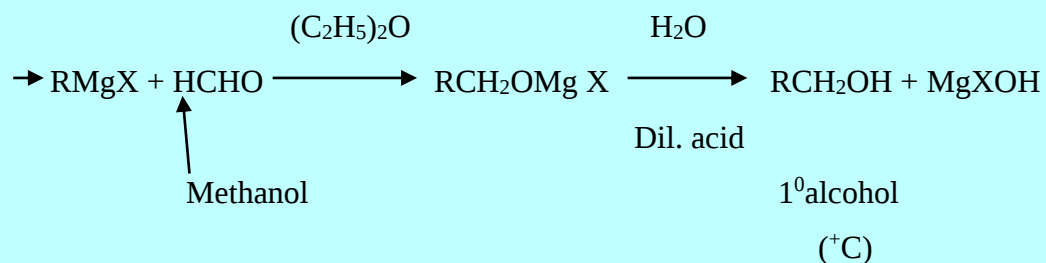
Preparation of Alkynes

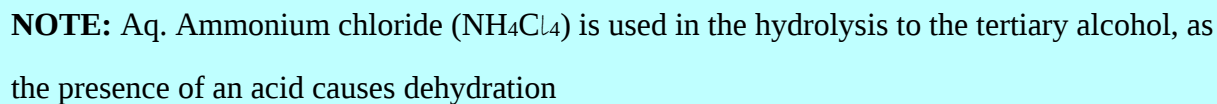
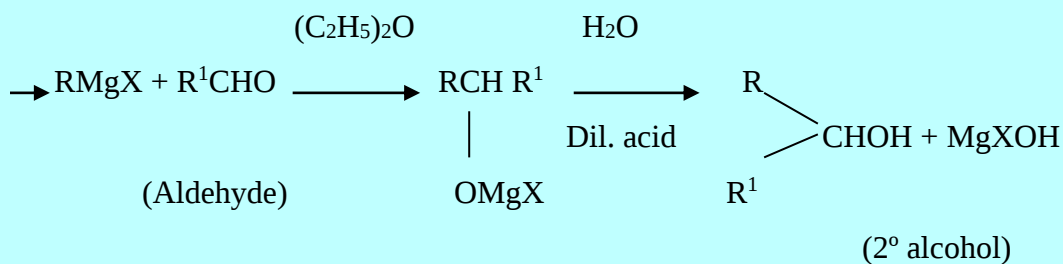
Suitable for higher homologous of Ethyne



Preparation of Alcohols

Suitable for 1^o, 2^o, and 3^o alcohols




$$\text{RMgX} + \text{H}-\underset{\text{OCH}_2\text{CH}_3}{\overset{\text{OCH}_2\text{CH}_3}{\text{C}}}-\text{OCH}_2\text{CH}_3 \xrightarrow{(\text{C}_2\text{H}_5)_2\text{O}} \text{H}-\underset{\text{OCH}_2\text{CH}_3}{\overset{\text{OCH}_2\text{CH}_3}{\text{C}}}-\text{R} + \text{MgXOCH}_2\text{CH}_3$$

Triethoxymethane

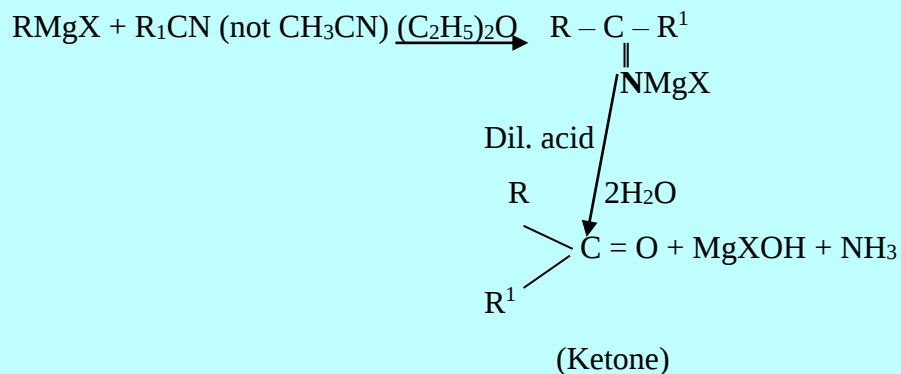
dil. $\searrow$ $2\text{H}_2\text{O}$

R

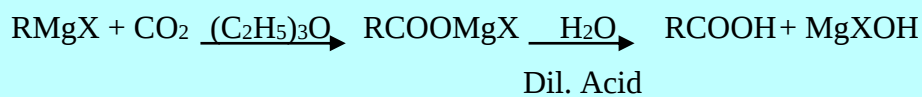
$\text{H} \searrow \text{C} = \text{O} + 2\text{CH}_3\text{CH}_2\text{OH}$

(Aldehyde)

Preparation of Ketones



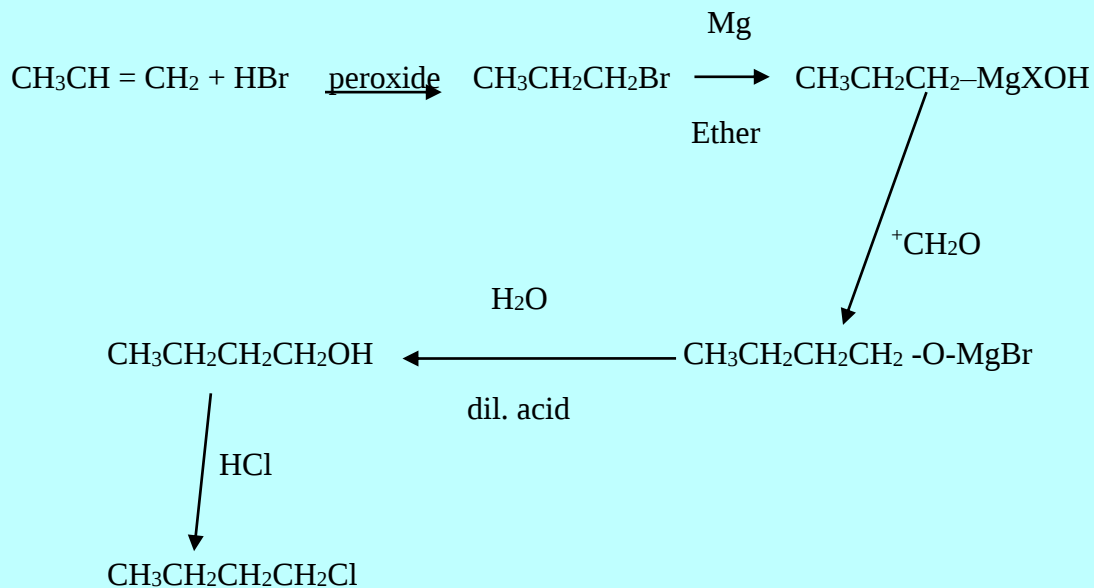
Preparation of carboxylic acids



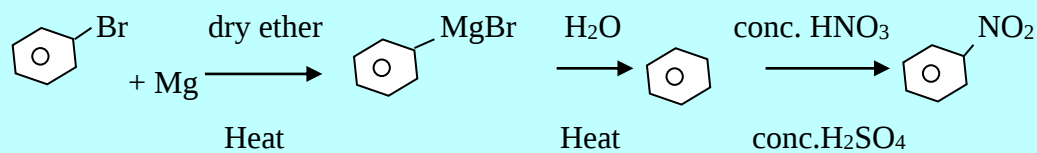
NB: (C₂H₅)₃O $\equiv$ dry ether

Qn. Show how the following conversions can be effected.

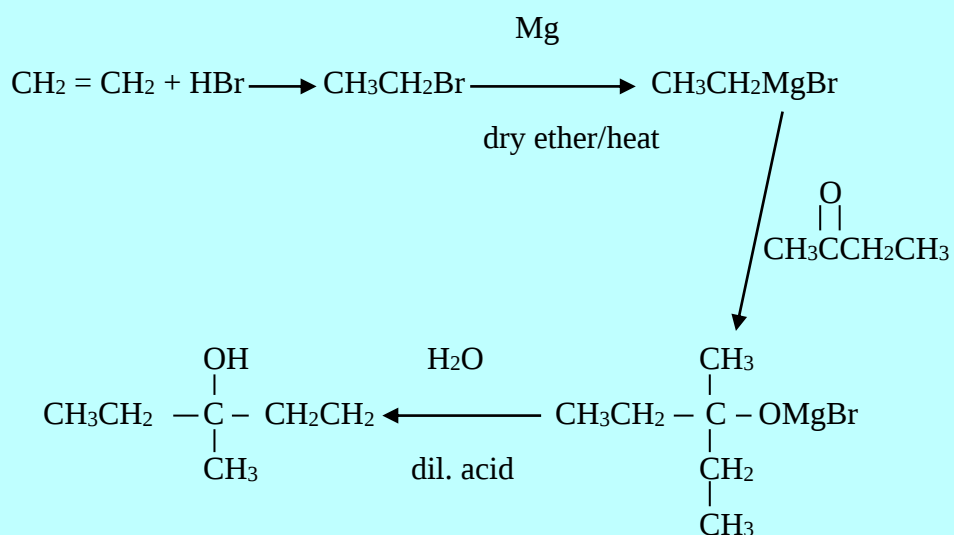
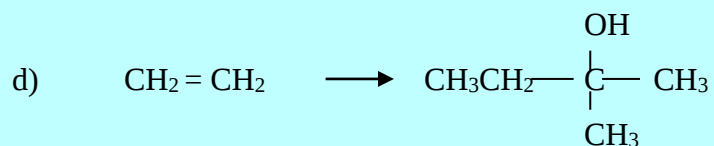
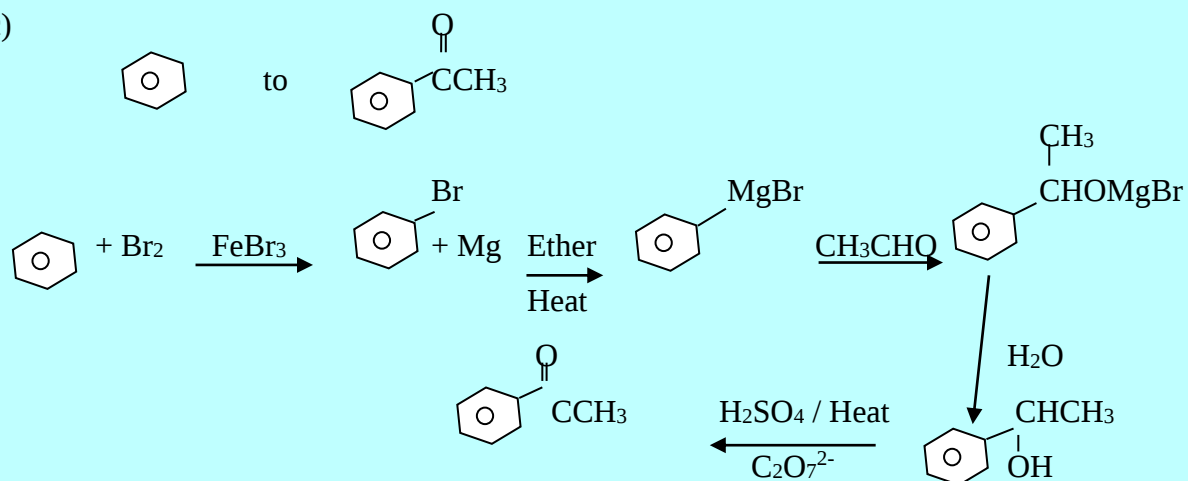
a) Propene to chlorobutane



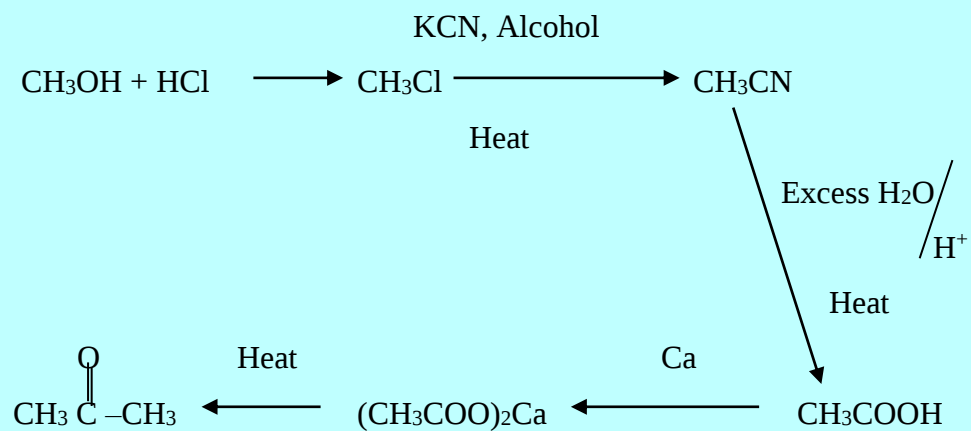
b) Bromobenzene to nitrobenzene



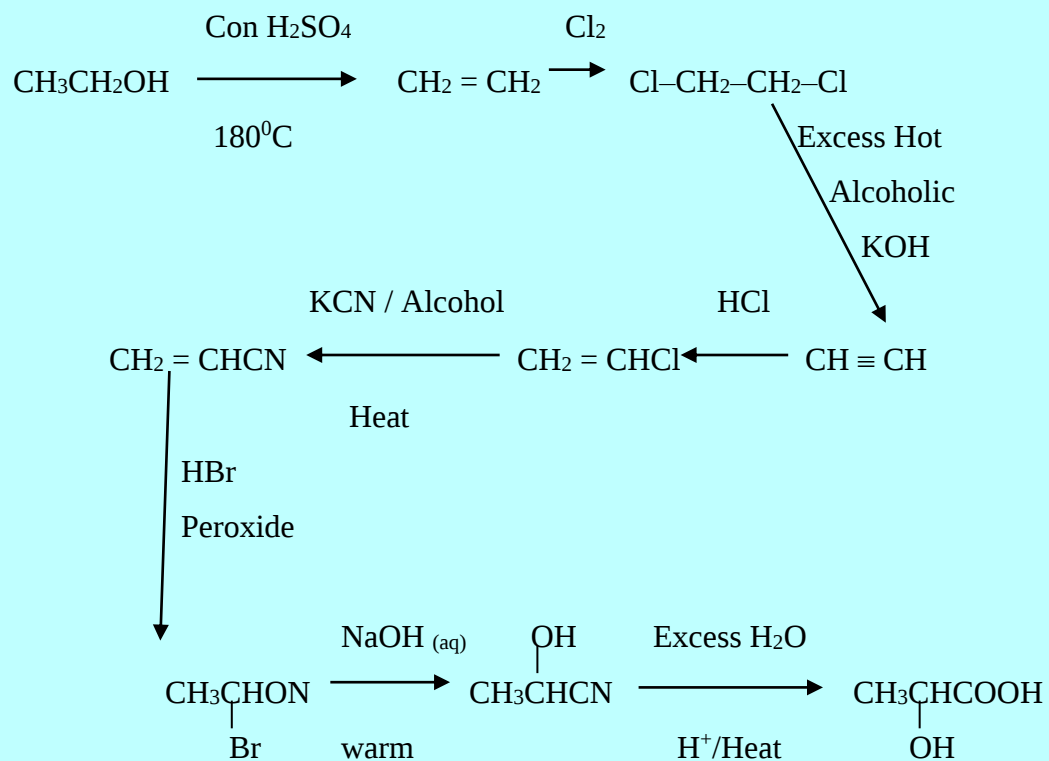
c)



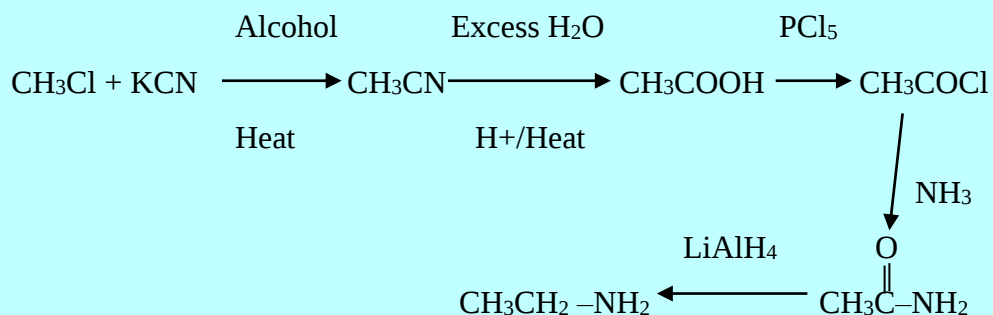
e) CH_3OH to CH_3COCH_3



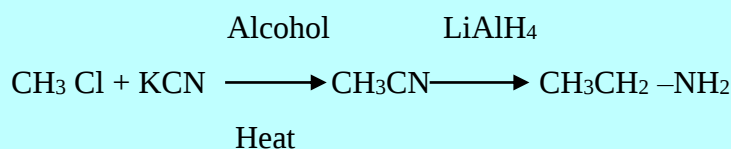
f) $\text{CH}_3\text{CH}_2\text{OH}$ to $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$



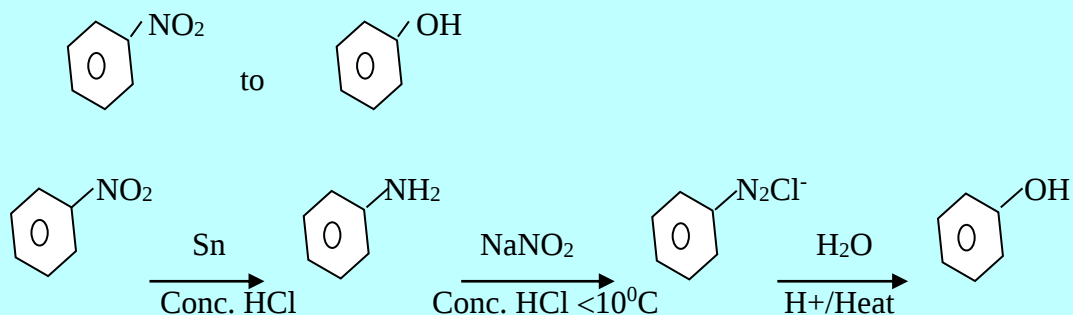
g) CH_3Cl to $\text{CH}_3\text{CH}_2 - \text{NH}_2$



OR



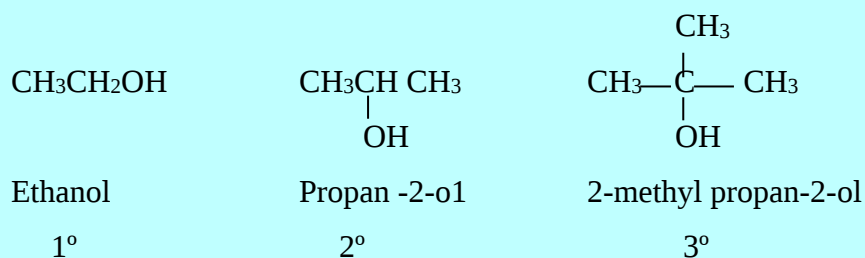
h)



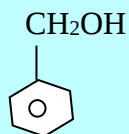
ALCOHOLS

Monohydroxyl derivatives of alkanes are called Aliphatic monohydric compounds containing more than one hydroxyl group are called Polyhydric alcohols

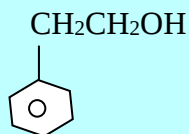
They may be classified as primary (1°) secondary (2°) or tertiary (3°) according to the nature of carbon atom to which the hydroxyl group is attached i.e.



Aromatic alcohols are aryl substituents of aliphatic alcohols in which the hydroxyl group is separated from the benzene ring by at least one methylene (-CH₂-) group e.g.



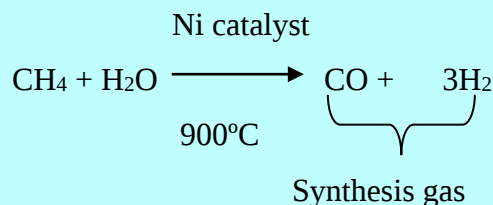
Phenyl methanol



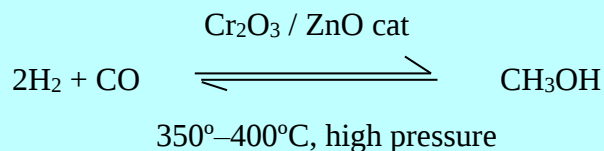
2-phenyl ethanol

Industrial source

1st stage: Steam reforming



2nd stage: Synthesis gas is passed over a chromium (III) oxide /Zinc oxide catalyst at 350^o-400^oC.



The equilibrium, is maintained by high pressure

NOTE:

Ordinary commercial alcohol is an azeotropic mixture of 95.6% ethanol and 4.4% water by mass, therefore separation by fractional distillation is not possible as that of Zeotropic mixture which boils at only a marginally lower temperature (78.2°C) than the absolute that contains 95% ethanol and this is then fractionally distilled.

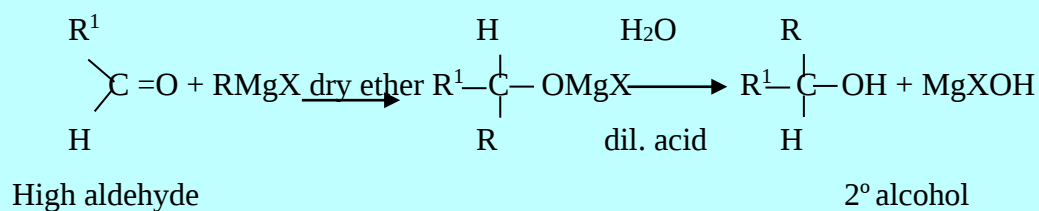
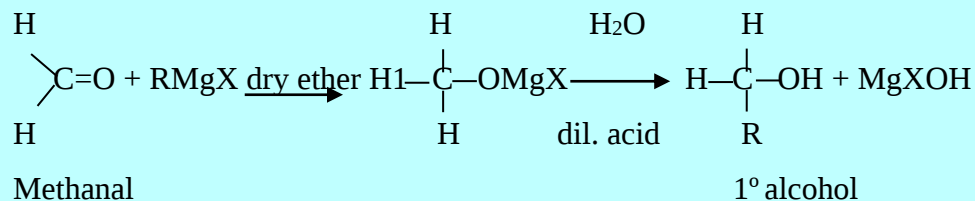
The distillate being collected in three separate parts.

1 st fraction	:	over at 64.8°C, Benzene ethanol water
2 nd fraction	:	at 68.2°C, Benzene / ethanol
Final fraction	:	at 78.3°C, is absolute ethanol

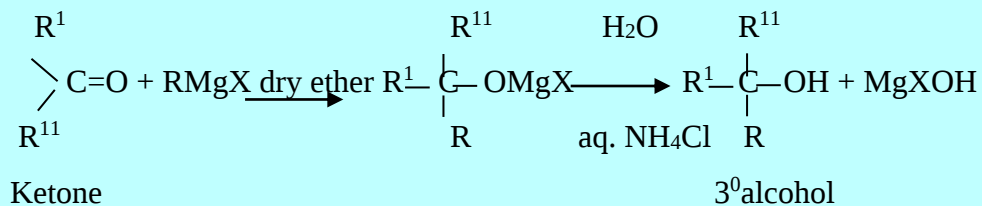
Absolute ethanol is highly hygroscopic and must be stored away from atmospheric moisture if its purity is to be maintained.

Using: Synthetic preparations of Aliphatic Alcohols

a) Grignard synthesis



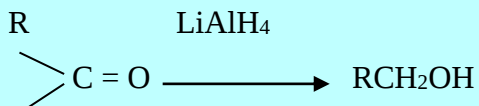
Such as ethanal



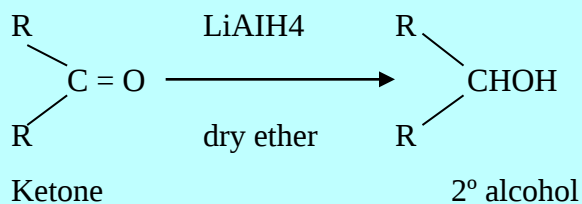
Such as propanone

b) Lithium Tetrahydrido aluminate (III) in dry water

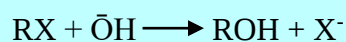
Its suitable for 1° and 2° alcohol, the reactions are performed at 0°C and its use in elementary practical work is not really desirable since it reacts violently with water and moisture.



$\begin{matrix} \text{H} \\ | \\ \text{C} = \text{O} \\ | \\ \text{R} \end{matrix}$ dry ether
 Aldehyde 1° alcohol

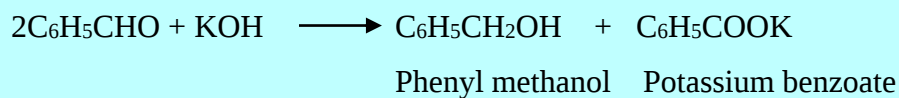


Hydrolysis of Haloalkanes

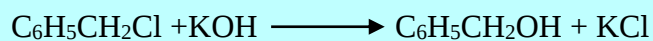


Preparations of Aromatic Alcohols

(The Cannizzaro reaction)



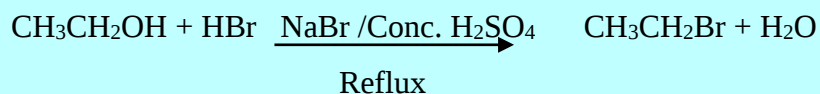
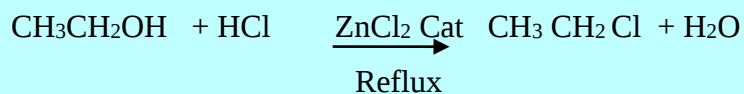
Hydrolysis of chloro methyl benzene (Benzyl chloride)



REACTIONS

Halogenation

Using hydrogen halides



NB

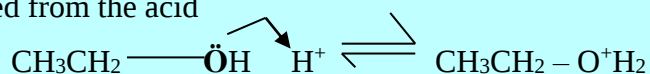
Bromination may be carried out by treating the alcohol with red phosphorous and bromine

→ An iodine and sulphuric acid cannot be used to bring about iodination as the hydrogen iodide produced, being a powerful reducing agent, it oxidized to iodine by the acid. Instead, the alcohol is treated with red phosphorous and iodine.

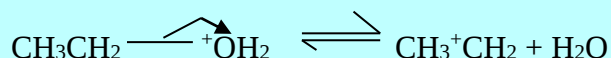
→ Tertiary and aromatic alcohols are predictably more readily halogenated by the hydrogen halides, the reactions taking place fairly rapidly on shaking in the cold.

Mechanism

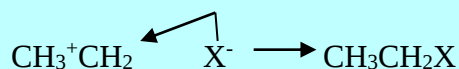
Step I: Donation of lone pair of electrons from the oxygen atom of the alcohol to a proton released from the acid



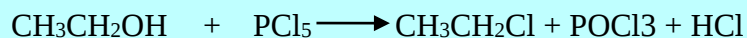
Step II: Ions of water molecule form the protonated alcohol to form a carbocation (Carbonium ion)



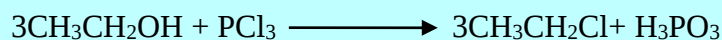
Step III: Nucleophilic attack by a halide upon the carbocation to form the halo alkane



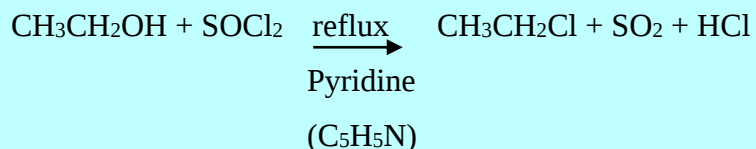
Using phosphorous



Phosphorus trichloride reacts similarly, although slightly less readily.

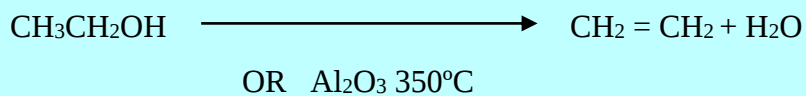


Using sulphur Dichloride oxide (Thionyl Chloride)

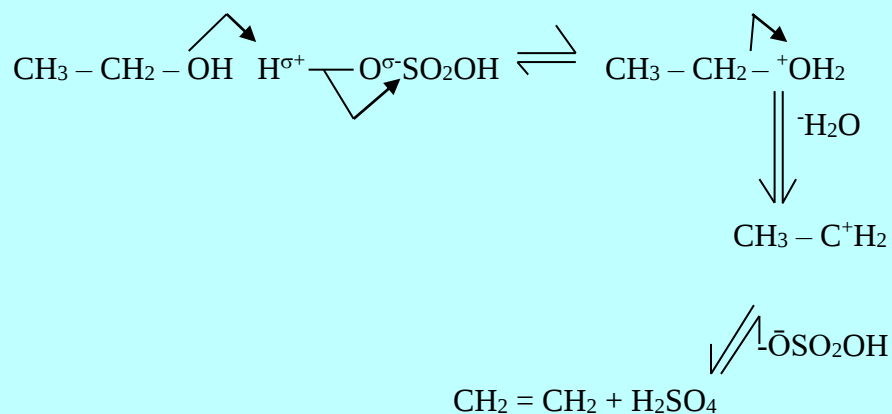


Dehydration to Alkenes

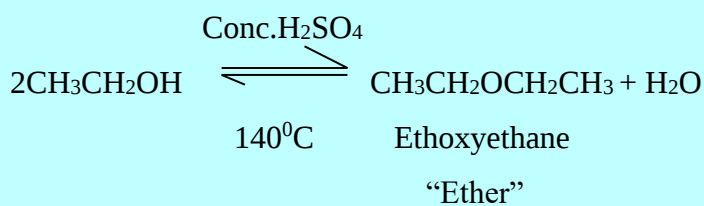
Excess Conc. H_2SO_4 . 170°C



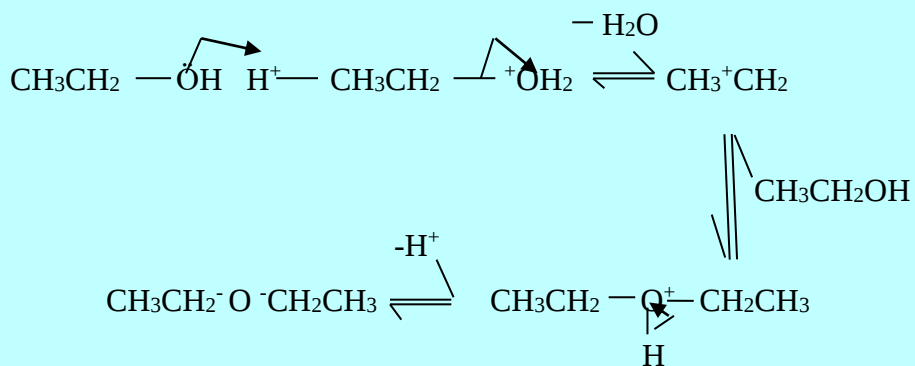
Mechanism



Ether formation



Mechanism



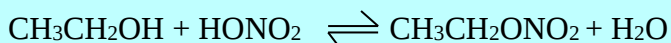
With metals



Esterification

The process whereby an alcohol reacts reversibly with an acid to form an ester is known as esterification. This involves the replacement of a hydroxyl group of an acid by an alkyl group of an alcohol.

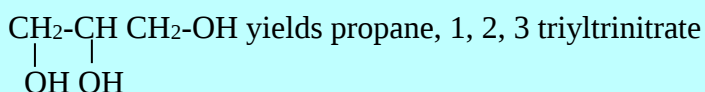
E.g. Ethanol reacts with concentrated sulphuric and nitric acid in the cold to form ethyl hydrogen sulphate and ethyl nitrate (dangerous reaction)



Ethyl nitrate

Nitrate esters are especially important in manufacturing explosives

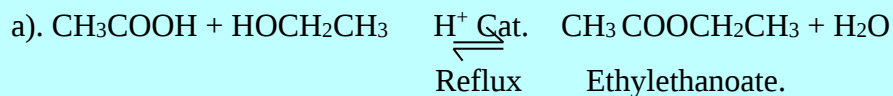
➤ Nitration of propane, 1, 2, 3 triol (glycerol)



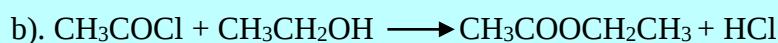
(Nitroglycerine $\text{CH}_2\text{NO}_3\text{CHNO}_3\text{CH}_2\text{NO}_3$ which when mixed with finely divided silicon (IV) oxide in the correct proportions is used in manufacturing dynamite.

NB

The most important class of esters is that formed between alcohol and carboxylic acids. The alcohol and the carboxylic acid are boiled under reflux in the presence of 5% concentrated sulphuric acid

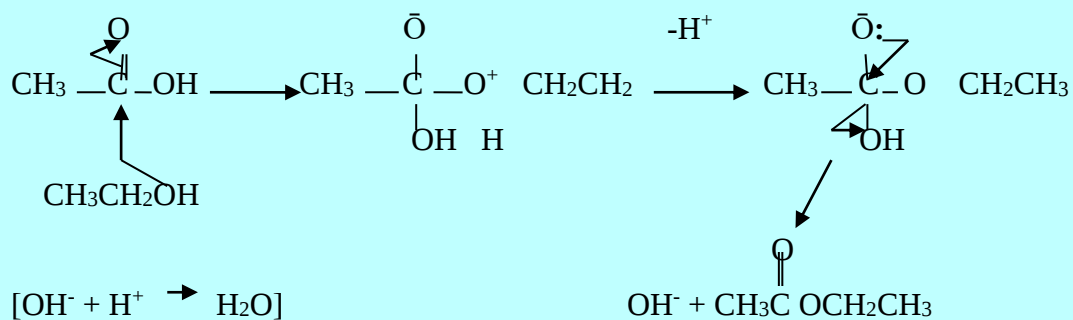


Esterification may also be accomplished using an acyl or benzene carbonyl (benzoyl) chloride.

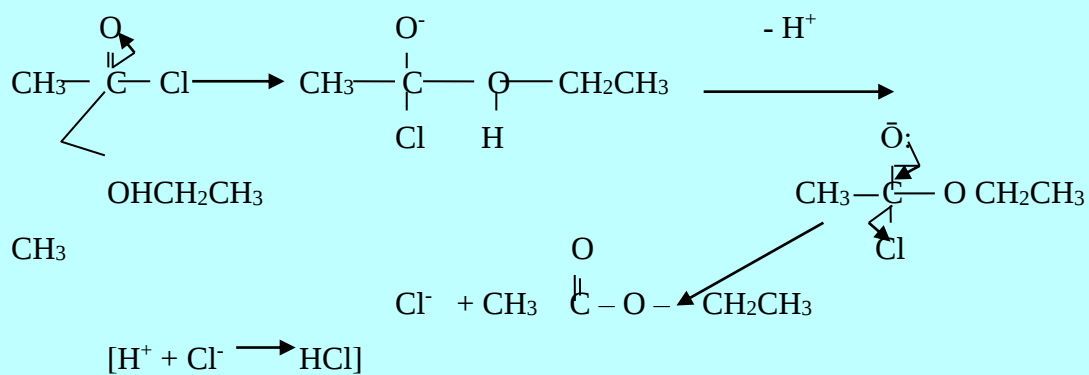


Ethanoylchloride

Mechanism

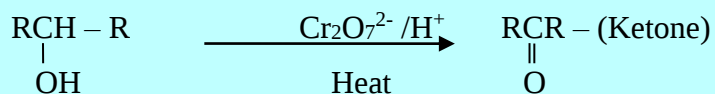
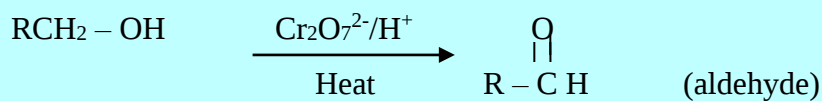


b)

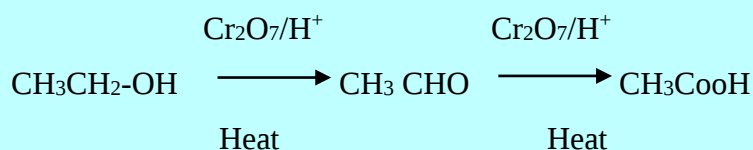


Oxidation

Potassium manganate (VII) (permanganate) and potassium dichromate (VI) are the most popular oxidizing agent. The manganate (VII) can be used in a neutral alkaline or acidic medium whereas the dichromate (VI) functions only in a medium of sulphuric acid



NB: Tertiary alcohols are comparatively stable for oxidation and are not oxidized at all in neutral or alkaline media. But under the same conditions primary and secondary alcohols retain the same carbon skeleton in undergoing oxidation to the aldehyde, acid or Ketone e.g.



TESTS OF ALCOHOLS

- Lower alcohols dissolve in water to give solution which have no effect on methyl orange and phenolphthalein indicators and are neutral to litmus.
- Addition of acidified solution of potassium dichromate to a primary or secondary alcohol and warming turns the mixture green if the alcohol is primary, unpleasant smelling aldehyde is formed but if it is a secondary alcohol fruity pleasant-smelling Ketone is formed

NB: Tertiary alcohols do not give positive test with acidified potassium dichromate solution. Formation of aldehyde or Ketone in the experiment is confirmed by adding a few drops of Brady's reagent to the product. Formation of a yellow precipitate then confirms

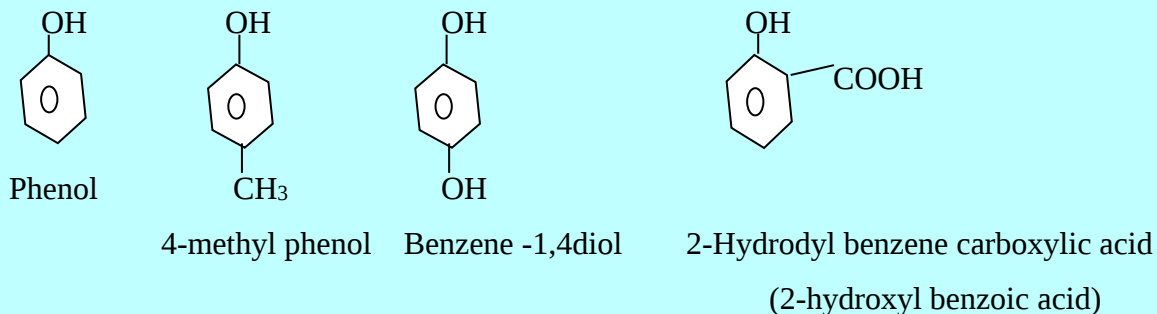
- With ethanoic acid, addition of some ethanoic acid & a few drops of sulphuric acid to primary, secondary or tertiary alcohol and warming the product sweet pleasant smell ester.
- Iodine solution and sodium hydroxide solution (Iodo form test). This gives positive results with only secondary alcohol which have methyl group attached to carbon atom

$$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{-CH-R} \end{array}$$

carrying the -OH group i.e. $\text{CH}_3\text{-CH(R)-OH}$. Ethanol is the only primary alcohol which gives a positive iodo form test. To the alcohol is added sodium hydroxide followed by iodine. A pale yellow precipitate is formed

PHENOLS

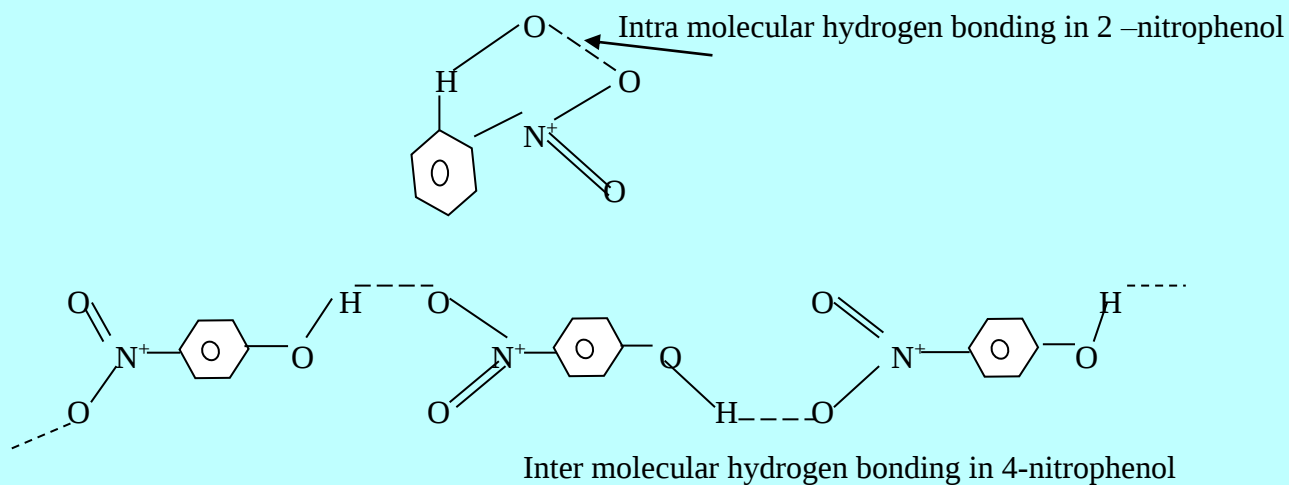
Are compounds containing a hydroxyl group attached directly to an aromatic nucleus.



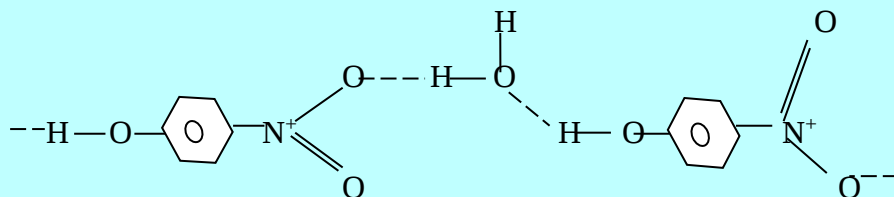
Phenol is a colourless, hygroscopic crystalline solid.

NB:

The greater volatility of 2-nitrophenol is attributed to intramolecular hydrogen bonding, where as the higher boiling points of the 3-and 4- isomers are a direct result of intermolecular hydrogen bonding.



As a result of their ability to associate with themselves and also with water molecules, 3 - and 4 - nitrophenol are appreciably more soluble in water than 2 nitro phenol, which cannot form inter molecular hydrogen bonds.

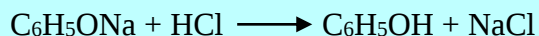
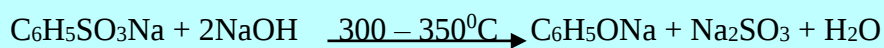


(Inter molecular hydrogen bonds between water and 4-nitrophenol)

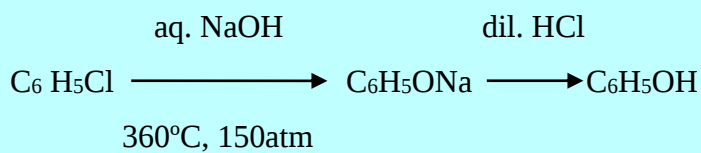
Hence the low miscibility and higher volatility of 2-nitrophenol enables it to be easily separated from other isomers by steam distillation.

PREPARATIONS

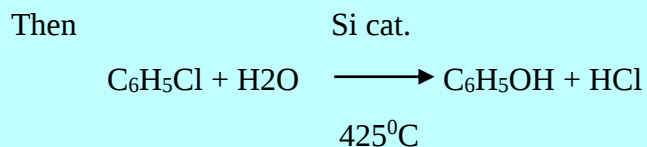
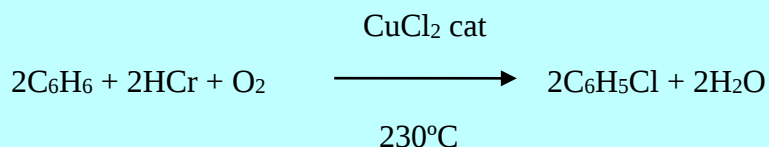
Alkali fusion with sodium benzene sulphate



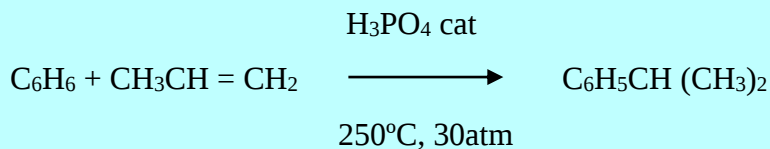
Hydrolysis of chloro benzene

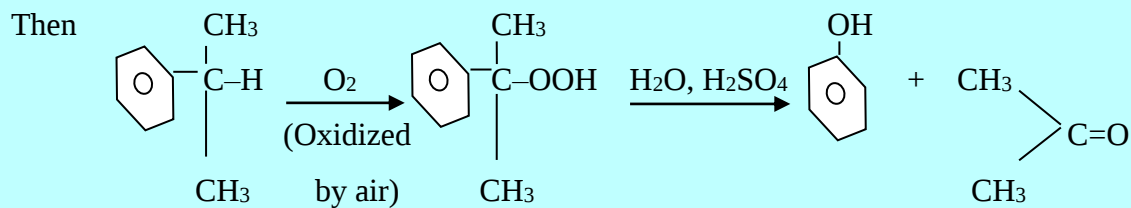


From Benzene (Rasching process)

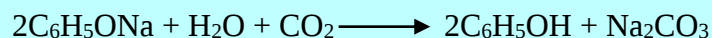


From petroleum products

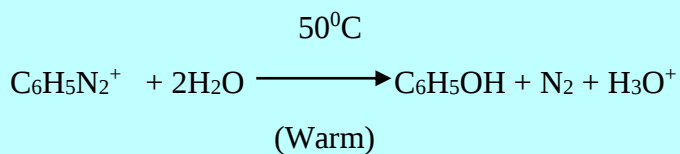




From Coal tar



Hydrolysis of Diazonium salts



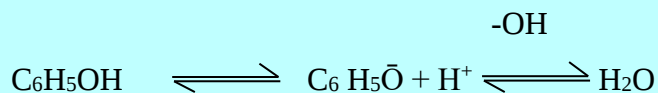
REACTIONS

Phenol undergoes two distinctive types of reaction

- Side –chain substitution, which generally involves replacement of the acidic proton
- And
- Electrophilic substitution in the ring.

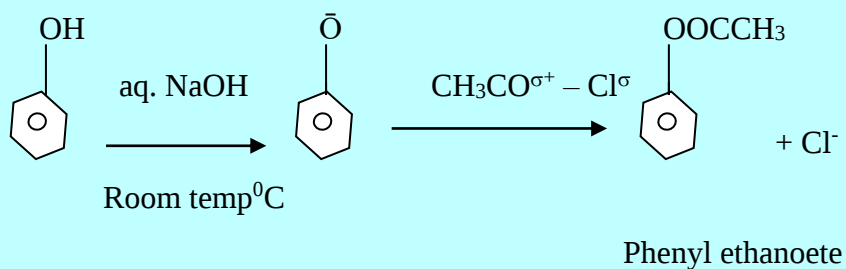
Reactions of the hydroxyl group

Reactions involving the hydroxyl group resemble those of the alcohols to a certain extent, but differ in as much as phenol exhibits much stronger acidic characteristics

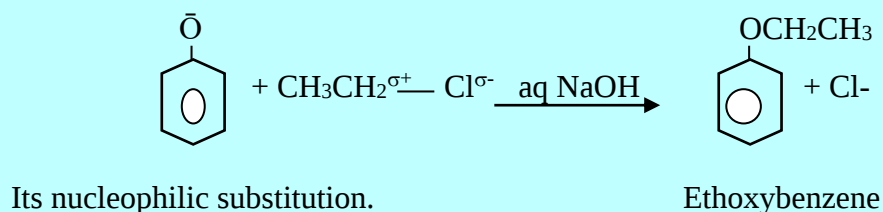


Esterification

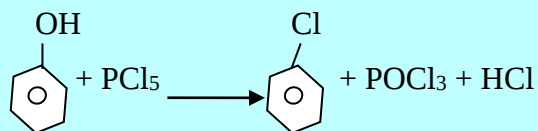
Phenol does not esterify with ethanoic acid, but in alkaline solution the nucleophilic phenoxide ion readily attacks the electrophilic acyl RCO- and aroyl, Aro-, centres of ethanoyl chloride, CH_3COCl , benzene carbonyl chloride $\text{C}_6\text{H}_5\text{COCl}$



Ether formation, Williamson's synthesis



Displacement of the hydroxyl group

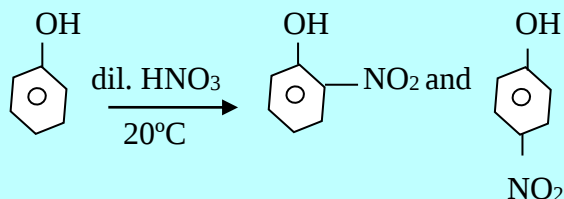


Ring Substitution

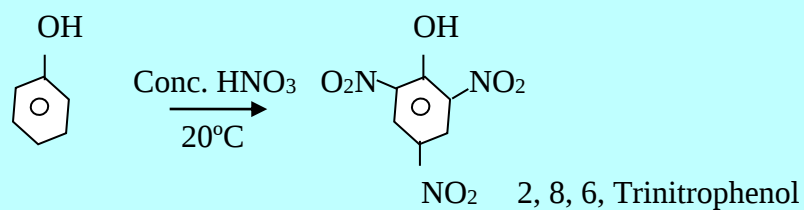
In addition to exhibiting acidic properties phenol is characterized by electrophilic substitution in the 2- and 4- positions of the aromatic ring.

Nitration

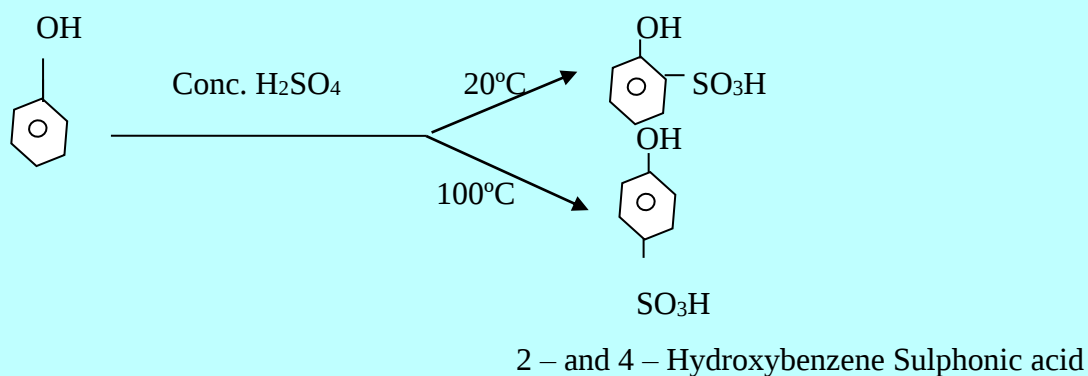
The nitration of Phenol is carried out at room temperature using dilute nitric acid.



The two isomers can be separated by steam distillation but the use of conc. nitric acid yields 2, 4, 6, - tri nitro product

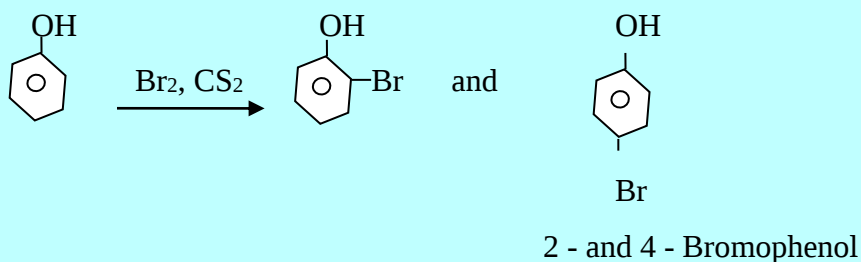


Sulphonation

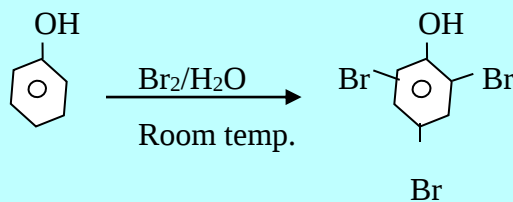


Halogenations

Halogenation of the ring occurs at room temperature and without the use of a halogen carrier catalyst, in order to facilitate the formation of the mono substituted derivatives, Bromination is carried out in a solvent of low polarity e.g. anhydrous carbon disulphide or tetra chloromethane.

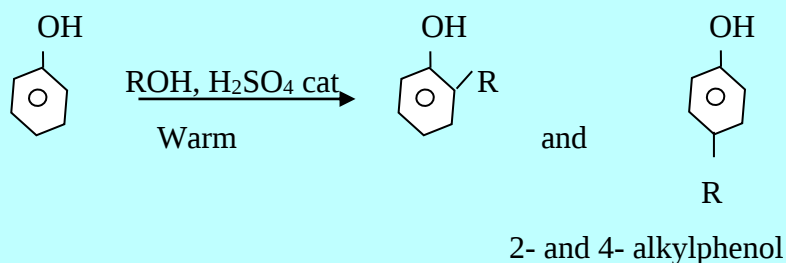


In aqueous solution, bromine forms an immediate white precipitate of 2, 4, 6 tri bromophenol, which is sometimes used as an antiseptic

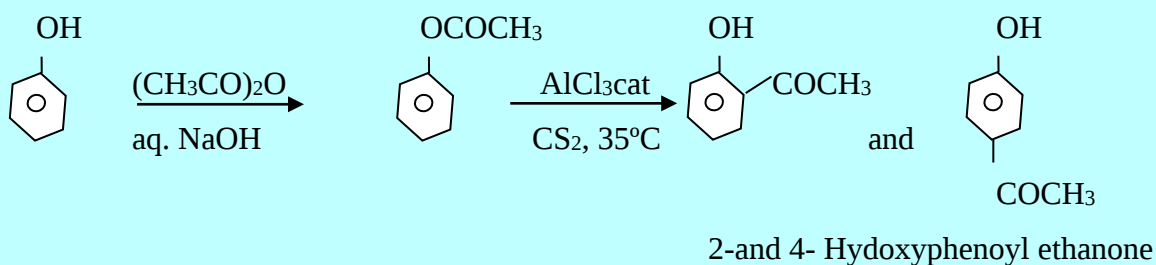


A similar reaction takes place with chlorine water yielding 2, 4, 6, trichlorophenol chlorination of phenol without the use of a solvent at temperatures between 40°C and 150°C yields a mixture of 2- and 4- chlorophenol (major product)

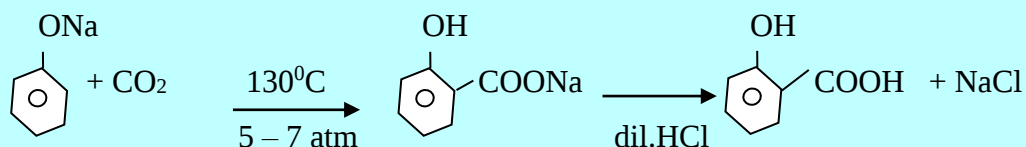
Alkylation



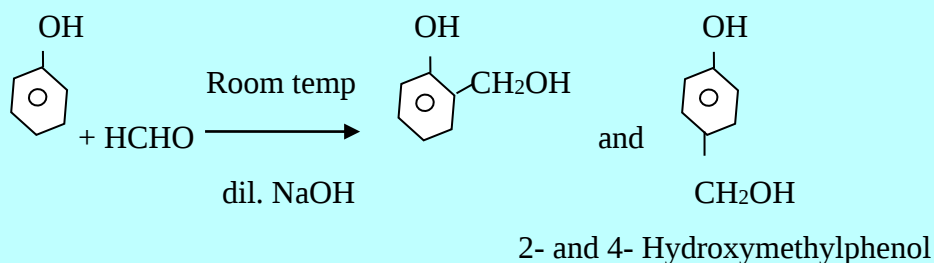
Acylation



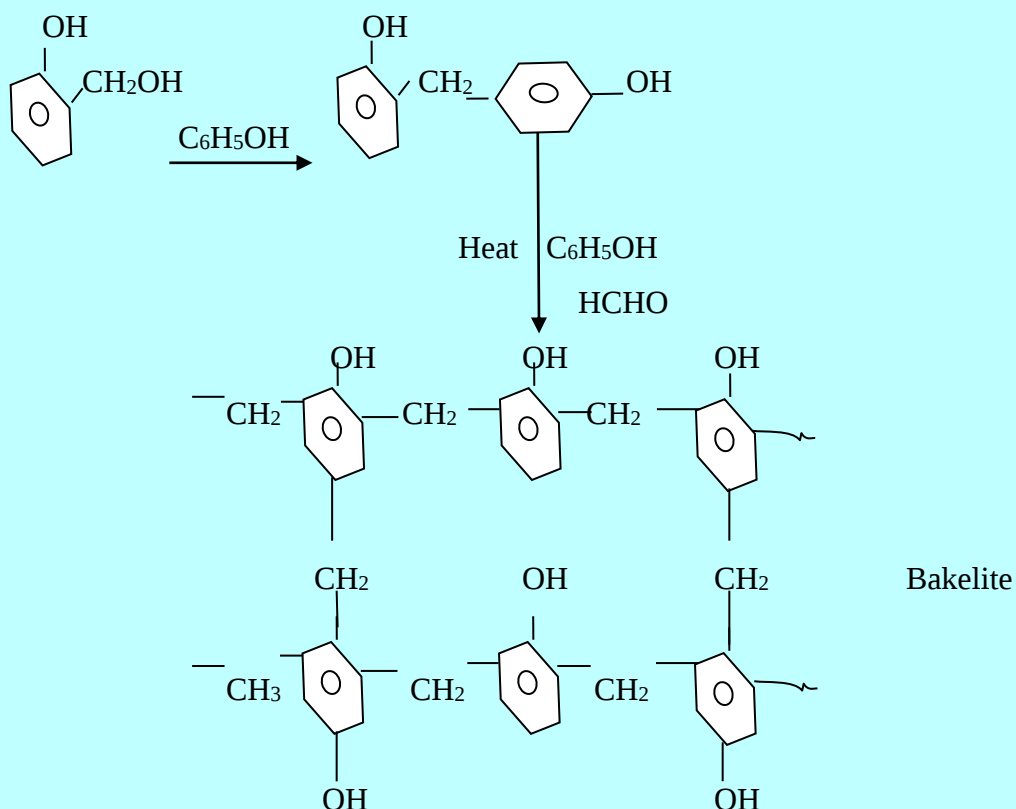
Carbonation, kolbe-schmitt reaction



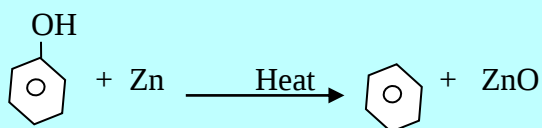
Phenol methanol



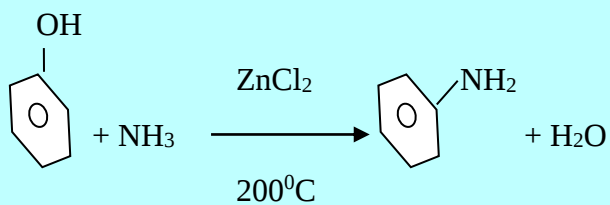
Heating with a larger quantity of methanol in an acidic medium produces rigid, three-dimensional, cross-linked polymers e.g. Bakelite



Reaction with Zinc dust



Reaction with ammonia



Differences of reactions between phenol and alcohol

- ✓ Phenol is a stronger acid than alcohol and turns litmus blue red.
- ✓ Phenol does not undergo substitution reactions with HX example HCl, PCl₃ or PCl₅ to form, aryl halides
- ✓ Phenol is not oxidized in a simple way as primary and secondary alcohol

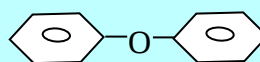
- ✓ Phenol reacts with neutral iron (III) chloride solution to give a purple violet colouration.

Similarities of reactions between phenol and alcohol

- ✓ React with Na to give bubbles of gas.
- ✓ React with carboxylic acids and acid anhydrides to give esters.

ETHERS

They possess the structure $R-O-R^1$ where R and R^1 may be aliphatic or aromatic e.g.



Ethoxyethane

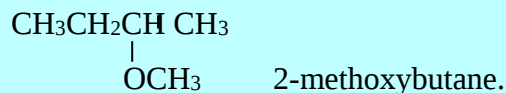
Methoxybenzene

Phenoxy benzene

Compounds in which R and R^1 are identical are described as symmetrical or simple ethers and where R and R^1 are different as unsymmetrical or mixed ethers.

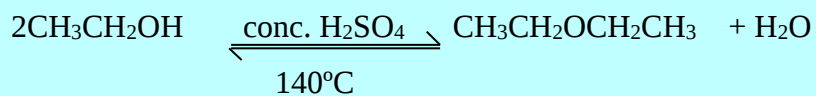
NOMENCLATURE

The IUPAC system regards them as alkoxy derivatives of alkanes or of the aryl nucleus e.g.

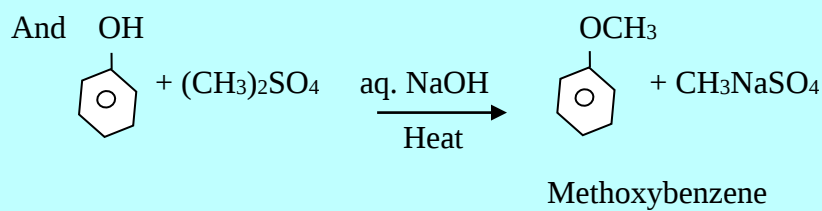
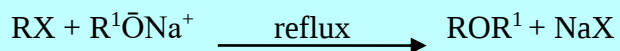


CH_3OCH_3	Methoxymethane
$CH_3OCH_2CH_3$	Methoxyethane
$CH_3CH_2OCH_2CH_3$	Ethoxyethane
$C_6H_5OCH_3$	Methoxybenzene
$C_6H_5OCH_2CH_3$	Ethoxybenzene
$C_6H_5OC_6H_5$	Phenoxybenzene

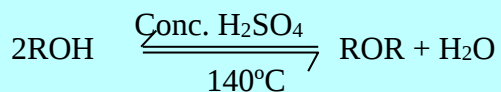
Industrial source



Synthetic preparations

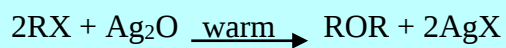


Partial Dehydration of alcohols



This method is limited only to symmetrical ethers

From Haloalkanes and dry silver (I) oxide

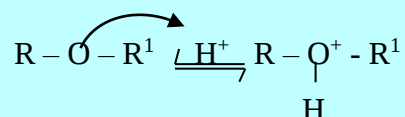


This preparation is for symmetrical ethers only.

REACTIONS

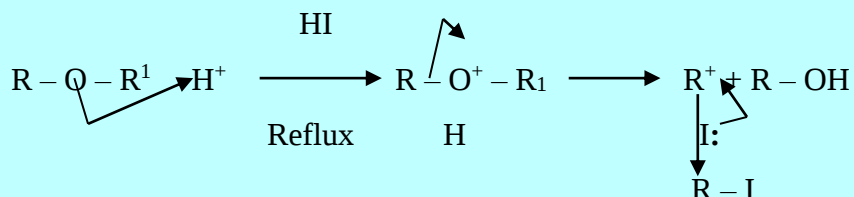
Hydrolysis

Unlike alcohols, ethers do not contain a replaceable proton and are generally unreactive compounds, not reacting with metals, strong bases or phosphorous pentahalides and not easily undergoing substitution with ionic species. However, the oxygen atom is sufficiently basic to undergo protonation in an acidic medium by the donation of a lone pair of electrons i.e.

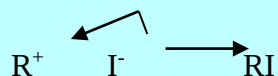
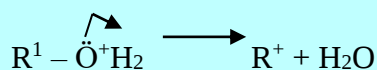
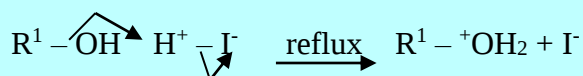


The protonated species is then susceptible to subsequent attack by a Nucleophile.

Reactions involving HX

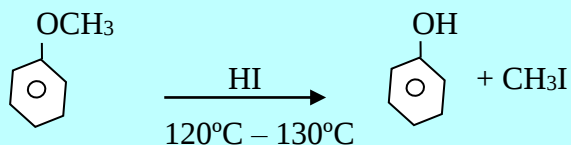


An alcohol is formed as one of the initial products but then reacts with more hydrogen iodide to yield the iodo alkane



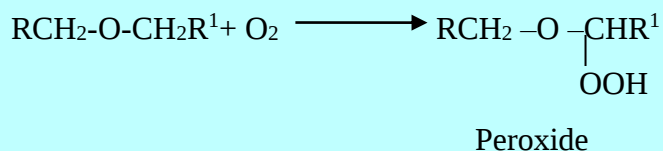
The alcohol may be isolated by employing milder conditions

e.g.



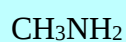
Reactivity $\text{HI} > \text{HBr} > \text{HCl}$

Autoxidation

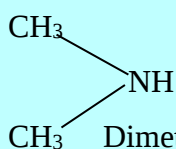


AMINES

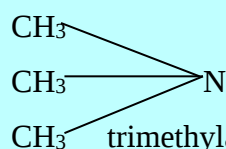
Amines are alkyl or aryl derivatives of ammonia and may be classified as primary, secondary or tertiary according to the number of alkyl or aryl groups attached to the nitrogen atom.



Methyl amine (1°)



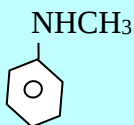
Dimethylamine (2°)



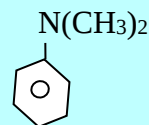
Trimethylamine (3°)



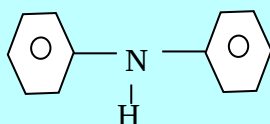
Phenyl amine (1°)



Methyl phenyl amine (2°)



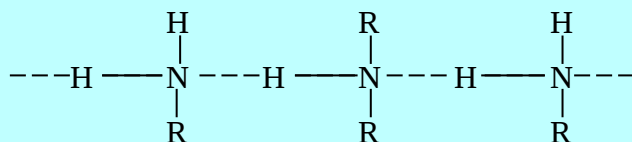
Dimethylphenylamine (3°)



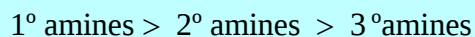
Diphenylamine (2°)

NB: Aromatic amines are compounds in which the nitrogen atom is attached directly to the aromatic ring.

They are polar compounds and their molecules, with the exception of tertiary amines, form intermolecular hydrogen bonds with each other, thus increasing their boiling points above those of less polar compounds of comparable relative molecular mass.



Hence the boiling point decreases in the order



Due to the progressive decrease in intermolecular hydrogen bonding. Volatility is enhanced by branching in the carbon chain.

NB: Amines are named as amino alkanes e.g.

CH_3NH_2 Amino methane.

$\text{CH}_3\text{NHCH}_2\text{CH}_3$ Methyl amino ethane

 NH_2 Amino benzene

Also can be named after the alkyl group attached to the nitrogen atom each name ending in the suffix 'amine' e.g.

CH_3NH_2 Methyl amine

CH_3NHCH_3 Dimethyl amine

$\text{CH}_3\text{NHCH}_2\text{CH}_3$ Methyl ethylamine

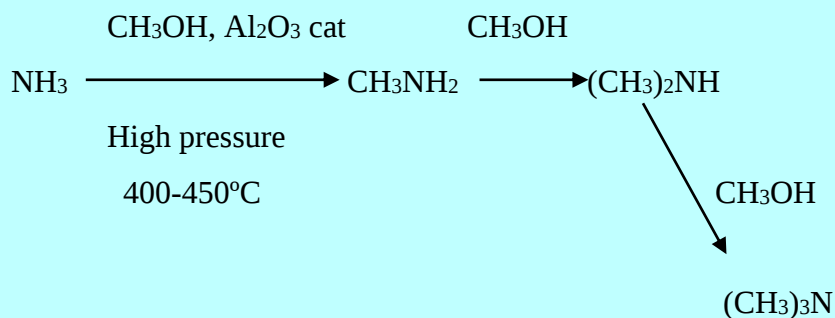
$\text{CH}_3\text{CHN}(\text{CH}_3)\text{CH}_2\text{CH}_3$ methyl diethyl amine

 NH_2 Phenyl amine (Aniline)

 CH_2NH_2 Benzyl amine

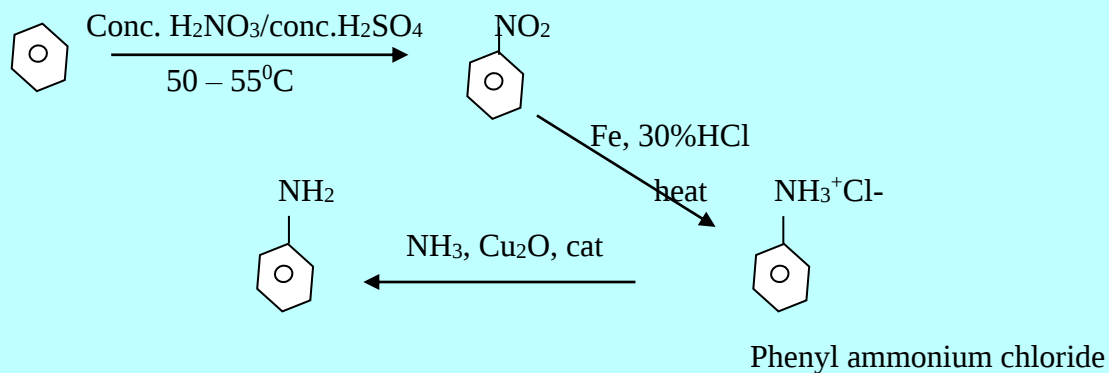
Industrial source

Methyl amines

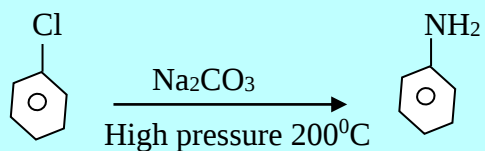


Ethyl amines are manufactured by passing ethanol, ammonia and hydrogen under pressure, over a metallic hydrogenation catalyst at $150-240^\circ\text{C}$.

Phenyl amine (ANILINE) is manufactured from nitrobenzene which is itself prepared from the abundantly available benzene i.e.



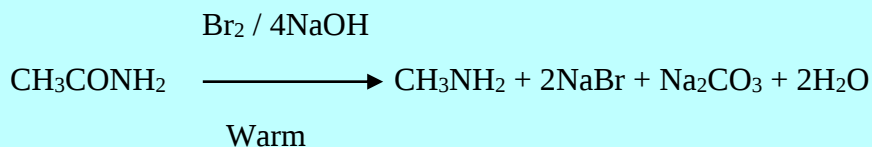
Aromatic amines are sometimes obtained by treating Chlorobenzene with ammonia at a high temperature and high pressure in the presence of a Copper (II) Oxide catalyst



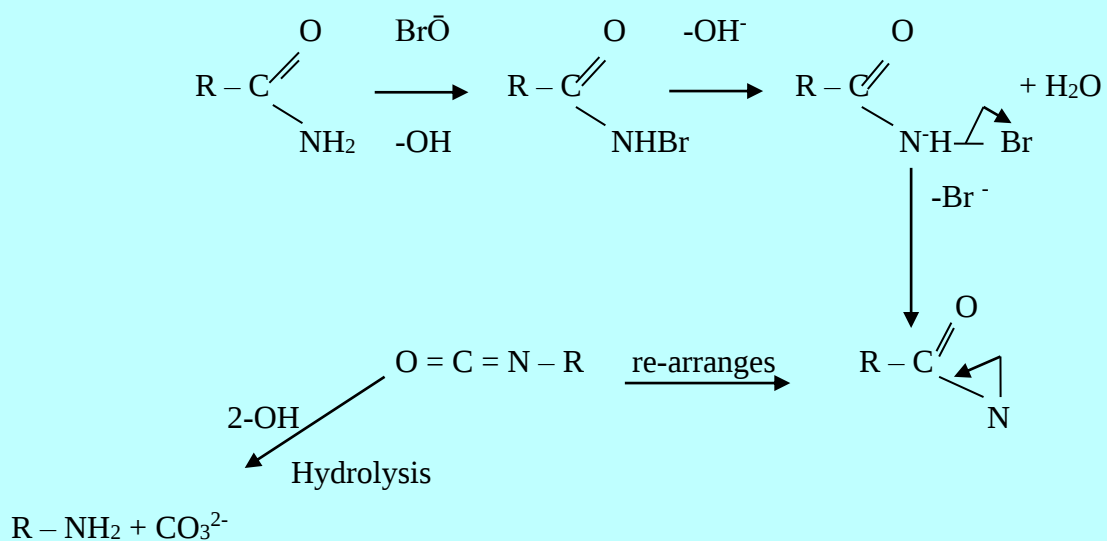
Synthetic preparations

Hofmann Degradation of amides

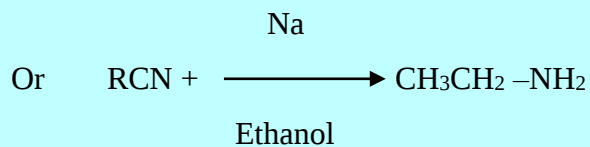
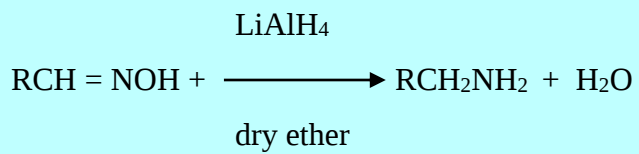
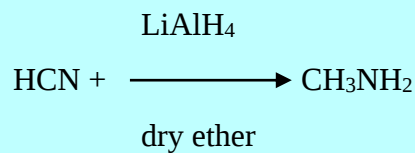
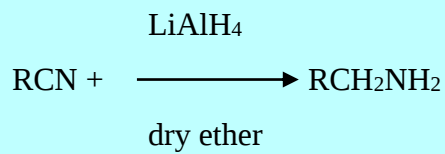
The amide is warmed with bromine and concentrated aqueous solution of alkali.



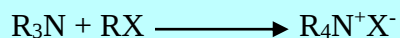
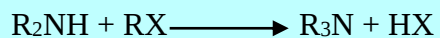
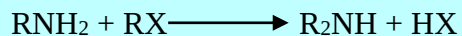
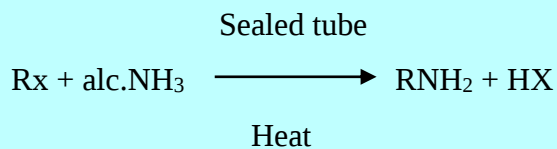
Mechanism



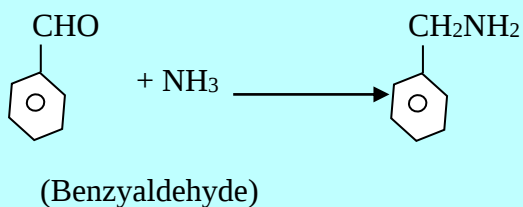
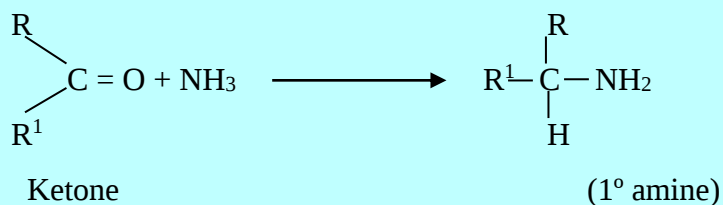
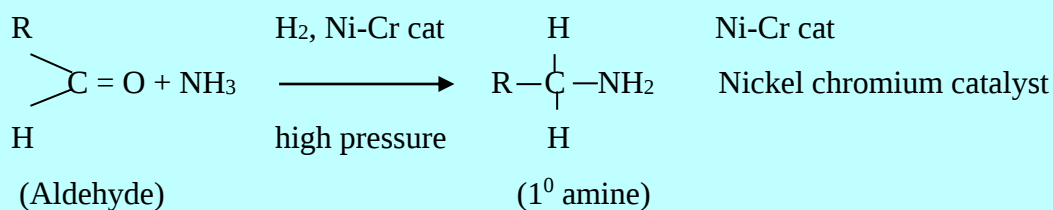
Reduction of Nitrites



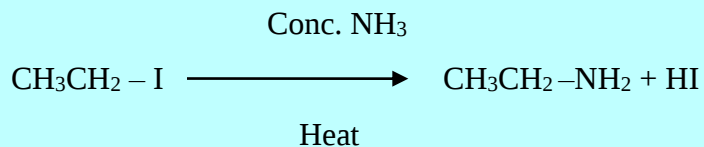
From Haloalkanes



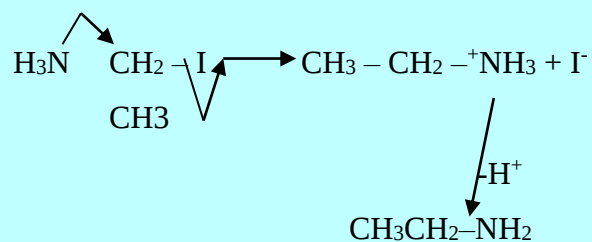
Reductive Amination of aldehyde and ketones



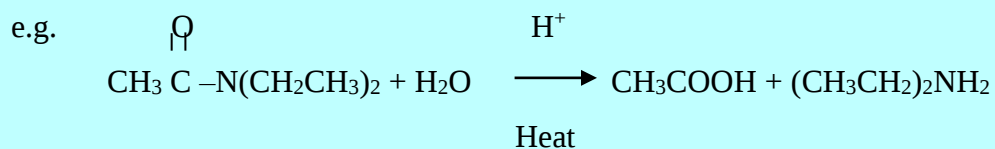
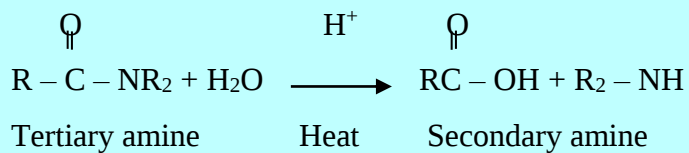
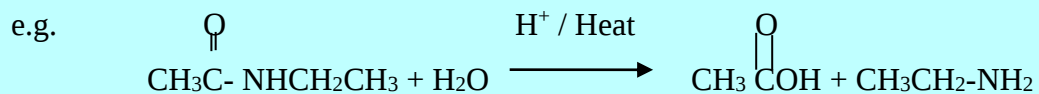
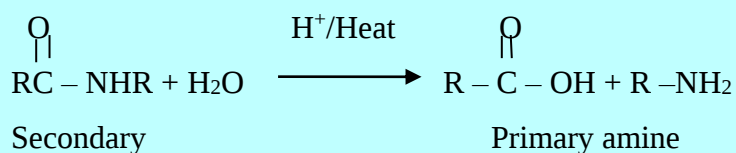
From alkyl halides



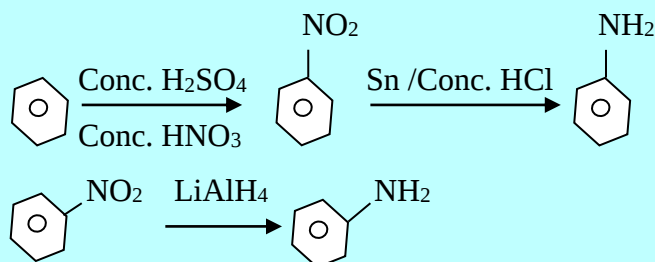
Mechanism



From secondary and tertiary amides



From nitro compounds



REACTIONS

Basic properties

- ✓ Amines dissolve in water to give weakly alkaline solution like ammonia the solution turns red litmus blue.
$$\text{R-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R}^+\text{NH}_3 + \text{OH}^-$$
- ✓ The basic characters of amines are due to the presence of the non-bonded electron pair on nitrogen atom which donate electrons. Therefore, the strength of the base will depend on the availability of the non-bonded electron pair. Hence basically of amines should be in the order

Tertiary > 2° > 1° > ammonia

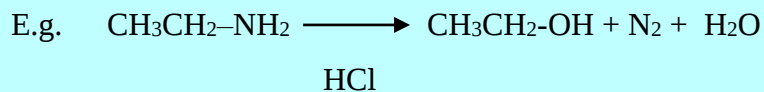
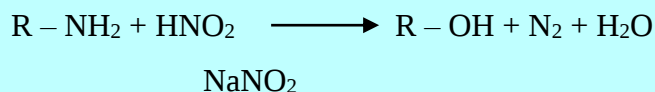
But the order is 2° > 1° > 3° > ammonia

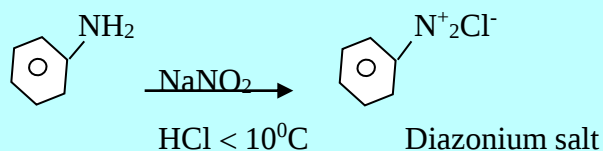
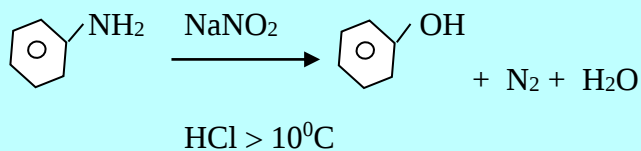
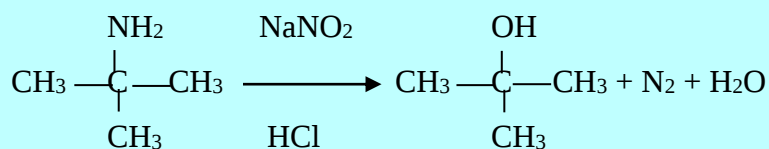
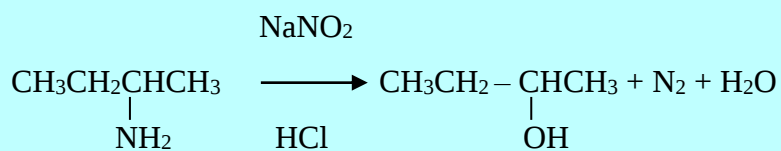
Qn. Explain why propyl amine is a stronger base than phenyl amine.

Solution

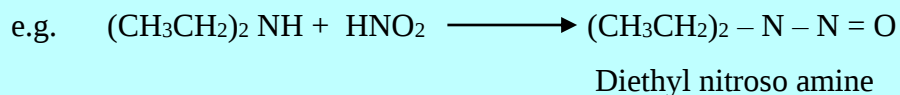
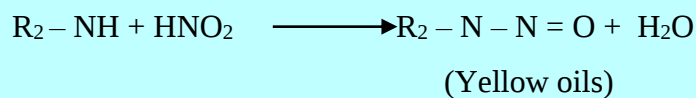
The propyl group of propyl amine releases electrons (positive inductive effect) to the nitrogen atom making the lone pair of electrons more available for proton attraction. In phenyl amine the lone pair of electrons on the nitrogen atom interacts with the delocalized electrons of the benzene ring and thus the electrons are less available for proton attraction.

Reaction with nitrous acid





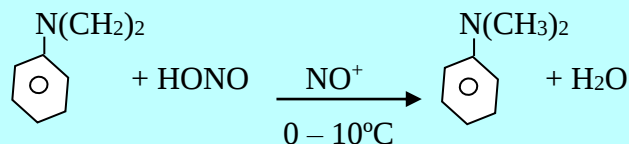
Secondary amines react with nitrous acid to give products which are yellow oils called nitroso amines



NB: Addition of phenol and Conc. H_2SO_4 to nitroso amine produces an intense blue colour when made alkaline. This is used as a test for 2° amines.

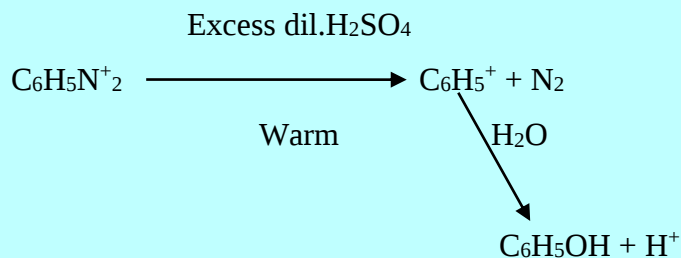


NB: The high reactivity of the ring enables Tertiary aromatic amines to undergo nitrosation in the 4-position (of phenol)



Reactions of Benzenediazonium salt

1. Nucleophilic substitution reaction, in which the diazonium group is liberated as nitrogen to form a carbocation (Carbonium ion) prior to attack by the nucleophile.

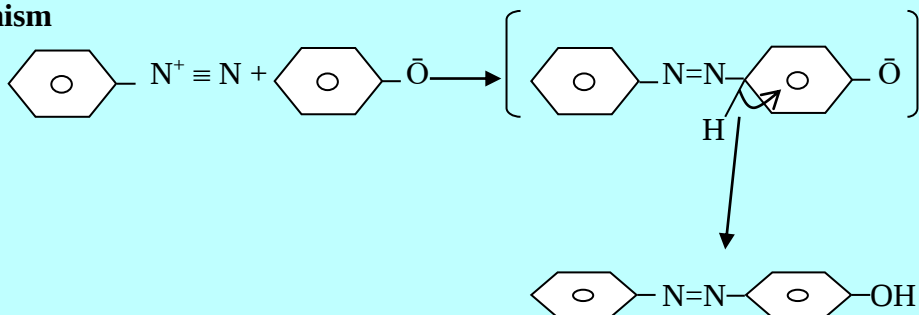


NB: The presence of excess, dilute sulphuric acid prevents coupling

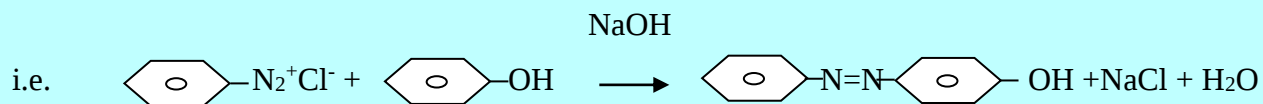
2. Coupling reaction

The coupling of a diazonium cation with a phenoxide or similar anion is of immense importance, especially in the synthesis of Azodyes

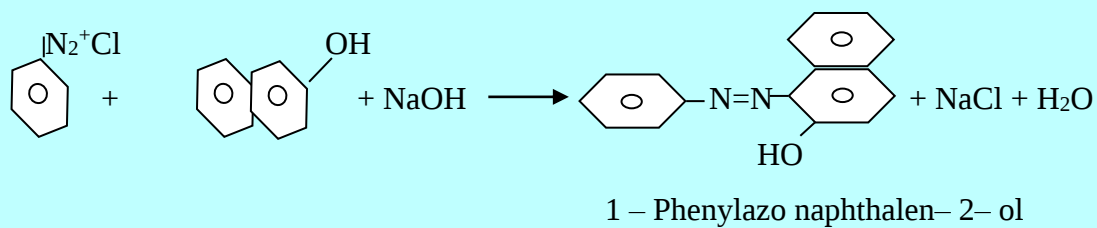
Mechanism



4 – Hydroxyphenyl azobenzene
(Bright yellow precipitate)

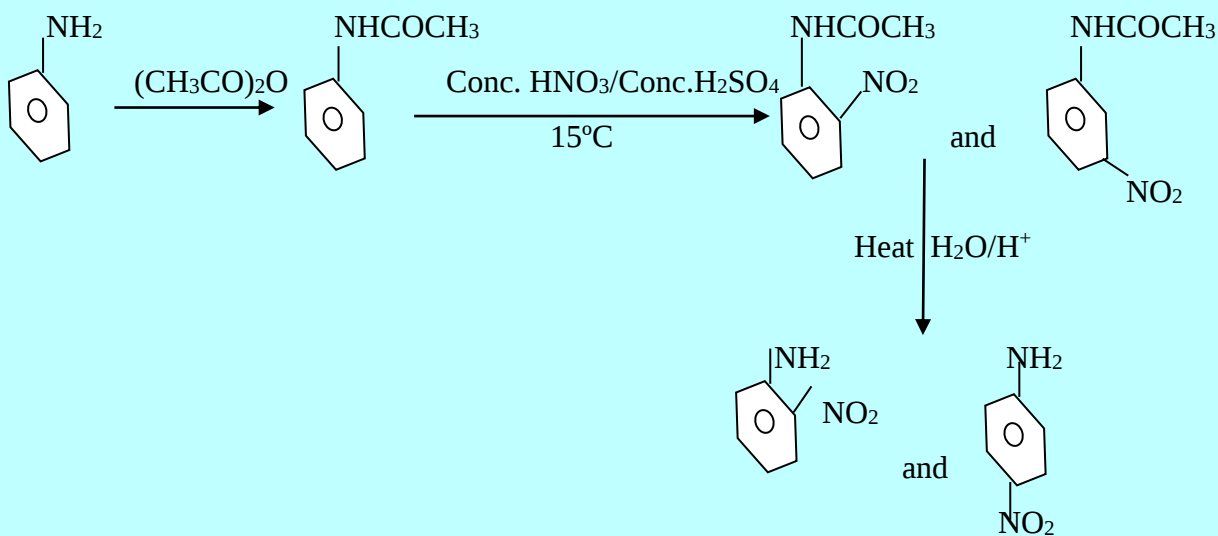


With naphthalene- 2-ol (2 naphthol), Benzenediazonium salts form bright red crystalline dyes i.e.

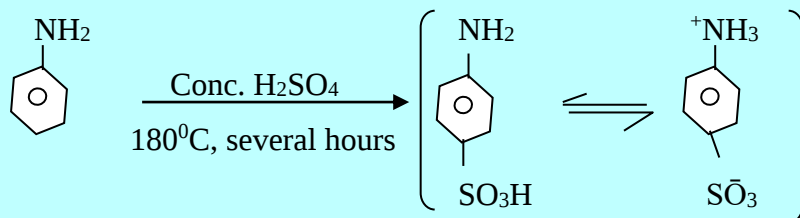


Ring substitution

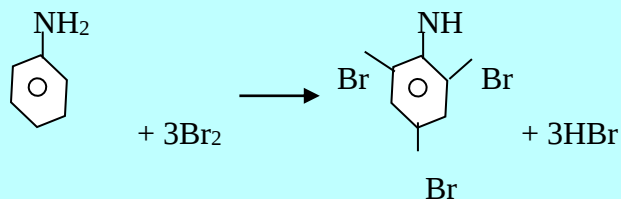
Nitration



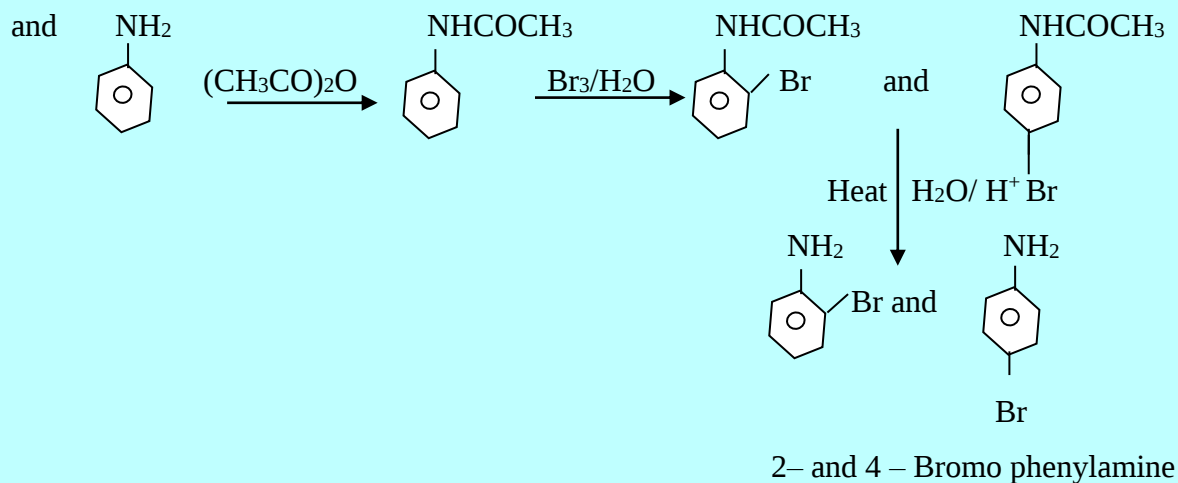
Sulphonation



Halogenation



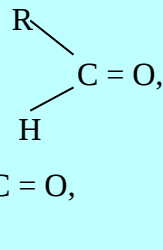
2, 4, 6-, Tribromo phenyl amine



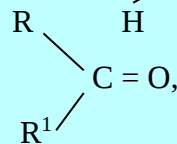
ALDEHYDES AND KETONES

Aldehydes and ketones are referred to as carbonyl compounds; they both contain the carbonyl, > C=O functional group. General formula C_nH_{2n}O

Aldehydes all possess a single hydrogen attached to the carbonyl carbon (–CHO)



Ketones always contain two hydro carbon groups



R and R¹ may be aliphatic or aromatic

NOMENCLATURE

Aldehydes

IUPAC names are obtained by dropping the ending “e” of the corresponding alkane and replacing it with suffix “al”

HCHO Methanal (form aldehyde)

CH₃CHO Ethanal

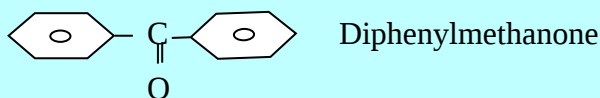
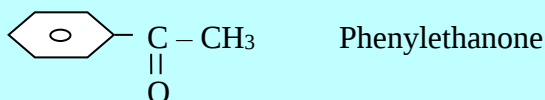
C₆H₅CH₂CHO Phenylethanal

Ketones

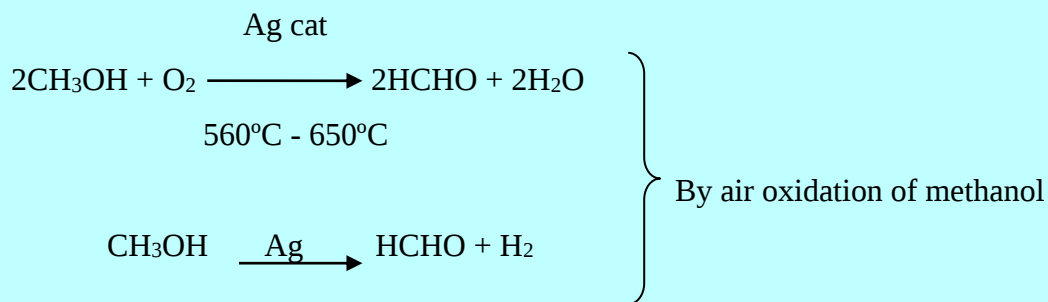
IUPAC names are derived by taking the stem of the name of the corresponding alkane and replacing the ending “e” with the suffix “one”

CH₃COCH₃ Propanone (Acetone)

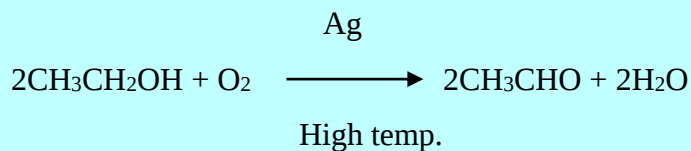
CH₃COCH₂CH₃ Ethanone

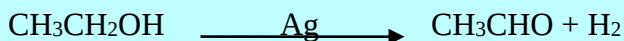


Industrial source

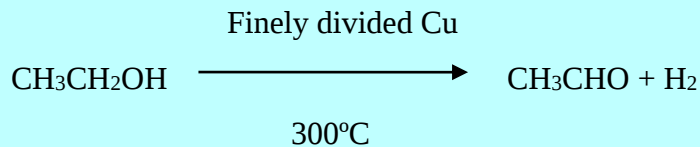


Also large quantities of ethanal are obtained by the air oxidation of ethanol

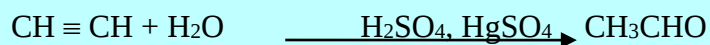




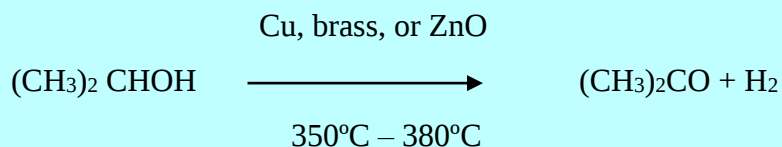
And also by direct dehydrogenation



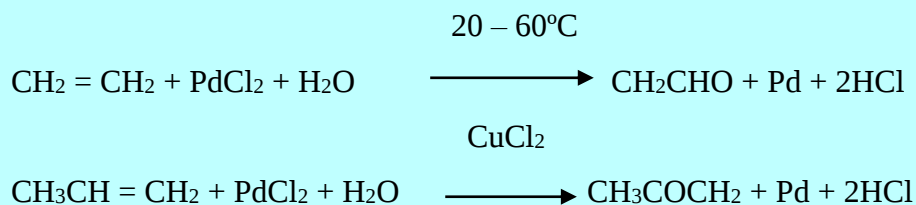
Also by acid hydrolysis of Ethyne



Propanone (acetone) is obtained by dehydrogenating propan-2-ol over a copper, brass or zinc oxide catalyst at 350°C– 380°C

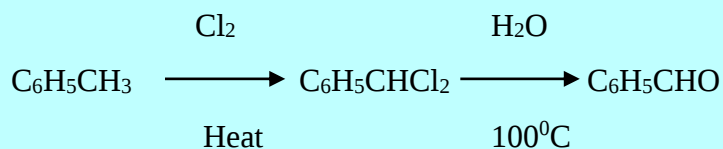


Also

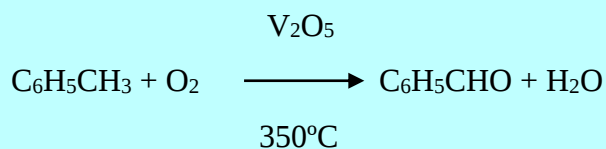


Butanone is prepared similarly, but from but-1-ene.

Benzaldehyde is manufactured by chlorinating the side chain of methyl benzene to dichloromethyl benzene and then hydrolyzing

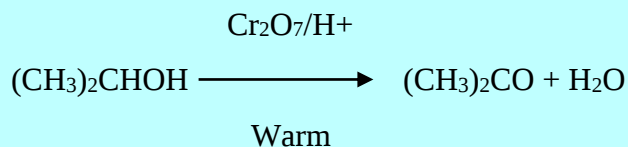
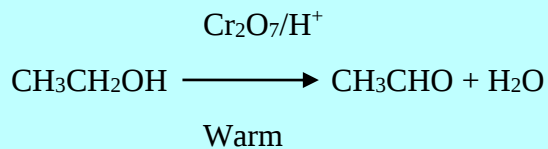


Other technique is to pass methylbenzene vapour and air over a vanadium (V) oxide catalyst heated to 350°C



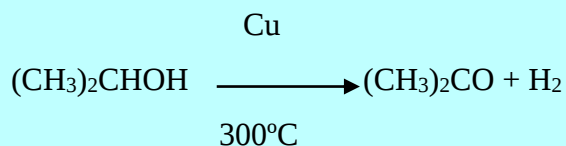
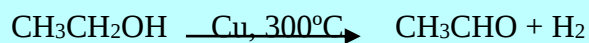
Synthesis preparations

Oxidation of alcohols



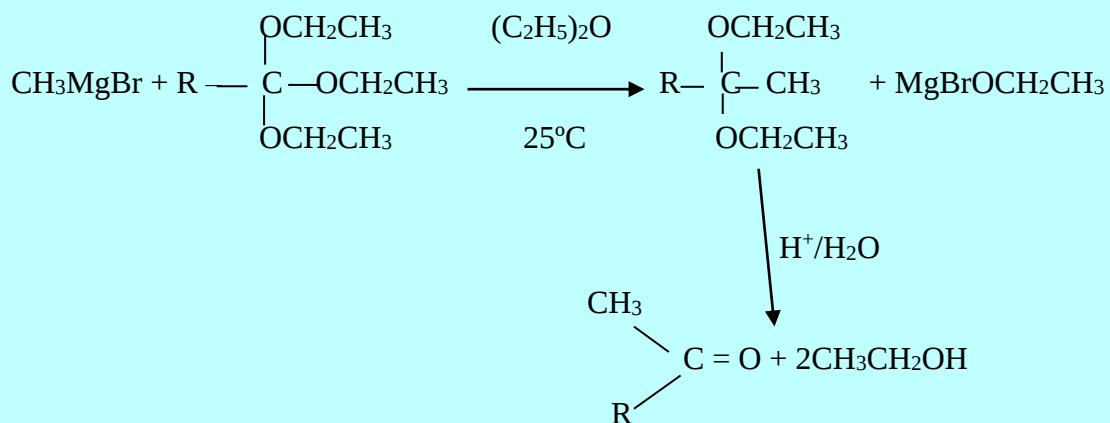
NOTE: An acidified solution of manganate (VII) can be used.

Alternatively, oxidation may be accompanied by dehydrogenation of the alcohol, using copper catalyst heated to about 300°C.

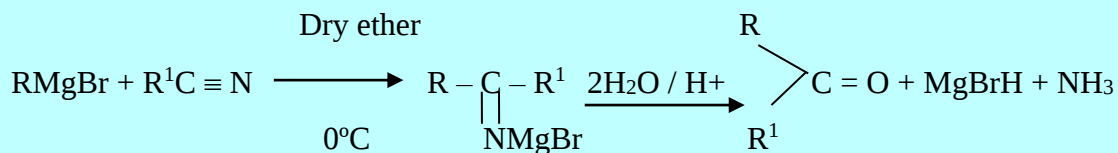


From Grignard reagents

a) Using a 1,1,1-Triethoxyalkane



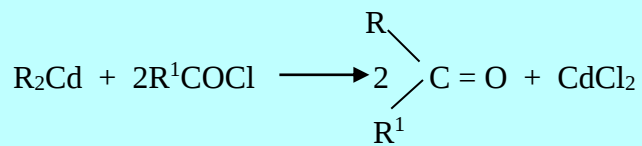
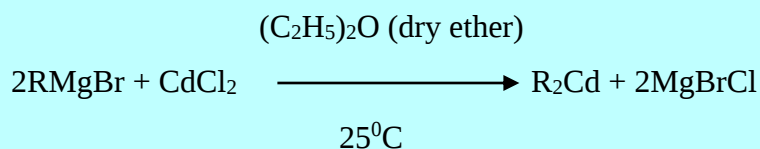
From alkyl and Aryl nitriles



(Only suitable for ketones)

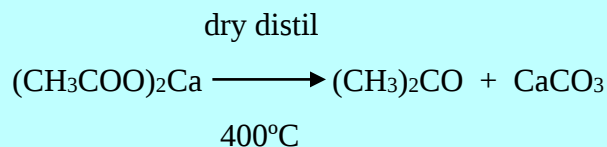
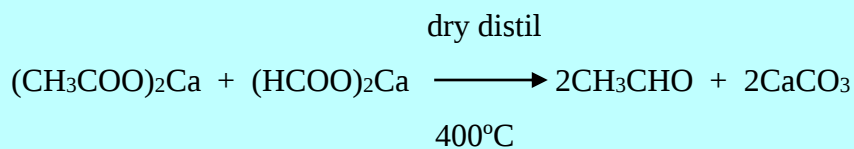
From acyl chlorides

The Grignard reagent must be converted first into the less reactive di alkyl cadmium compound; otherwise the reaction proceeds to yield the tertiary alcohol

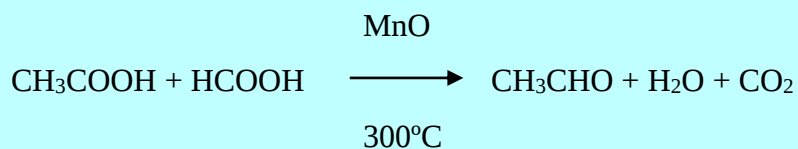


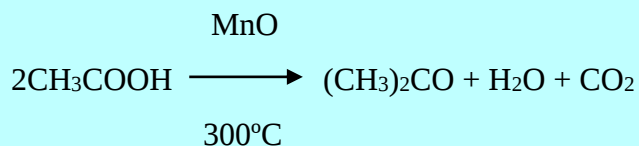
R and R¹ may be primary alkyl or aryl groups

Decarboxylation of calcium salts



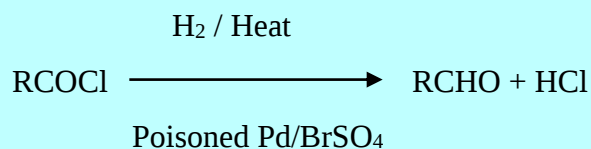
Decarboxylation of carboxylic acid





Hydrogenation of acyl chlorides using a poisoned catalyst.

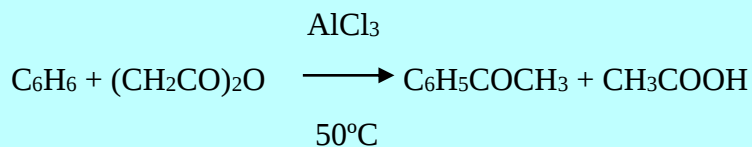
A Palladium / Barium Sulphate catalyst is deactivated by addition of a poison such as quinoline / sulphur to prevent further reduction to the alcohol



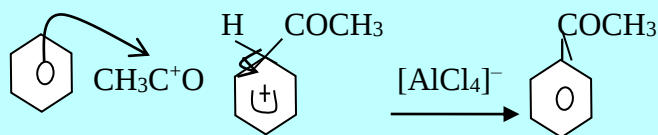
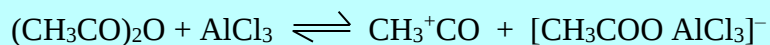
Only suitable for aldehydes

Preparation of Phenylethanone

Friedel – crafts Acylation



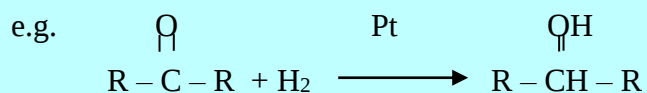
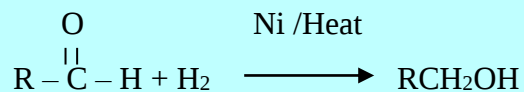
Mechanism



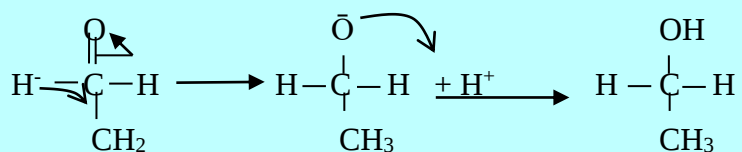
REACTIONS

Reaction with hydrogen

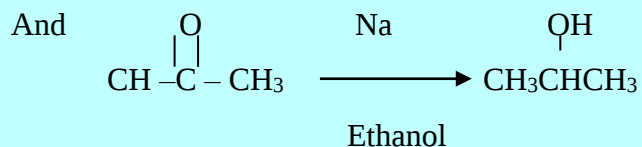
Both aldehydes and ketones are reduced by hydrogen in the presence of catalyst like Ni, Pt or Pd to 1° and 2° alcohols respectively.



The metal (Pt) aids splitting of H₂



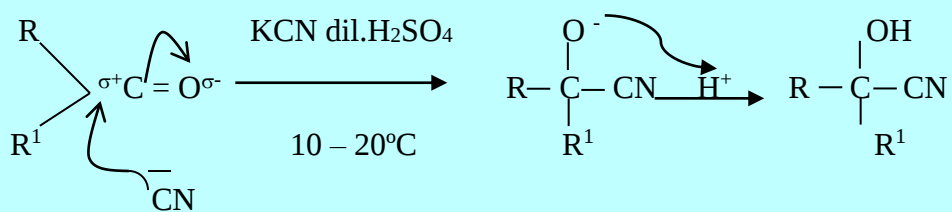
Reduction also can be affected using LiAlH₄ or NaBH₄ or Na/alcohol



Addition of hydrogen cyanide

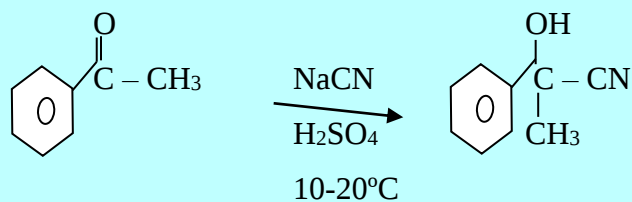
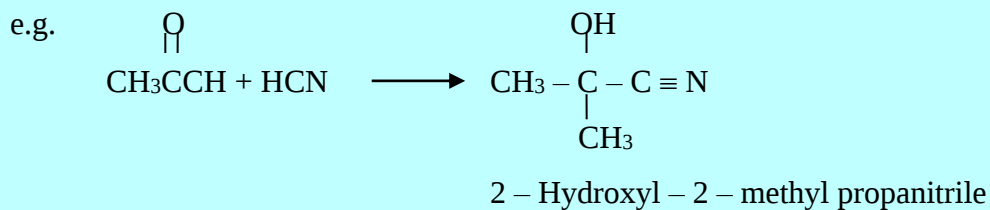
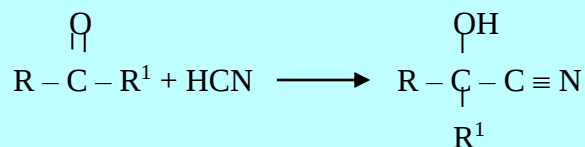
Mechanism

Aldehydes and simple ketones undergo addition of hydrogen cyanide.

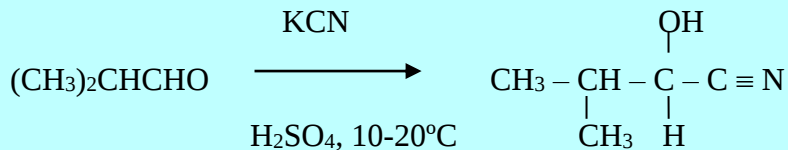
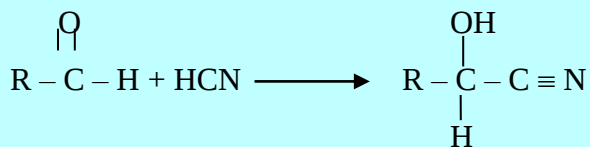


NB

Hydrogen cyanide is usually generated during the reaction by the action of dil. H_2SO_4 on alkali metal cyanide at $10-20^{\circ}\text{C}$

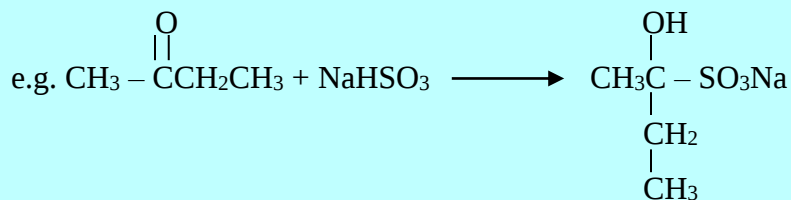
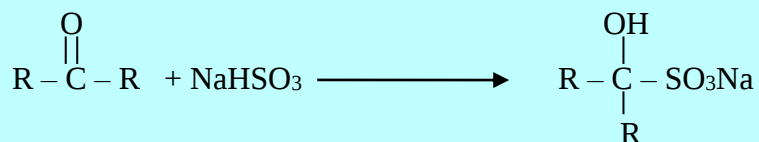
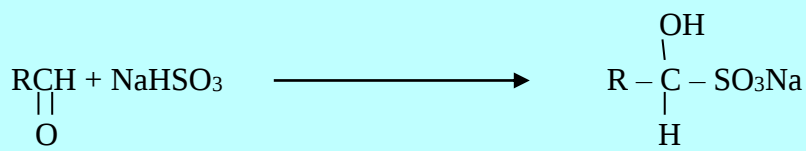
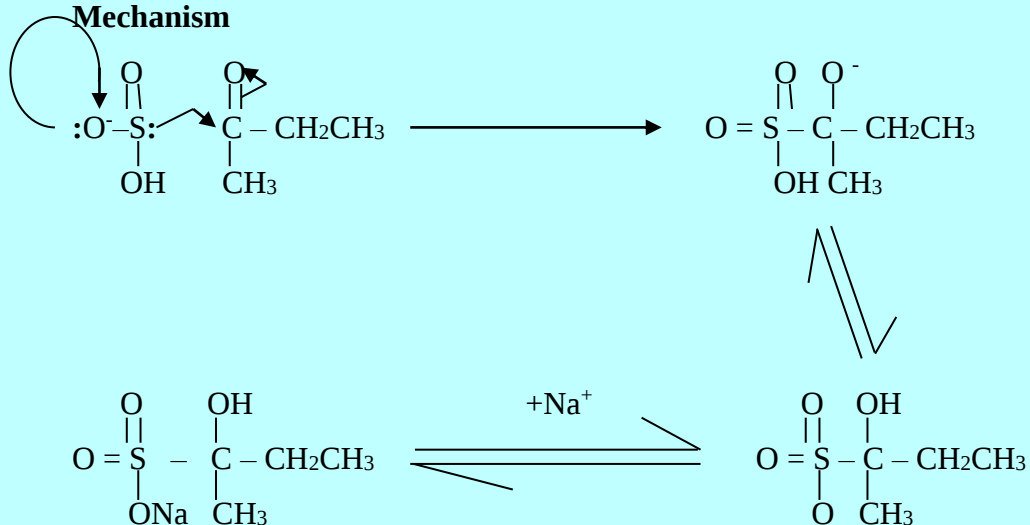


2-hydroxy-2-phenyl propanitrile



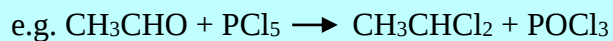
Reaction with sodium hydrogen sulphite (Sodium Bisulphite)

Mechanism

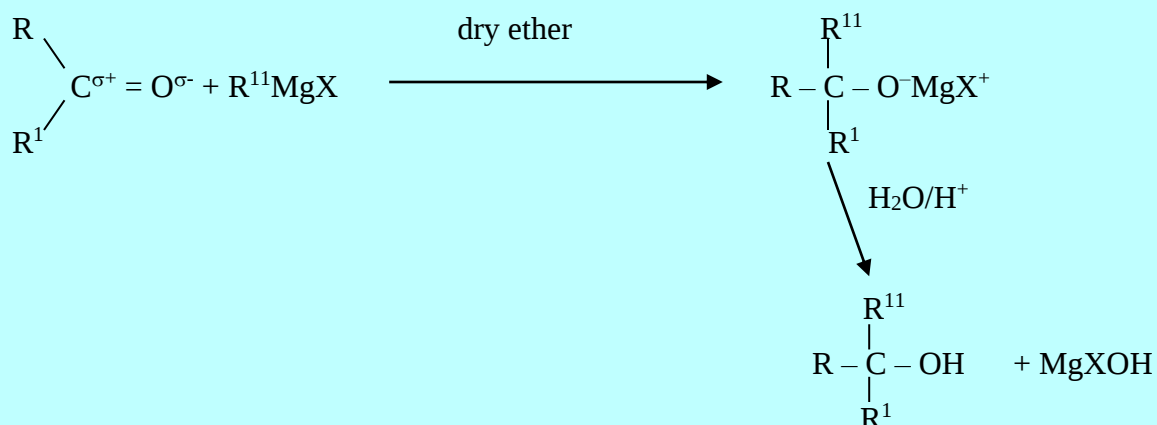


Reaction with phosphorous pentachloride

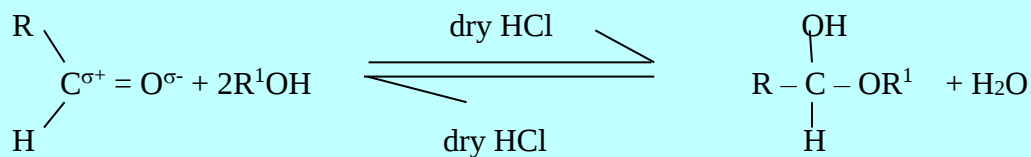
Both aldehyde and ketones react with PCl_5 to give gem dihalides



Addition of Grignard reagent

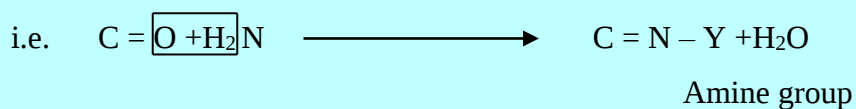
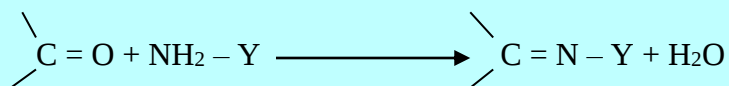


Addition of alcohol

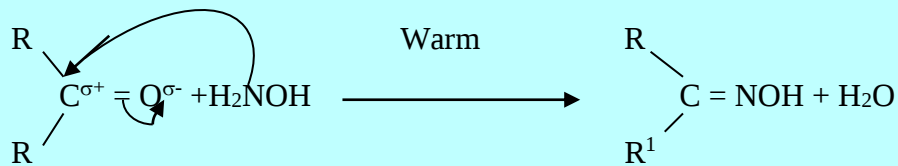


Condensation

Both Aldehydes and ketones react with compounds containing -NH_2 with loss of water molecule.



a) With hydroxylamine NH_2OH

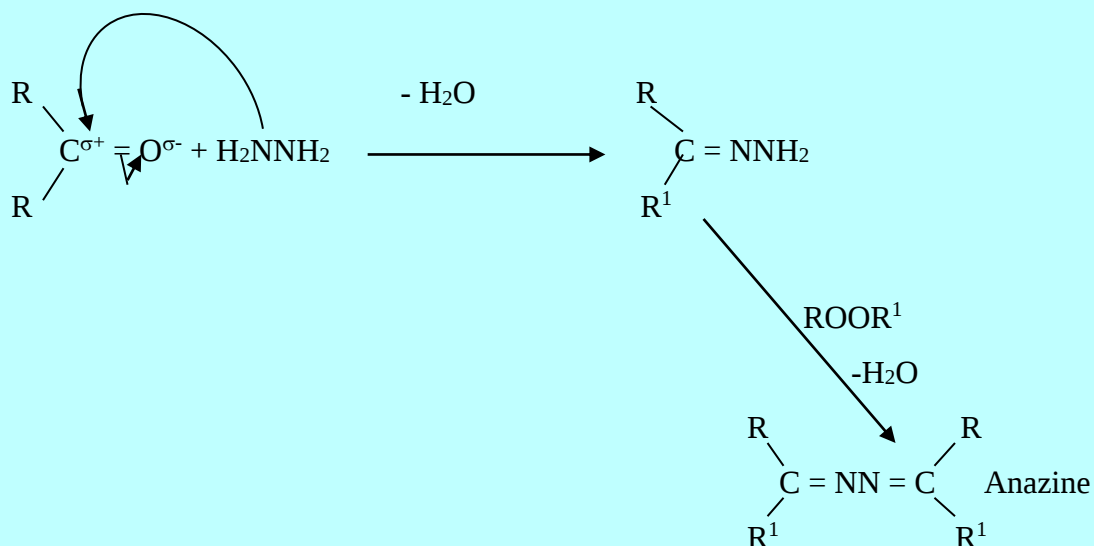


An oxime

Ethanal and propanone yield ethanal oxime and propanone oxime respectively



With hydrazine NH_2NH_2

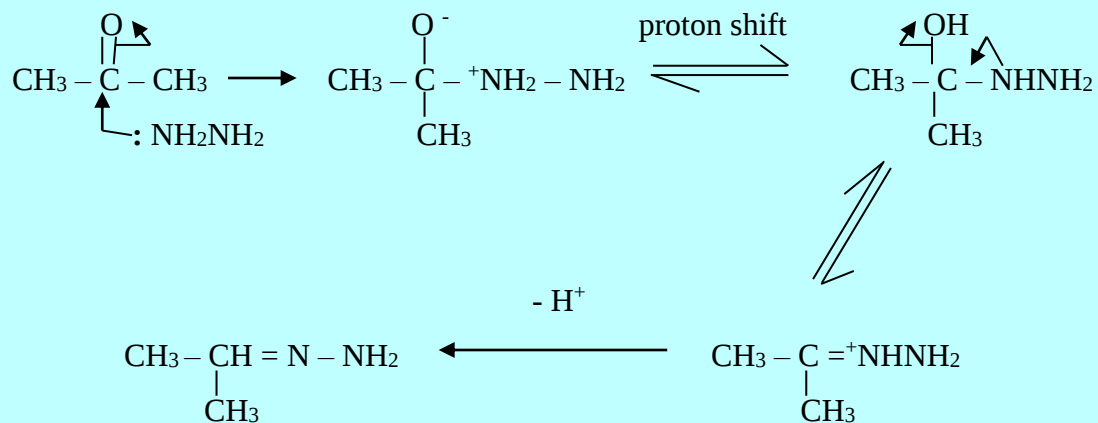


Both hydrazones and azines are crystalline solids

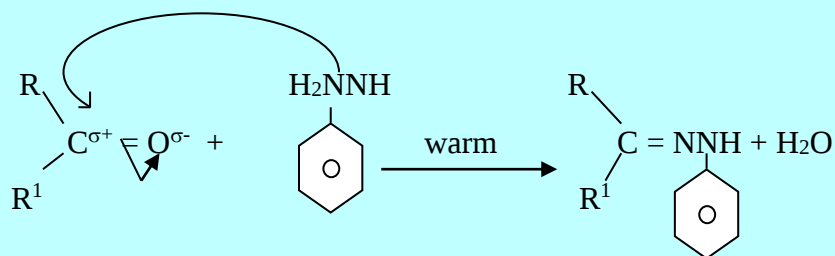
e.g.

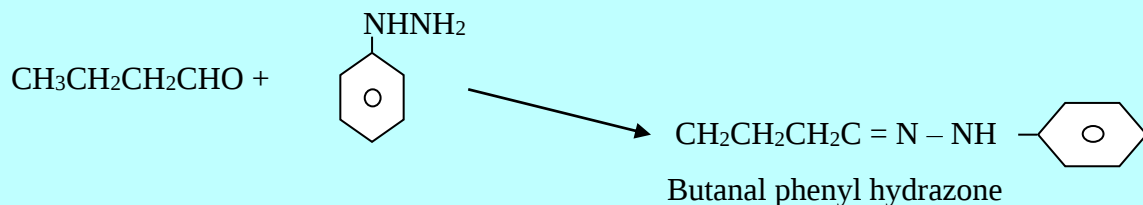
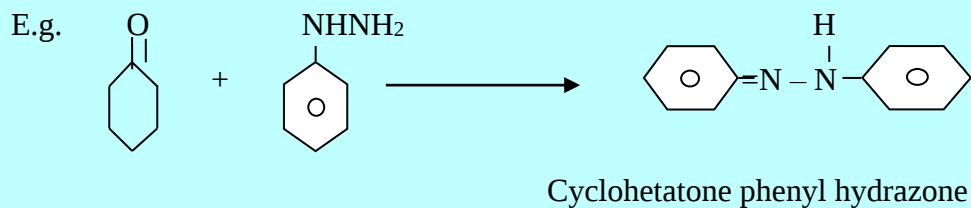


Mechanism

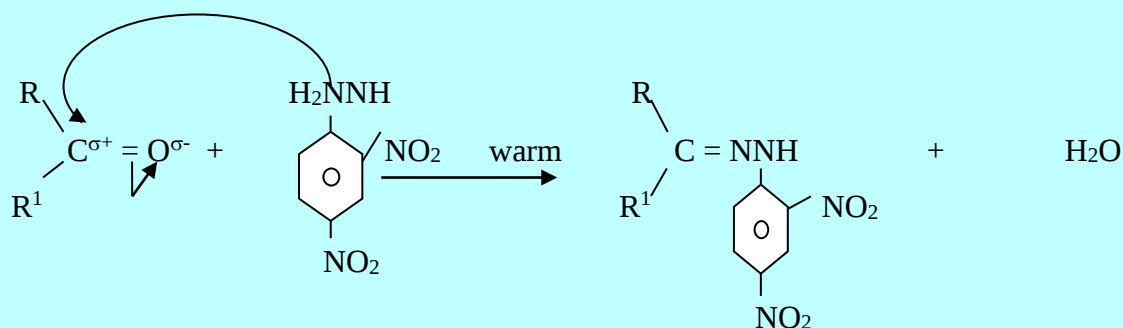


With phenyl hydrazine $\text{C}_6\text{H}_5\text{NHNH}_2$





With 2, 4-dinitrophenyl hydrazine $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{NHNH}_2$

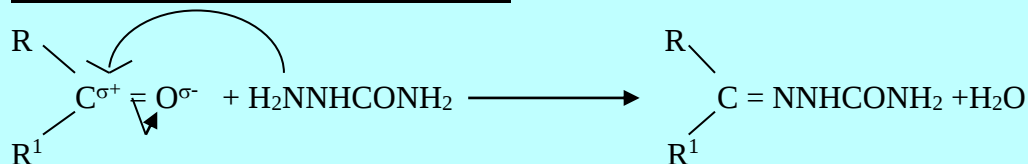


NOTE

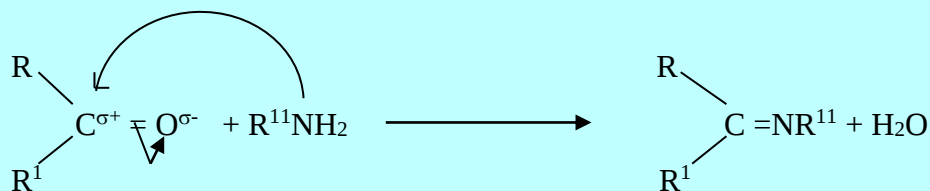
2-4-dinitrophenyl hydrazine is utilized in Brady's reagent for the detection of a carbonyl functional group.

It is moistened with methanol and then shaken with a few drops of concentrated sulphuric acid in order to convert it into the yellow sulphate. On adding the carbonyl compound, the 2-4 dinitro phenyl hydrazone crystallizes out fairly rapidly although the reaction occurs rather more slowly with ketones than with aldehydes.

With Semicarbazide $\text{NH}_2\text{NHCONH}_2$

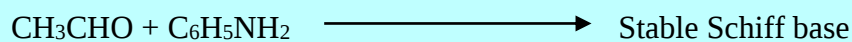


With primary Amines (formation of Schiff Bases)

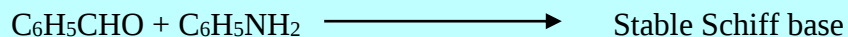


NB

Unless the carbon-nitrogen double bond is stabilized by conjugation with an aromatic nucleus, these bases tend to be unstable in aqueous solution and revert back into the starting reagents i.e. in a non-aqueous medium they polymerize i.e. stable Schiff bases can be formed between the aliphatic carbonyl compound and phenyl amine i.e.

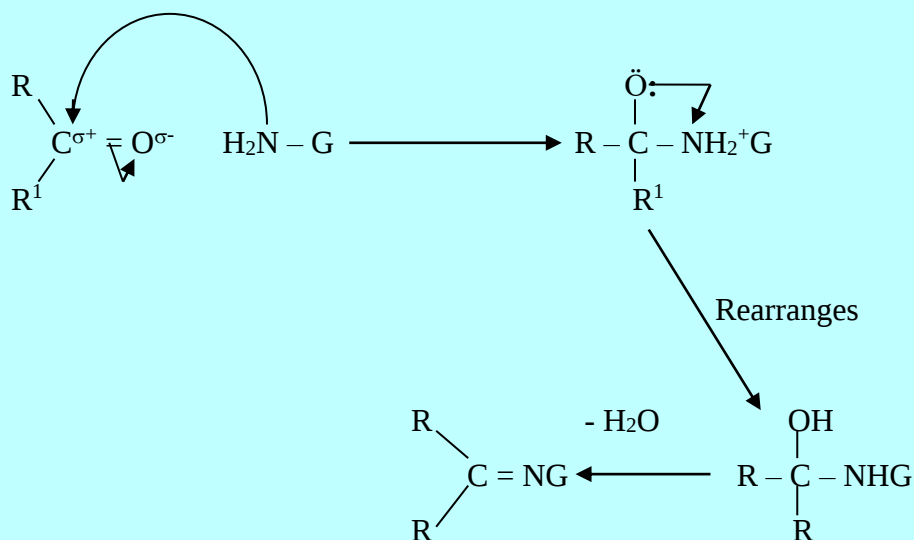


Benzene carbaldehyde and phenyl amine and so on



Mechanism for condensation reactions

Consider an amino derivative $NH_2 - G$, where G represents the attached group.



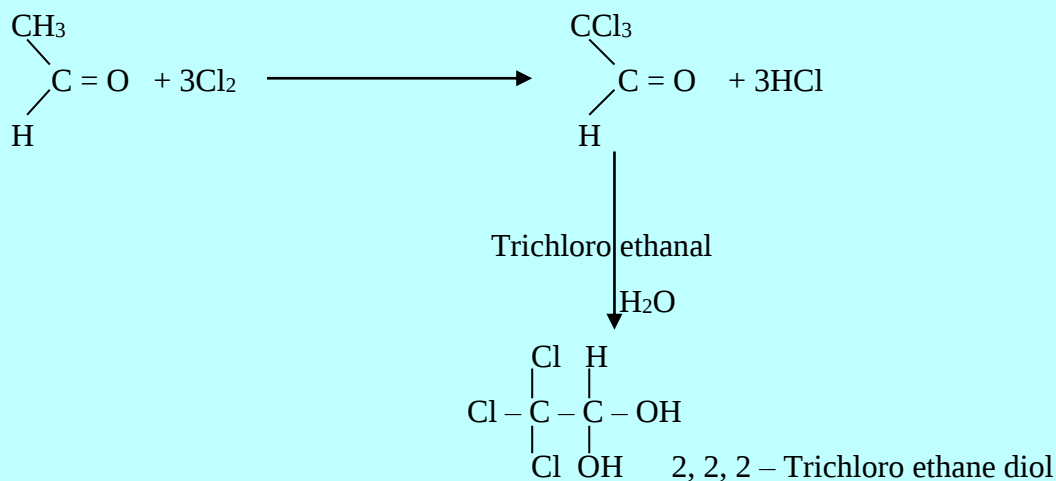
Chlorination

With phosphorus pentachloride

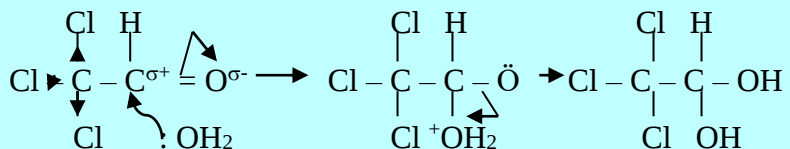
With anhydrous conditions, aliphatic and simple aromatic carbonyl compounds undergo replacement of the oxygen atom by two chlorines to yield the dichloro hydrocarbon



Lower dichloro alkanes are colourless liquids



Mechanism

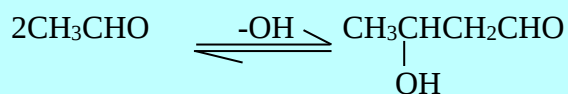


NB

Electron withdrawing inductive effects of the three chlorine atoms carbonyl carbon is more positive

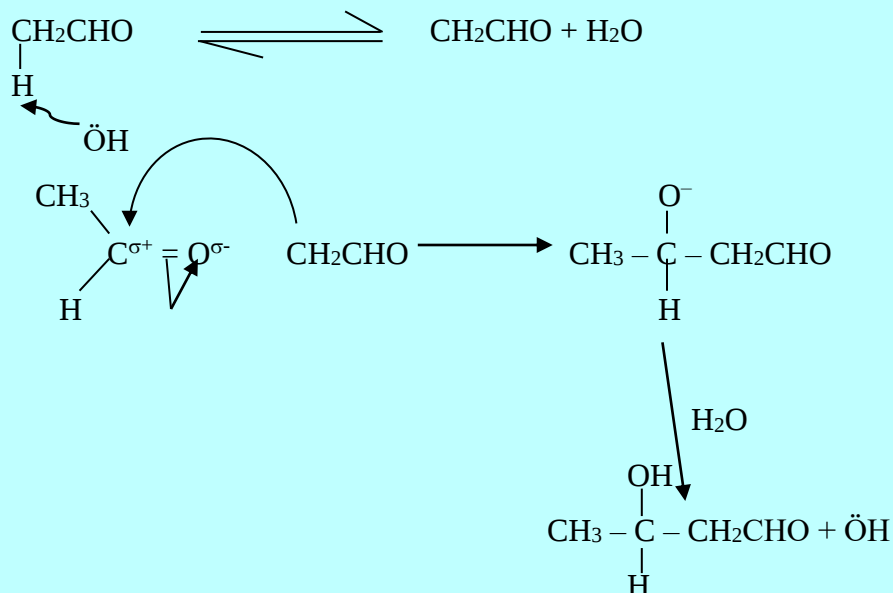
Under similar conditions, benzene carbaldehyde (benzaldehyde) is converted into a colourless liquid, benzene carbonyl (benzoyl) chloride $\text{C}_6\text{H}_5\text{COCl}$

Aldol condensation



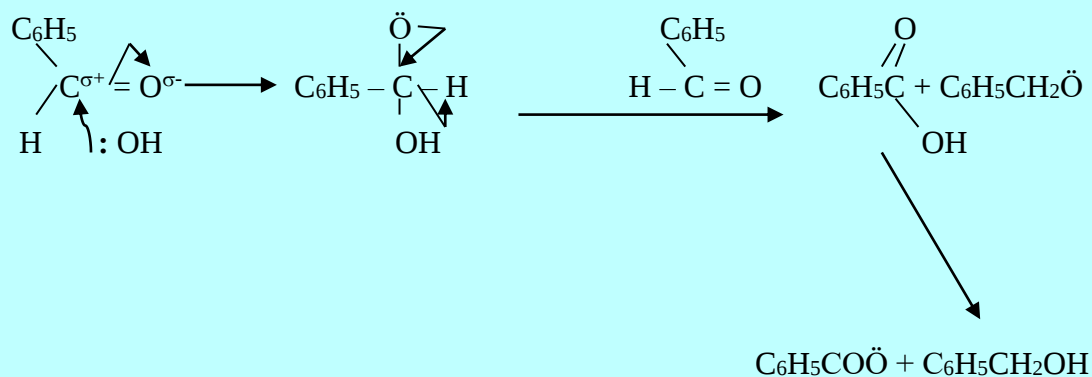
If the concentration of hydroxide ions is too large, the reaction continues to give eventually a polymeric resin.

Mechanism

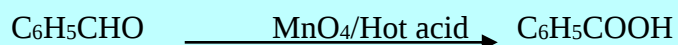
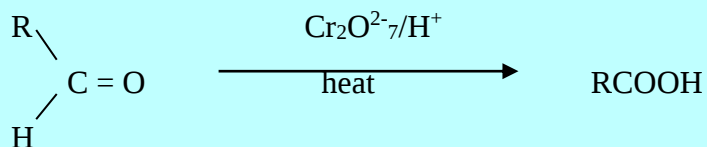


Cannizzaro reaction

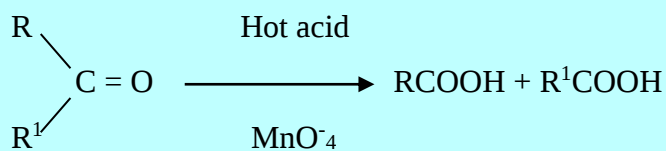
This reaction is limited to aromatic and aliphatic compounds in which the carbonyl carbon is attached to a tertiary alkyl carbon atom



Oxidation

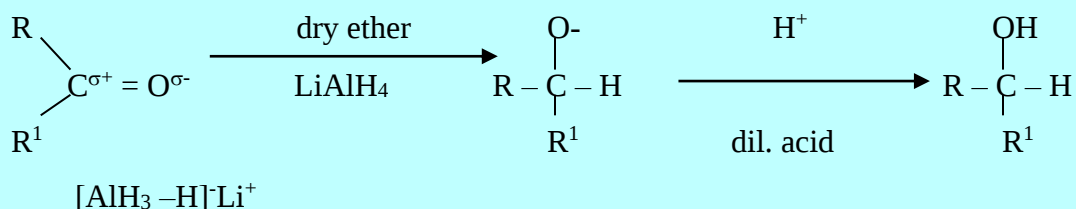


And



Reduction

By Lithium Tetra hydridoaluminate (III)



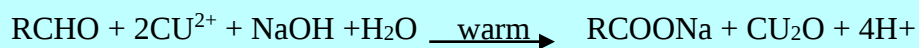
Distinguishing between Aldehydes and Ketones

Fehling's Test

A solution of copper (I) sulphate is added to a solution of Rochelle salt, Potassium sodium 2,3-dihydroxylabutanedioate, in excess sodium hydroxide. A deep blue coloration is obtained on mixing the solution owing to the formation of complex copper (II) ions

Observation

Aliphatic aldehyde reduces the Copper (II) to the reddish-brown copper(I) oxide which is precipitated



Ketones and aromatic aldehydes give no reaction.

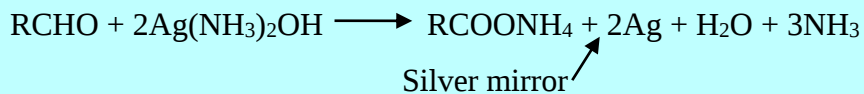
Silver mirror test

The reagent consists of a solution of Silver (I) nitrate in excess ammonia solution.

Observations

Aldehydes reduce the Ag^+ to silver which is precipitated and forms a mirror effect in the bottom part of the test-tube

Safety: residues from this reaction should never be left in the tube as explosive silver (I) oxide may form



NB

Ethanal reacts almost immediately but with benzene carboaldehyde (benzaldehyde) the reaction mixture requires warming

Ketones give no reaction.

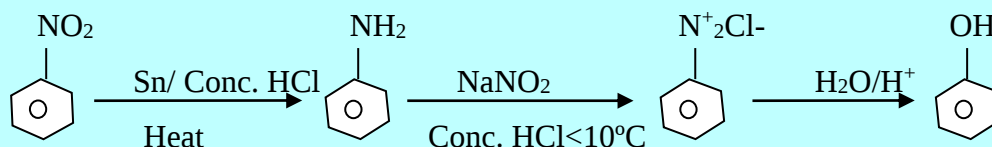
Also, Tollen's reagent (Ammonia solution is added drop wise to a solution of silver (I) nitrate in dilute aqueous sodium hydroxide until the brown precipitate just dissolves). Addition of the aldehyde brings about the formation of a silver mirror and no reaction with ketones.

NB

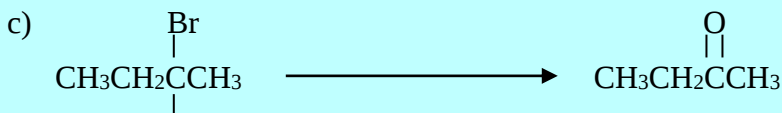
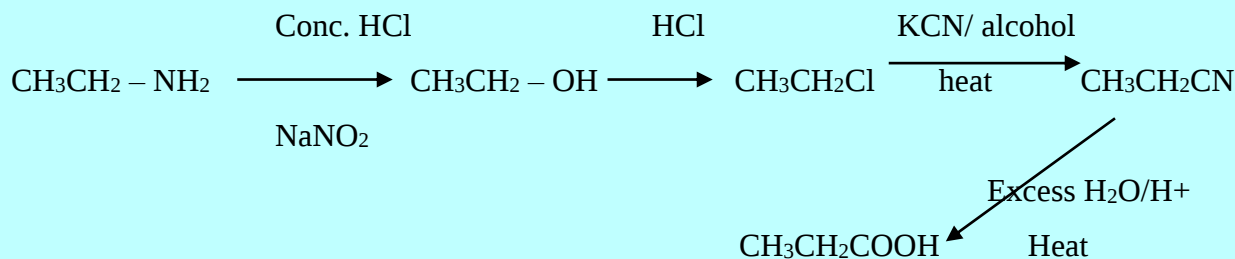
Ammoniacal silver (I) nitrate and Tollen's reagent are both, Unstable and should always be freshly prepared.

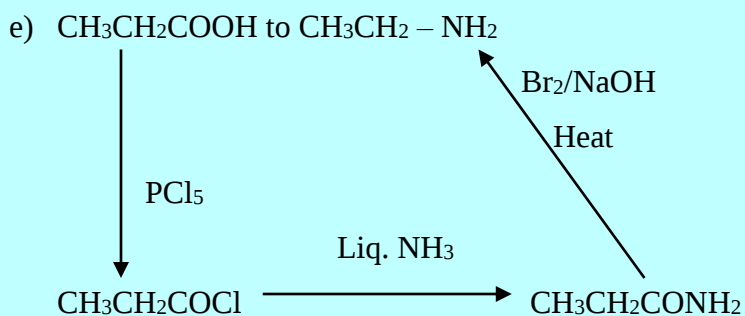
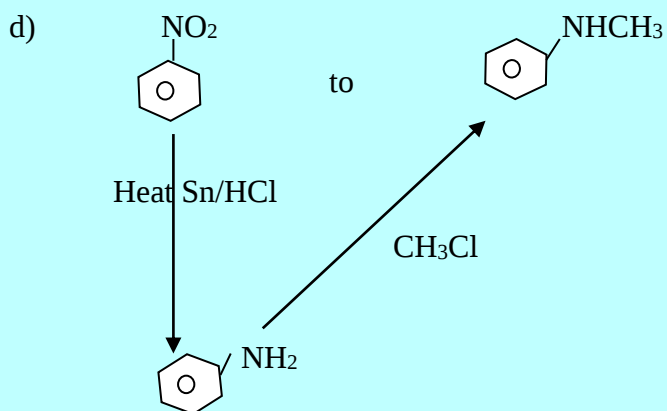
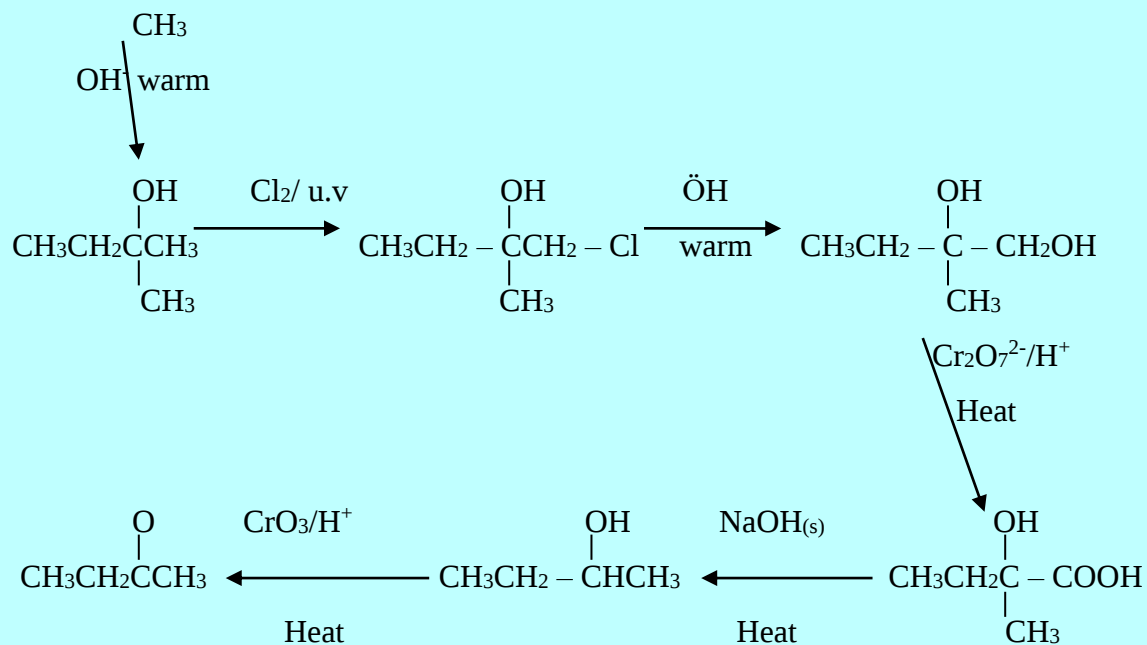
Qn: Show how the following compounds can be synthesized

a) Phenol from nitrobenzene

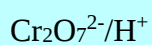


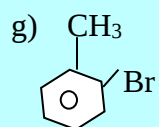
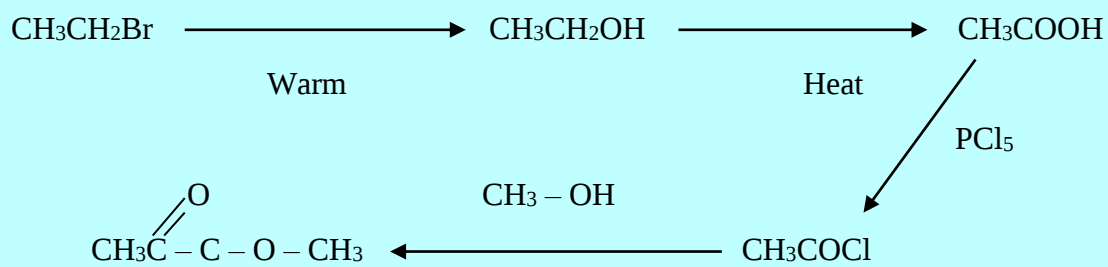
b) Propanoic acid from amino ethane.



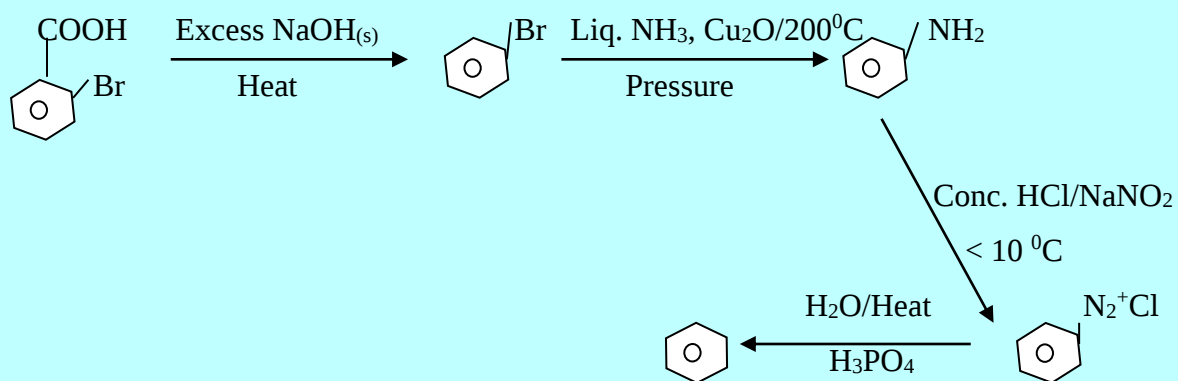


f) Methyl ethanoate from bromo ethane





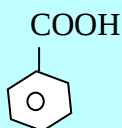
to



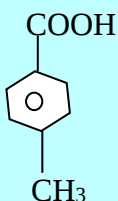
CARBOXYLIC ACIDS

Saturated aliphatic mono carboxylic acids form a homologous series of general molecular formula $C_nH_{2n+1}COOH$ the functional group is $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{OH} \end{array}$

Compounds classified as aromatic carboxylic acids all contain the carboxyl group attached directly to an aromatic nucleus,



Benzoic acid
(Benzoic acid)



4 – methyl benzoic acid

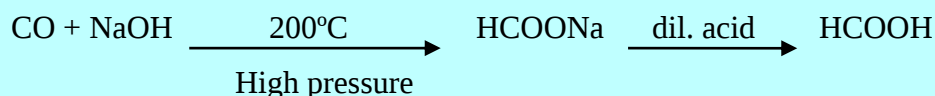
Nomenclature

IUPAC names are afforded by taking the name of the appropriate alkane and replacing the ending “e” with the suffix “-oic” positions of substitution are denoted in the usual way by numbering the longest un branched chain containing the carboxyl group.

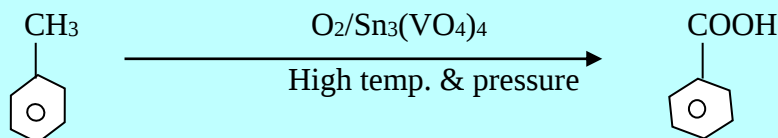
HCOOH	Methanoic acid
CH ₃ COOH	Ethanoic acid
(CH ₃) ₂ CHOOH	2 - methyl propanoic acid
C ₆ H ₅ COOH	Phenyl ethanoic acid

Industrial source

Methanoic acid is manufactured by the reaction

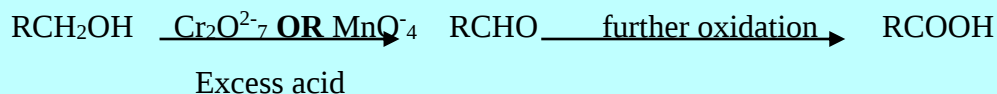


Benzoic acid is obtained by the air oxidation of methylbenzene using a tin (IV), Vanadate (V) catalyst



Synthetic preparations

Oxidation of primary alcohols



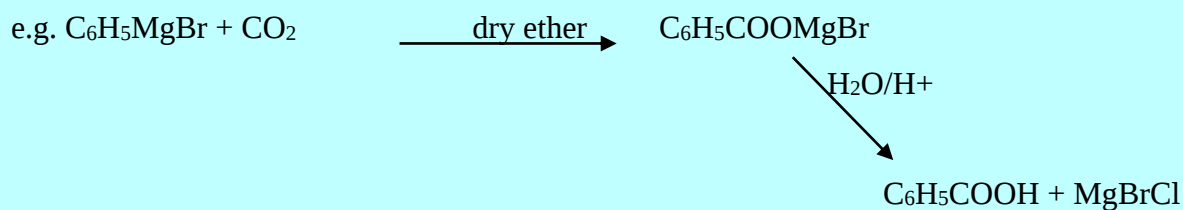
This method is suitable for preparing aromatic as well aliphatic acids.

Grignard synthesis; Carbonation

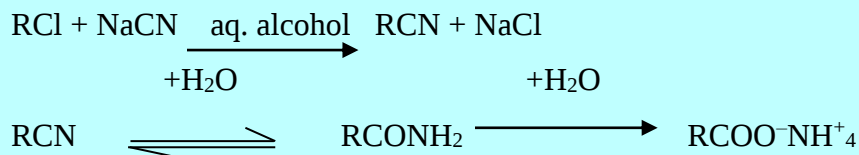
Aliphatic acids are obtained by bubbling carbon dioxide into the Grignard reagent and then treating with dilute acid.



R may be 1°, 2°, 3° or aromatic

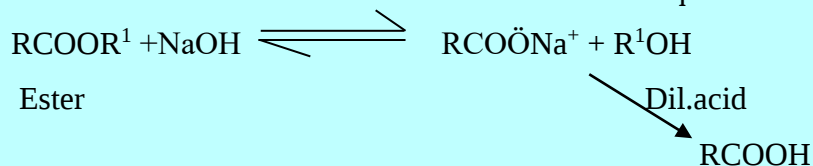


Hydrolysis of nitriles

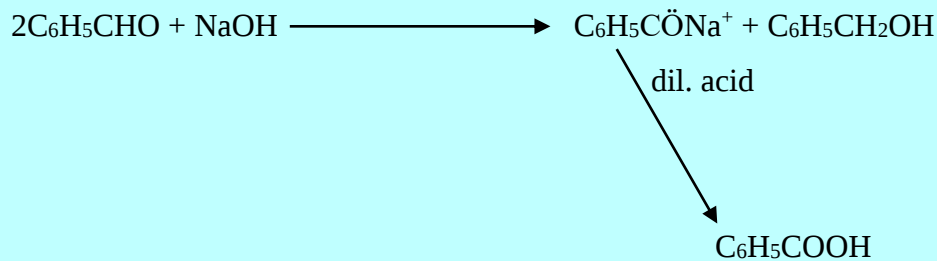


Hydrolysis of Esters; saponification

The ester is boiled under reflux with concentrated aqueous sodium hydroxide



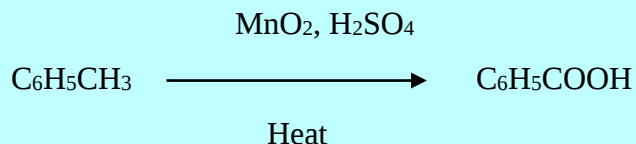
Cannizzaro reaction



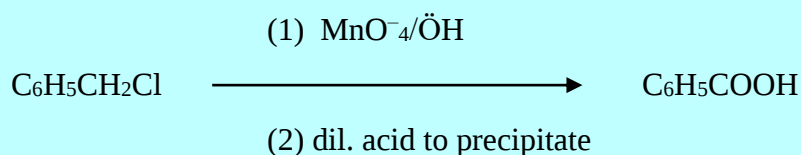
This reaction is only undergone by aromatic aldehydes and those aliphatic ones containing no – hydrogen atoms.

Synthesis of Benzoic Acid

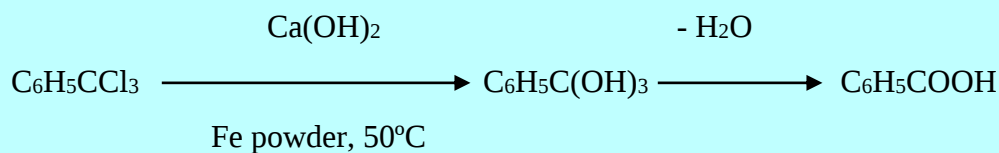
1. From methylbenzene (Toluene)



2. From chloromethyl benzene

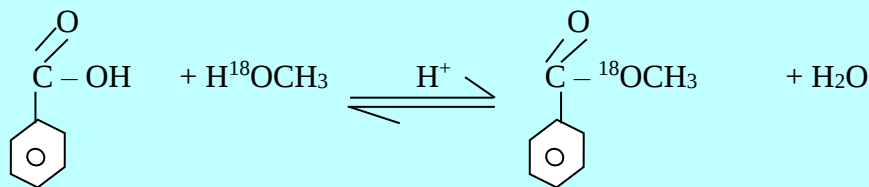


3. From Trichloromethyl benzene



REACTIONS

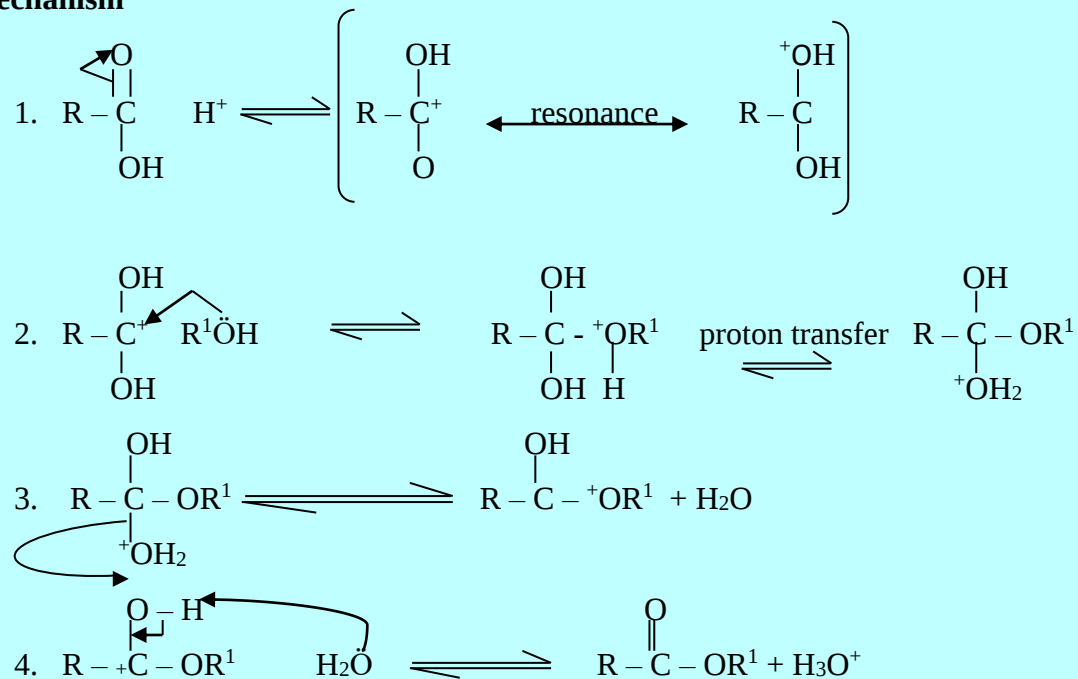
Esterification



NB

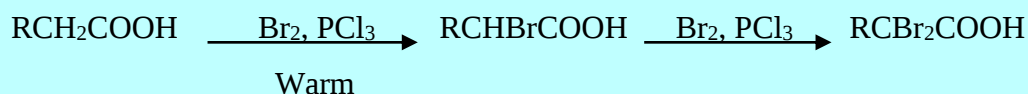
Isotopic labeling of the oxygen atom on the alcohol using ^{18}O show that primary and some secondary alcohols undergo alkoxy-hydrogen fusion i.e. mass spectrometry detects the radioactive oxygen only in the fragment prevented from the ester and not from the water.

Mechanism

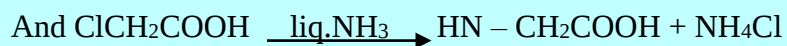
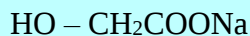


The overall reaction is reversible.

Halogenation

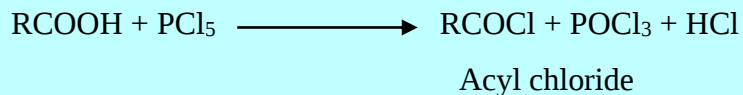


NaOH

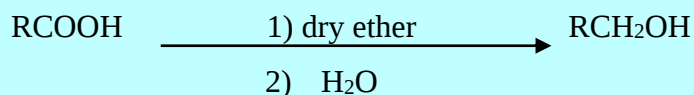


Conversion into Acyl chlorides

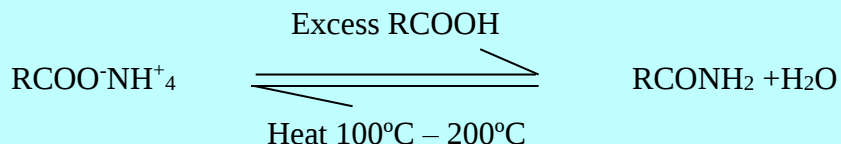
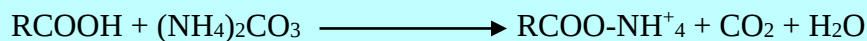
Both aliphatic and aromatic carboxylic acids readily undergo replacement of a hydroxyl group on reacting with PCl_3 , PCl_5 and SOCl_2



Reduction

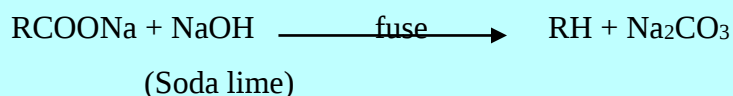


Amide formation

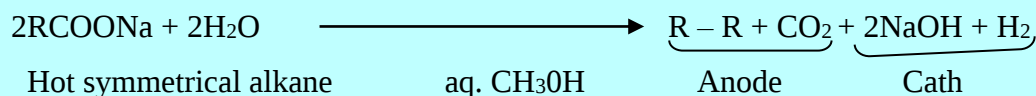


Decarboxylation of the sodium salt

1. Heating with soda lime



2. Kolbe's synthesis



Qn. Show how the following can be obtained

FATS AND OILS

Fats and oils are one of the three major groups of foods used by humans, the word oil is used by chemists in a wide sense it includes the fats and oils to be studied in this section. Three contexts are used, namely.

- Fatty oils- obtained from plant and animal sources example palm oil, fallow and white sperm wax
- Mineral oils obtained from petroleum (crude oil), coal and shale, example lubricating oil and paraffin oil.
- Essential oils-volatile and pleasant, sometimes sharp smelling(fragrant) extracts from plants example oil of turpentine, menthol, cinnamon oil and orange-peel oil.

NOTE:

Generally, fats are considered as high melting point substances, compared with oils which have low melting points. At room temperature fats usually occur as solids and oils as liquids.

- Fats and oils such as palm oil and groundnuts oil are a mixture of esters mainly of glycerol, propane-1,2,3,-triol
- They are commonly known as glycerides or esters of glycerol and can be amino-di-or tri-esters

Uses of fats and oils

- ✓ They are used as food mainly to provide energy, when fats are stored in the body it protects animals from cold since it is a poor conductor of heat.
- ✓ Some oils such as linolein are used to treat one side of a cotton material. The dried oil produces the water proof material linoleum
- ✓ However, the two important uses of fats and oils are from their direct use as food is in the making hardened oil such as margarine, and soap.

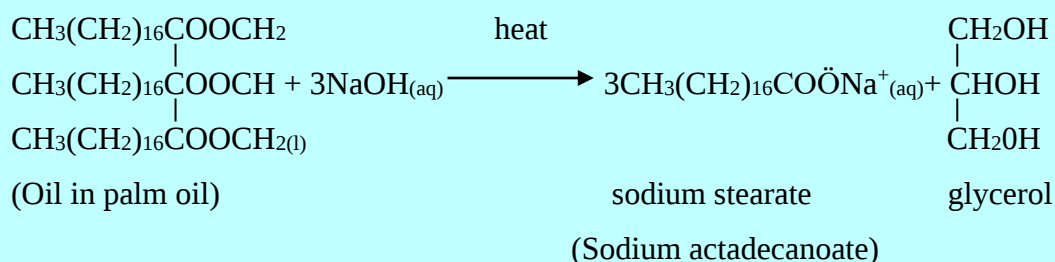
Soap making- saponification

Saponification is the chemical process of an alcohol breaking down an alkyl alkanoate or ester to form soap. Soap is sodium or potassium salt of along chain alkanoic acid or fatty acid.

The saponification process can be represented generally for fats and oils which contain one or ester groups followed by a specific example using tristearism, a common fat in most oils and fats

Vegetable oil / + alkali $\longrightarrow$ Soap + glycerol

animal fat



Fats, oils, sodium hydroxide or potassium hydroxide, brine solution and water are the main raw materials in the production of soap.

Oil and a measured quantity of alkali are mixed together in a container. The mixture is heated with steam and then boiled to mix well to form crude soap. Hot brine (saturated salt solution) is

added to the product mixture to throw up the crude soap known as grained soap. This process is called salting out.

The lower aqueous layer is glycerol dissolved in salt solution and it is called lye. Glycerol is extracted from it and purified. The grained soap is then washed many times to remove remaining salt and glycerol impurity and then bleached. Repeated washing and bleaching removes undesirable colouring, smell and other impurities. After this stage, special colouring, perfume and preservatives are added and mixed with the soap.

Structure and Cleansing action of soaps

The structure of soap is made up of a

- Long chain non-polar hydrocarbon
- Ionic, polar head.

The non-polar hydrocarbon tail $\text{CH}_3(\text{CH}_2)_n$ in which n is usually large is insoluble in water, but soluble in oils and grease which are organic substances. The tail end is called the hydrophobic end because it is insoluble in water.

The ionic head ($-\text{COO}^-\text{Na}^+$) is soluble in water but does not dissolve in organic substance such as oil and grease. The head is called the hydrophilic end because of its ability to dissolve in water.

NOTE:

Soap cleanses by

- Wetting the material
- Emulsifying the grease or oil to which the dirt is held.

Other processes such as lathering aid the removal of the dirt

Wetting action of soap

When water is mixed with soap, it spreads and wets the cloth. Soap lowers the surface tension of water and allows the aqueous soap solution to spread, wet and cleanse. Dissolution removes some nearby water molecules on the surface of the droplet and weakens the hydrogen bond forces on the surface. As a result, the surface tension is lowered and the water spreads, pushing out more detergent species to take part in the cleansing action.

Cleansing action of soap

Dirt is held to a material by oil or grease. In the cleansing process the material is first wetted. The hydrocarbon tail of the soap dissolves in the grease which remains suspended in the water by the attraction of the ionic end of the soap species. The model of the sequence through which the grease holding the dirt to the material is removed. Agitation by hand or machine heating and removal of the soap solution and its latter finally removes the dirt.

POLYMERS

The simplest molecules which form the giant single molecule are known as monomers and the large molecule is called a polymer. Poly means many and mono mean one.

Polymerization is the chemical process of joining a large number of small molecules to form one giant molecule of very high molecular mass. The giant molecule product of polymerization is known as a polymer. A monomer is a simple molecule from which a polymer can be made. Some polymers found in nature are known as natural polymers. Those made artificially by man are known as synthetic or man-made polymers.

Examples of natural polymers

- Carbohydrates such as monosaccharides, disaccharides and polysaccharides
- Starch
- Proteins.

Synthetic polymers

Examples

- Plastics, plastics can be partly identified by two simple tests namely
 - ✓ Gentle heating.
 - ✓ Strong and prolonged heating.

Two groups can be identified from experiments. Some of the plastics melt and turn back to solids when cooled, they can be moulded or remoulded into other shapes. The other types of plastics do not melt on heating. They may become hard or clear on strong heating.

Examples of plastics which can be melted and reshaped are polythene, Polypropene, polyvinylchloride (PVC) and nylon.

Examples of the type which does not melt include Bakelite (phenol-methanal) and urea-methanal.

Types of plastics

- Thermoplastics are plastics which soften and melt on heating and become solid again on cooling. They have weak inter-chain forces which can be easily broken by heating.
- Thermosets or thermosetting plastics are plastics which do not melt on heating. They have strong covalent bonds, called cross –links between polymer chains which cannot be broken easily.

NOTE:

The difference between thermoplastics and thermosets arises through the arrangement and bonding in the long chains in all polymers. The chains in the thermoplastics are held together by weak vanderwaal's forces. These weak inter-chain forces can be easily broken. When heated, the chains break loose, and slide over each other. The molten liquids can be poured into shaped containers to give different forms. Thermoset chains are bonded to each other by strong cross-link covalent bonds from one chain to others all through the polymer. These strong cross-links cannot be broken easily. Extreme heating decomposes the thermosets.

Preparation and manufacture of polymer

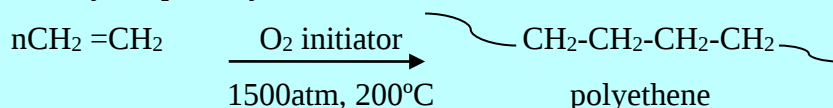
Two types of reactions are used to form polymers. The two differ mainly in the way the products are formed during the formation of the chains of the polymer. In one way, only one single large molecule is formed. In the other, small molecules such as water or hydrogen chloride are condensed out in addition to the large molecule of the polymer.

- **Addition polymerization.** In addition, polymerization a large number of unsaturated molecules gain to form the polymer, which is saturated. An example is polythene, the monomer is $\text{CH}_2 = \text{CH}_2$, the repeating unit is $-\text{CH}_2-\text{CH}_2-$ and its polymer is represented as $\text{---}(\text{CH}_2-\text{CH}_2)_n$ where n is a large number. Monomers of addition polymers always contain an unsaturated bond which is the source of its reactivity.
- **Condensation polymerization.** In condensation polymerization, a large number of molecules join together by the elimination of a small molecule often, but not always

water. An example is nylon. Condensation polymers are made by joining molecules which have two reactive function groups. The functional group of different molecules react together to form a chain with the elimination of small molecules.

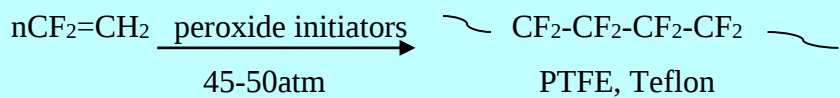
Poly ethene (polythene)

Simple alkenes polymerize to form a family of long-chain addition polymers which are flexible solids and may adopt many forms.



Polytetrafluoroethene (PTFE, Teflon, Fluon)

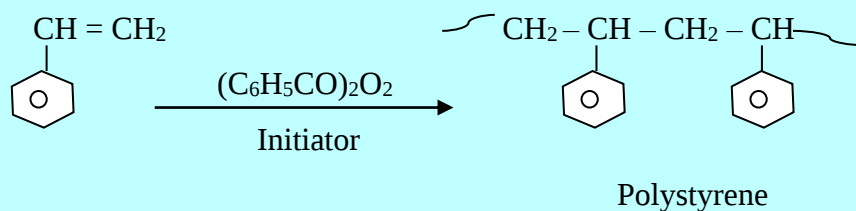
This is obtained by the pyrolysis of chlorodifluoromethane like contain other chlorofluoro-derivatives of methane and ethane, is available refrigerant and is known as freon-22



Suitable for manufacturing non-stick cooking utensils and low friction bearings since it's highly resistant to chemical and possesses an extremely low coefficient of friction.

Polyphenylethene (polystyrene)

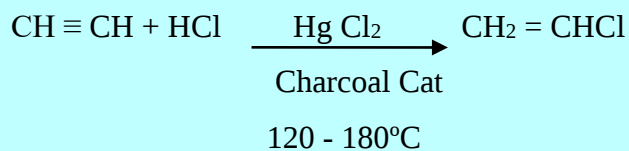
Free-radical polymerization of phenylethene (styrene) is brought about by a dibenzene carboxyl peroxide initiator at a temperature of 85-100°C



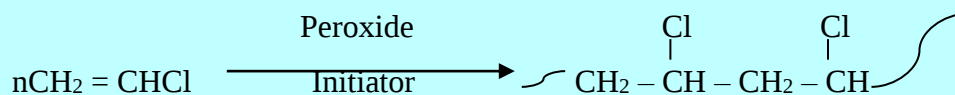
Ethenyl (vinyl) polymers

Polychloroethene (polyvinyl chloride, PVC)

i.e.

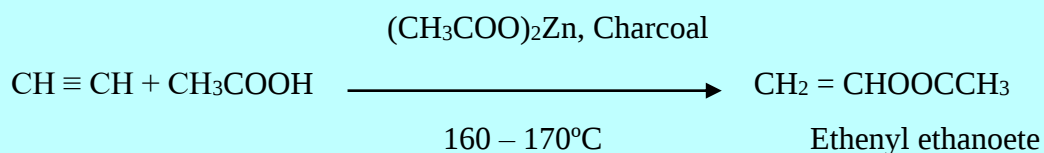


Then

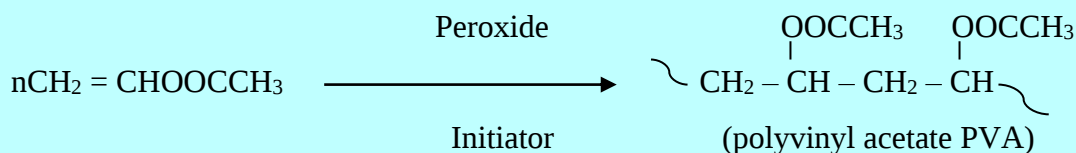


It's a thermosoftening plastic which can easily be moulded and it is used in the manufacture of plastic raincoats, curtains, furniture coverings, records, water piping and guttering etc

Polyethenyl ethanoate (polyvinyl Acetate PVA)



Free –radical polymerization can be brought about by light, peroxides etc

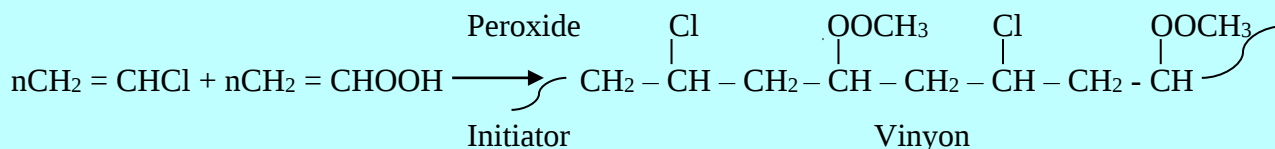


It is used in sheets as the middle layer of Triplex safety glass

NB: Its uses are limited as it tends to be too soft for many practical applications

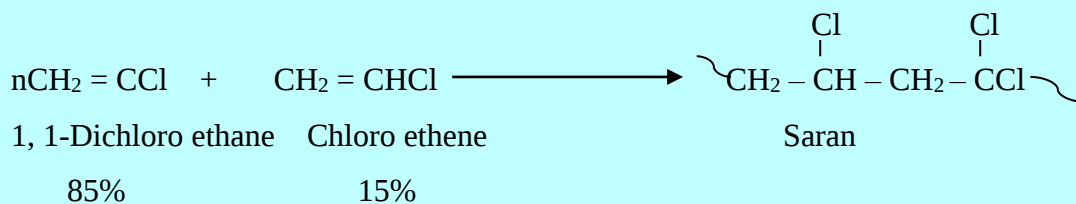
Vinyon

Is a copolymer of chloroethene and ethanylethanoate



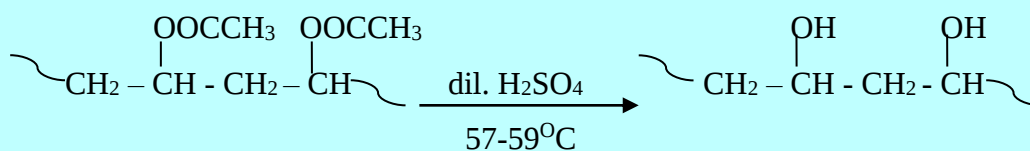
Vinyon fibre exhibits the flexible properties of PVA and has the strength of PVC, although its uses are still limited owing to its comparatively low softening temperature of 65°C

Saran



Polyethenol (polyvinyl/ alcohol)

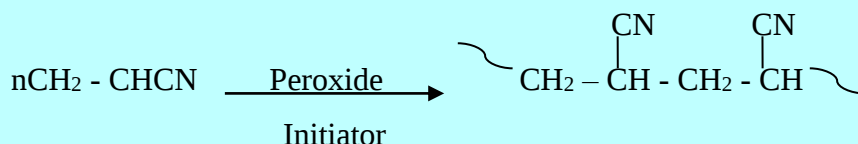
Obtained by the acid hydrolysis of polyethenylethanoate



It provides a useful intermediate for preparing other polymers

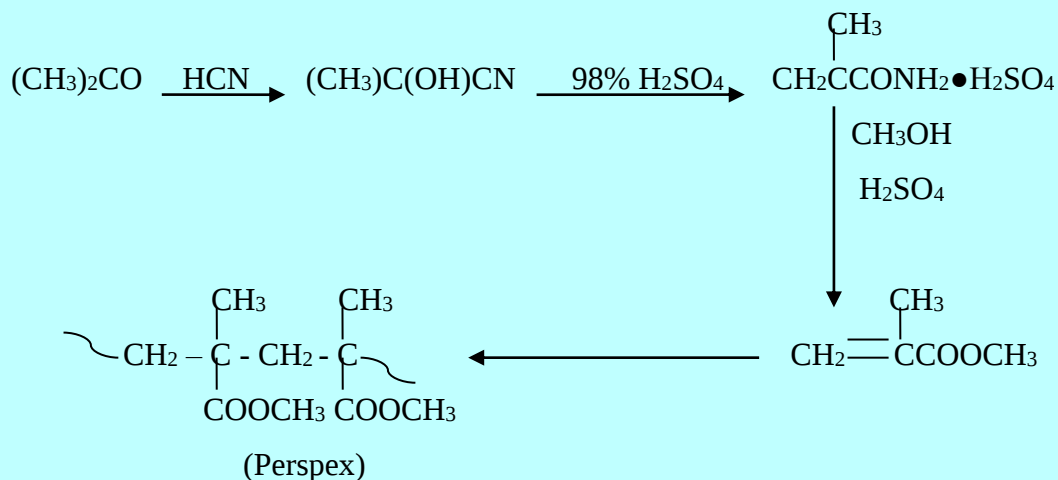
Is also used in making water-soluble coatings and adhesives.

Polypropenenitrile (polyacrylonitrile, Orlon)



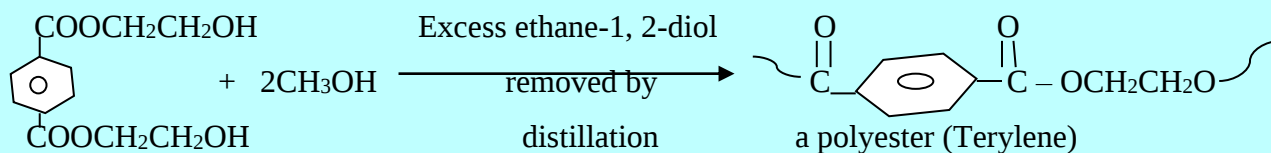
Perspex (polymethyl-2-methylpropenoate)

Perspex is a strong, transparent thermoplastic which has a variety of uses although it is probably most frequently encountered as a replacement for glass. It is obtained from propanone (acetone)



Condensation polymers

- Polyesters



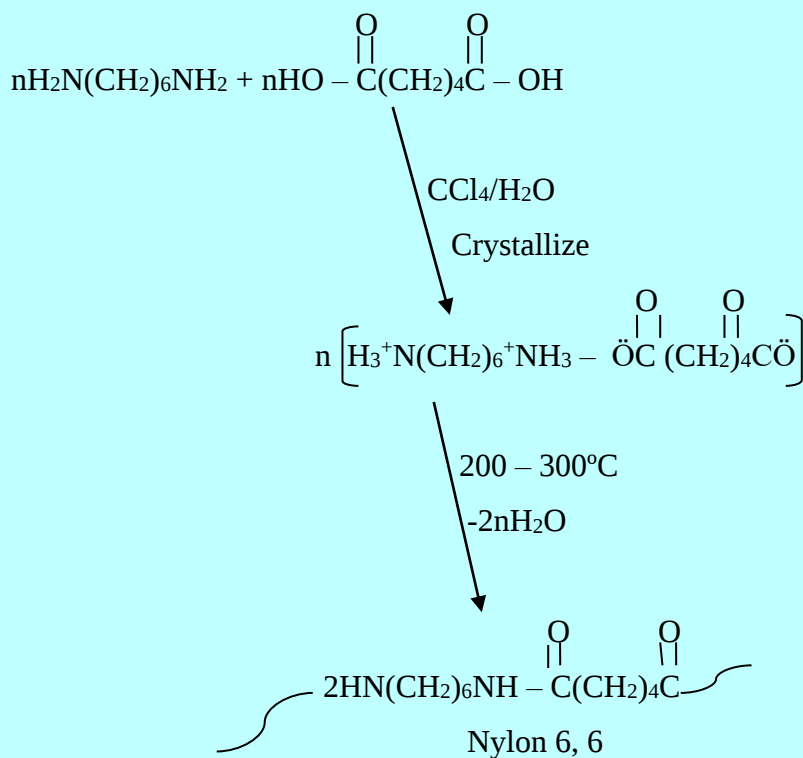
Dihydroxyethyl benzene -1, 4, - dicarboxylate

(Hydroxyethyl terephthalate)

It is used in the textile industry to make clothing materials

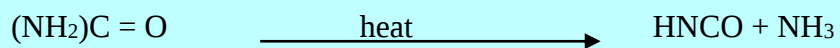
- **Nylon 6.6**

It is manufactured from hexane-1, 6-dioic, acid, dissolved in tetrachloromethane (carbon tetrachloride) and an aqueous solution of hexane-1, 6-diamine and used in making threads, ropes, stockings, shirts, finishing nets, toothbrushes, electrical equipment etc

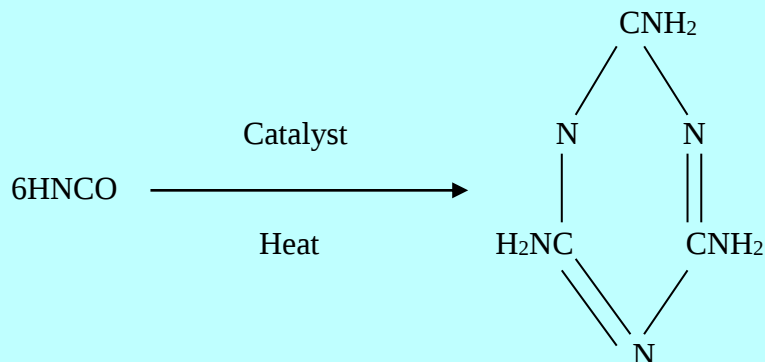


- **Melamine –methanal resins**

Is manufactured from urea by strong heating it to form, acid, HNCO and ammonia.



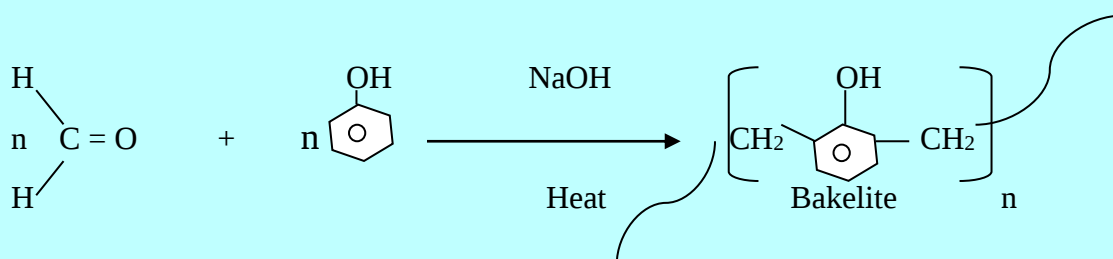
Then passing it over a heated catalyst



- **Bakelite (Phenol-methanal)**

Phenol and aqueous solution of methanol in the presence of a little sodium hydroxide is heated. The reaction goes through two stages to finally form cross-links with the elimination of water molecules.

It is used for electric switches, handles of cooking utensils, parts of cars and boats, radio, television and telephone equipment and cameras.



LET US REVISE

1. 1.86g of a compound X contains carbon, hydrogen and nitrogen only. X on combustion liberated 5.28g of carbon dioxide gas and 224cm³ of nitrogen gas at s.t.p

a) Determine the empirical formula of X

Solution

$$\begin{aligned}\text{Mass of carbon in carbondioxide} &= \frac{12}{44} \times 5.28 \\ &= 1.44\text{g}\end{aligned}$$

$$\begin{aligned}\text{Mass of nitrogen} &= \frac{28}{22400} \times 224 \\ &= 0.28\text{g}\end{aligned}$$

$$\begin{aligned}\text{Mass of hydrogen} &= 1.86 - (1.44 + 0.28) \\ &= 0.14\text{g}\end{aligned}$$

Elements	C	:	H	:	N
Moles of atoms	$\frac{0.144}{12}$		$\frac{0.14}{1}$		$\frac{0.28}{14}$
	0.12		0.14		0.02
Divided by smallest	$\frac{0.12}{0.02}$		$\frac{0.14}{0.02}$		$\frac{0.02}{0.02}$
	6	:	7	:	1

Empirical formula is C₆H₇N

b) When vapourised, 0.2g of X occupied 81cm³ at 184.1⁰C and 101.325KPa. Determine the molecular formula of X.

Solution

$$V_1 = 81\text{cm}^3 \quad V_2 = ?$$

$$\begin{aligned}T_1 &= 273 + 184.1 \\ &= 457.1\text{K}\end{aligned} \quad T_2 = 273\text{K}$$

$$P_1 = 101.325\text{KPa} \quad P_2 = 101.325\text{Pa}$$

$$\text{Using } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\begin{aligned}V_2 &= \frac{101.325 \times 81 \times 273}{457.1 \times 101.325} \\ &= 48.377\text{cm}^3\end{aligned}$$

But 48.377cm³ of X contain 0.2g of X

22400cm³ of X contain $\frac{0.2 \times 22400}{48.377}$

= 92.6g of X

Then (C₆H₇N)_n = 92.6

(16 x 12 + 1 x 7 + 1 x 14)_n = 92.6

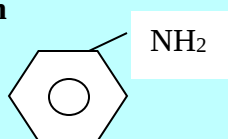
$$\frac{93n}{93} = \frac{92.6}{93}$$

n = 1

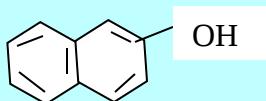
Hence molecular formula of X is C₆H₇N.

c) X burns with a sooty flame and the PH of its aqueous solution is greater than 7. Write the molecular structure of X.

Solution



d) X was reacted with sodium nitrate in the presence of hydrochloric acid at 5°C and the product treated with 2-naphthol,



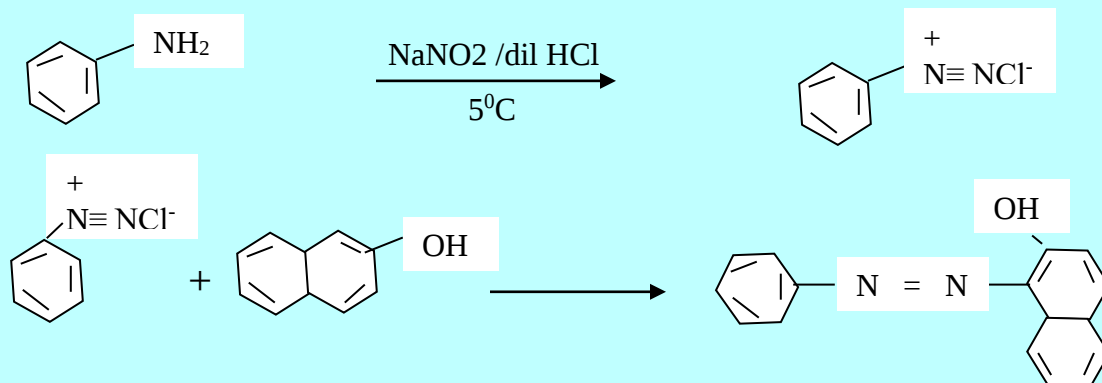
i) State what was observed

Solution

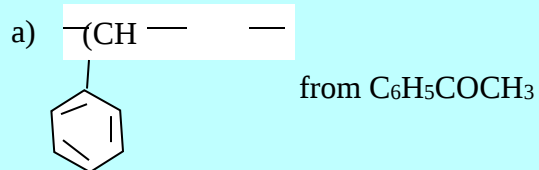
Red precipitate

ii) Write equations for the reactions that took place

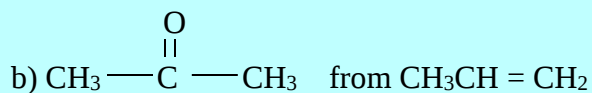
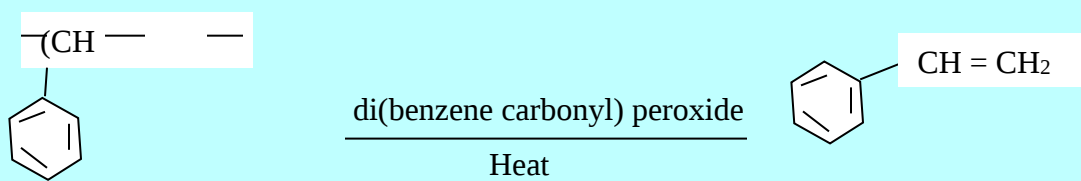
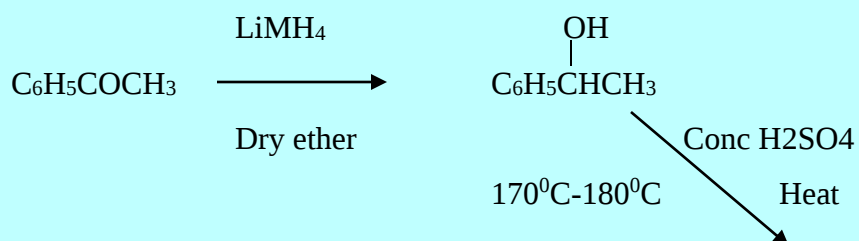
Solution



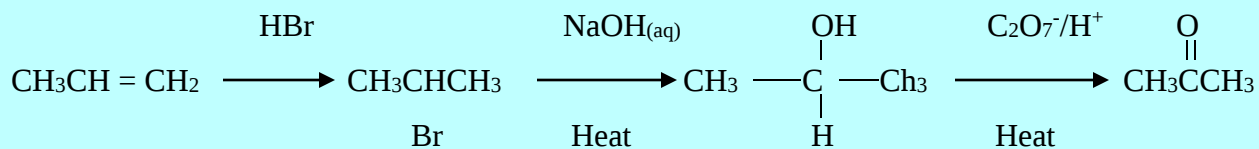
2. Write equations to show how the following compounds can be synthesized and, in each case, indicate the conditions for the reaction.



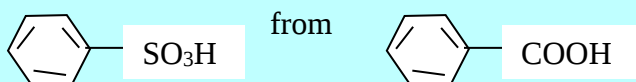
Solution



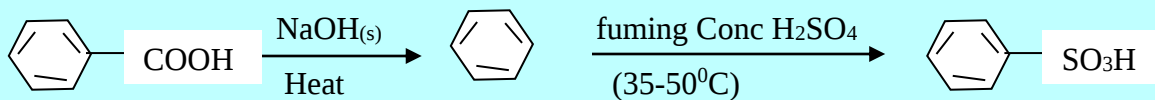
Solution



c)



Solution

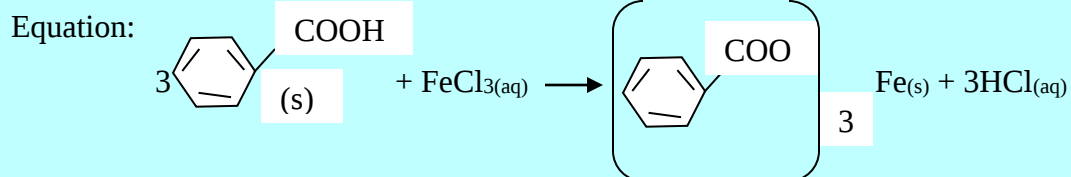


3.a) State what would be observed and, in each case, write equation for the reaction that would take place if a mixture of the following compounds were heated.

i) Benzoic acid and Iron (II) Chloride solution.

Solution

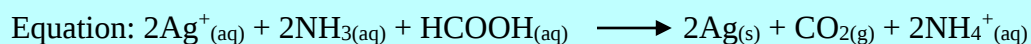
Observation: Reddish-brown precipitate



ii) Methanoic acid and ammoniacal silver nitrate.

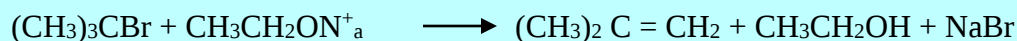
Solution

Observation: Silver mirror

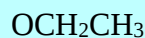
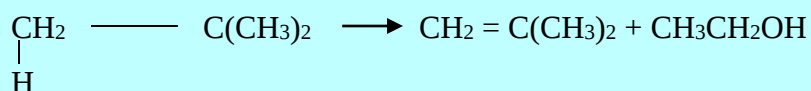
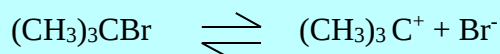


b(i) Write equation and outline a mechanism for the reaction between 2 – bromo – 2 – methylpropane and sodium ethoxide.

Solution



Mechanism



ii) Write the name given to the type of mechanism you have outlined in b(i) above.

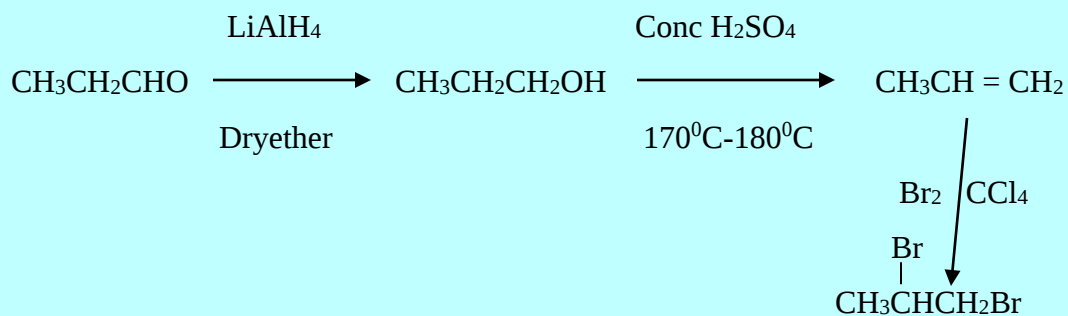
b) Solution

Elimination unimolecular

4. Write equations to show how the following conversions can be carried out in each case indicate the reagents and condition for the reactions.

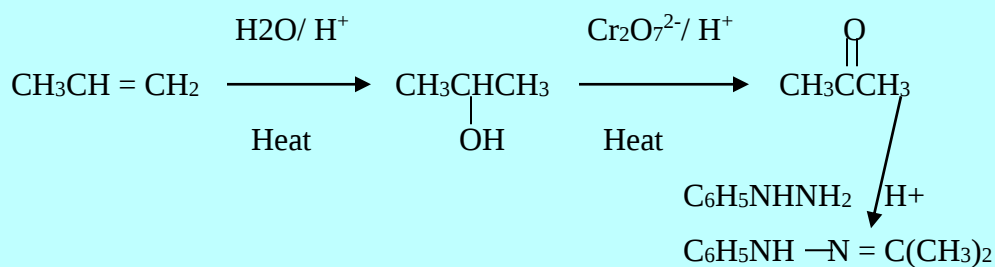
a) $\text{CH}_3\text{CH}_2\text{CHO}$ to $\text{CH}_3\text{CHBrCH}_2\text{Br}$

Solution



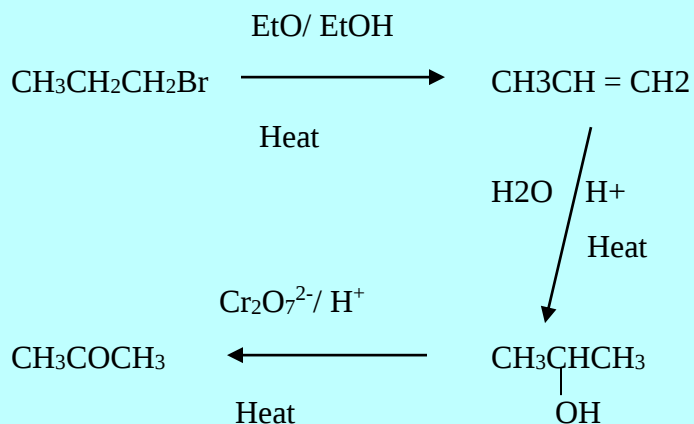
b) $\text{CH}_3\text{CH}=\text{CH}_2$ to $\text{C}_6\text{H}_5\text{NH}-\text{N}=\text{C}(\text{CH}_3)_2$

Solution



c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ to CH_3COCH_3

Solution



5(a) Name one source of vegetable oil

Solution

Sunflower, simsim, ground nuts, soya beans, cotton seeds, shea nuts, coconut, palm oil seed, etc.

b) Describe briefly show how soap can be prepared from one of the sources of vegetable oil you have named in (a) above.

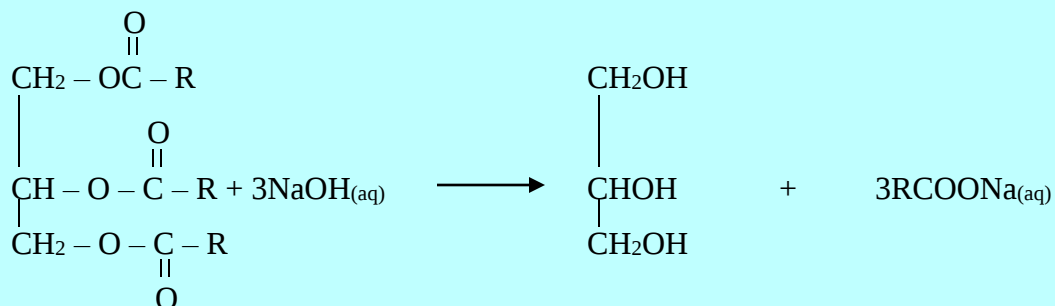
Solution

Roast/dry the seeds, crush/grind to make paster with water until oil floats on top and decant off the oil. Mix the oil with excess concentrated sodium hydroxide solution and heat/boil with constant stirring for a long time. Add concentrated sodium chloride solution to precipitate the soap.

c) Write the general equation for the;

i) formation of soap

Solution



ii) reaction between hard water and soap.

Solution



d) A sample of soap was prepared from 9.5g of a vegetable oil containing the ester of hexadecanoic acid ($\text{C}_{15}\text{H}_{31}\text{COOH}$). Calculate the mass of soap formed.

Solution

$$\begin{aligned}
 \text{RMM of ester} &= (12 \times 15) + (1 \times 31) + (12 \times 1) + (16 \times 2) + (1 \times 1) \\
 &= 806
 \end{aligned}$$

$$\text{Moles of ester} = \frac{9.5}{806} = 1.179 \times 10^{-2}$$

But

1 mole of ester produces 3 moles of soap

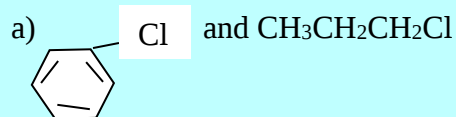
$$\begin{aligned}
 \text{50 moles of soap} &= 3 \times 1.179 \times 10^{-2} \\
 &= 3.537 \times 10^{-2}
 \end{aligned}$$

$$\text{RMM of soap } \text{C}_{15}\text{H}_{31}\text{COONa} = 278$$

Then 1 mole of soap contain 278g of soap

$$3.537 \times 10^{-2} \text{ moles of soap contain } \frac{278 \times 3.537 \times 10^{-2}}{1} \\ = 9.839$$

6. Name one reagent that can be used to distinguish between each of the following pairs of compounds. In each cases state what is observed if each member of the pair is treated with the reagent.

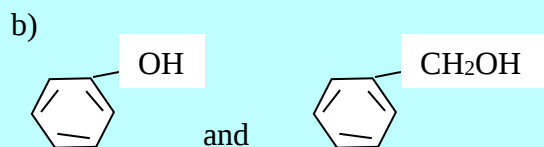
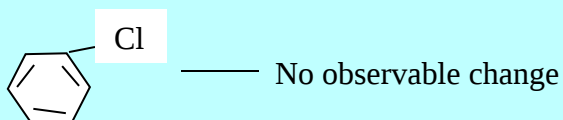


Solution

Reagent: Hot sodium hydroxide solution followed by silver nitrate solution.

Observation:

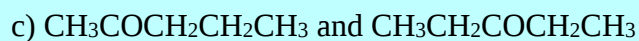
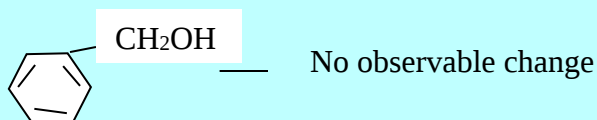
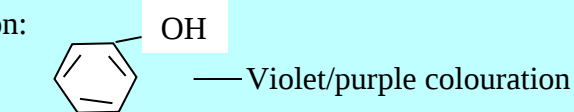
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ ——— White precipitate



Solution

Reagent: Neutral Iron (II) chloride solution

Observation:



Solution

Reagent: Iodine solution and sodium hydroxide solution

Observation:

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$ – yellow precipitate

$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ – No observable change

d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{NHCH}_2\text{CH}_3$

Solution

Reagent: Sodium nitrate and cold concentrated hydrochloric acid.

Observations

$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ - gives bubbles of a colourless gas and a colourless solution

$\text{CH}_3\text{NHCH}_2\text{CH}_3$ – gives a yellow oil

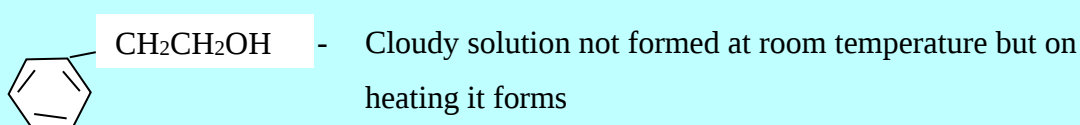
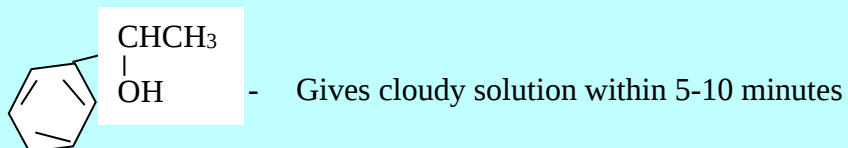
e)



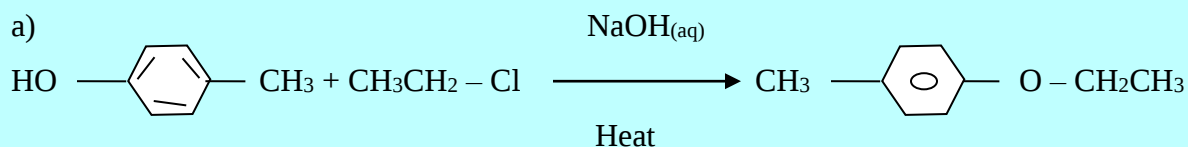
Solution

Reagent: Anhydrous Zinc chloride and concentrated hydrochloric acid

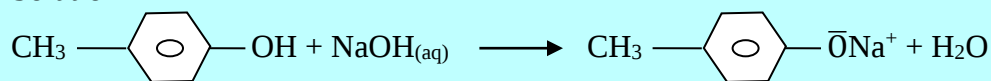
Observation:

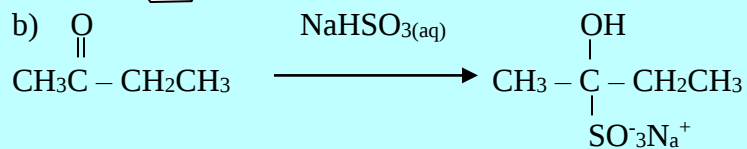
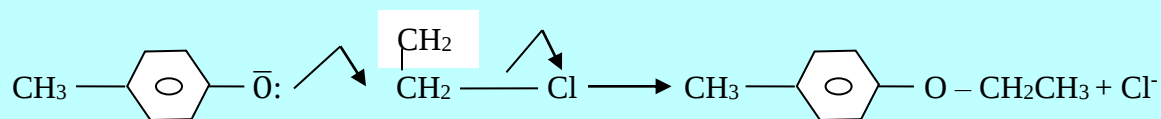


7. Complete the following equations and in each case write the accepted mechanism for the reaction.

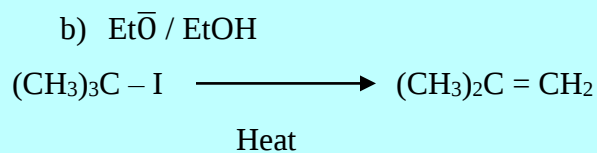
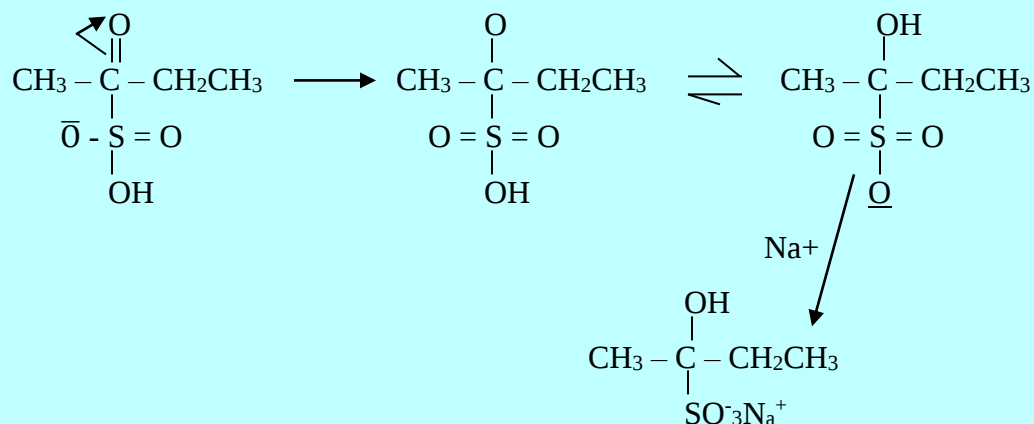


Solution

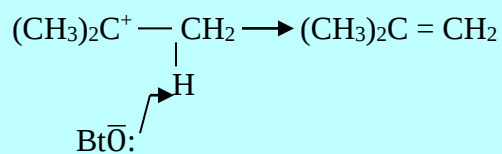
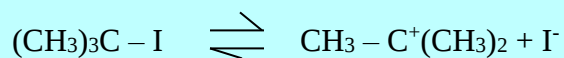




Solution

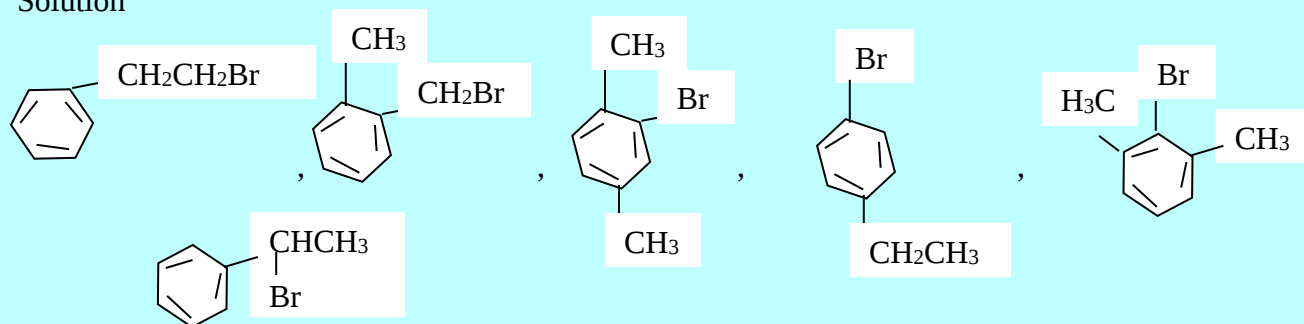


Solution



8(a) A compound X $\text{C}_8\text{H}_9\text{Br}$ burns with a sooty flame write all the possible structural formulae of X.

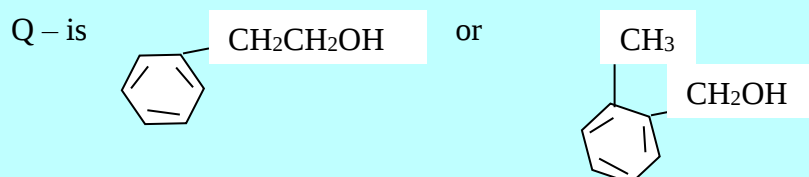
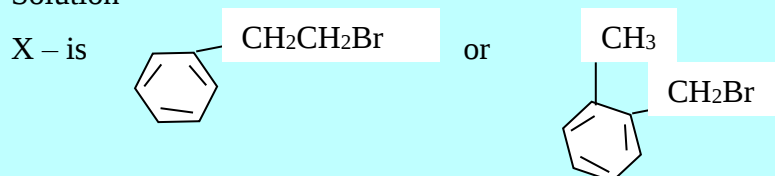
Solution



b) When X was heated under reflux with aqueous sodium hydroxide solution, a compound Q, C_8H_9Br was formed.

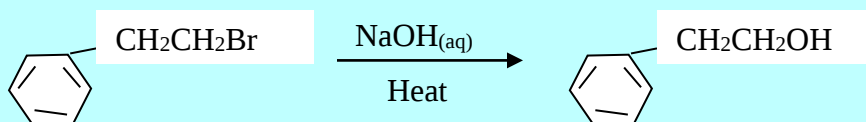
i) Identify X and Q

Solution

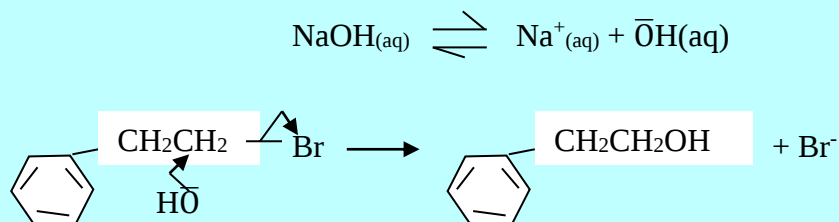


ii) Write an equation and indicate a mechanism for the reaction leading to the formation of Q from X.

Solution

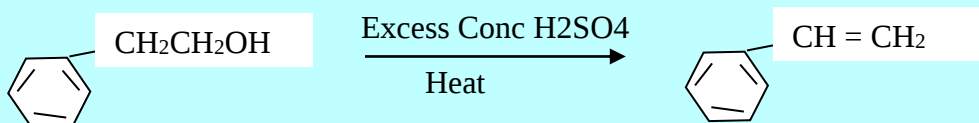


Mechanism

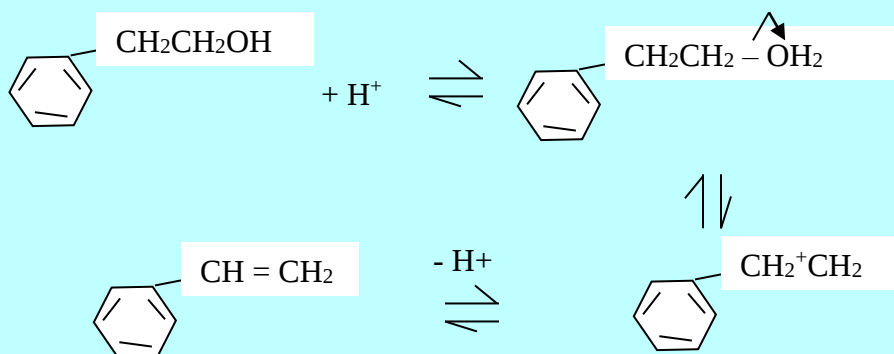
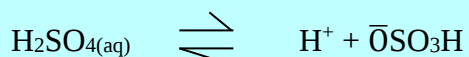


c. Q was converted in a one-step reaction to an alkene. Write equation and outline a mechanism for the reaction.

Solution



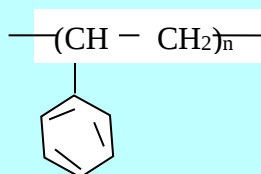
Mechanism



d. The Alkene in (c) above was polymerized.

i) Write the structural formulae of the polymer

Solution

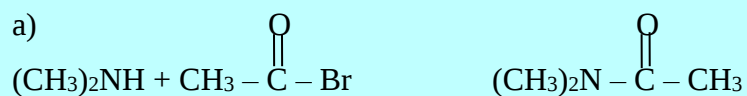


ii) State the type of polymerization involved

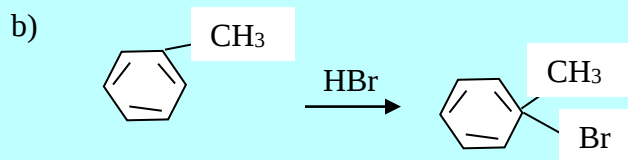
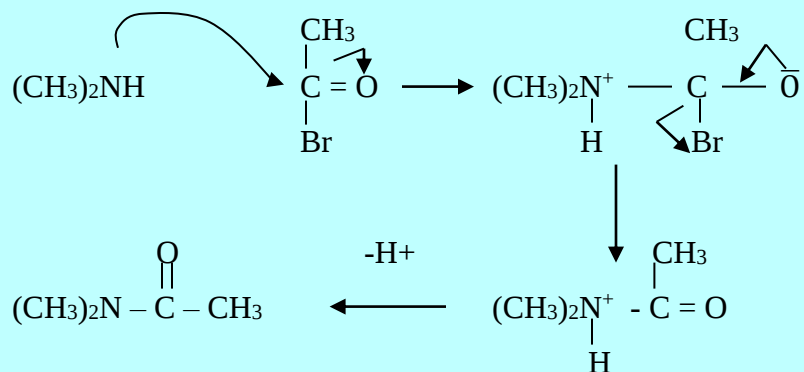
Solution

Addition polymerization.

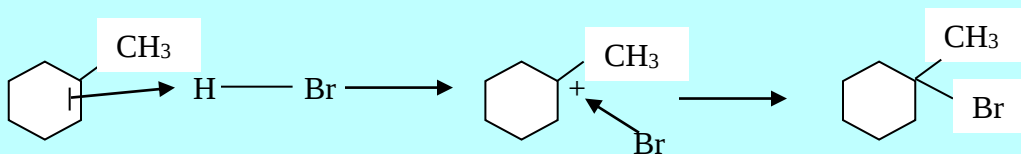
9. Complete the following equations and in each case outline the accepted mechanism for the reaction.



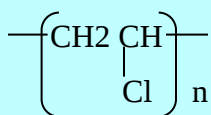
Solution



Solution



10(a) State the conditions for the formation of polyvinyl chloride.



Solution

- Heat/ High temperature/ or 100°C
- Peroxide or Hydrogen peroxide, Dibenzoyl peroxide
- High pressure

b) The osmotic pressure of a solution containing 4.00gdm^{-3} of polyvinyl chloride in dioxin is 65Pa at 20°C . Calculate the number of monomers in polyvinyl chloride.

Solution

$$V_1 = 1000\text{cm}^3(1\text{dm}^3)$$

$$V_2 = ?$$

$$P_1 = 65\text{Pa}$$

$$P_2 = 1.0 \times 10^5\text{Pa}$$

$$T_1 = 20 + 273 = 293\text{K}$$

$$T_2 = 273\text{K}$$

$$\text{Using } \frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1}$$

$$V_2 = \frac{1 \times 65 \times 273}{293 \times 1.01 \times 10^5}$$

$$= 60.56314 \times 10^{-5}\text{dm}^3$$

Now

$60.56314 \times 10^{-5}\text{dm}^3$ of polyvinyl chloride contain 4g of polyvinyl chloride

22.4dm^3 of polyvinyl chloride contain 22.4×4

$$60.56314 \times 10^{-5}$$

$$= 1.4794477 \times 10^{-5}$$

$$= 147944.77\text{g}$$

So

Molar mass of monomer ($\text{CH}_2 = \text{CHCl}$) = $(12 \times 2) + 3 + 35.5$

$$= 62.5$$

Therefore $\frac{62.5n}{62.5} = \frac{147944.77}{62.5}$

$$62.5 \quad 62.5$$

$$n = 2367.1$$

Hence $n \approx 2367$

c) State one use of polyvinyl chloride

Solution

Making pipes, films, records, insulators for cables rain coats, etc

Self-check

1.a) Ethyne was bubbled through an ammoniacal silver nitrate

Solution

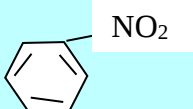
- i) State what was observed
- ii) Write equation of reaction that occurs in (a)(i) above.

b) Give a reaction scheme to show how the following conversions can be effected in each case indicate the reagents required and the conditions of reaction.

i) ethanol to ethyne

ii) ethyne to ethanamide

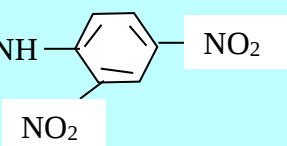
iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ to $\text{CH}_3\text{CH}_2\text{NH}_2$

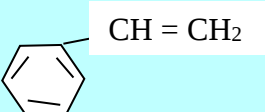
iv)  to 

2. Complete the following equations and in each case suggest the mechanism of reaction.

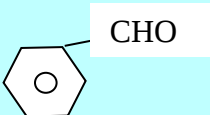
a)  + $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3}$

b) $\text{CH}_3\text{COCH}_3 + \text{NaHSO}_3 \longrightarrow$

c) $\text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \xrightarrow{\text{H}^+}$


d)  $\xrightarrow[\text{H}_2\text{O}]{\text{Br}_2}$

e) $(\text{CH}_3)_3\text{C}-\text{OH} \xrightarrow[\text{Heat}]{\text{Conc H}_3\text{PO}_4}$

f)  $\xrightarrow{\text{O}^-\text{A}_{(\text{aq})}}$

3(a) Compound M contains 61% by mass of carbon, 15.3% by mass of hydrogen, the rest being nitrogen. Calculate;

i) The empirical formula of M

ii) The molecular formula of M (Vapour density of M is 29.5)

b) M reacts with nitrous acid forming gas N and a compound O. O reacts with acidified potassium dichromate (VI) solution on warming forming compound P, which reacts with iodine and potassium hydroxide solution forming a yellow precipitate.

- i) Identify the compounds O, P and M and the gas N.
- ii) Write an equation leading to the formation of the yellow precipitate.
- iii) Write an equation and outline a mechanism for the reaction between P and phenylhydrazine in the presence of dilute sulphuric acid.
- c) Write equations to show how the following conversion can be effected. Indicate reagents and conditions for the reaction.

(i) P to propan – 1 – ol

(ii) propene to P

4. When 0.10g of an organic compound X containing carbon, hydrogen and oxygen only was subjected to combustion, it gave 0.227g of carbon dioxide and 0.0929g of water. 0.368g of X when vaporized at 37°C and 760mmHg it occupied a volume of 161.4cm³

a(i) Calculate the empirical formula of X.

(ii) Deduce the molecular formula of X

b) Determine the structural formulae and their IUPAC names of all the possible Isomers of X.

c) X reacts with hydroxyl amine in acidic medium but does not react with ammoniacal silver nitrate solution. Identify X.

d) Write equations to show how;

i) X can be synthesized from ethanol

ii) X can be converted to ethanoic acid

e) Write equation for the reaction between X and dilute sodium hydroxide solution at room temperature.

5.a) Describe the reactions of amines with nitrous acid. Write equations for the reactions and state the observations.

b) 0.354g of a compound X containing carbon, hydrogen and nitrogen gave 0.981g of carbon dioxide, and 0.233g of water when burnt in excess air. The same mass of X gave 41.5cm³ of nitrogen at 0°C and 760mmHg calculate the empirical formula of X.

c) When X was steam distilled at 98°C and 760mmHg, the distillate was found to contain 72.1% of water. If the vapour pressure of water at 98°C is 707mmHg.

i) Calculate the relative molecular mass of X.

ii) Determine molecular formula of X.

d) Write equations to show how X can be;

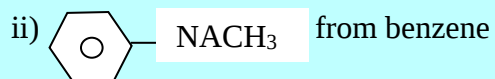
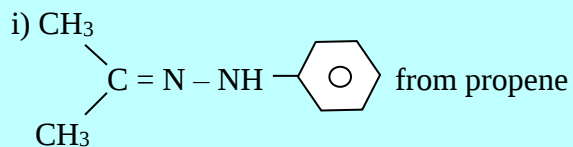
i) prepared from benzene

ii) converted to benzoic acid

6(a) Define the term catenation

i) Why does carbon have such a high-profile ability to catenate?

b) Write equation to show how the following compounds can be synthesized.



iii) $\text{CH}_3\text{CO}_2\text{CH}_3$ from bromoethane

iv) $\text{CH}_3\text{CA}_2\text{C} \equiv \text{CH}$ from ethanol

v) $(\text{CH}_3)_2\text{C} = \text{NOH}$ from propene

7. Write short notes on the following;

a) Elimination uni -molecular reaction

b) Sulphonation reaction

c) Nitration reaction

-END-