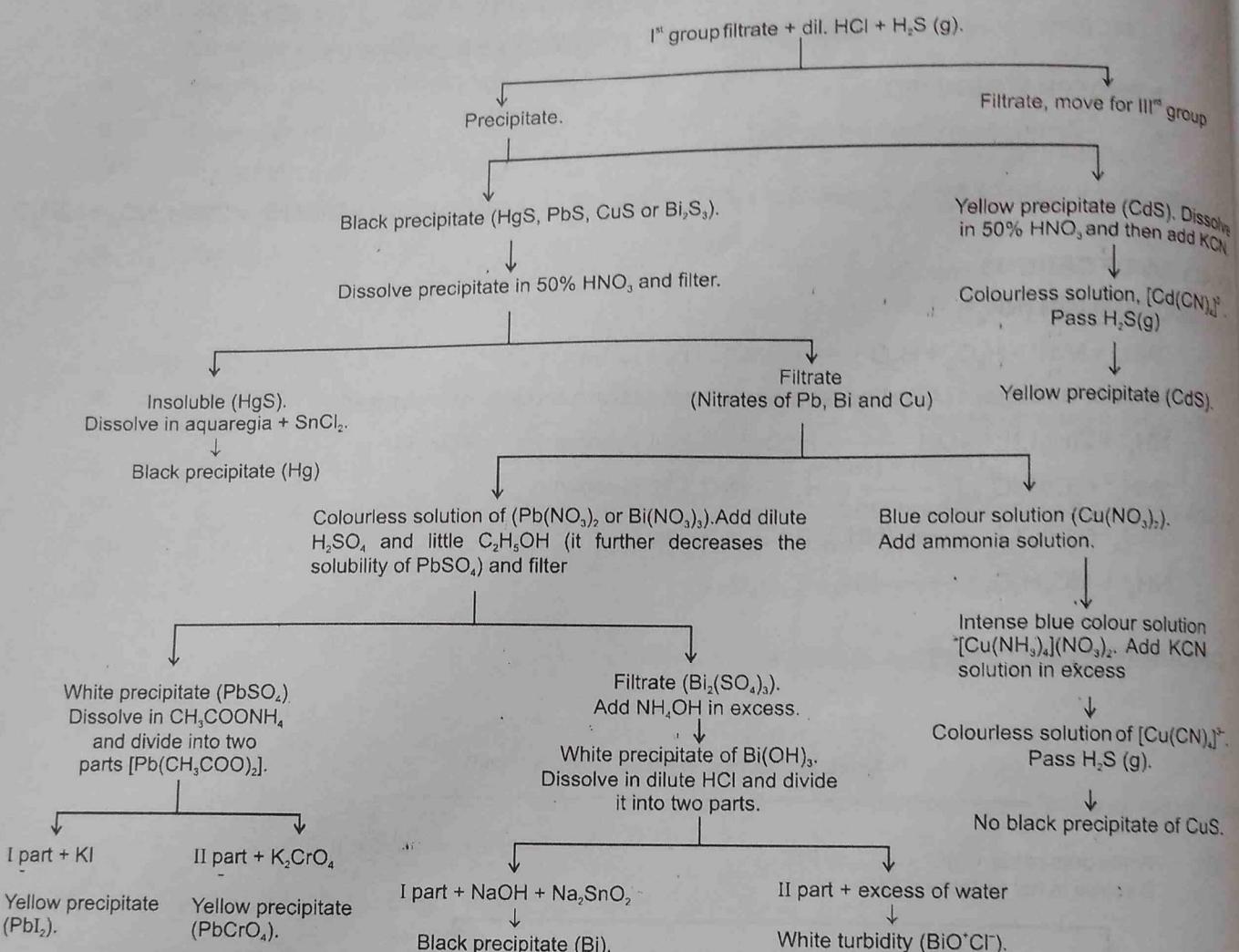
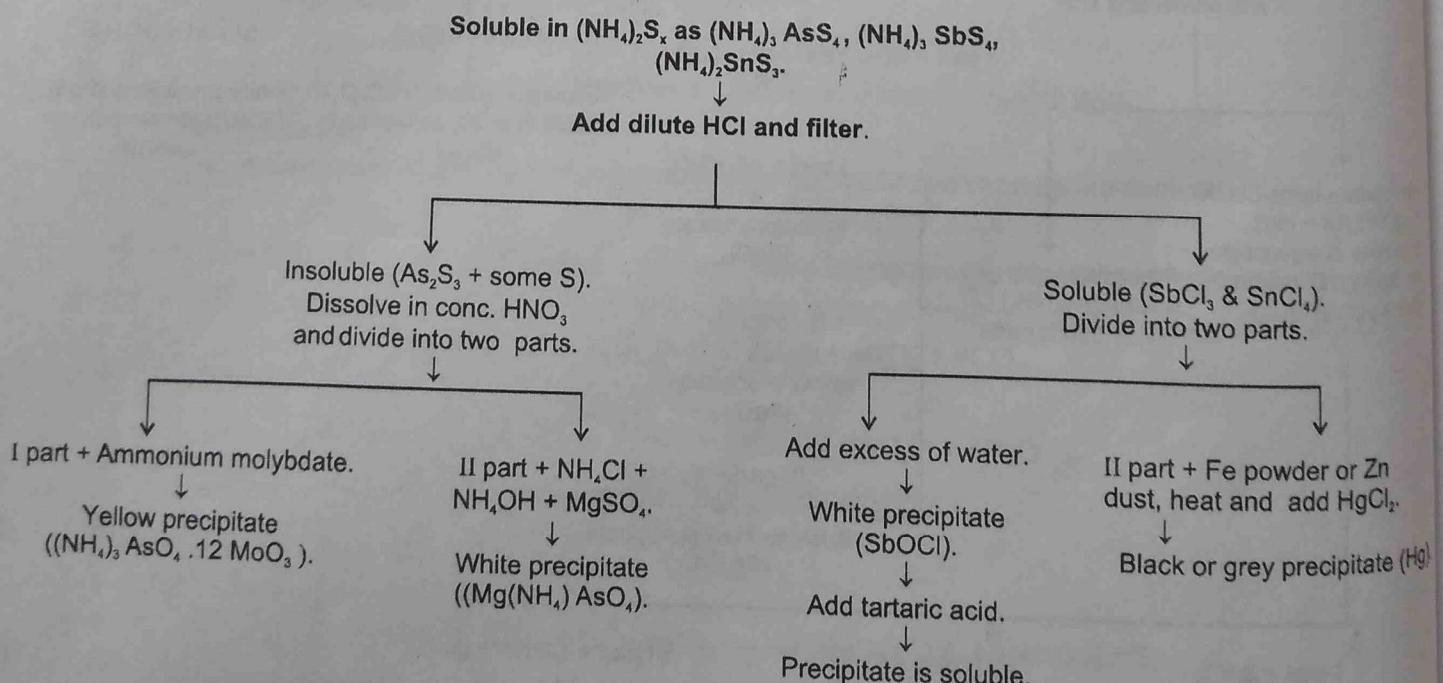
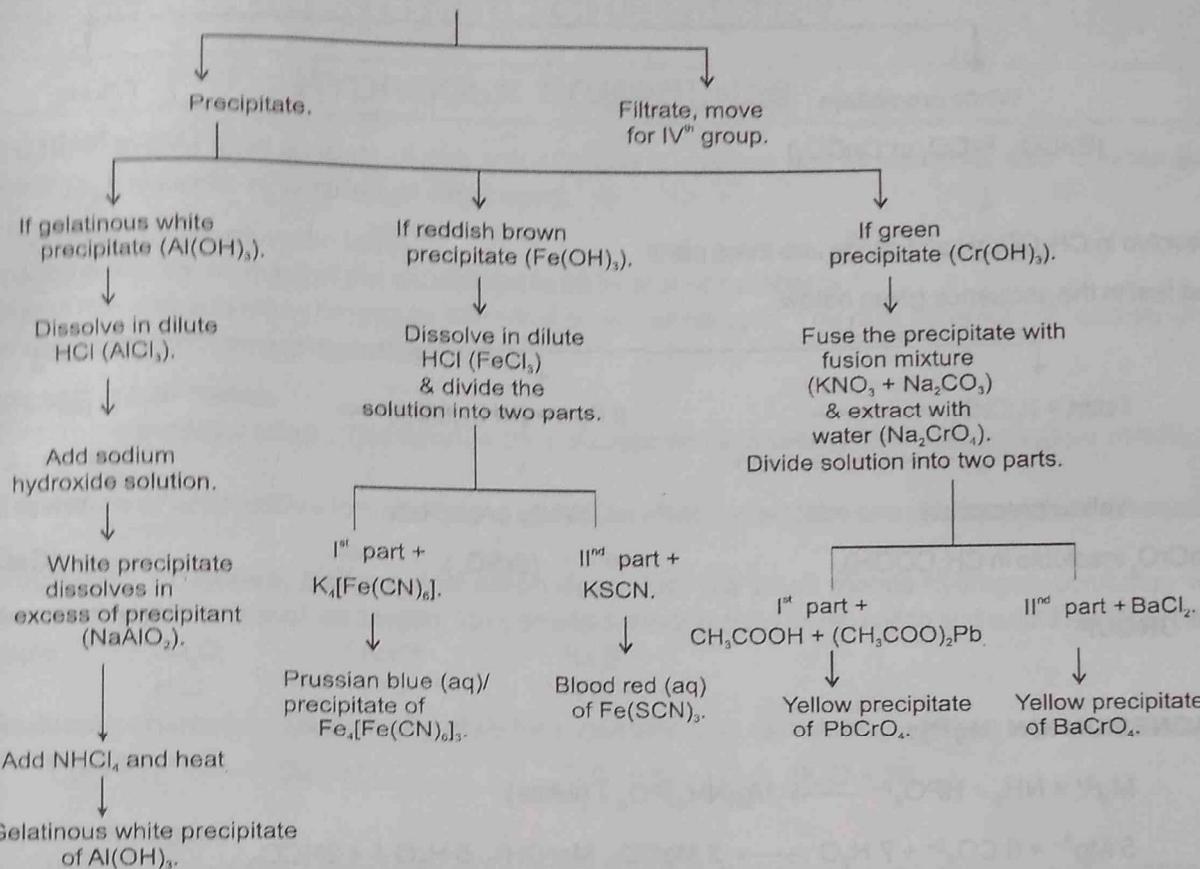


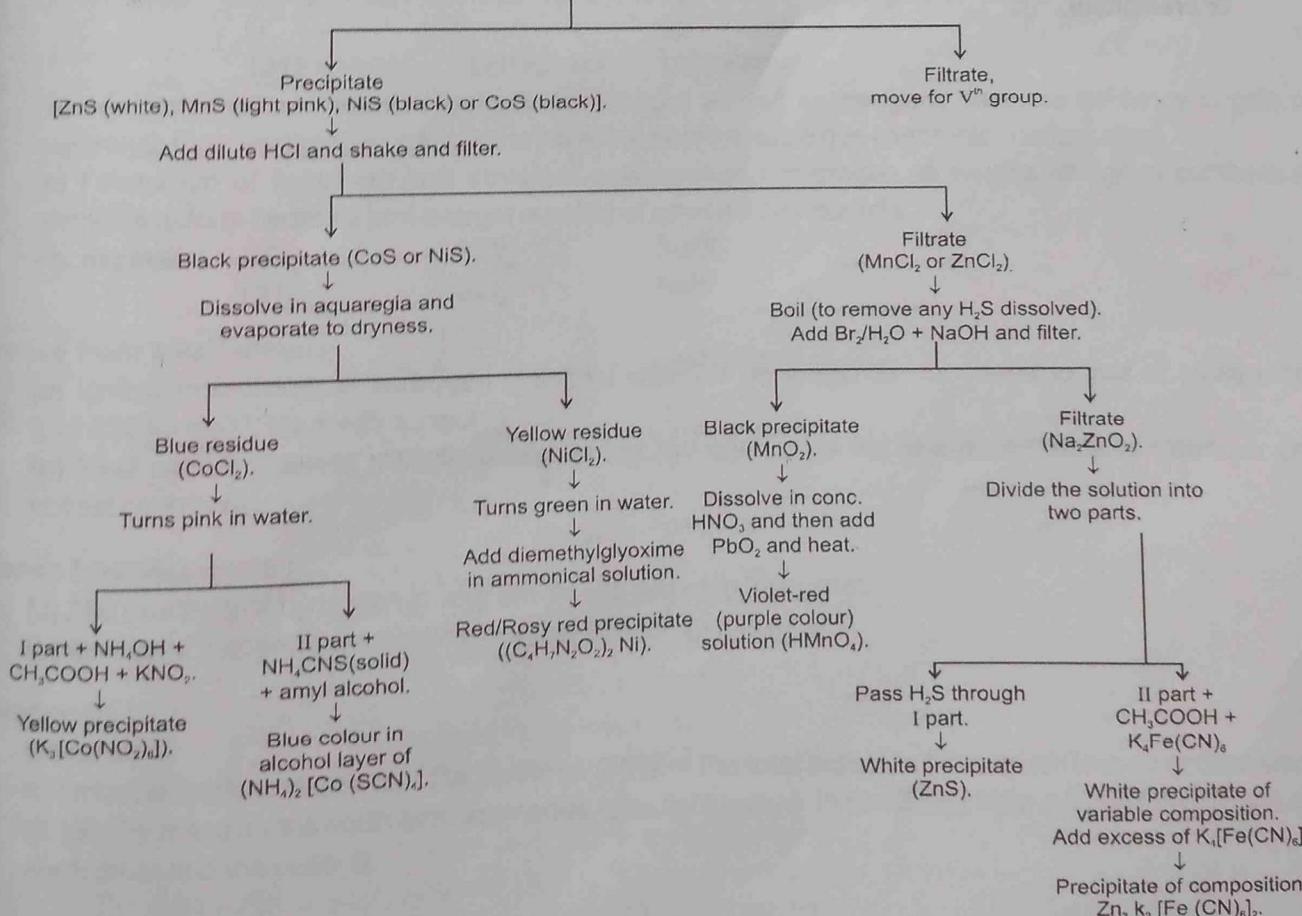
IIA Group ( $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ )IIB Group ( $As^{3+}$ ,  $Sb^{3+}$ ,  $Sn^{2+}$ ,  $Sn^{4+}$ )

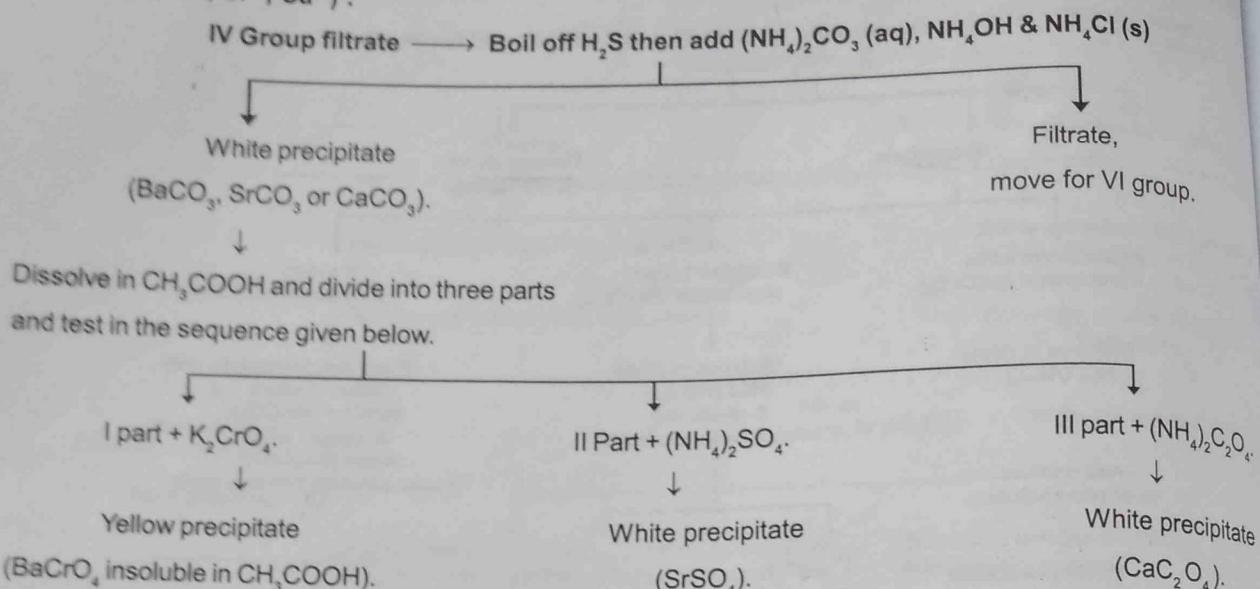
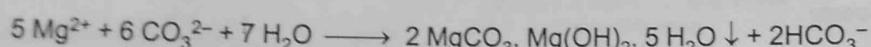
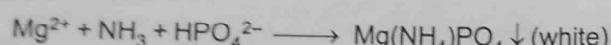
III<sup>rd</sup> Group ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ )

II Group Boil off,  $\text{H}_2\text{S} \uparrow$  then add conc.  $\text{HNO}_3$  (1-2 drops) +  $\text{NH}_4\text{Cl}$  (solid) +  $\text{NH}_4\text{OH}$

IV<sup>th</sup> GROUP ( $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ):

III Group filtrate +  $\text{NH}_4\text{OH}$  (excess) &  $\text{NH}_4\text{Cl}$ , then pass  $\text{H}_2\text{S}$



V<sup>th</sup> Group ( $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ) :VI<sup>th</sup> GROUP :MAGNESIUM ION ( $\text{Mg}^{2+}$ ) :

**Titan Yellow (a water soluble yellow dyestuff)** : It is adsorbed by  $\text{Mg}(\text{OH})_2$  producing a deep red colour or precipitate.

# FOR JEE(MAIN)

## INORGANIC CHEMISTRY

### HYDROGEN COMPOUNDS

Hydrogen in atomic form consists of one proton and one electron but, in elemental form it exists as a diatomic ( $H_2$ ) molecule.  $H_2$  is called as dihydrogen.

#### Position of hydrogen in the periodic table :

Hydrogen is the first element of the periodic table as its atomic number is 1.

Hydrogen resembles in many properties with alkali as well as halogen. This dual behaviour of hydrogen may arise due to its electronic configuration i.e.  $1s^1$ .

#### Resemblance with alkali metals :

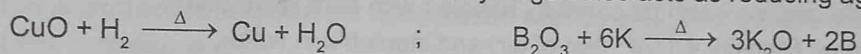
(a) **Electronic configuration** : The valence shell electron configuration of hydrogen and alkali metals are similar i.e.  $ns^1$

(b) **Formation of unipositive ion** : Hydrogen as well as alkali metals lose one electron to form unipositive ions.

(c) **Formation of oxides, halides and sulphides** : Just like alkali metals hydrogen combines with electronegative elements such as oxygen, halogen and sulphur forming oxide, halide and sulphide respectively.

Example	$Na_2O$	$NaCl$	$Na_2S$
	$H_2O$	$HCl$	$H_2S$

(d) **Reducing character** : Like, alkali metals hydrogen also acts as reducing agent.



#### Resemblance with halogens .

(a) **Electron configuration** : Both have one electron less than that of preceding inert gas configuration.

(b) **Atomicity** : Like halogens, hydrogen forms diatomic molecule too. For example,  $Cl_2$ ,  $Br_2$ ,  $I_2$  etc.

(c) **Ionization enthalpy** : Hydrogen as well as halogens both have higher ionization enthalpies.

H	F	Cl
1312 kJ/mol	1680 kJ/mol	1255 kJ/mol

(d) **Formation of uninegative ion** : Both hydrogen as well as halogens have the tendency to gain one electron to form uninegative ion so as to have the nearest noble gas electronic configuration.

(e) **Formation of hydrides and covalent compounds** : Hydrogen as well as halogens combine with elements to form hydrides and a larger number of covalent compounds.

For example ;	$CCl_4$	$SiCl_4$	$NaCl$
	$CH_4$	$SiH_4$	$NaH$

#### Difference from alkali metals

(a) Ionization enthalpy of hydrogen ( $1312 \text{ kJ mol}^{-1}$ ) is very high as compared to that of alkali metals. ( $Li = 520 \text{ kJ mol}^{-1}$ ,  $Na = 495 \text{ kJ mol}^{-1}$ )

(b) Alkali metals possess metallic character but hydrogen does not possesses metallic character under normal conditions.

#### Difference from Halogens :

(a) The reactivity of hydrogen is very low as compared to halogens.

(b) Oxides of halogens are acidic while that of hydrogen is neutral.

#### Dihydrogen ( $H_2$ ) :

##### Occurrence

It is most abundant element of the universe (70% of the total mass) but it is much less abundant element (0.15% by mass) in the earth atmosphere due to its light nature. In combined form it constitutes 15.4% of the earth crust and the oceans.

**Isotopes**

Hydrogen has three isotopes namely protium,  $^1\text{H}$ , deuterium,  $^2\text{H}$  or D and tritium  $^3\text{H}$  or T. They differ from one another by the number of neutrons present in them. Protium has no neutrons. Deuterium which is also known as heavy hydrogen has one and Tritium has two neutrons in the nucleus.

**Property**

	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	$10^{-5}$
Relative atomic mass ( $\text{g mol}^{-1}$ )	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point / K	20.39	23.67	25.0
Density / $\text{g L}^{-1}$	0.09	0.18	0.27
Enthalpy of fusion / $\text{kJ mol}^{-1}$	0.117	0.197	-
Enthalpy of vaporization / $\text{kJ mol}^{-1}$	0.904	1.226	-
Enthalpy of bond dissociation / $\text{kJ mol}^{-1}$ at 298.2 K	435.88	443.35	-
Internuclear distance / pm	74.14	74.14	-
Ionization enthalpy / $\text{kJ mol}^{-1}$	1312	-	-
Electron gain enthalpy / $\text{kJ mol}^{-1}$	-73	-	-
Covalent radius / pm	37	-	-
Ionic radius ( $\text{H}^+$ ) / pm	208	-	-

**Properties of dihydrogen :****Physical properties :**

- (a) It is a colourless, odourless tasteless gas.
- (b) It is combustible gas; so it can be carefully handled with care while using.
- (c) It is lighter than air (density =  $1/24^{\text{th}}$  that of air) and insoluble in water.

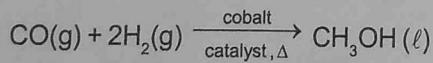
**Chemical properties :**

The chemical reactivity of dihydrogen is very low at room temperature. It is attributed to its very high H-H bond dissociation enthalpy ( $439.9 \text{ kJ mol}^{-1}$ ). This bond enthalpy in fact is the highest for any single bond enthalpy between two atoms of any element. The relatively inert nature of dihydrogen due to the high H-H bond enthalpy may be understood by the fact that the dissociation of dihydrogen into atoms is only 0.081 % around 2000 K which increases to 95.5% at 5000 K. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations with its incomplete  $1s^1$  electronic configuration. It does combine with almost all the elements. It undergoes chemical reaction by :

- (a) loss of the only electron to give  $\text{H}^+$
- (b) gain of an electron to form  $\text{H}^-$ , and
- (c) sharing an electron to form a single covalent bond.

**Uses :**

- (i) In the manufacture of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers
- (ii) In the manufacture of vanaspati ghee by hydrogenation of polyunsaturated vegetable oils like, soyabean, cotton seed etc.
- (iii) In the manufacture of bulk organic chemicals, particularly methanol.



- (iv) In preparation of metal hydrides and hydrogen chloride which are highly useful chemicals.
  - (v) It is used in the metallurgical process to reduce heavy metal oxides into metals.
  - (vi) Atomic hydrogen (where temperature required is 2500 K) and oxy-hydrogen torches (where temperature required is 4000 K) are used for cutting and welding purposes.
- Dissociation of dihydrogen with the help of an electric arc produces atomic hydrogen atoms. The atomic hydrogen atoms are allowed to recombine on the surface to be welded to regenerate the temperature of 4000K.
- (vii) Mixed with liquid oxygen, it is used as a rocket fuel in space research.
  - (viii) It is used in fuel cells for generating electrical energy because it does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

**Hydrides :**

Dihydrogen combines with a large number of non-metals and metals, except noble gases, under certain suitable reaction conditions to form compounds. These binary compounds are called hydrides. The hydrides can be represented by the general formula  $EH_x$  (e.g.  $MgH_2$ ) or  $E_mH_n$  (e.g.  $B_2H_6$ )

**Hydrides**

Ionic or saline  
or Salt like hydrides

Covalent or Molecular  
hydrides

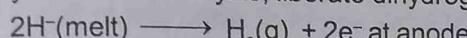
Metallic or Non stoichiometric  
hydrides

**Ionic or saline hydrides :**

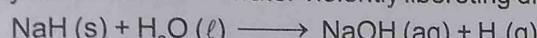
These are stoichiometric compounds of dihydrogen with most of the s-block elements which are highly electropositive in nature.

However, the lighter metal hydrides such as  $LiH$ ,  $BeH_2$  and  $MgH_2$  have significant covalent character. Infact  $BeH_2$  and  $MgH_2$  are polymeric in nature.

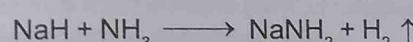
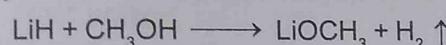
Ionic hydrides are crystalline, nonvolatile and non conducting in solid state. But their molten state conduct electricity and on electrolysis, liberate dihydrogen gas at anode. Which confirms the existence of  $H^-$  ion.



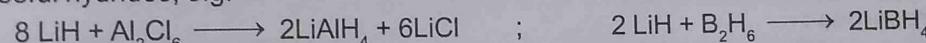
These hydrides react with water violently liberating dihydrogen gas.



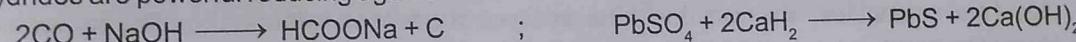
Similarly with protonic solvent such as ethanol and ammonia, they combine and liberates dihydrogen gas.



Note :  $LiH$  is unreactive at moderate temperature with  $O_2$  or  $Cl_2$  and therefore, it is used in the synthesis of other useful hydrides, e.g.



Ionic hydrides are powerful reducing agents

**Covalent or molecular hydrides**

These are the binary compounds of hydrogen with most of the p-block elements which have relatively high electronegativity. Covalent hydrides involves the formation of covalent bonds between H-atoms and other atoms by sharing of electrons. Some important examples of covalent hydrides are  $HCl$ ,  $H_2O$ ,  $CH_4$ ,  $PH_3$ ,  $NH_3$  etc.

Being covalent they are volatile compounds and more soluble in organic solvents.  
Molecular hydrides are further classified according to the relative numbers of electrons and bond in their Lewis structures.

**Molecular hydrides**

**Electron deficient hydrides**  
They have too few electrons for writing their conventional Lewis structures, examples :  $B_2H_6$  and all elements of group 13<sup>th</sup> form electron deficient compounds. They acts as Lewis acid, i.e. electron acceptor

**Electron precise hydrides**  
They have required number of electron for writing their conventional Lewis structures. Example :  $CH_4$  and hydrides of group 14<sup>th</sup> elements. They have tetrahedral geometry.

**Electron rich hydrides** They have excess of electrons which are present as lone pairs  
Examples : Elements of group 15-17 form such hydrides  
 $NH_3$ -1 lone pair ;  
 $H_2O$  - 2 lone pairs  
 $HF$  - 3 lone pairs  
They acts as Lewis base, i.e. electron donors.

**Note :** The presence of lone pairs on highly electronegative atoms like N, O, and F in hydrides results in hydrogen bond formation between the molecules leading to the association of molecule.

**Metallic or non - stoichiometric (or interstitial) hydrides :**

These are formed by many d-block and f-block elements except the metals of group 7,8 and 9. Chromium only the 6<sup>th</sup> group metals which form metallic hydrides, (CrH). These hydrides conduct electricity and heat not as efficiently as their parent metals do.

They are almost always non-stoichiometric, being deficient in hydrogen.

Examples :  $\text{LaH}_{2.87}$ ,  $\text{YbH}_{2.55}$ ,  $\text{TiH}_{1.5-1.8}$ ,  $\text{ZrH}_{1.3-1.75}$ ,  $\text{VH}_{0.56}$ ,  $\text{NiH}_{0.6-0.7}$ ,  $\text{PdH}_{0.6-0.8}$  etc.

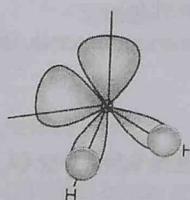
Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. This gave the name interstitial hydrides to this type of hydrides but recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metals.

This property of absorption of hydrogen on transition metal is largely used in the catalytic reduction, hydrogenation reaction for the preparation of large number of compounds.

Pd, Pt etc. can accommodate a very large volume of hydrogen and therefore can be used as its storage media.

**Water :**

It is an important constituent of animal and vegetable matter and plays a vital role in their life processes. It constitutes about 65% of human body and about 95% by weight of some plants. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform.

**Physical properties :**

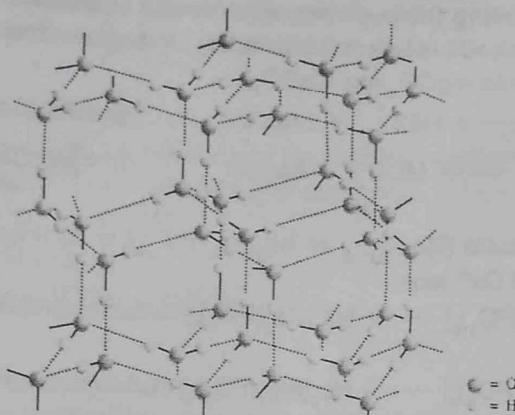
It is a colourless and tasteless liquid. It has some unique and unusual properties in the condensed phase (liquid and solid states) which are due to the presence of extensive hydrogen bonding between water molecules. Hydrogen bonding leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$ .

Water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant etc than most of the other liquids. Because of these properties water play a vital and key role in the biosphere.

Property	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$
Molecular mass ( $\text{g mol}^{-1}$ )	18.0151	20.0276
Melting point / K	273.0	276.8
Boiling point / K	373.0	374.4
Enthalpy of formation / $\text{kJ mol}^{-1}$	-285.9	-294.6
Enthalpy of vaporisation (373K) / $\text{kJ mol}^{-1}$	40.66	41.61
Enthalpy of fusion / $\text{kJ mol}^{-1}$	6.01	-
Temp of max. density / K	276.98	284.2
Density (298K) $\text{g cm}^{-3}$	1.0000	1.1059
Viscosity / centipoise	0.8903	1.107
Dielectric constant / $\text{C}_2/\text{N.m}^2$	78.39	78.06
Electrical conductivity	$5.7 \times 10^{-8}$	-

**Structure of ice**

Ice has a highly ordered three dimensional hydrogen bonded structure



According to X-rays analysis of ice crystals, each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 2.76 Å. There are four H atoms around each O atom. Two of the four H atoms are bonded by covalent bonds (bond lengths 100 pm) whereas the other two are bonded through H-bonds (bond lengths 176 pm)

**Soft water and Hard water :****Soft water**

- Water free from soluble salts of calcium and magnesium is called soft water.  
It gives lather with soap easily.
- Distilled water and rain water are common examples of soft water.
- It does not form scum/precipitate with soap.
- It is suitable for laundry as well as for boilers.

**Hard water**

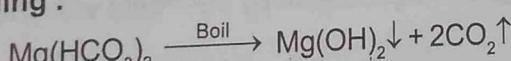
- Water containing calcium and magnesium in the form of hydrogen carbonate, chloride and sulphate does not give lather with soap. This type of water is called hard water.
- River water, sea water, tap water are common examples of hard water.
- It forms scum/precipitate with soap. It reacts with soap (containing sodium stearate) to precipitate out Ca/Mg stearate.  

$$2C_{17}H_{35}COONa(aq) + M^+(aq) \downarrow \\ (C_{17}H_{35}COO)_2M \downarrow + 2Na^+(aq) \quad M = Ca/Mg$$
- It is not suitable for laundry because of the above reason. It is also harmful for boilers because of the deposition of salts in the form of scales. The scale formation reduces the efficiency of the boiler.

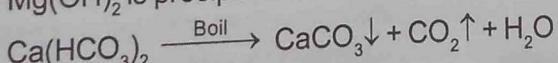
**Hardness of water :****(1) Temporary hardness :**

It is due to the presence of the soluble bicarbonates of magnesium and calcium.

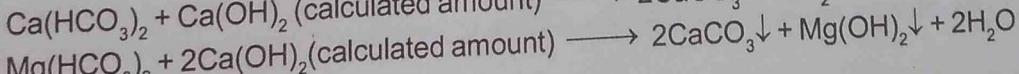
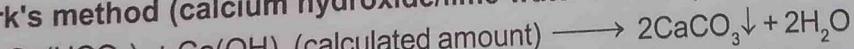
Methods used for removing the temporary hardness of water are as follows -

**(a) Boiling :**

$Mg(OH)_2$  is precipitated because of high solubility product of  $Mg(OH)_2$  as compared to that of  $MgCO_3$ .



Filtrate is soft water.

**(b) Clark's method (calcium hydroxide/lime water method) :**

**(2) Permanent hardness :**

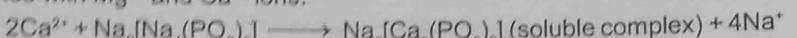
It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates.

Methods used for removing the permanent hardness of water are as follows -

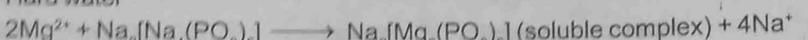
(a) **Addition of washing soda (sodium carbonate)** : It reacts with chloride and sulphate of  $Mg^{2+}$  and  $Ca^{2+}$  to precipitate out as  $MgCO_3$  and  $CaCO_3$ .

**(b) Calgon's method :**

Sodium hexametaphosphate ( $Na_6P_6O_{18}$  or  $Na_2[Na_4(PO_3)_6]$ ) is commercially called 'calgon' forms soluble complexes with  $Mg^{2+}$  and  $Ca^{2+}$  ions.

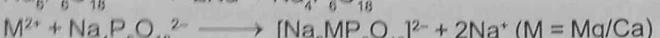
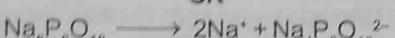


Hard water

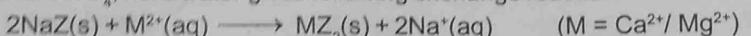


Hard water

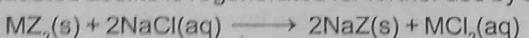
**OR**



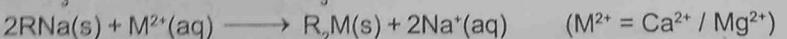
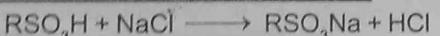
(c) **Ion-exchange method** : (Zeolite/permuntit method) With zeolite (hydrated sodium aluminium silicate)  $NaAlSiO_4$ , hard water gives following exchange reaction.



The exhausted zeolite is regenerated for further use by treating with aqueous solution of  $NaCl$



(d) **Synthetic resin method** : This method is more efficient than zeolite. It involves the use of cation exchange resin and anion exchange resin for softening of water. Cation exchange resin contain large organic molecules with  $-SO_3H$  group and are insoluble. Anion exchange resin contain large organic molecules with  $-OH$  group and are insoluble.

**Reaction with cation exchange resin.**

Hard water

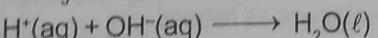
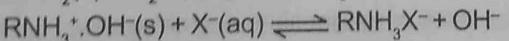
Exhausted resin is then regenerated by treating with  $NaCl$  solution.

Pure de-mineralised water which is free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the  $H^+$  form) and an anion exchange (in the  $OH^-$  form).



Here in this  $H^+$  exchange for  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and other cation present in the water. This process results in the release of proton and thus makes the water acidic.

In the anion exchange process as given below,  $OH^-$  exchanges for anion like,  $Cl^-$ ,  $HCO_3^-$ ,  $SO_4^{2-}$  etc, present in the water, this process results in the release of  $OH^-$  which neutralise the  $H^+$  ions released in the cation exchange.



The exhausted cation and anion exchange resin are regenerated by treatment with dilute acid and dilute alkali solutions respectively.

**Heavy water ( $D_2O$ ) :****Preparation :**

(a) By prolonged/exhaustive electrolysis of water.

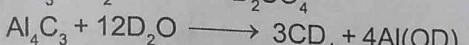
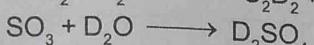
(b) Obtained as a by product in some fertilizer industries.

**Properties :**

Heavy water is colourless, tasteless and odourless liquid. All physical constants of heavy water are higher than the corresponding values of ordinary water. Chemically heavy water is similar to ordinary water but the chemical reactions are slower than those of ordinary water.

**Uses :**

- It is widely used as moderator in nuclear reactors.
- It is used in exchange reactions for the study of the reaction mechanism.
- It is used for the preparation of other deuterium compounds.

**Properties of H<sub>2</sub>O<sub>2</sub> :****(a) Physical properties :**

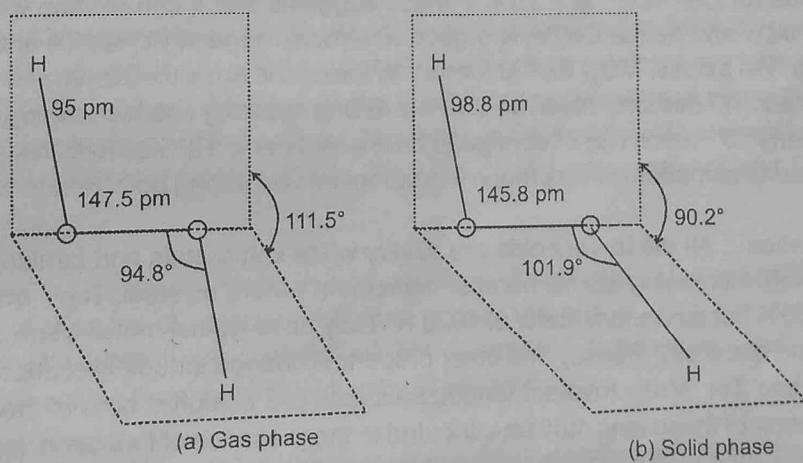
- It is a colourless viscous liquid which appears blue in the large quantity.
- It is H-bonded and therefore, miscible with water in all proportions and forms a hydrate H<sub>2</sub>O<sub>2</sub>.H<sub>2</sub>O (melting point 221 K).
- Its boiling point (144°C) is more than water, freezing point (-4°C) is less and density is more than water. Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O<sub>2</sub>, slowly on exposure to light.



H<sub>2</sub>O<sub>2</sub> is not kept in glass/metal containers because traces of alkali metal ions and metal ions from the glass and metal surface respectively can catalyse the explosive decomposition of H<sub>2</sub>O<sub>2</sub>. Therefore, H<sub>2</sub>O<sub>2</sub> aqueous solution is stored in the plastic or wax-lined glass containers in dark and some urea, phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H<sub>2</sub>O<sub>2</sub>. It is also kept away from the dust because dust can also induce explosive decomposition. Commercially it is marketed as 10 V, which means it contains 3% H<sub>2</sub>O<sub>2</sub>.

**Structures :**

Hydrogen peroxide is non planar structure. The two oxygen atoms are linked to each other by a single covalent bond and each oxygen is further linked to a hydrogen atom by a single covalent bond. The O-H bonds are in different planes due to repulsions between different bonding and antibonding orbitals.

**Uses :**

- It is used as a hair bleach and as a mild disinfectant. As an antiseptic, it is sold in the market as perhydrol.
- It is used to manufacture chemicals like sodium perborate and per carbonate used in high quality detergents.
- It is used in synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- Also used in Environmental (Green) chemistry. e.g., in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.?

## f-BLOCK ELEMENTS

### The inner transition elements (f-block)

#### INTRODUCTION :

The elements constituting the f-block are those in which the 4f and 5f orbitals are progressively filled. These elements are the members of group 3.

The f-block elements comprises of the two series, (i) lanthanoids (the fourteen elements following lanthanum) and (ii) actinoids (the fourteen elements following actinium).

#### [A] Lanthanoids (4f - series) :

**Electronic configuration :** The atoms of these elements have electronic configuration with  $6s^2$  common but with variable occupancy of 4f level. However, the electronic configurations of all the tripositive ions which is the most stable oxidation state of all the lanthanoids, are of the form  $4f^n$  ( $n = 1$  to 14 with increasing atomic number)

**Atomic sizes :** There is decrease in atomic and ionic radii from lanthanum to lutetium due to lanthanoid contraction. The decrease in atomic radii is not quite regular as it is regular in  $M^{3+}$  ion. This contraction is of course, similar to that observed in an ordinary transition series and is attributed to the imperfect shielding of one electron by another in the same subshell. However, the shielding of one 4f electron by another is less than a d-electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.

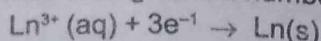
The cumulative effect of the contraction of the lanthanoids series, known as lanthanoids contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm) is a result of the lanthanoid contraction. This accounts for their occurrence together in nature and for the difficulty in their separation.

**Oxidation state :** In the lanthanoids, La(III) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half filled or filled f subshell. Thus the formation of  $Ce^{IV}$  is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The  $E^\circ$  value for  $Ce^{4+}/Ce^{3+}$  is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent; Pr Nd, Tb and Dy also exhibit +4 state but only in oxides,  $MO_2$ .  $Eu^{2+}$  is formed by losing the two s electrons and its  $f^7$  configuration accounts for the formation of this ion. However,  $Eu^{2+}$  is a strong reducing agent changing to the +3 common oxidation state. Similarly  $Yb^{+2}$  which has  $f^{14}$  configuration is a reductant.  $Tb^{IV}$  has half filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

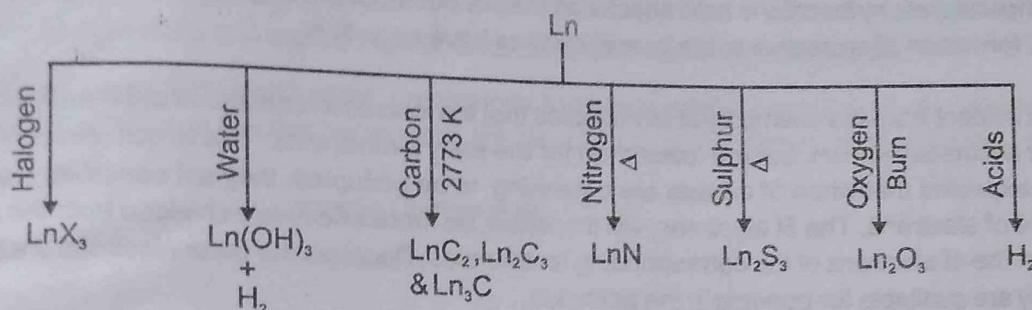
**General characteristics :** All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium is hard as steel. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm. Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solution. Colour of these ions may be attributed to the presence of f electron. Neither  $La^{3+}$  nor  $Lu^{3+}$  ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f level. The lanthanoids ions other than the  $f^0$  type ( $La^{+3}$  and  $Ce^{4+}$ ) and the  $f^{14}$  type ( $Yb^{2+}$  and  $Lu^{3+}$ ) are all paramagnetic. The paramagnetism rises to maximum in neodymium.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol<sup>-1</sup>s, the second about 1200 kJ mol<sup>-1</sup> comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3d orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals f level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number. They behave more like aluminium. Values for  $E^\circ$  for the half reaction



are in the range of  $-2.2$  to  $-2.4$  V except for Eu for which the value is  $-2.0$  V. This is of course, a small variation. The metals combine with hydrogen when gently heated in the gas. They form oxides  $\text{M}_2\text{O}_3$  and hydroxides  $\text{M(OH)}_3$ . The hydroxides are definite compounds, not just hydrate oxides. They are basic like alkaline earth metals oxides and hydroxides.



### Uses of lanthanoids :

1. Used for the production of alloy steels for plates and pipes. e.g mischmetall which consists of lanthanoid metal (~95%) and iron (~5%) and traces of S,C,Ca and Al. Mischmetall is used in Mg based alloy to produce bullets, shell and lighter flint.
2. Mixed oxides of lanthanoids are employed as catalyst in petroleum cracking.
3. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.
4. Because of their paramagnetic and ferromagnetic character, their compounds are used in making magnetic & electronic devices.
5. Ceric sulphate is a well known oxidizing agent in volumetric analysis.

### [B] Actinoids (5f - series) :

The actinoids include the fourteen elements from Th to Lr. The actinoids are radioactive elements and the earlier members have relatively long half lives, the latter ones have half life values ranging from a day to 3 minutes for lawrencium ( $Z = 103$ ).

**Electronic Configuration :** All the actinoids are believed to have the electronic configuration of  $7s^2$  and variable occupancy of the 5f and 6d subshell. The fourteen electrons are formally added to 5f, through not in thorium ( $Z = 90$ ) but from Pa onwards the 5f orbitals are complete at element 103. The irregularities in the electronic configuration of the actinoid, like those in the lanthanoids are related to the stabilities of the  $f^0$ ,  $f^1$  and  $f^{14}$  occupancies of the 5f orbitals. Thus the configurations of Am and Cm are  $[\text{Rn}] 5f^7 7s^2$  and  $[\text{Rn}] 5f^7 6d^1 7s^2$ .

**Ionic Sizes :** The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or  $\text{M}^{3+}$  ions across the series. This may be referred to as the actinoids contraction (like lanthanoids contraction). The contraction is, however, greater from elements to element in this series resulting from poor shielding by 5f electrons.

**Oxidation states :** There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies.

The actinoids show in general +3 oxidation state. The elements, in the first half to the series frequently exhibit higher oxidation state. e.g. The maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However +3 and +4 ions tends to hydrolyse.

**General characteristics and comparison with Lanthanoids :**

1. The actinoids metals are all silvery white in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.
2. The actinoids are highly reactive metals, especially when divided, the action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most metals takes place at moderate temperatures; hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.
3. It is evident from the chemistry of lanthanoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

**Note :** The lanthanoids contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

**Uses of actinoids :**

1. Thorium is used in atomic reactors and in the treatment of cancer. Its salts are used in making incandescent gas mantles.
2. Uranium is used as a nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
3. Plutonium it is used as a fuel for atomic reactors as well as for making atomic bombs.

# ORGANIC CHEMISTRY

## CLASSIFICATION AND IUPAC NAMING OF ORGANIC COMPOUNDS

### Classification of Organic Compounds :

Generally organic compounds classify into Aliphatic or Aromatic compounds.

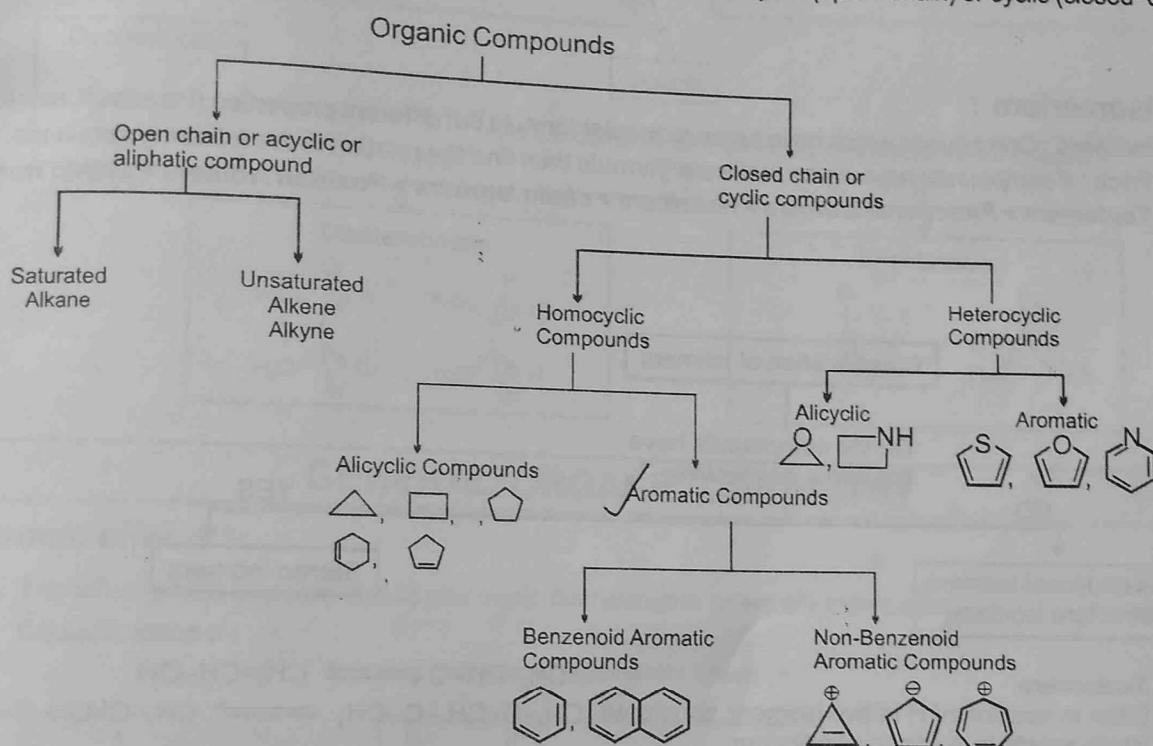
**Aromatic compounds :** Aromatic compounds are those compounds which are cyclic, planar and close

cyclic conjugation of  $(4n + 2)\pi$ -electrons.

**Aliphatic compounds :** All organic compounds other than aromatic compounds.

If we look at the vast number of organic compounds, two things will strike in our mind – the skeleton is either open

or closed. Based on this, organic compounds are classified as acyclic (open-chain) or cyclic (closed-chain)



### IUPAC Naming of Aliphatic compounds and their derivatives :

**IUPAC Scheme:** Secondary Prefix + Primary prefix + word root + Primary suffix + Secondary suffix

- Number of carbon atoms in the longest continuous parent chain is consider for word root. (Meth, eth, prop, but, pent.....)

- Senior most functional group is consider as sec. suffix. Seniority order of functional groups is :

$\text{COOH} > \text{SO}_3\text{H} > \text{CO-O-CO} > \text{COOR} > \text{COX} > \text{CONH}_2 > \text{CN} > \text{CHO} > -\text{CO}- > \text{OH} > \text{SH} > \text{NH}_2$

- Functional groups which are not covered in IUPAC seniority, consider as substituents and write alphabetically as secondary prefix :

### Parent chain selection :

Use following sequence for parent chain selection. A carbon chain, which have :

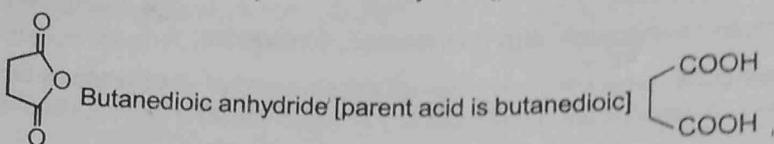
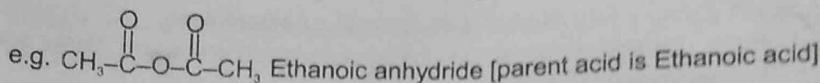
- (i) Maximum number of senior most functional groups.
- (ii) Maximum number of multiple bonds ( $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$ )
- (iii) Maximum number of carbon atoms
- (iv) Maximum number of substituents including junior functional groups.
- (v) [Now cyclic is prefer over acyclic chain]
- (vi) Nearest locants (follow lowest set of locant rule till first point of difference.)
- (vii) Alphabetical seniority and [ $\text{C}=\text{C}$  prefer over  $\text{C}\equiv\text{C}$ ]

**Numbering :**

Starts from that end of the parent chain where carbon atom bearing senior most functional group is terminating.

- If senior most functional group is chain terminating then numbering starts from that carbon only.
- Priority order : senior functional group > (C=C/C=C) > substituents.

**Note :** • In the naming of **acid anhydride** use only parent acid name.



3.

**Isomerism :**

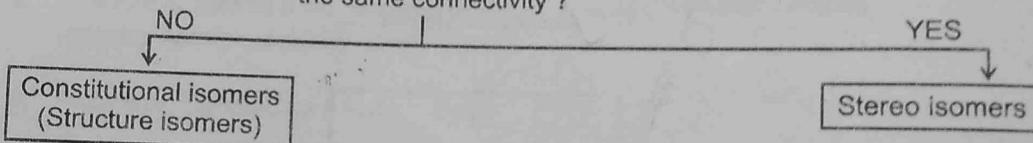
**Isomers :** Compounds which have same molecular formula but different properties (Physical/Chemical).

**Trick :** If compounds have same molecular formula then find the relation in the following sequence.

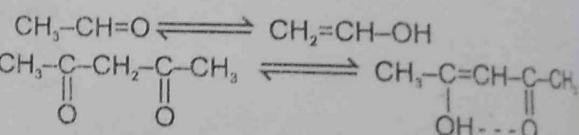
Tautomers > Functional isomers > Metamers > chain Isomers > Position isomers > stereo Isomers

## Classification of isomers

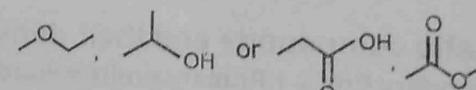
Do the compounds have  
the same connectivity ?

→ **Tautomers**

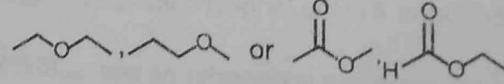
Differ in position of H in two isomeric structures which exists in dynamic equilibrium.

→ **Functional isomer**

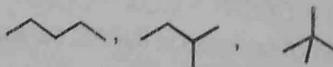
Differ in nature of functional group

→ **Metamers**

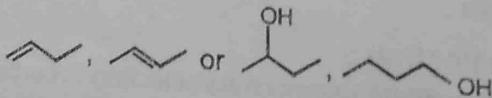
Different nature of alkyl groups along a polyvalent hetero atom in compound.

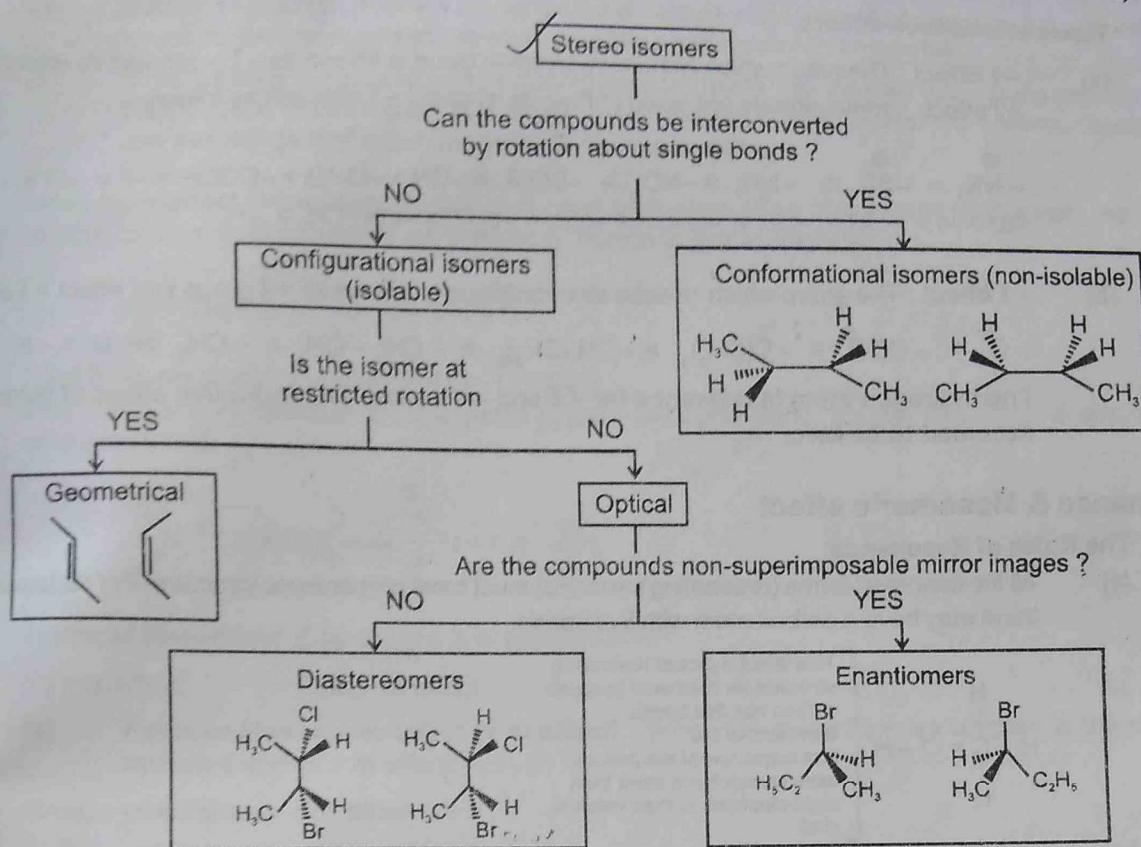
→ **Chain isomers**

Differ in no. of carbon atoms in main chain or side chain

→ **Position isomers**

Differ in position of functional group / multiple bond/substituent in same Carbon skeleton



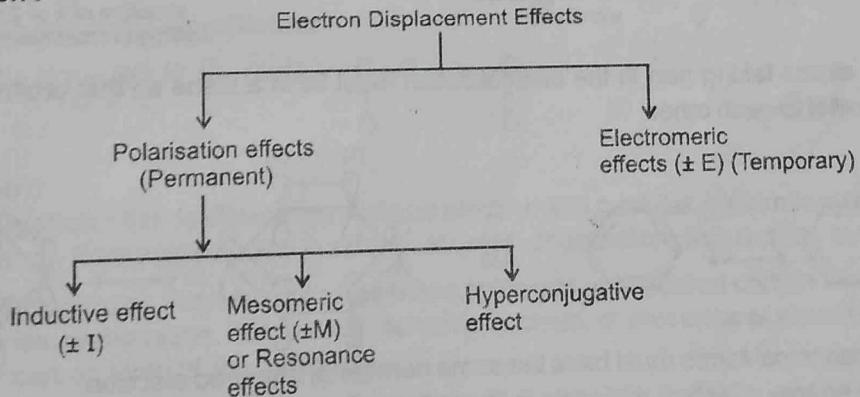


## GENERAL ORGANIC CHEMISTRY

### Electronic effects :

The effect which appears due to electronic distribution is called electronic effect.

#### Classification :



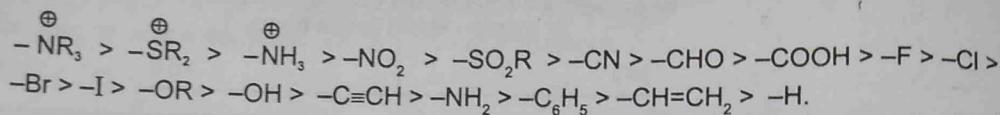
### Inductive Effect

Thus inductive effect may be defined as a permanent displacement of  $\sigma$  bond pair electrons due to a dipole. (Polar bond)

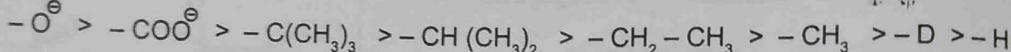
- It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.
- It is also called transmission effect.
- It causes permanent polarisation in molecule, hence it is a permanent effect
- The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.
- The electrons never leave their original atomic orbital.
- Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.
- The inductive effect is always operative through  $\sigma$  bond, does not involve  $\pi$  bond electron.

## Types of inductive effect :

- (a) **- I Effect** : The group which withdraws electron cloud is known as - I group and its effect is called - I effect. Various groups are listed in their decreasing - I strength as follows.



- (b) **+ I effect** : The group which releases electron cloud is known as + I group and effect + I effect.

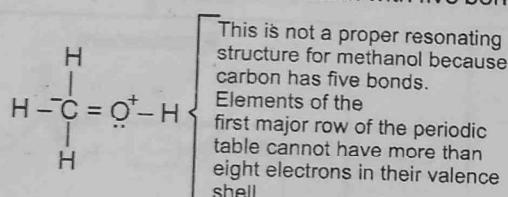


The hydrogen atom is reference for + I and - I series. The inductive effect of hydrogen is assumed to be zero.

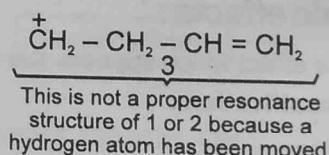
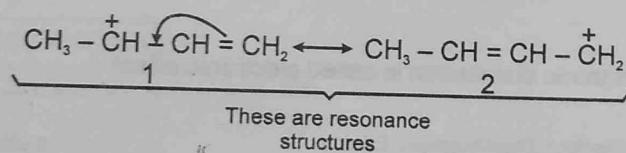
## Resonance &amp; Mesomeric effect

## The Rules of Resonance

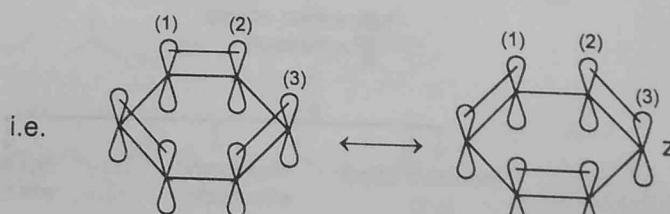
- (a) All the canonical forms (resonating structure) must have proper Lewis structure. For instance none of them may have a carbon atom with five bonds.



- (b) The positions of the nuclei of the atoms must remain the same in all of the structures. Structure 3 is not a resonance structure of 1 or 2, for example, because in order to form it we would have to move a hydrogen atom and this is not permitted :



- (c) All atoms taking part in the delocalisation must lie in a plane so that orbitals overlapping become parallel to each other.

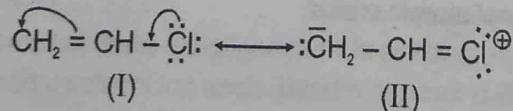


All canonical forms must have the same number of unpaired electron. The energy of actual molecule is lower than of any form. Therefore delocalisation is a stabilizing phenomenon.

All canonical forms do not contribute equally to the true molecule. The more stable structure is the greater contribution to its resonance hybrid.

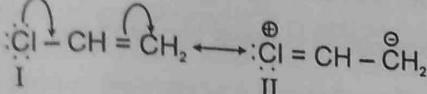
## Relative stability of the canonical form

- (a) Nonpolar (uncharged) structure are most stable. Charge separation decreases stability. Separating opposite charges requires energy. Therefore, structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation.



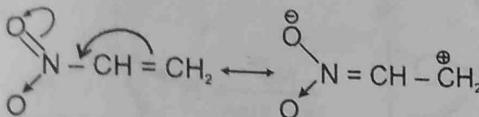
- (b) Structures in which all of the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are especially stable and make large contributions to the hybrid.
- (c) If all the atoms of two resonating structure have complete valence shell of electrons (complete octet) then that one will be more stable in which -ve charge is present over more electronegative atom and +ve charge is present over less electro negative atom.

**Mesomeric effect :** Mesomeric effect is defined as permanent effect of  $\pi$  electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond.



I and II are resonating structures of  $\text{Cl}-\text{CH}=\text{CH}_2$ .

This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect.

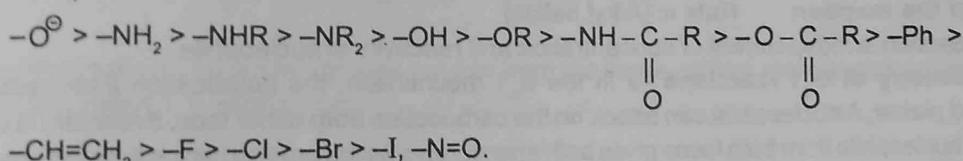


**Types of Mesomeric Effect :** This is of two types

- (a) + m effect      (b) - m effect

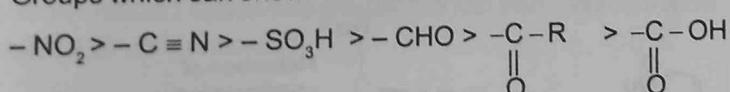
(a) **Positive Mesomeric effect (+ m effect)** : When the group donates electron to the conjugated system it shows + m effect.

Groups which shows '+ m' effect are :



(b) **Negative Mesomeric Effect (- m effect)** : When the group withdraws electron from the conjugated system, it shows - m effect

Groups which can show - m effect are

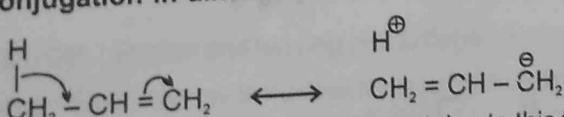


## Hyperconjugation

**Hyperconjugation** : It is delocalisation of sigma electron with p-orbital. Also known as  $\sigma\pi$ -conjugation or no bond resonance. It may take place in alkene, alkynes, carbocation, free radical, benzene nucleus.

**Necessary Condition** : Presence of at least one hydrogen at saturated carbon which is  $\alpha$  with respect to alkene, alkynes, carbocation, free radical, benzene nucleus. or presence of atleast one hydrogen atom at adjacent  $\text{sp}^3$  carbon atom of  $\text{sp}^2$  carbon.

### Hyperconjugation in alkene



(a) The effect of electron displacement due to this type of resonance is called hyperconjugative effect.  
 (b) Since canonical forms of this resonance may not contain any bond between H and C so  
 (c) hyperconjugation is also known as no bond resonance.

These resonating structures only suggest that

- \* There is some ionic character between C - H bond.
- \* Carbon - carbon double bond acquires some single bond character.
- (d) Number of no bond resonating structures due to hyperconjugation = Number of  $\alpha$ -hydrogens (In aliphatic systems).

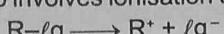
## FUNDAMENTAL CONCEPT IN ORGANIC REACTION MECHANISM

**Nucleophilic substitution reaction ( $S_N$ ):**

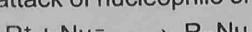
**Unimolecular nucleophilic substitution reaction ( $S_N1$ ):**

Nucleophilic substitution which involves two step process

(a) First step : Slow step involves ionisation to form carbocation.

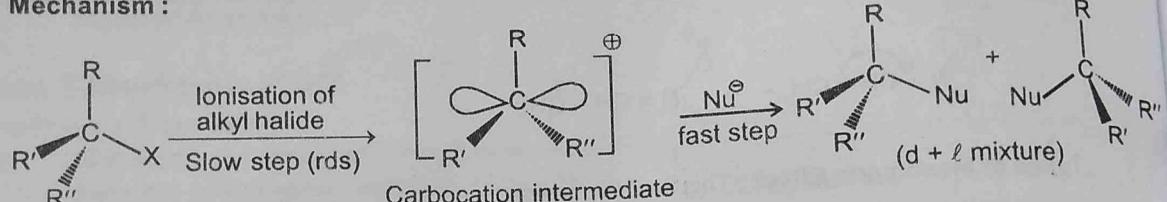


(b) Second step : Fast attack of nucleophile on carbocation to result into product.



### **$S_N1$ Reaction of Alkyl halide**

Mechanism :



**Characteristics of  $S_N1$  reactions :**

1. It is unimolecular, two step process.
2. Carbocation intermediate is formed so rearrangement is possible in  $S_N1$  reaction.
3. It is first order reaction

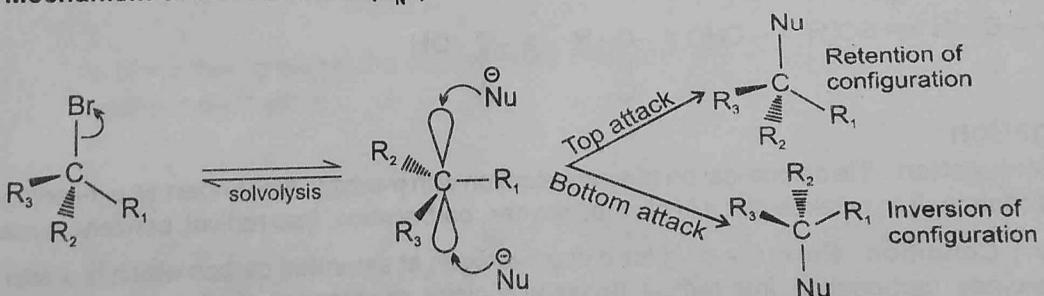
4. **Kinetics of the reaction**      Rate  $\propto$  [Alkyl halide]

Rate of  $S_N1$  reaction is independent of concentration and reactivity of nucleophile.

5. **Stereochemistry of  $S_N1$  reactions** → In the  $S_N1$  mechanism, the carbocation intermediate is sp<sup>2</sup> hybridized and planar. A nucleophile can attack on the carbocation from either face, if reactant is chiral then after attack of nucleophile from both faces gives both enantiomers as the product, which is called racemisation.

6. Practically it is found that % of inversion product is more than % of retention product due to close ion pair formation.

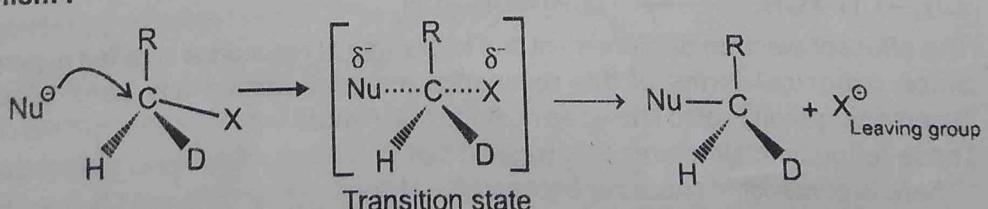
**Mechanism of racemisation ( $S_N1$ ) →**



### **Bimolecular nucleophilic substitution reaction ( $S_N2$ )**

**$S_N2$  Reaction of Alkyl halide :**

Mechanism :

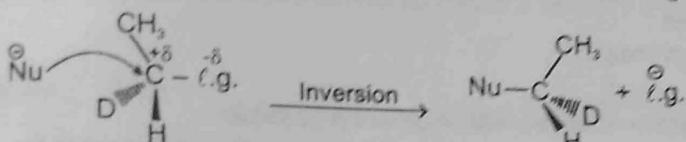


**Characteristic of S<sub>N</sub>2**

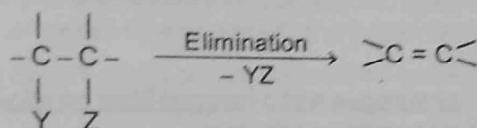
1. It is bimolecular, one step concerted process
2. It is second order reaction because in the rds both species are involved
3. Kinetics of the reaction :  $\text{rate} \propto [\text{alkyl halide}] [\text{nucleophile}]$   
 $\text{rate} = k[\text{alkyl halide}] [\text{nucleophile}]$

If the concentration of alkyl halide in the reaction mixture is doubled, the rate of the nucleophilic substitution reaction is double. If the concentration of nucleophile is doubled the rate of reaction is also double. If the concentration of both are doubled then the rate of the reaction quadruples.

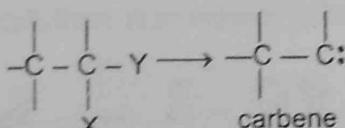
4. The stereochemistry of S<sub>N</sub>2 reactions → As we seen earlier, in an S<sub>N</sub>2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as Walden inversion. Thus we get an stereoisomer during S<sub>N</sub>2 reaction.

**Elimination reactions :**

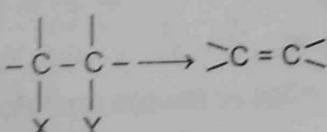
In an elimination reaction two atoms or groups (YZ) are removed from the substrate and generally resulting into formation of π bond.



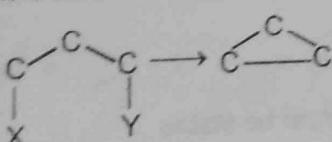
$\alpha$ -elimination : When two groups are lost from the same carbon atom to give a carbene (or nitrene). This is also called 1,1- elimination.



$\beta$ -elimination : When two groups are lost from adjacent atoms so that a new π bond is formed. This is also called 1,2- elimination.



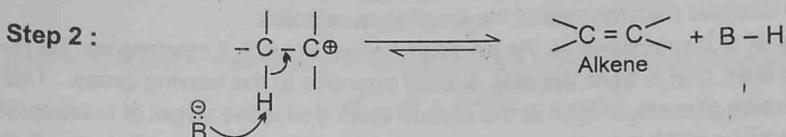
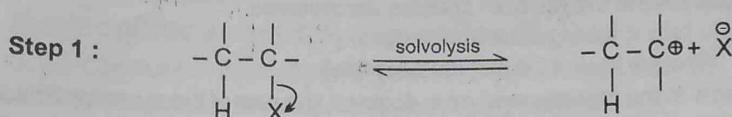
$\gamma$ -elimination : It is also called 1,3- elimination. In this a three membered ring is formed.



**E1 Reaction** : Proton and leaving group depart in two different step.

(a) First step : Slow step involves ionisation to form carbocation

(b) Second step : Abstraction of proton

**E1 Reaction of Alkyl halide :****Mechanism :**

E1 CBF

**Characteristics of E1 reaction :**

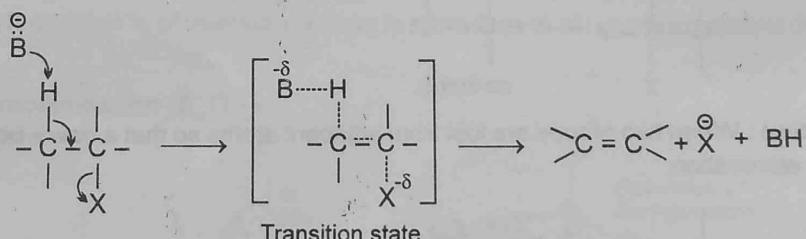
- It is unimolecular, two step process.
- It is a first order reaction.
- Reaction intermediate is carbocation, so rearrangement is possible
- In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.
- Kinetics :** Rate  $\propto$  [Alkylhalide]  
Rate = k [Alkylhalide]

**E2 Reaction :****E2 Reaction of Alkyl halide :**

Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene. Dehydrohalogenation can take place by E1 and E2 mechanism.

**Reagent**

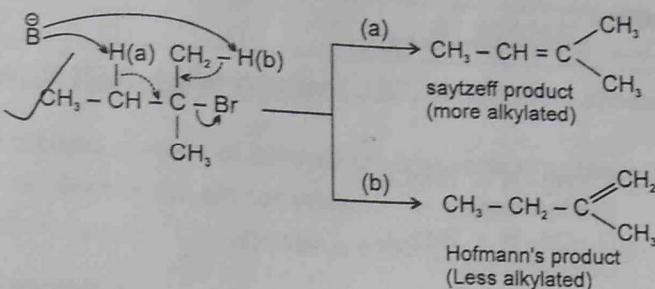
- Hot alcoholic solution of KOH or EtO<sup>-</sup> / EtOH
- NaNH<sub>2</sub>
- t-BuO<sup>-</sup>K<sup>+</sup> in t-BuOH

**Mechanism :****Characteristics of E2 reaction :**

- This is a single step, bimolecular reaction
- It is a second order reaction
- Kinetics  $\rightarrow$  Rate  $\propto$  [R-X] [Base]  
Rate = k [R-X] [B]
- Rearrangement is not possible
- For the lower energy of activation, transition state must be stable
- E2 follows a concerted mechanism
- The orientation of proton & leaving group should be antiperiplanar.
- Here  $\beta$  - H is eliminated by base hence called  $\beta$  elimination
- Positional orientation of elimination  $\rightarrow$  In most E1 and E2 eliminations where there are two or more possible elimination products, the product with the most highly substituted double bond will predominate. This rule is called the saytzeff or zaitsev rule.

**Reactivity towards E2  $\rightarrow$  R-I > R-Br > R-Cl > R-F**

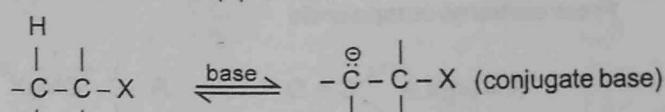
For example : Dehydrohalogenation of 2-bromo-2-methylbutane can yield two products.



### E1cB Reaction (Unimolecular conjugate base reaction):

In the E1cB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism : Step 1 :



Step 2 :



Remarks :

First step consists of the removal of a proton,  $\text{H}^+$ , by a base generating a carbanion.

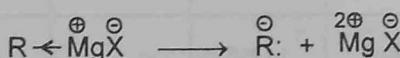
In second step carbanion loses a leaving group to form alkene

Condition : For the E1cB, (i) substrate must be containing acidic hydrogens and (ii) poor leaving groups.

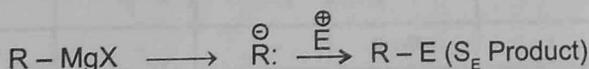
## GRIGNARD REAGENT

### Reactions of Grignard reagents

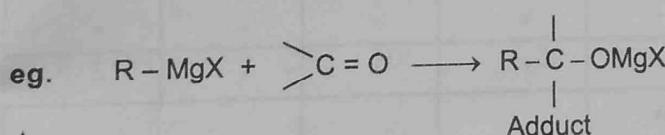
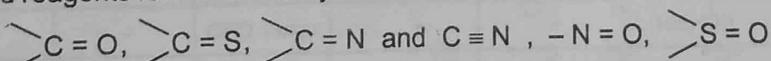
It has been found out by estimation that there is 35% ionic character in carbon-magnesium bond of Grignard reagent. Therefore, there is a tendency of forming carbanion by heterolysis of this polar coordinate bond as follows.



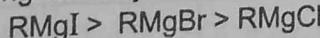
The carbanion (a nucleophile) formed as shown above, attacks the positively charged electrophilic centre of other compound. Therefore, it can be said that if a Grignard reagent is regarded as the substrate, then electrophile displaces  $\text{MgX}$ , i.e. electrophilic substitution ( $S_E$ ) reaction takes place.



Grignard reagents form adducts by addition on the following types of pi bonds.

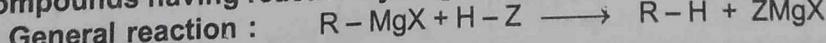


On having same hydrocarbon radical, the order of reactivity of Grignard reagents will be as follows :



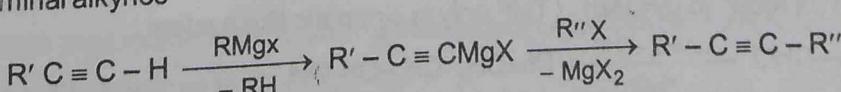
### Synthesis of Alkanes

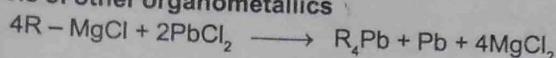
With compounds having reactive hydrogen atom



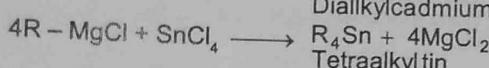
### Synthesis of higher alkynes

Non-terminal alkynes

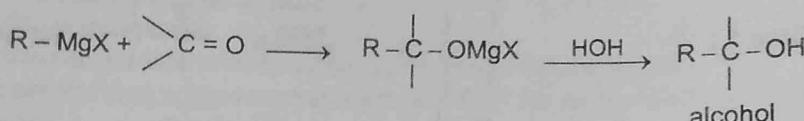


**Synthesis of other organometallics**

Two important antiknocking compounds, tetraethyllead (T.E.L.) and tetramethyllead (T.M.L.) are manufactured by the above reaction.

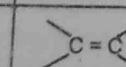
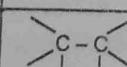
**Synthesis of Alcohols**

There are following methods to obtain alcohols from Grignard reagent.

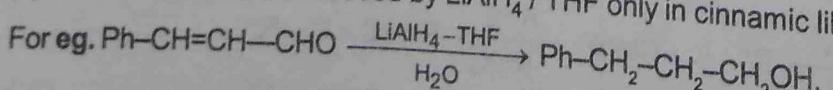
**From carbonyl compounds**

This is nucleophilic addition reaction.

**REDUCTION**

S.No.	F.G.	Reduced into	(1) LiAlH <sub>4</sub> /Ether (2) H <sub>2</sub> O H <sup>-</sup> by LiAlH <sub>4</sub> , H <sup>+</sup> by H <sub>2</sub> O	H <sub>2</sub> /Ni	DIBAL-H	(1) NaBH <sub>4</sub> , (2) EtOH H <sup>-</sup> by NaBH <sub>4</sub> , H <sup>+</sup> by EtOH	Na/EtOH e <sup>-</sup> by Na H <sup>+</sup> by EtOH
1	RCH = O	RCH <sub>2</sub> OH	+	+	+	+	+
2	R - C - R 	R - CH - R 	+	+	+	+	+
3	R - C - Cl 	RCH <sub>2</sub> OH	+	+	+	+	+
4	R - C - OR' 	RCH <sub>2</sub> OH + R'OH	+	difficult	+ (at 25°C) (upto -CHO at -78°)	-	+
5	 O  O R - C - O - C - R	R-CH <sub>2</sub> OH	+	difficult	-	-	+
6	RCOOH	RCH <sub>2</sub> OH	+	difficult	-	-	-
7	RCONH <sub>2</sub>	RCH <sub>2</sub> NH <sub>2</sub>	+	difficult	-	-	-
8	RC ≡ N	RCH <sub>2</sub> NH <sub>2</sub>	+	+	upto - CHO	-	+
9	RN ≡ C	RNH-CH <sub>3</sub>	+	+	-	-	+
10	RNO <sub>2</sub>	RNH <sub>2</sub>	+	+	-	-	-
11			*	+	-	-	-
12	-C ≡ C-	-CH <sub>2</sub> - CH <sub>2</sub> -	*	+	-	-	-
13	R - X	R - H	1° > 2° (SN <sup>2</sup> ) 3° (E-2)	Δ	-	3° > 2° > 1° (SN <sup>1</sup> )	-

(\*) double bond can be reduced by LiAlH<sub>4</sub> / THF only in cinnamic like system.



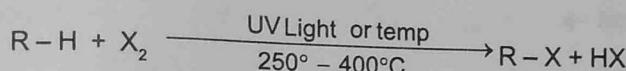
## ALKANE

### Chemical Reactions of Alkanes :

Characteristic reaction of alkanes are **free radical substitution** reaction, these reactions are generally chain reactions which are completed in three steps.

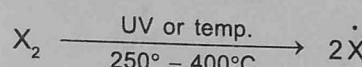
- (i) chain initiation      (ii) chain propagation.      (iii) chain termination

#### Halogenation :



#### Mechanism of halogenation of alkane →

- (i) Chain initiation → it is an endothermic step.



- (ii) Chain propagation →



- (iii) Chain termination → it is always **exothermic**



#### Steps of halogenation,

#### Value of $\Delta H$ for each step. (Kcal/mole)

	F	Cl	Br	I
(i) $X_2 \longrightarrow 2\dot{X}$	+ 38	+ 58	+ 46	+ 36
(ii) $\dot{X} + CH_4 \longrightarrow CH_3 + HX$	- 32	+ 1	+ 16	+ 33
(iii) $CH_3 + X_2 \longrightarrow CH_3X + \dot{X}$	- 70	- 26	- 24	- 20

**Reactivity of  $X_2$  :**  $F_2 > Cl_2 > Br_2 > I_2$

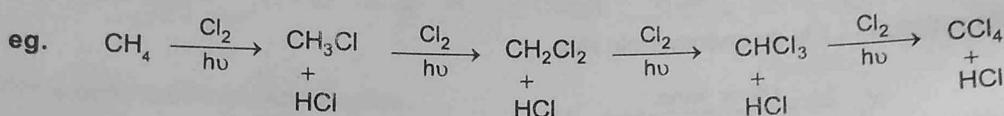
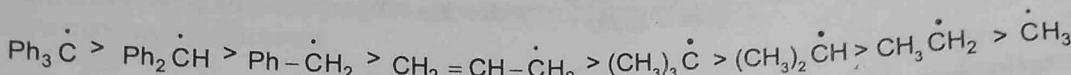
**Reactivity of H :**  $3^{\circ}H > 2^{\circ}H > 1^{\circ}H$

With  $F_2$  alkanes react so vigorously that even in the dark and at room temperature, reactant is diluted with an inert gas. Iodination is reversible reaction, since HI formed as a by product and it is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidising agent like  $HIO_3$ ,  $HNO_3$  or  $HgO$ .



Formation of alkyl free radical is rate determining step.

### Order of stability of Free radical →

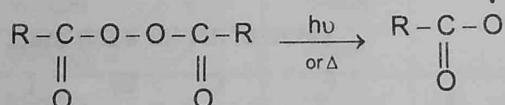
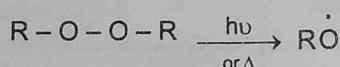


When equimolar amount of methane and  $Cl_2$  is taken, a mixture of four possible products are formed, but when we take excess of  $CH_4$  then yield of  $CH_3Cl$  will be high.

Each photon of light cleaves one chlorine molecule to form two chlorine radicals, each chlorine atom starts a chain and on an average each chain contains 5000 repetitions of the chain propagating cycle so about 10,000 molecules of  $CH_3Cl$  are formed by one photon of light.

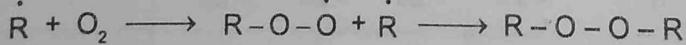
### In a chain reaction following reagents are involved -

(i) **Initiators** → they initiate the chain reaction, Initiators are peroxide ( $R_2O_2$ ), Peroxester's etc.



(ii) **Inhibitors** → A substance that slows down or stops the reaction is known as inhibitors

For example  $O_2$  is a good inhibitor



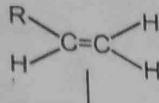
all reactive alkyl free radicals are consumed so reaction stops for a period of time.

### Relative reactivity of halogen towards methane →

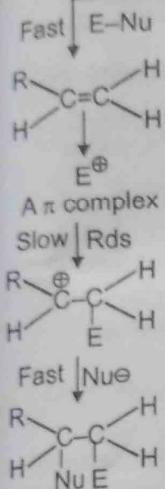
Order of reactivity is  $F_2 > Cl_2 > Br_2 > I_2$  which can be explained by the value of  $\Delta H$  (enthalpy change)

## ALKENE & ALKYNE

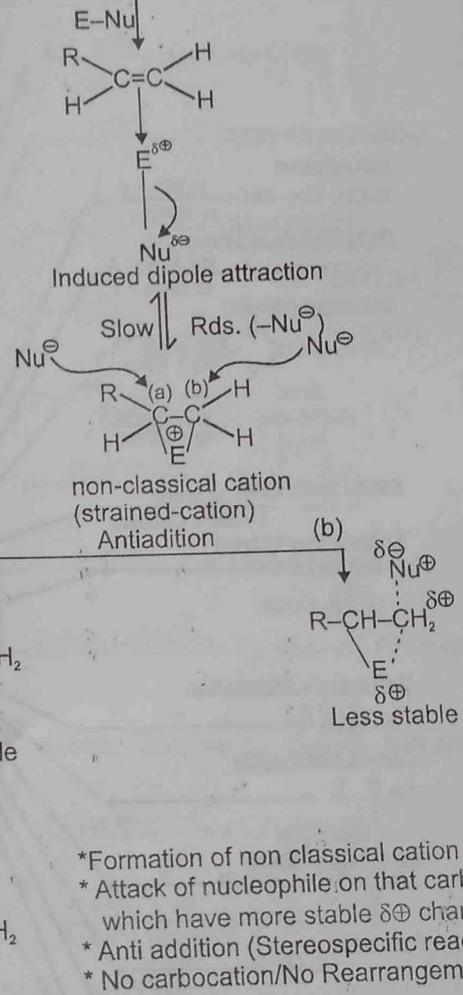
### Chemical reactions of alkene (Electrophilic addition Reaction)



Mechanism-I



Mechanism-II



#### Example of mechanism-I

- (1) Addition of hydrogen halide
- (2) Acid-catalysed hydration.
- (3) Addition of  $H_2SO_4$ .

- (1)
- (2)
- (3)
- (4)

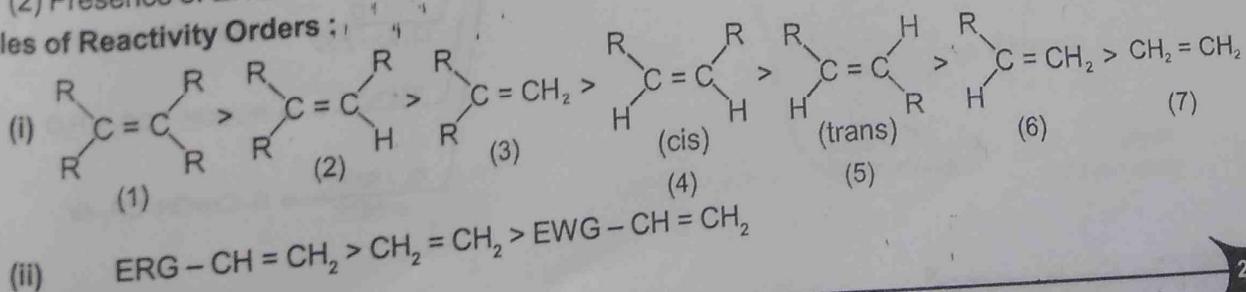
#### Example of mechanism-II

- Addition of halogen.
- Addition of hypohalous acid.
- Oxymercuration-demercuration
- Addition of  $NOCl$

#### Reactivity of an Alkene:

- (1) Presence of electron releasing groups (+m, +I) at  $C = C$  increases electrophilicity and reactivity.
- (2) Presence of ERG stabilises the intermediate carbocation. (3) More stable  $C^+$ , more is reactivity.

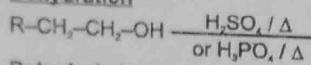
#### Examples of Reactivity Orders :



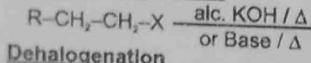
## Preparation and Properties of alkenes

## General Method of Preparation (GMP)

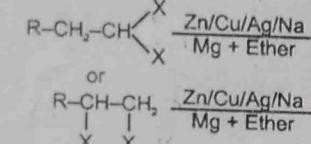
## Dehydration



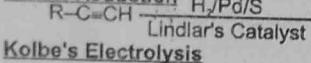
## Dehydrohalogenation



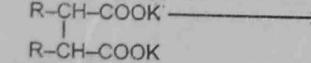
## Dehalogenation



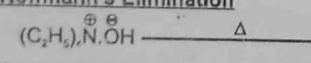
## Partial Reduction



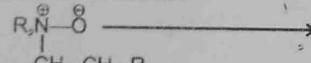
## Kolbe's Electrolysis



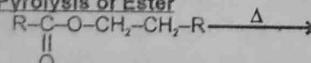
## Hoffmann's Elimination



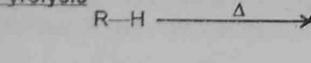
## Cope's Elimination



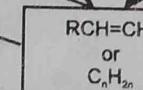
## Pyrolysis of Ester



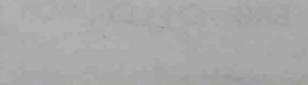
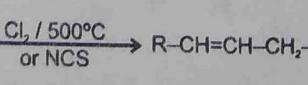
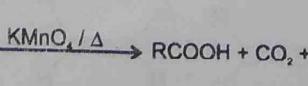
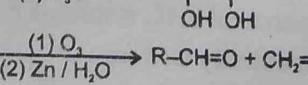
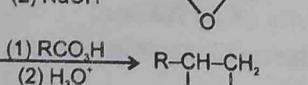
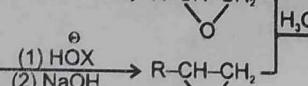
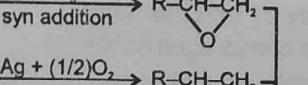
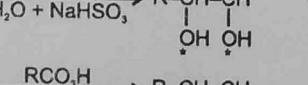
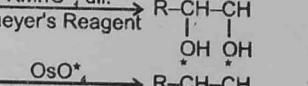
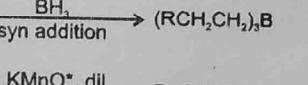
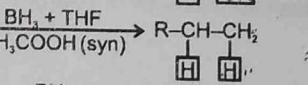
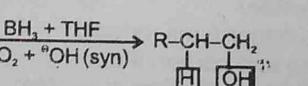
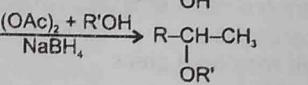
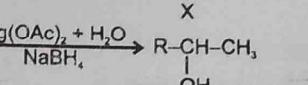
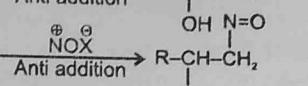
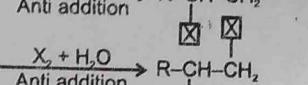
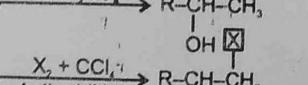
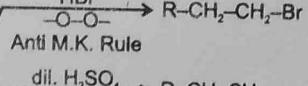
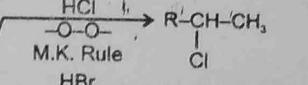
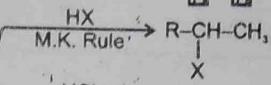
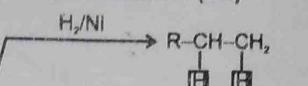
## Pyrolysis



## Birch reduction in Non Terminal alkyne

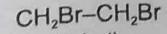


## General Reactions (GR)

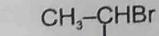


## General Method

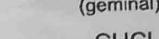
## Dehydrohalogenation



(vicinal)

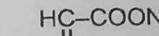
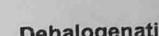


(geminal)



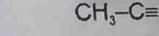
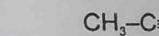
(chlorof).

## Dehalogenation



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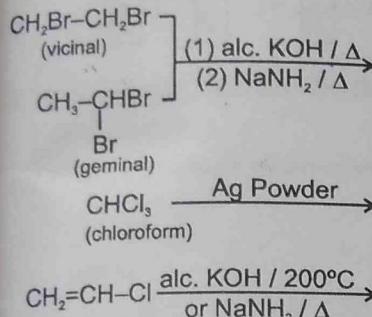
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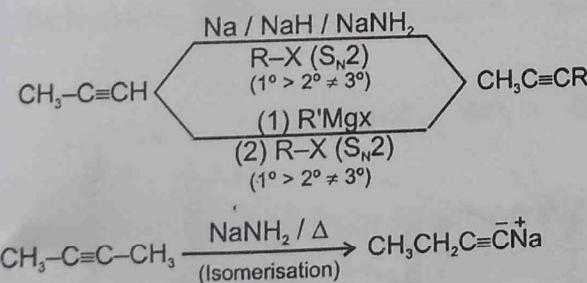
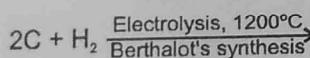
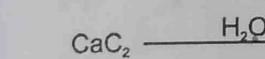
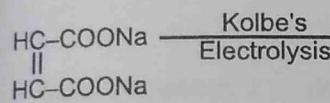
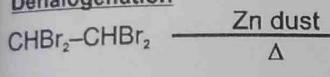
## Preparation and Properties of alkynes

### General Method of Preparation (GMP)

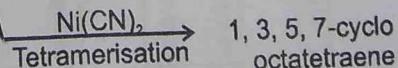
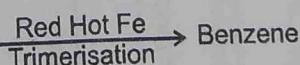
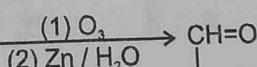
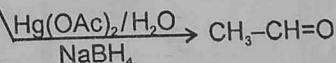
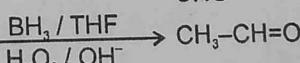
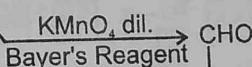
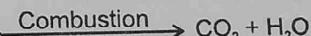
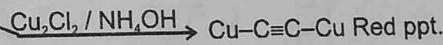
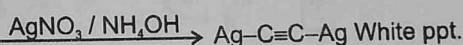
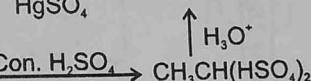
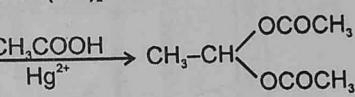
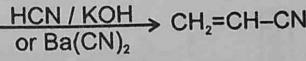
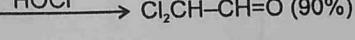
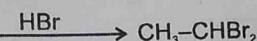
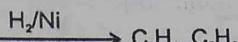
#### Dehydrohalogenation



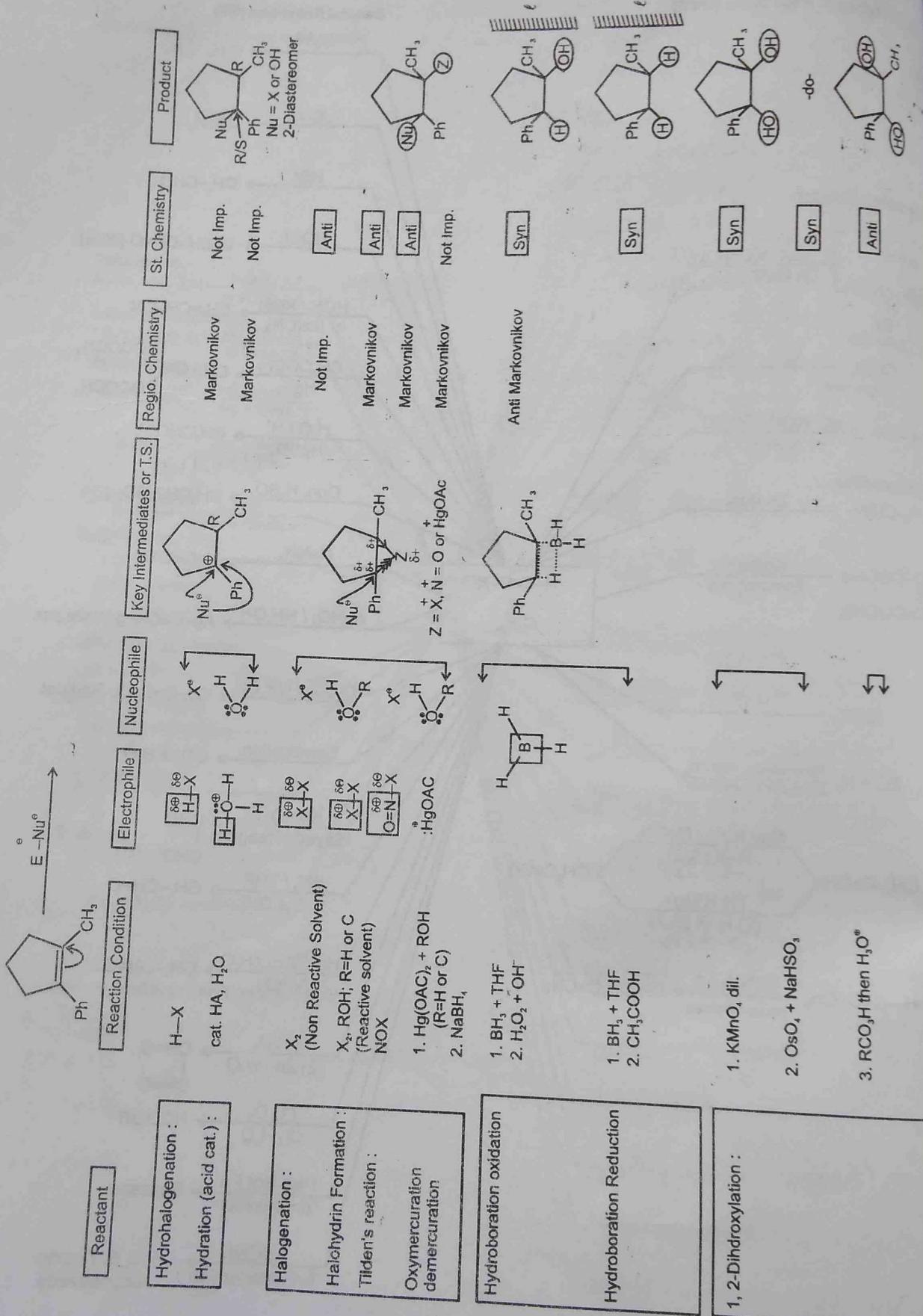
#### Dehalogenation



#### General Reactions (GR)



## Mechanism Review : Summary of Alkene addition reactions



## AROMATIC COMPOUNDS

### Aromatic Character : [The Huckel ( $4n + 2\pi$ ) rule]

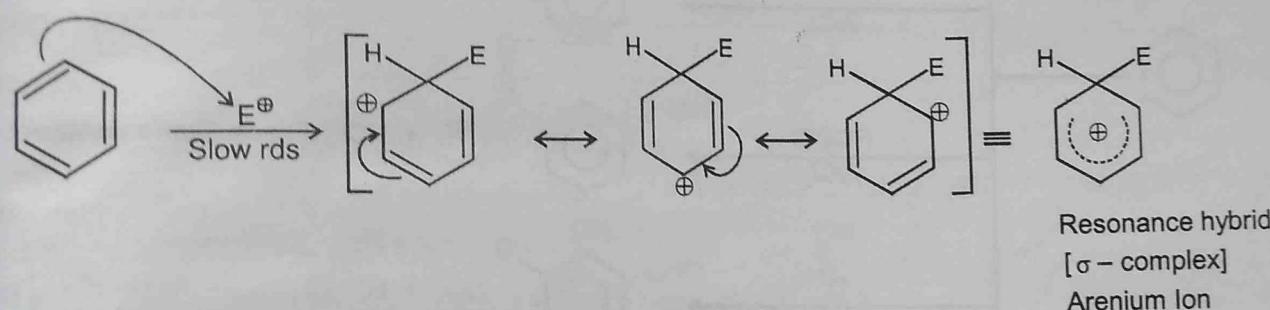
The following three rules are useful in predicting whether a particular compound is aromatic or non-aromatic.

- (I) Aromatic compounds are cyclic and planar.
- (II) Each atom in an aromatic ring is  $sp^2$  or  $sp$  hybridised.
- (III) The cyclic  $\pi$  molecular orbital (formed by overlap of p-orbitals) must contain  $(4n + 2)\pi$  electrons, i.e., 2, 6, 10, 14 .....  $\pi$  electrons. Where  $n$  = an integer 0, 1, 2, 3,.....

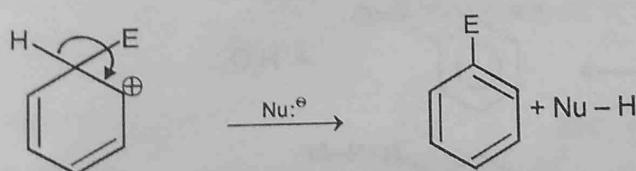
### Aromatic Electrophilic Substitution ( $ArS_E$ ) Reactions in Benzene Ring

Mechanism :

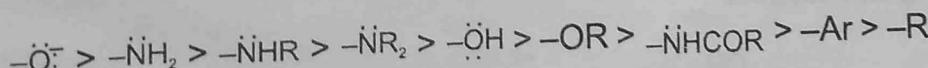
Step 1 : Attack of an electrophile on benzene ring forms the sigma complex



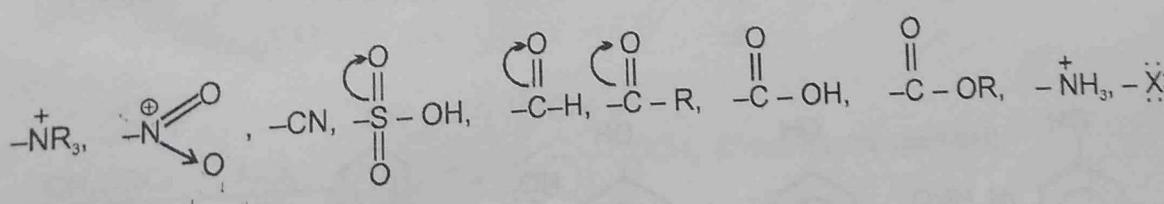
Step 2 : Loss of a proton gives the substitution product.



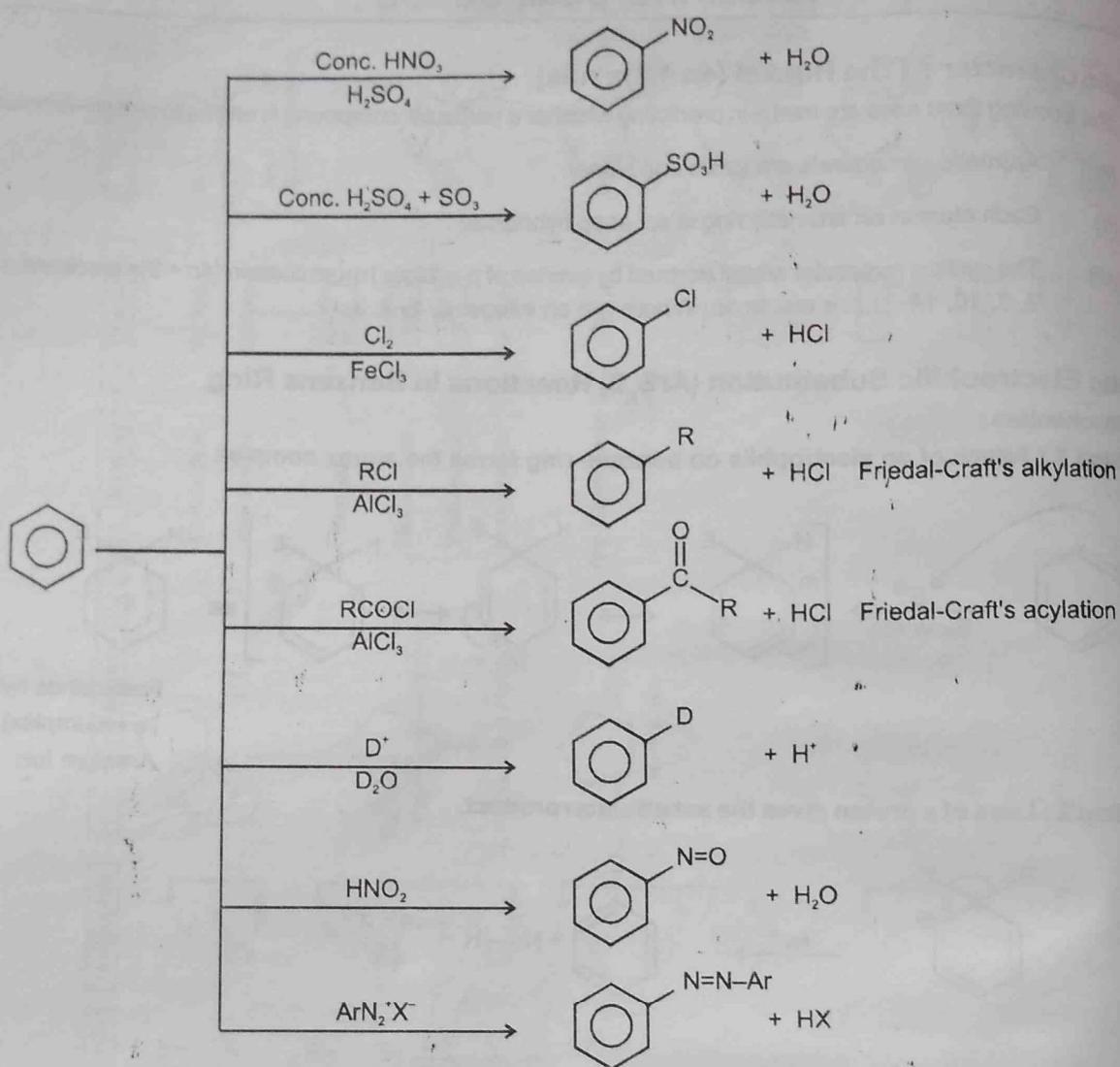
### Activating Groups or Electron Releasing Groups (ERG)



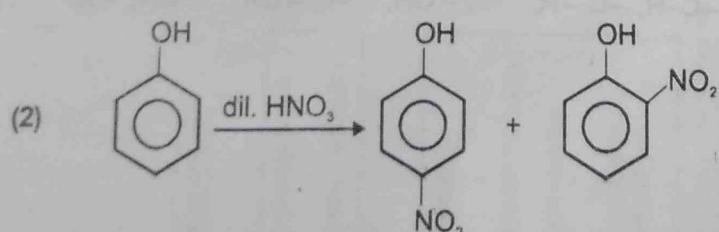
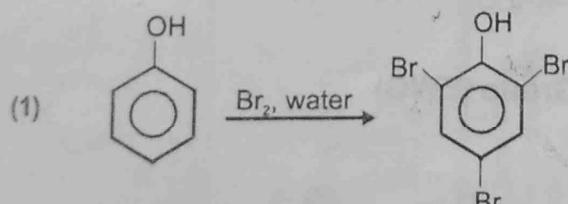
### Deactivating Group or Electron Withdrawing Group (EWG)

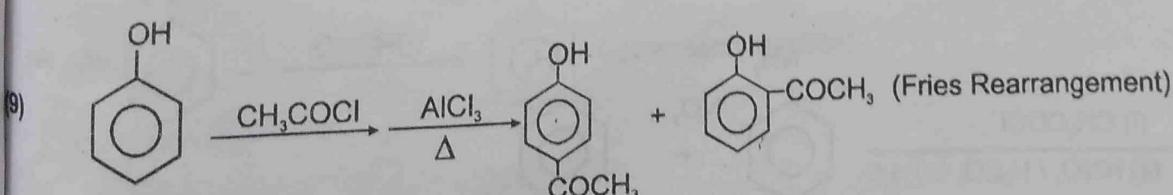
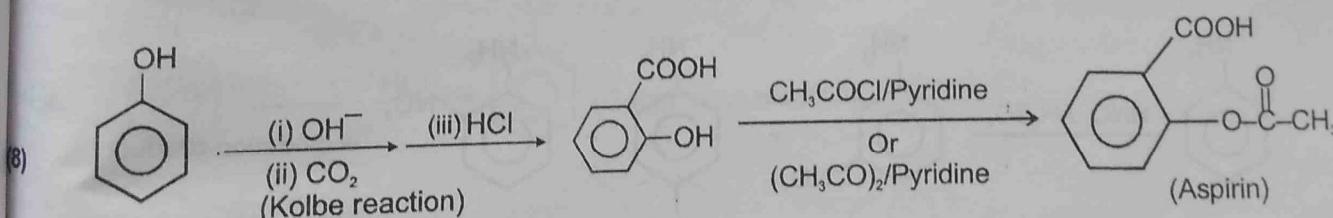
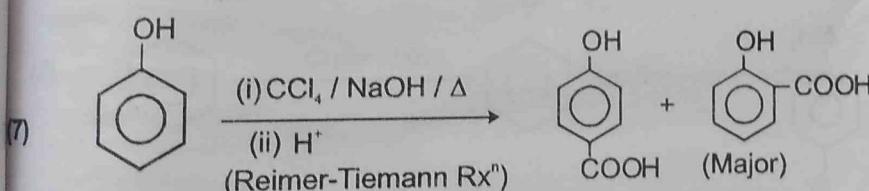
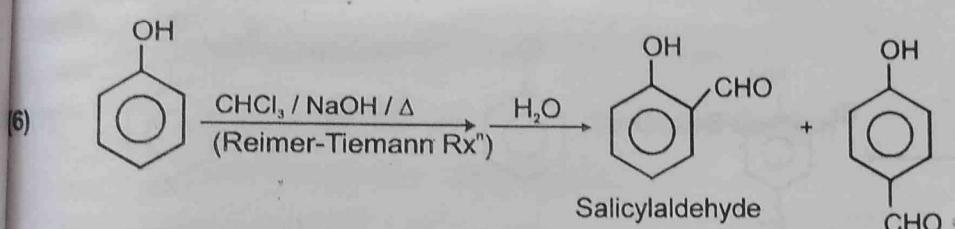
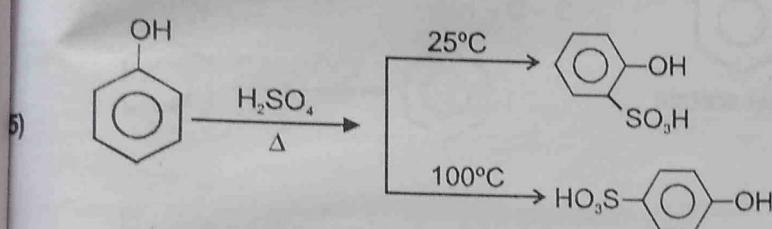
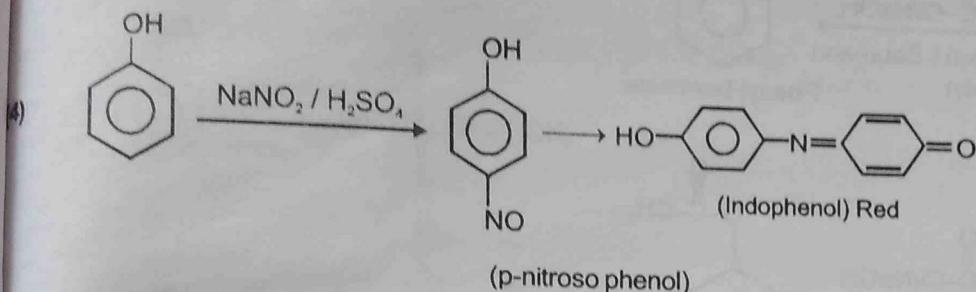
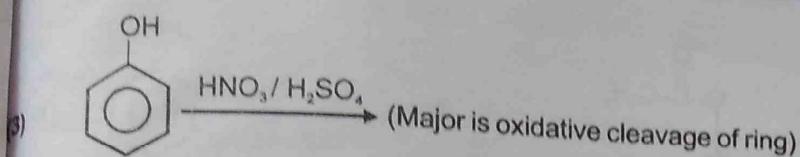


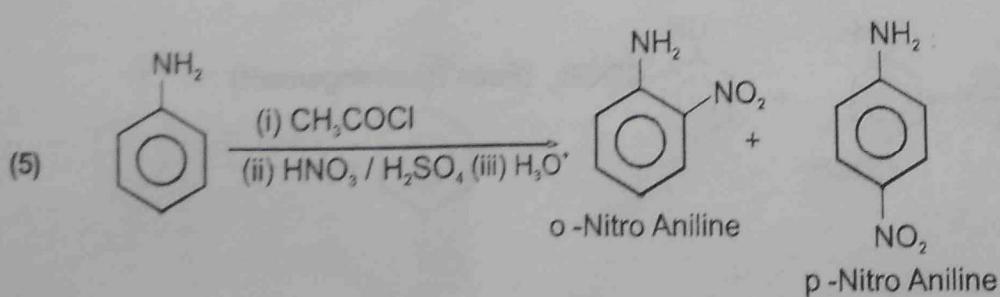
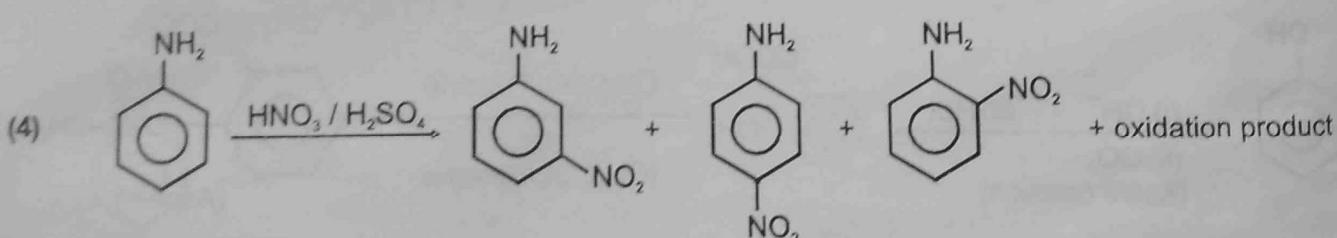
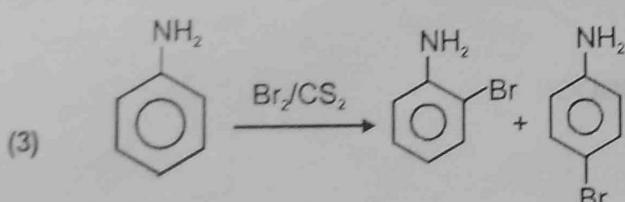
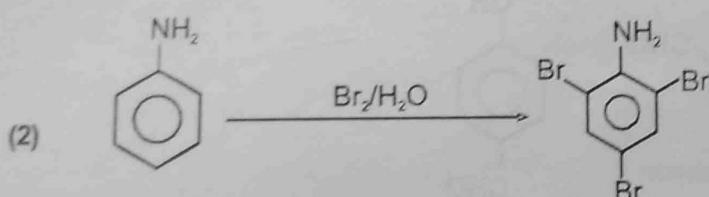
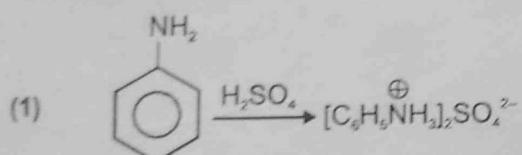
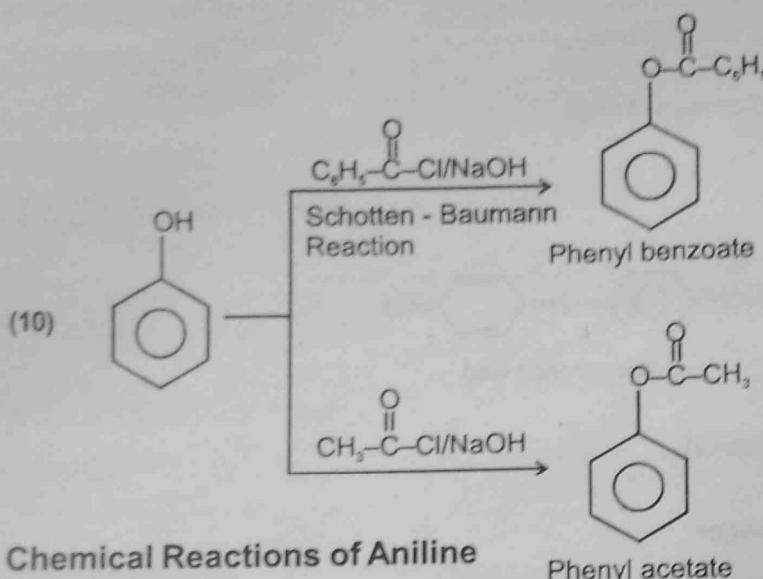
## Reactions of Benzene :

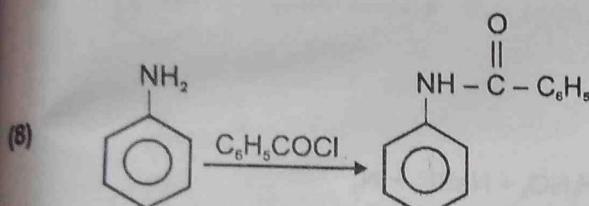
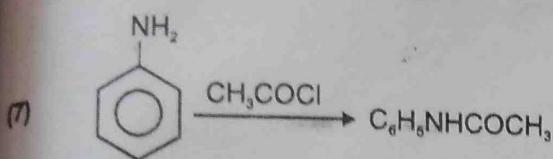
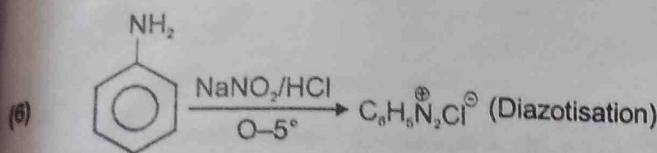


## Chemical Reactions of Phenols

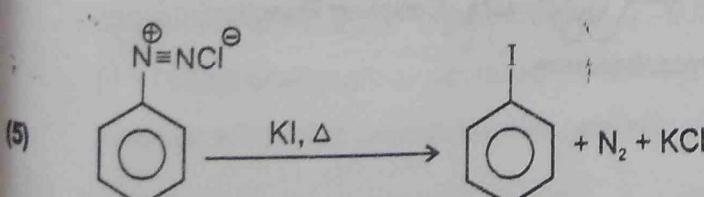
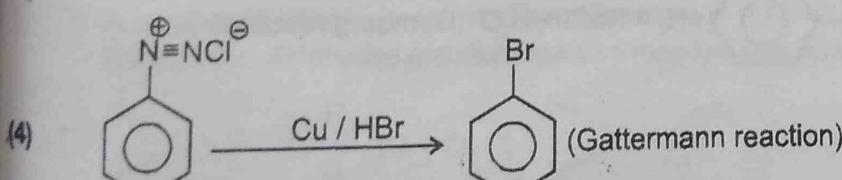
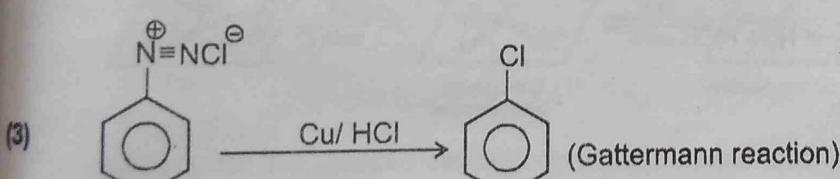
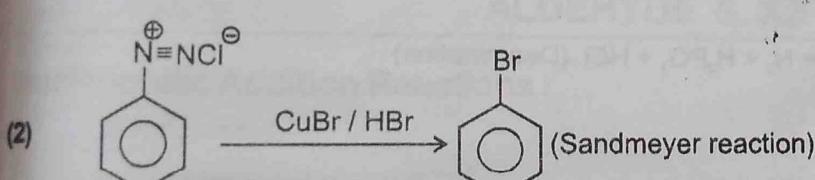
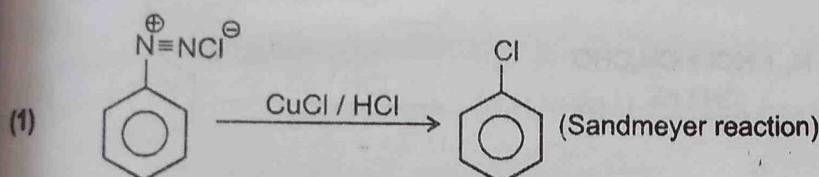


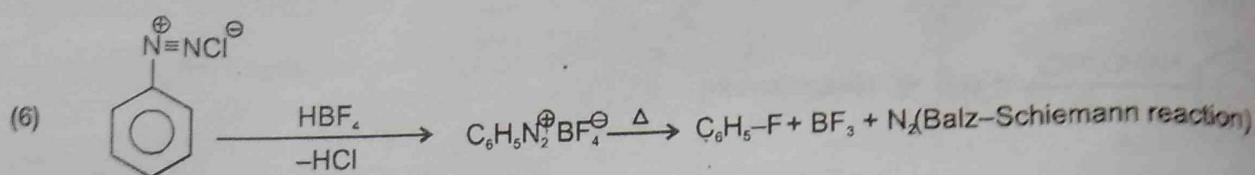




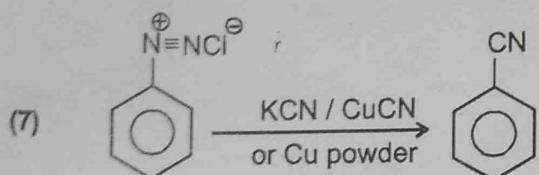


### Benzenediazonium chloride

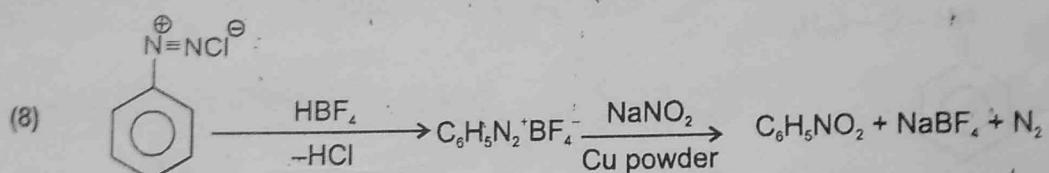




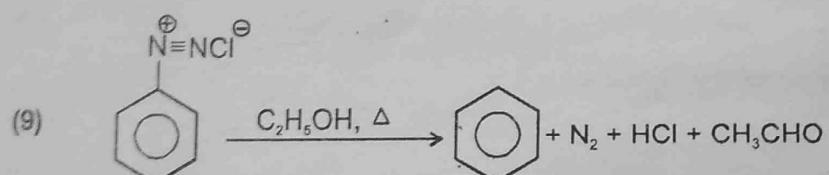
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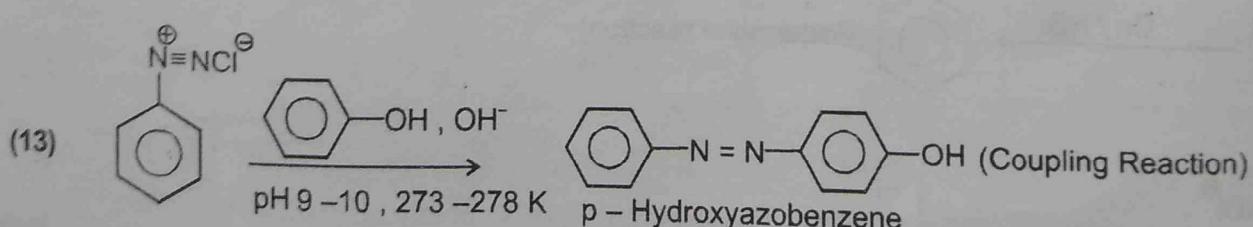
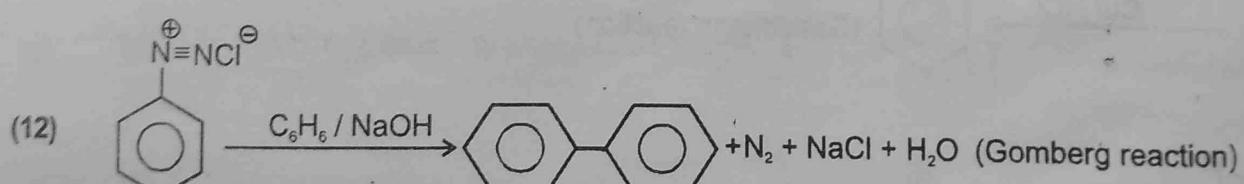
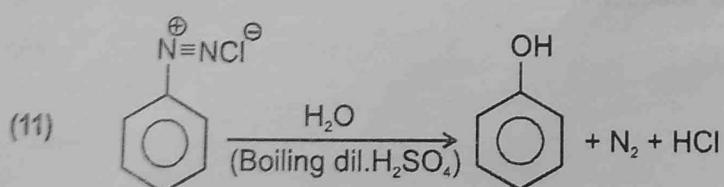
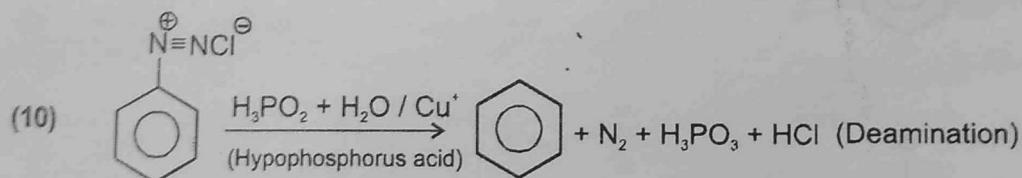
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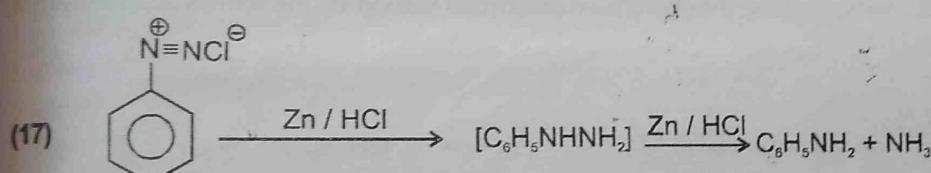
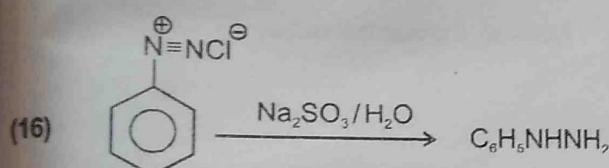
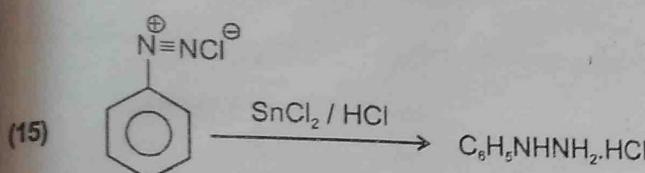
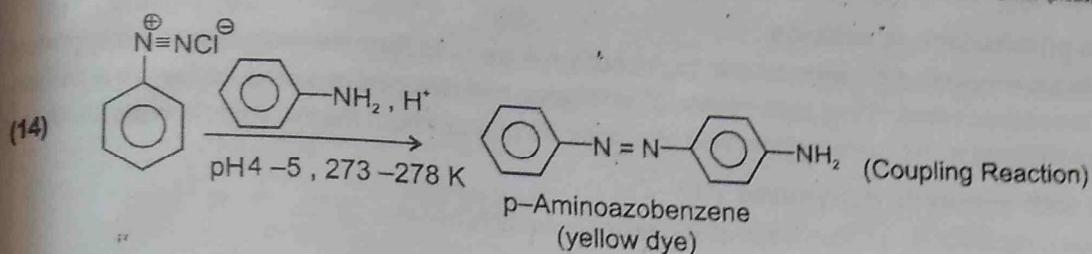


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(17)

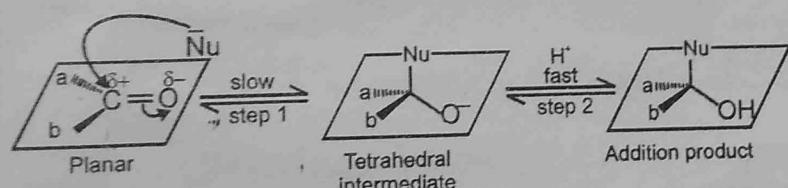




## ALDEHYDE & KETONE

### Nucleophilic Addition Reactions :

Mechanism :

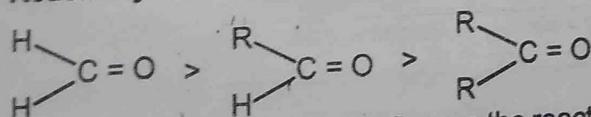


Nucleophile ( $\text{Nu}^-$ ) attacks the carbonyl group perpendicular to the plane of  $\text{sp}^2$  hybridised orbitals of carbonyl carbon.

In the process, hybridisation of carbon changes from  $\text{sp}^2$  to  $\text{sp}^3$ .

A tetrahedral alkoxide is formed as intermediate.

**Reactivity :** Aldehydes are more reactive than ketones in nucleophilic addition reactions.



There are two factors which influence the reactivity of ketone and aldehyde.

(i) Inductive effect      (ii) steric factor

(i) + I effect of alkyl group decrease the amount of charge on  $\text{C}^+$  ( $\text{C}^+ - \text{O}^-$ ). in ketones.

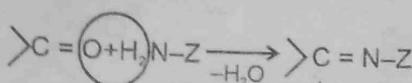
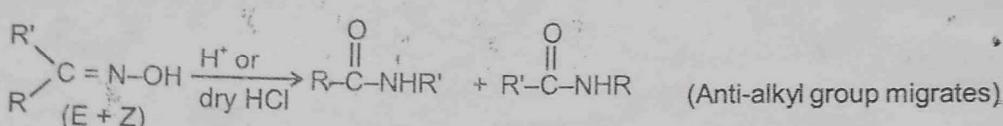
(ii) Steric effect also causes the less reactivity of carbonyl group.

**Addition elimination reactions :**

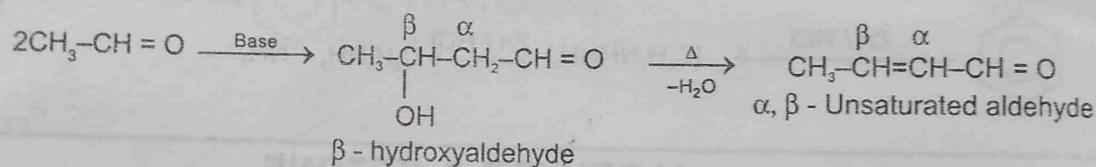
Certain compounds related to ammonia add to the carbonyl group to form derivatives that are important chiefly for the characterization and identification of aldehydes and Ketones, the product contain a carbon-nitrogen double bond resulting from elimination of a molecule of water from the initial addition products.

**Reaction with ammonia derivatives ( $H_2N-Z$ ) :**

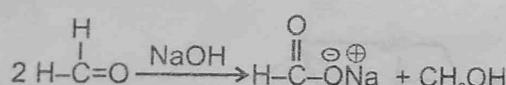
This reaction is nucleophilic addition followed by water elimination.

**Beckmann Rearrangement in Oxime:****Aldol Condensation :**

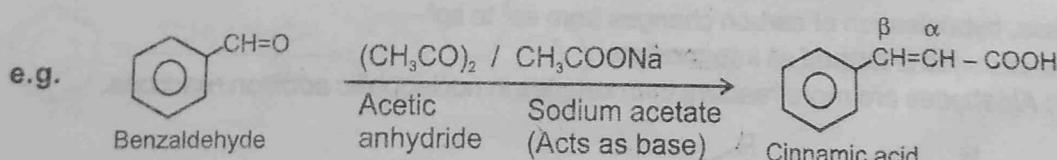
It is condensation between two moles of carbonyl compounds among which at least one must have  $\alpha$ -hydrogen atom in dilute basic media to get  $\alpha, \beta$ -unsaturated aldehyde / ketone via the formation of  $\beta$ -hydroxy aldehyde / ketone.

**Cannizzaro reaction :**

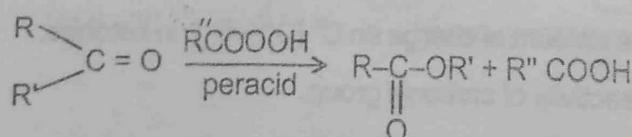
Carbonyl compounds not having  $\alpha$ -hydrogen atom undergo disproportionation or redox reaction in strong basic media.

**Perkin reaction :**

When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get  $\alpha, \beta$ -unsaturated acid.

**Baeyer-Villiger oxidation :**

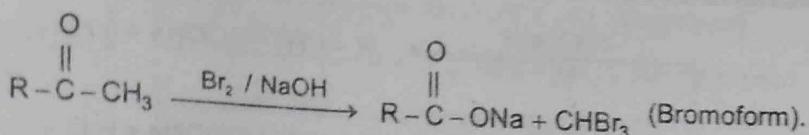
It is preparation of ester from ketone using peracid.



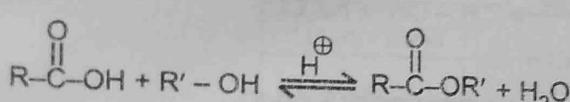
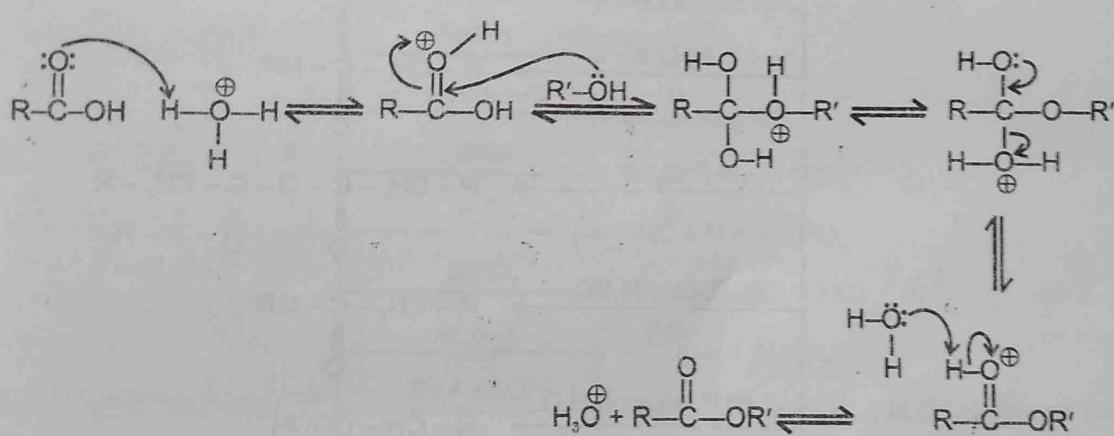
If migratory aptitude of  $\text{R}'$  is greater than  $\text{R}$ .

**Haloform reaction :**

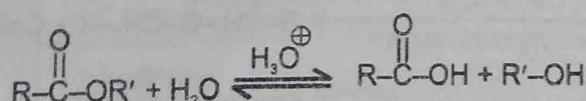
Acetaldehyde and methylalkyl ketones react rapidly with halogen ( $\text{Cl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$ ) in the presence of alkali to give haloform and acid salt.

**ESTER FORMATION****Fisher Esterification**

Carboxylic acid react with alcohol to form esters through a condensation reaction known as esterification.

**General Reaction :****Mechanism : (Acid catalysed esterification)**

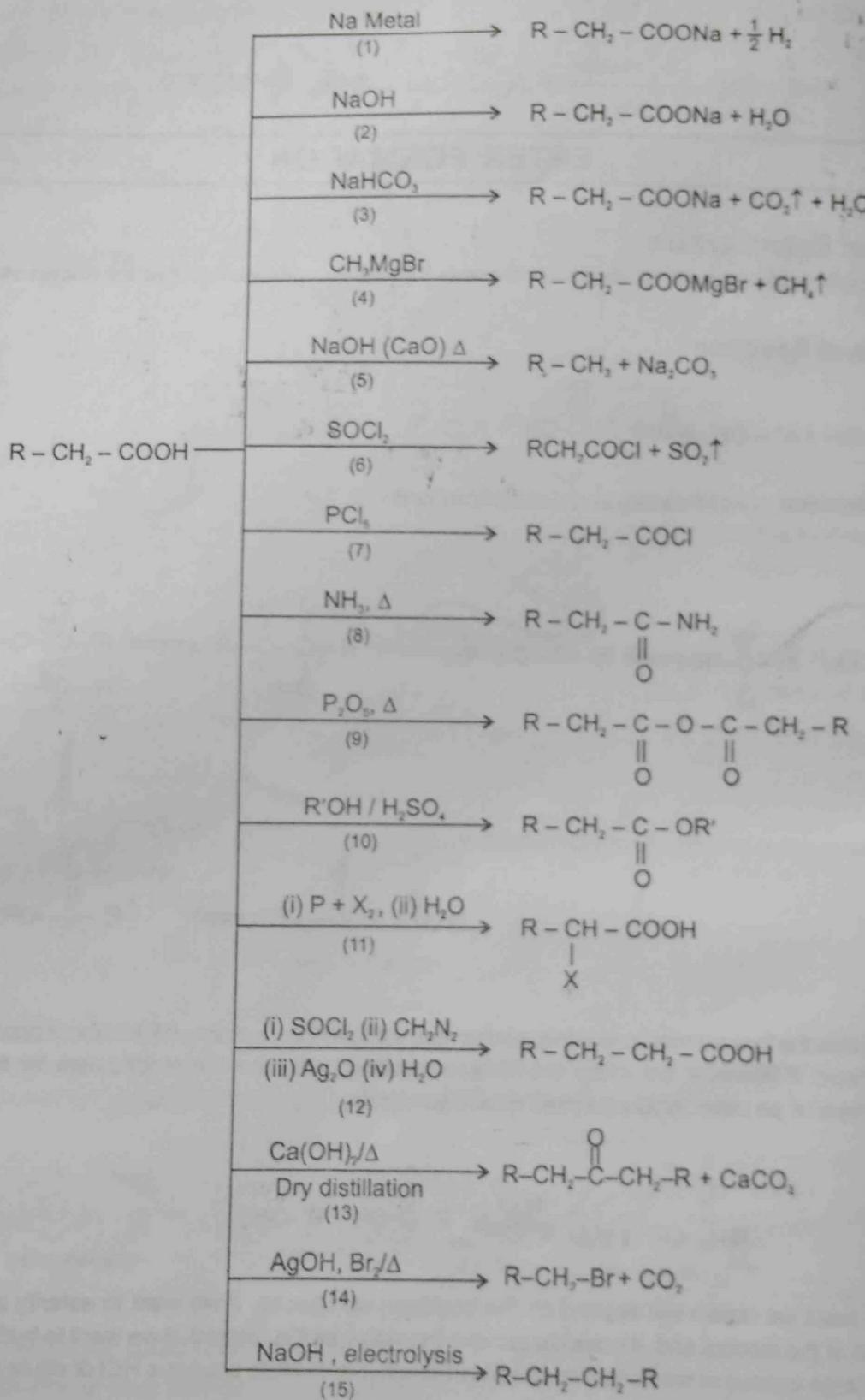
If we follow the forward reactions in this mechanism, we have the mechanism for the acid catalysed esterification of an acid. If however, we follow the reverse reactions, we have the mechanism for the acid catalysed hydrolysis of an ester. Acid catalysed ester hydrolysis.



which result we obtain will depend on the condition we choose. If we want to esterify an acid, we use an excess of the alcohol and, if possible remove the water as it is formed. If we want to hydrolyse an ester, we use a large excess of water that is we reflux the ester with dilute aqueous HCl or dilute aqueous  $\text{H}_2\text{SO}_4$ .

## CARBOXYLIC ACIDS &amp; DERIVATIVE

Summary of reactions of carboxylic acids :



## Summary of reactions of acid halide

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \\ \text{Acid chloride} \end{array}$	$\text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{HCl}$ (Hydrolysis)
	$\text{R}'\text{OH} \rightarrow \text{RCOOR}' + \text{HCl}$ (Alcoholysis)
	$2\text{NH}_3 \rightarrow \text{RCONH}_2 + \text{NH}_4\text{Cl}$ (Ammonolysis)
	$2\text{R}'\text{NH}_2 \rightarrow \text{RCONHR}' + \text{R}'\text{NH}_2\text{Cl}^-$
	$\text{RCOOH} / \text{Pyridine} \rightarrow (\text{RCO})_2\text{O} + \text{HCl}$
	$\text{RCOONa} \rightarrow (\text{RCO})_2\text{O} + \text{NaCl}$
	$\text{C}_6\text{H}_6 / \text{Anhyd. AlCl}_3 \rightarrow \text{C}_6\text{H}_5\text{COR} + \text{HCl}$ (Friedal-Crafts reaction)
	$\text{H}_2 / \text{Pd-BaSO}_4 + \text{S or quinoline} \rightarrow \text{RCHO} + \text{HCl}$ (Rosenmund's reduction)
	$\text{R}'\text{Cd/Ether} \rightarrow 2\text{RCOR}' + \text{CdCl}_2$
	$\text{LiAlH}_4 / \text{Ether} \rightarrow \text{RCH}_2\text{OH}$
	$\text{KCN} \rightarrow \text{R}-\text{CO}-\text{CN} \xrightarrow{\text{H}^+ / \text{H}_2\text{O}} \text{R}-\text{CO}-\text{COOH} + \text{NH}_3$

## Summary of reaction of amide:

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \\ \text{Acid amide} \end{array}$	$\text{H}^+ / \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{NH}_4^+$
	$\text{NaOH} \rightarrow \text{RCOONa} + \text{NH}_3$
	$\text{Conc. HCl} \rightarrow \text{RCONH}_2\text{HCl}$
	$2\text{Na} \rightarrow \text{RCONHNa} + 1/2\text{H}_2$
	$\text{P}_2\text{O}_5 \rightarrow 3\text{RC}\equiv\text{N} + 2\text{H}_3\text{PO}_4$
	$\text{SOCl}_2 \rightarrow \text{RC}\equiv\text{N} + \text{SO}_2 + \text{HCl}$
	$\text{HONO} \rightarrow \text{RCOOH} + \text{N}_2 + \text{H}_2\text{O}$
	$\text{Br}_2 + 4\text{KOH} \rightarrow \text{RNH}_2 + \text{CO}_2 + 2\text{KBr} + \text{H}_2\text{O}$ (Hoffmann bromide reaction)
	$\text{LiAlH}_4 / \text{dry ether} \rightarrow \text{RCH}_2\text{NH}_2$ $1^\circ \text{ Amine}$

## Summary of reaction of esters :

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \\ \text{Ester} \end{array}$	$\text{H}^+ / \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{R}'\text{OH}$ (Hydrolysis)
	$\text{NaOH} / \text{H}_2\text{O} \rightarrow \text{RCOONa} + \text{R}'\text{OH}$ (Saponification)
	$\text{NH}_3 \rightarrow \text{RCONH}_2 + \text{R}'\text{OH}$ (Amonolysis)
	$\text{R}''\text{NH}_2 \rightarrow \text{RCONHR}'' + \text{R}'\text{OH}$
	$\text{R}''\text{OH} / \text{H}^+ \text{ or } \text{R}''\text{ONa} \rightarrow \text{RCOOR}'' + \text{R}'\text{OH}$ (Trans-esterification)
	$\text{H}_2 / \text{Copper chromite} \rightarrow \text{RCH}_2\text{OH} + \text{R}'\text{OH}$
	$\text{or LiAlH}_4 / \text{Na/alcohol} \rightarrow \text{RCH}_2\text{OH} + \text{R}'\text{OH}$ (Bouveault-Blanc reduction)
	$(i) 2\text{R}''\text{MgX}' \rightarrow \begin{array}{c} \text{R}'' \\   \\ \text{R}-\text{C}-\text{OH} \\   \\ \text{R}'' \end{array}$ (In case of esters of formic acid, $(ii) \text{H}^+ / \text{H}_2\text{O}$ $2^\circ$ alcohols are obtained) $3^\circ \text{ Alcohol}$