



Mount Abu Public School

H-Block, Sector-18, Rohini, New Delhi-110085 India

SUBJECT : CHEMISTRY

CLASS XII

Week : 1 February 6 February 2021

CHAPTER 7 : P BLOCK ELEMENTS

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/CzpC1ECQzEU>

<https://youtu.be/kNFXJxX72uY>

<https://youtu.be/CzpC1ECQzEU>

Learning outcomes

- Appreciate general trends in the chemistry of elements of group 15 16 17 and 18
- Learn the preparation properties and uses of dinitrogen and phosphorus and some of their important compounds
- Describe the preparation properties and uses of dioxygen and Ozone and the chemistry of some simple oxides.
- Learn allotropic forms of Sulphur and Chemistry of its important compounds and the structure of its oxoacids
- Describe the preparation properties and uses of chlorine and hydrochloric acid
- Understand chemistry of interhalogen And The structures of oxoacids of halogens
- Learn the uses of noble gases.
- Appreciate the importance of these elements and their compounds in our day to day life

Sub Topics

- *Group 15 Elements*
- *Dinitrogen*

- Ammonia
- Oxides of Nitrogen
- Nitric Acid
- Phosphorus — Allotropic Forms
- Phosphine
- Phosphorus Halides
- Oxoacids of Phosphorus
- Group 16 Elements
- Dioxygen
- Simple Oxides
- Ozone
- Sulphur — Allotropic Forms
- Sulphur Dioxide
- Oxoacids of Sulphur
- Sulphuric Acid
- Group 17 Elements
- Chlorine
- Hydrogen Chloride
- Oxoacids of Halogens
- Interhalogen Compounds
- Group 18 Elements

LESSON DEVELOPMENT

GROUP 15 ELEMENTS

- **The p-Block elements:** Elements belonging to groups 13 to 18 of the periodic table are called p-block elements.
- **General electronic configuration of p-block elements:** The p-block elements are characterized by the ns^2np^{1-6} valence shell electronic configuration.
- **Representative elements:** Elements belonging to the s and p-blocks in the periodic table are called the representative elements or main group elements.
- **Inert pair effect:** The tendency of ns^2 electron pair to participate in bond formation decreases with the increase in atomic size. Within a group the higher oxidation state becomes less stable with respect to the lower oxidation state as the atomic number increases. This trend is called 'inert pair effect'. In other words, the energy required to unpair the electrons is more than energy released in the formation of two additional bonds.

GROUP 15 ELEMENTS

- **Nitrogen family:** The elements of group 15 – nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) belong to configuration is ns^2np^3 .
- **Atomic and ionic radii:**
 1. Covalent and ionic radii increase down the group.
 2. There is appreciable increase in covalent radii from N to P.

3. There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.

- **Ionisation energy:**

1. It goes on decreasing down the group due to increase in atomic size.

2. Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements.

3. Group 15 elements have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half-filled p-orbitals.

- **Allotropy:** All elements of Group 15 except nitrogen show allotropy.

- **Reactivity towards hydrogen:**

1. All group 15 elements form trihydrides, MH_3 .

2. It belongs to sp^3 hybridisation.

3. The stability of hydrides decreases down the group due to decrease in bond dissociation energy down the group.



- **Boiling point:**



1. Boiling point increases with increase in size due to increase in van der Waals forces.

2. Boiling point of NH_3 is more because of hydrogen bonding.

- **Bond angle:**



As we move from ammonia to bismuth hydride, the electronegativity of central atom decreases therefore the Bond pair lie away from the central atom as a result there is maximum repulsion between Bond pairs of ammonia and minimum repulsion between Bond pair of of Bismuth hydride bond angle decreases

- **Basicity**

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3 . It will decrease down the group exercise increases comment on density over the central atom decreases.

- **Reducing power**

The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group as a result the tendency to liberate hydrogen increases.

- Ammonia has one lone pair of electrons over nitrogen atom that is available for donation and Ammonia act as a Lewis base.

- **Solubility**

Only ammonia is available in water due to the formation of hydrogen bonding with water but other hydride are insoluble in water as they do not able to form hydrogen bonding with water

- **Reactivity towards hydrogen:**

4. All group 15 elements form trihydrides, MH_3 .
5. It belongs to sp^3 hybridisation.
6. The stability of hydrides decreases down the group due to decrease in bond dissociation energy down the group.



- **Boiling point:**



3. Boiling point increases with increase in size due to increase in van der Waals forces.
4. Boiling point of NH_3 is more because of hydrogen bonding.

- **Bond angle:**

1. Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs. Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.
2. Basicity decreases as $NH_3 > PH_3 > AsH_3 > SbH_3 < BiH_3$. This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3 . It will decrease down the group as the electronegativity decreases down the group. The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.

- **Reactivity towards halogen:**

Group 15 elements form trihalides and pentahalides.

1. Trihalides: These are covalent compounds and become ionic down the group with sp^3 hybridisation, pyramidal shape.
2. Pentahalides They are lewis acids because of the presence of vacant d – orbitals. They possess sp^3d hybridisation and hence possess trigonalbipyramidal shape.
 $PCl_5 + Cl^- \rightarrow [PCl_6]^-$
3. PCl_5 is ionic in solid state and exist as $[PCl_4]^+ [PCl_6]^-$
4. In PCl_5 , there are three equatorial bonds and two axial bonds. The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.
5. Nitrogen does not form pentahalides due to absence of d– orbitals.

- **Catenation:**

1. Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent.
2. The tendency to show catenation decreases down the group.

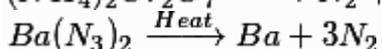
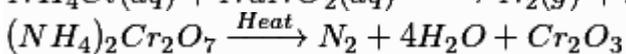
- **Anomalous behaviour of nitrogen:** The behaviour of nitrogen differs from rest of the elements.

Reasons:

- i. It has a small size.
- ii. It does not have d – orbitals
- iii. It has high electronegativity
- iv. It has high ionization enthalpy

- **Dinitrogen:**

a) Preparation:



b) Physical Properties:

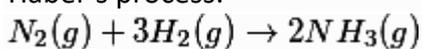
i) It is a colourless, odourless, tasteless and non – toxic gas.

ii) It is chemically un-reactive at ordinary temperature due to triple bond in $N \equiv N$ which has high bond dissociation energy.

- **Ammonia:**

1. Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex.
2. It has 3 bond pairs and 1 lone pair.
3. N is sp^3 hybridised.
4. Preparation:

Haber's process:

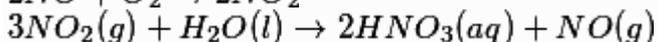
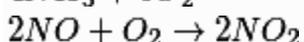
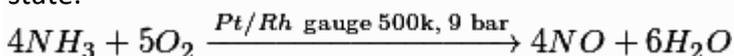


$$\Delta_f H^0 = -46.1 kJ mol^{-1}$$

Pressure 200×10 Pa Temperature 773 K Catalyst is FeO with small amounts of K_2O and Al_2O_3

- **Nitric Acid:**

Ostwald Process: The NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4 . Nitric acid is strong oxidizing agent in the concentrated as well as in the dilute state.



GROUP 16

Group-16 Elements Oxygen Family

16th group elements are sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). This is sometimes known as group of chalcogens (due to ore forming nature). Oxygen is the most abundant of all the

elements on earth. Oxygen and sulphur are non-metals, selenium and tellurium are metalloids and polonium is radioactive metal.

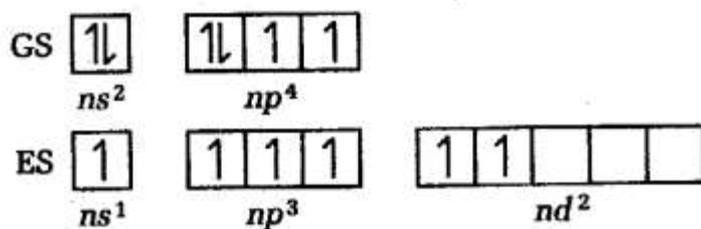
Important Properties

The group 16 elements exhibit the properties may be given as:

Physical Properties

- Group-16 elements show following trends in their physical properties

General configuration ns^2np^4

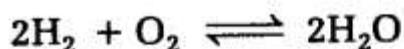


- Ionisation energies On moving down the group from oxygen to polonium, the ionisation energy decreases because of increase in atomic size.
- Metallic character On moving down the group, the metallic character increases down the group from oxygen to polonium because of decrease in ionisation energy.
- Oxidation states **Group VIA** elements show oxidation state of + 2, + 4 and + 6 due to the promotion of electrons to vacant d-orbitals. But down the group +4 oxidation state becomes more stable.
- Allotropy Oxygen exists in two allotropic forms as O_2 and O_3 (ozone). Sulphur exists in a number of allotropic forms such as rhombic, monoclinic and plastic sulphur. Selenium has two common forms red (non-metallic) and white grey (metallic). Tellurium occurs in two allotropic forms, crystalline and amorphous. Polonium also exists in a- and p- forms (both metallic).

Chemical Properties

Following are the main chemical properties of group-16 elements

Hydrides All the elements of the oxygen family form stable hydrides of the type H_2M either by directly combining with hydrogen or by the action of acids on metal sulphides, selenides and tellurides.



H_2O is a liquid due to hydrogen bonding and others are colourless gases with unpleasant smell.

Compounds $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$

(all sp^3 -hybridised)

Bond angle 104.5° 92.5° 91° 90°

The decreasing bond dissociation enthalpy of the $\text{M}-\text{H}$ bond is due to increase in the size of M which explains the increasing acidic character of hydrides down the group.

Halides All the elements of the oxygen family form a number of halides.

Element	Fluorides	Chlorides	Bromides	Iodides
O	$\text{OF}_2, \text{O}_2\text{F}_2$	$\text{ClO}_2, \text{Cl}_2\text{O}_7$	—	—
S	$\text{S}_2\text{F}_2, \text{SF}_4, \text{SF}_6$	$\text{S}_2\text{Cl}_2, \text{SCl}_2$	S_2Br_2	—
Se	$\text{SeF}_2, \text{SeF}_4, \text{SeF}_6$	$\text{Se}_2\text{Cl}_4, \text{SeCl}_4$	$\text{SeBr}_2, \text{SeBr}_4$	—
Te	$\text{TeF}_4, \text{TeF}_6$	$\text{TeCl}_2, \text{TeCl}_4$	$\text{TeBr}_2, \text{TeBr}_4$	TeI_4
Po	—	$\text{PoCl}_2, \text{PoCl}_4$	$\text{PoBr}_2, \text{PoBr}_4$	PoI_4

Oxides These form oxides of the type MO_2 and MO_3 .

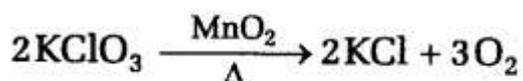
Oxide	S	Se	Te	Po
Monoxides	SO	—	TeO	PoO
Dioxides	SO_2	SeO_2	TeO_2	PoO_2
Trioxides	SO_3	SeO_3	TeO_3	PoO_3
Heptoxides	S_2O_7	—	—	—
Other oxides	$\text{S}_2\text{O}, \text{S}_2\text{O}_3, \text{SO}_4$	—	—	—

Some Important Compounds of Oxygen

Dioxygen

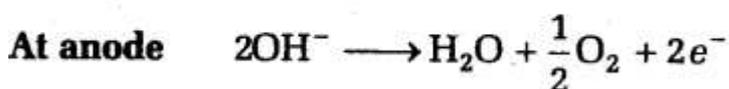
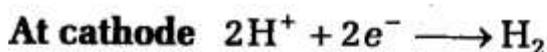
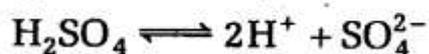
Preparation

- **Laboratory method**



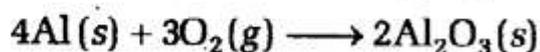
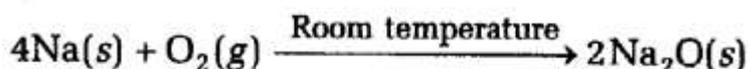
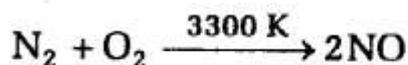
- It is manufactured from liquid air. Air is liquefied by making use of Joule Thomson effect. Liquid air is a mixture of liquid nitrogen and liquid oxygen. The difference in their boiling points is about 12.8°C, hence, they are easily separated by fractional evaporation.
- **By electrolysis of water (acidified water)**

By electrolysis of water (acidified water)

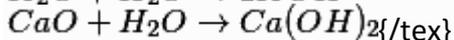
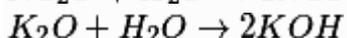
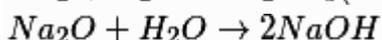


Properties

- Colourless, odourless, tasteless gas which is slightly soluble in water. Liquid oxygen exhibits paramagnetism.
- It is non-inflammable but a supporter of combustion.
- $\text{O}=\text{O}$, bond dissociation energy is high, therefore it reacts with metals or non-metals after external heating to start the reaction.



- **Oxides:** The compounds of oxygen and other elements are called oxides.
- **Types of oxides:**



1. Acidic oxides: Non-metallic oxides are usually acidic in nature.
2. Basic oxides: Metallic oxides are mostly basic in nature. Basic oxides dissolve in water forming bases e.g.,
3. Amphoteric oxides: They show characteristics of both acidic as well as basic oxides. $\text{Al}_2\text{O}_3 + 6\text{HCl}(aq) \rightarrow 2\text{AlCl}_3(aq) + 3\text{H}_2\text{O}$
 $\text{Al}_2\text{O}_3 + 6\text{NaOH}(aq) + 3\text{H}_2\text{O}(l) \rightarrow 2\text{Na}_3[\text{Al}(\text{OH})_6](aq)$

4. Neutral oxides: These oxides are neither acidic nor basic. Example: Co, NO and N₂O

Uses

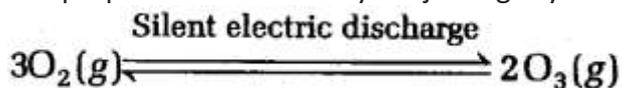
- In oxyacetylene and oxyhydrogen flames.
- Liquid O₂ is used as a rocket fuel.
- For life support systems, e.g. in hospitals and in water diving for divers, for miners and mountaineers.
- As an oxidising and bleaching agent.

Ozone(O₃)

It is formed in the upper layer of atmosphere by the action of UV rays from sun on oxygen. It prevents the UV rays from entering the earth's atmosphere. CFCs, common refrigerants deplete the ozone layer.

Preparation

It is prepared in ozoniser by subjecting dry and cold dioxygen to the action of silent electric discharge.



Properties

- It is pale blue gas with pungent odour. It is diamagnetic and poisonous.

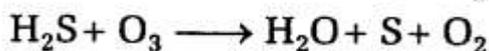
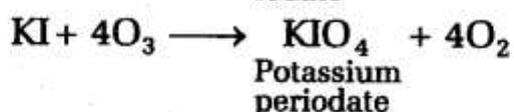
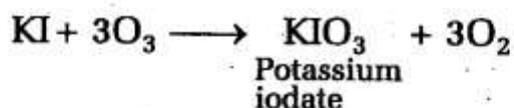
- Ozone is unstable



It acts as a powerful oxidising agent. It liberates iodine from neutral KI solution and the liberated I_2 turns starch paper blue.



Alkaline KI is oxidised to potassium iodate and periodate.



Mercury loses its meniscus in contact with ozone (tailing of mercury).



Uses

- As a germicide and disinfectant for sterilizing water.
- As a bleaching agent for oils, ivory wax and delicate fibre.
- For detecting the position of double bond in unsaturated compounds. In destroying odours coming from cold storage room, slaughter houses and kitchen of hotels.

- Reactivity with oxygen:** and EO_3

- Reducing character of dioxides decreases down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.
- Acidity also decreases down the group.
- SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

- Reactivity with halogens:** EX_2 , EX_4 and EX_6

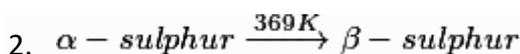
- The stability of halides decreases in the order $\text{F} - > \text{Cl} - > \text{Br} - > \text{I} -$.
- This is because E-X bond length increases with increase in size.
- Among hexa halides, fluorides are the most stable because of steric reasons.

- Dihalides are sp^3 hybridised and so, are tetrahedral in shape.
- Hexafluorides are only stable halides which are gaseous and have sp^3d^2 hybridisation and octahedral structure.
- H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.

- Sulphur:**

- Sulphur exhibits allotropy:

- Yellow Rhombic (α – sulphur)
- Monoclinic (β – sulphur)



- At 369 K both forms are stable. It is called transition temperature.
- Both of them have S_8 molecules.
- The ring is puckered and has a crown shape.
- Another allotrope of sulphur – cyclo S_6 ring adopts a chair form.
- S_2 is formed at high temperature (~ 1000 K).
- It is paramagnetic because of 2 unpaired electrons present in anti bonding π^* orbitals like O_2 .

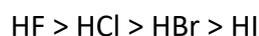
GROUP 17 ELEMENTS

- Atomic and ionic radii:** Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.
- Ionisation enthalpy:** They have very high ionization enthalpy because of small size as compared to other groups.
- Electron gain enthalpy:**
 - Halogens have maximum negative electron gain enthalpy because these elements have only one electron less than stable noble gas configuration.
 - Electron gain enthalpy becomes less negative down the group because atomic size increases down the group.
- Electronegativity:**
 - These elements are highly electronegative and electronegativity decreases down the group.
 - They have high effective nuclear charge.
- Bond dissociation enthalpy:**
 - Bond dissociation enthalpy follows the order: $Cl_2 > Br_2 > F_2 > I_2$
 - This is because as the size increases bond length increases.
 - Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2 .
- Colour:** All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher energy levels.
- Oxidising power:**

1. All halogens are strong oxidising agents because they have a strong tendency to accept electrons.
2. Order of oxidizing power is: $F_2 > Cl_2 > Br_2 > I_2$
 - **Reactivity with Hydrogen:**
 1. Acidic strength: $HF < HCl < HBr < HI$
 2. Stability: $HF > HCl > HBr > HI$. This is because of decrease in bond dissociation enthalpy.
 3. Boiling point: $HCl < HBr < HI < HF$. HF has strong intermolecular H bonding. As the size increases van der Waals forces increase and hence boiling point increases.
 4. % Ionic character: $HF > HCl > HBr > HI$ Dipole moment: $HF > HCl > HBr > HI$. Electronegativity decreases down the group.
 5. Reducing power: $HF < HCl < HBr < HI$
 - **Reactivity with metals:**
 1. Halogens react with metals to form halides.
 2. Ionic character: $MF > MCl > MBr > MI$. The halides in higher oxidation state will be more covalent than the one in the lower oxidation state.

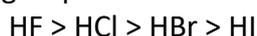
Ionic character

Due to the decrease in electronegativity down the group the ionic character of hydrogen halides also decreases down the group.



Dipole moment

Due to the decrease in electronegativity down the group the ionic character of hydrogen halides also decreases down the group.

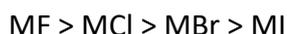


Reactivity towards metals:

Halogens react with metals to form metal halides of the form MX , where M is a monovalent metal.

Ionic character

Due to the decrease in electronegativity down the group the ionic character of metal halides also decreases down the group



Reactivity of halogens towards other halogens (Interhalogens):

Binary compounds of two different halogen atoms of general formula XX'_n are called interhalogen compounds where $n = 1, 3, 5, \text{ or } 7$. All the interhalogen compounds are covalent in nature.

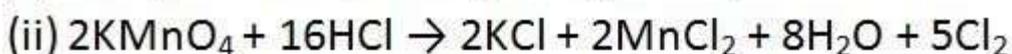
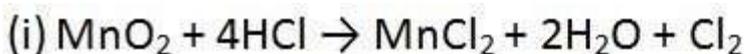
Some properties of interhalogen compounds are given in the following table:

Type	Formula	Physical state and colour	Structure
XX ₁	ClF	colourless gas	-
	BrF	pale brown gas	-
	IF ^a	detected spectroscopically	-
	BrCl ^b	gas	-
	ICl	ruby red solid (α-form)	-
		brown red solid (β-form)	-
XX ₃	IBr	black solid	-
	ClF ₃	colourless gas	Bent T-shaped
	BrF ₃	yellow green liquid	Bent T-shaped
	IF ₃	yellow powder	Bent T-shaped (?)
	ICl ₃ ^c	orange solid	Bent T-shaped (?)
XX ₅	IF ₅	colourless gas but solid below 77 K	Square pyramidal
	BrF ₅	colourless liquid	Square pyramidal
	ClF ₅	colourless liquid	Square pyramidal
XX ₇	IF ₇	colourless gas	Pentagonal bipyramidal

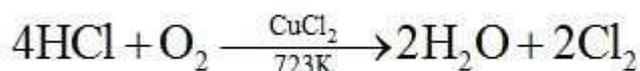
Chlorine (Cl)

Preparation:

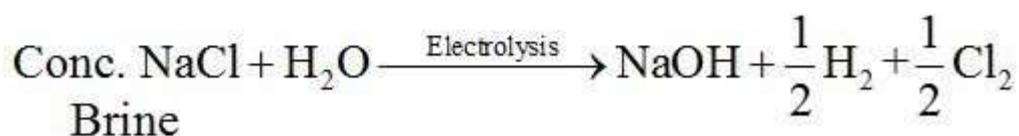
Chlorine can be prepared by any of the following processes:



(iii) Deacon's process



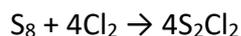
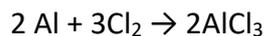
(iv) Electrolytic process



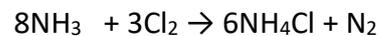
Properties:

- It is a greenish yellow gas with pungent and suffocating odour.
- It is soluble in H₂O
- Reaction with metals and non-metals: Chlorine reacts with a number of metals and non-metals to form chlorides.

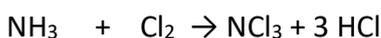
For example:



- Reaction with ammonia: When treated with excess ammonia, chlorine gives nitrogen and ammonium chloride whereas when excess chlorine reacts with ammonia, nitrogen trichloride is formed.



Excess

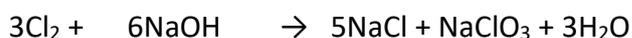


Excess

- Reaction with NaOH: Chlorine reacts differently with cold dilute NaOH and hot concentrated NaOH.

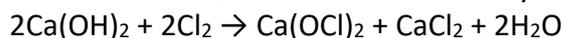


Cold dil.

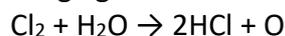


Hot conc.

Reaction with slaked lime: Cl_2 when treated With dry slaked lime it gives bleaching powder:



Cl_2 acts as a powerful bleaching agent and its bleaching action is due to its oxidizing nature.



Uses:

(i) Chlorine is used for bleaching woodpulp.

(ii) It is used in the extraction of gold and platinum

(iii) It is used in in sterilising drinking water.

(iv) It is used in the manufacture of dyes, drugs and organic compounds like CCl_4 , DDT, refrigerants, etc.

Hydrogen chloride (HCl)

Preparation:

It is prepared by heating sodium chloride with concentrated sulphuric acid.

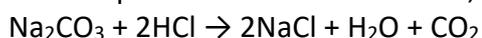


Properties:

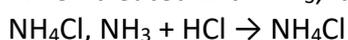
HCl is a colourless gas with pungent odour.

It is extremely soluble in water, $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$

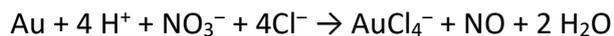
It decomposes salts of weaker acids,



When treated with NH_3 , it gives white fumes of



$3\text{HCl} : 1\text{HNO}_3$ is called aqua regia, which is used for dissolving noble metals.



Uses:

(i) Hydrogen chloride is used in medicine and as a laboratory reagent.

(ii) It is used in the manufacture of chlorine, NH_4Cl and glucose.

Oxoacids of halogens

Fluorine due to its small size and high electronegativity forms only one oxoacid HOF (Hypofluorous acid).

Other halogen form several oxoacids as given in the following table:

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	- -	HOClO (chlorous acid)	- -	- -
Halic (V) acid (Halic acid)	- -	HOClO ₂ (chloric acid)	HOBrO ₂ (bromic acid)	HOIO ₂ (iodic acid)
Halic (VII) acid (Perhalic acid)	- -	HOClO ₃ (perchloric acid)	HOBrO ₃ (perbromic acid)	HOIO ₃ (periodic acid)

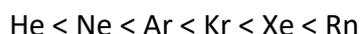
Group 18, Noble gases

Group 18 elements: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) having the electronic configuration $ns^2 np^6$, are named as noble gases. All these are gases and chemically unreactive.

General properties of noble gases

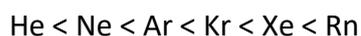
Atomic radii:

Atomic radii of noble gases increases down the group due to the addition of a new shell at each step.



Ionisation enthalpy:

They have very high ionization enthalpy because of completely filled orbitals. Ionisation enthalpy decreases down the group because of increase in size.



Electron gain enthalpy:

Because of stable electronic configuration, noble gases have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

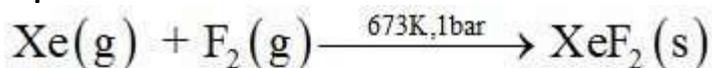
Melting and boiling point:

Due to the weak dispersion forces they have low melting and boiling point.

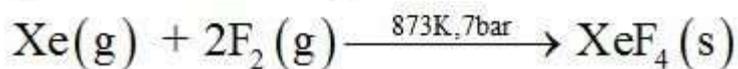
Xenon-fluorine compounds

Xenon forms three binary fluorides, XeF₂, XeF₄ and XeF₆.

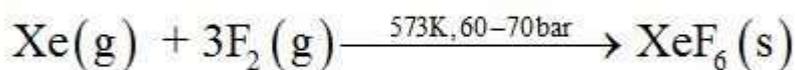
Preparation:



(Xenon in excess)



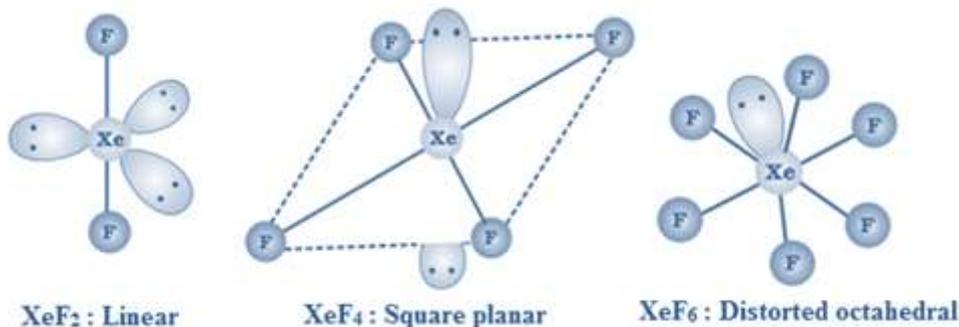
(1:5 ratio)



(1:20 ratio)

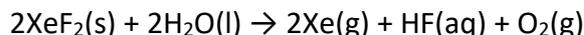
Properties:

XeF₂ is linear, XeF₄ is square planar and XeF₆ is distorted octahedral.

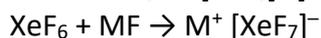
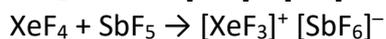
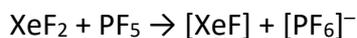


XeF₂, XeF₄ and XeF₆ are colourless crystalline solids

They are readily hydrolysed



They react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



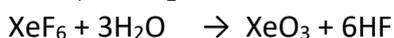
[Where, M = Na, K, Rb or Cs]

Xenon-oxygen compounds

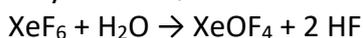
Xenon forms some important compounds with oxygen like XeO₃, XeOF₄ and XeO₂F₂.

Preparation:

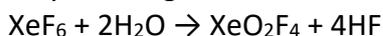
Various xenon-oxygen compounds are prepared as follows:



Partial Hydrolysis XeOF_4



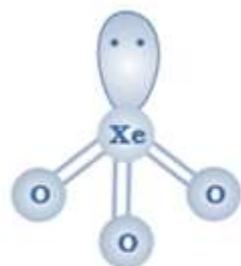
Partial Hydrolysis also gives XeO_2F_4



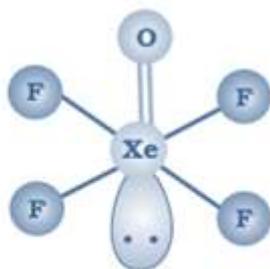
Properties:

XeO_3 is a colourless explosive solid having a trigonal pyramidal structure.

XeOF_4 is a colourless volatile liquid with a square pyramidal



XeO_3 : Pyramidal



XeOF_4 : Square pyramidal

Uses of inert gases

Helium is used:

- Gas cooled Nuclear reactors
- In filling balloons for meteorological observations.
- In the oxygen mixture of deep sea divers
- In inflating aeroplane tyres
- Used to provide an inert atmosphere in melting and welding of easily oxidizable metals.

Neon is used:

- In discharge tubes and fluorescent bulbs used for advertising purposes
- In beacon lights for the safety of air navigators as the light can easily pass through the fog for a clear view.

Argon is used:

- To provide an inert atmosphere in high-temperature metallurgical processes (arc welding of metals or alloys)
- For filling electric bulbs.
- In the laboratory for handling substances that are air-sensitive.
- Xenon and Krypton are also used in light bulbs.

ASSIGNMENT

1. Which is a stronger oxidizing agent Bi(v) or Sb(v)? (Delhi 2009)
2. Why does NO_2 dimerise? (Delhi 2010)
3. Fluorine does not exhibit any positive oxidation state. Why? (All India 2010)
4. Nitrogen is relatively inert as compared to phosphorus. Why? (All India 2010)
5. Draw the structure of XeF_4 molecule. (Delhi 2011)
6. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why? (Delhi 2012)
7. Noble gases have low boiling points. Why? (Comptt. Delhi 2012)
8. Why does PCl_3 fume in moisture? (Comptt. Delhi 2012)
9. Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15 elements? (Comptt. All India 2012)
10. Name two poisonous gases which can be prepared from chlorine gas. (All India 2013)
11. Why does NH_3 act as a Lewis base? (All India 2014)
12. $\text{Pb}(\text{NO}_3)_2$ on heating gives a brown gas which undergoes dimerization on cooling. Identify the gas. (All India 2016)
13. State reasons for each of the following :
 - (i) The N-O bond in NO_2 is shorter than the N-O bond in NO_3^- .
 - (ii) SF_6 is kinetically an inert substance. (Delhi 2011)
14. State reasons for each of the following :
 - (i) All the P-Cl bonds in PCl_5 molecule are not equivalent.
 - (ii) Sulphur has greater tendency for catenation than oxygen. (Delhi 2011)
15. Explain the following facts giving appropriate reason in each case :
 - (i) NF_3 is an exothermic compound whereas NCl_3 is not.
 - (ii) All the bonds in SF_4 are not equivalent. (All India 2012)
16. Which form of sulphur shows paramagnetic behaviour and why ?
17. Arrange the following in the order of property indicated against each set :
 - (i) HF, HCl, HBr, HI – increasing bond dissociation enthalpy.
 - (ii) H_2O , H_2S , H_2Se , H_2Te – increasing acidic character. (Delhi 2014)



Mount Abu Public School

H-Block, Sector-18, Rohini, New Delhi-110085 India

SUBJECT : CHEMISTRY

CLASS XII

Week : 8 February 13 February 2021

CHAPTER 8 : D and F BLOCK ELEMENT

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/LzZWHsYaxw>

<https://youtu.be/LzZWHsYaxw>

<https://youtu.be/LzZWHsYaxw>

Learning outcomes

Students will be able to learn about the properties of transition elements

Sub Topics

- Position in the Periodic Table
- Electronic Configurations of the d-Block Elements
- General Properties of the Transition Elements (d-Block)
- Some Important Compounds of Transition Elements
- The Lanthanoids

LESSON DEVELOPMENT

The elements lying in the middle of periodic table belonging to groups 3 to 12 are known as *d*- block elements.

Atomic number	Symbol	Electronic configuration	
21	Sc	[Ar]3d ¹ 4s ²	↑
22	Ti	[Ar]3d ² 4s ²	↑ ↑
23	V	[Ar]3d ³ 4s ²	↑ ↑ ↑
24	Cr	[Ar]3d ⁵ 4s ¹	↑ ↑ ↑ ↑ ↑
25	Mn	[Ar]3d ⁵ 4s ²	↑ ↑ ↑ ↑ ↑
26	Fe	[Ar]3d ⁶ 4s ²	↑↓ ↑ ↑ ↑ ↑
27	Co	[Ar]3d ⁷ 4s ²	↑↓ ↑↓ ↑ ↑ ↑
28	Ni	[Ar]3d ⁸ 4s ²	↑↓ ↑↓ ↑↓ ↑ ↑
29	Cu	[Ar]3d ¹⁰ 4s ¹	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
30	Zn	[Ar]3d ¹⁰ 4s ²	↑↓ ↑↓ ↑↓ ↑↓ ↑↓

3d-Series			4d-Series			5d-Series		
Atomic number	Element	Electronic configuration	Atomic number	Element	Electronic configuration	Atomic number	Element	Electronic configuration
21	Sc	$[Ar]3d^1 4s^2$	39	Y	$[Kr]4d^1 5s^2$	57	La	$[Xe]5d^1 6s^2$
22	Ti	$[Ar]3d^2 4s^2$	40	Zr	$[Kr]4d^2 5s^2$	72	Hf	$[Xe]4f^{14} 5d^2 6s^2$
23	V	$[Ar]3d^3 4s^2$	41	Nb	$[Kr]4d^4 5s^1$	73	Ta	$[Xe]4f^{14} 5d^3 6s^2$
24	Cr	$[Ar]3d^5 4s^1$	42	Mo	$[Kr]4d^5 5s^1$	74	W	$[Xe]4f^{14} 5d^4 6s^2$
25	Mn	$[Ar]3d^5 4s^2$	43	Tc	$[Kr]4d^5 5s^2$	75	Re	$[Xe]4f^{14} 5d^5 6s^2$
26	Fe	$[Ar]3d^6 4s^2$	44	Ru	$[Kr]4d^7 5s^1$	76	Os	$[Xe]4f^{14} 5d^6 6s^2$
27	Co	$[Ar]3d^7 4s^2$	45	Rh	$[Kr]4d^8 5s^1$	77	Ir	$[Xe]4f^{14} 5d^7 6s^2$
28	Ni	$[Ar]3d^8 4s^2$	46	Pd	$[Kr]4d^{10} 5s^0$	78	Pt	$[Xe]4f^{14} 5d^9 6s^1$
29	Cu	$[Ar]3d^{10} 4s^1$	47	Ag	$[Kr]4d^{10} 5s^1$	79	Au	$[Xe]4f^{14} 5d^{10} 6s^1$
30	Zn	$[Ar]3d^{10} 4s^2$	48	Cd	$[Kr]4d^{10} 5s^2$	80	Hg	$[Xe]4f^{14} 5d^{10} 6s^2$

What are transition element and write its properties (cbse 2016) • The general electronic configuration of *d*-block elements is $(n-1)d^{1-10} ns^{1-2}$, where $(n-1)$ stands for the inner *d* orbitals.

• The *d*-block elements should have incompletely filled *d*-subshell in its ground state or in its most common Oxidation State are called transition metals.

Properties

- Transition elements have high enthalpy of atomisation, low ionization enthalpy they have high melting and boiling point, paramagnetic behaviour, variable Oxidation State, show catalytic properties

EXAMPLE 1.1 Why Zn , Cd ,Hg are not regarded as transition element .(2008)

• Zinc, cadmium, mercury having the general electronic configuration as $(n-1)d^{10} ns^2$, are not regarded as transition metals due to completely filled *d* – orbital in the ground state as well as common oxidation state

General Properties of transition elements:

Metallic character

- Transition elements are metal because they have low ionization enthalpy as a result of loss of electron become easy
- Almost all the transition elements display metallic properties such as metallic luster, high tensile strength, ductility, malleability and high thermal and electrical conductivity.
- Metallic strength depend on the number of unpaired electron .greater the number of unpaired electrons, stronger is the metallic bonding and interatomic bonding

Why Cr, Mo , W have strong metallic bond

Because they all have maximum number of unpaired electron as a result stronger is the metallic bonding

Why Zn , Cd , Hg are called soft metals

Because they all have fulfilled stable electronic configuration that is there is absence of unpaired electron therefore they do not have strong metallic bonding .

EXAMPLE 1.2 Why do Transition Element exhibit higher enthalpy of atomisation

Transition elements have high enthalpy of atomisation due to presence of unpaired electron in their atoms they have stronger interatomic interactions and have stronger bonding between atoms result in higher enthalpy of atomisation

Boiling and melting point

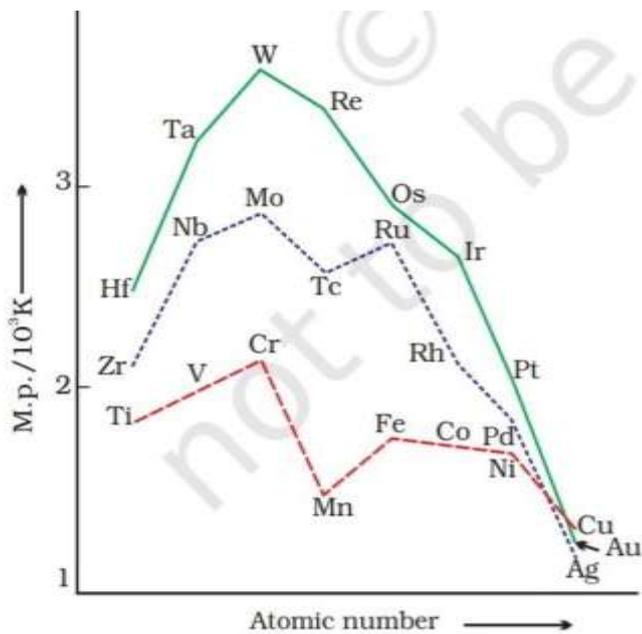


Fig. 8.1: Trends in melting points of transition elements

Transition elements have high melting and boiling point . In any row, the melting point of these metals rises to a maximum at d^5 and after that as the electrons start pairing up so the melting point decreases regularly as the atomic number increases and Mn and Tc are exception.

Reason : greater the number of unpaired valence electron, stronger is the bonding between atoms or stronger interatomic metallic bonding

Atomic and ionic radii

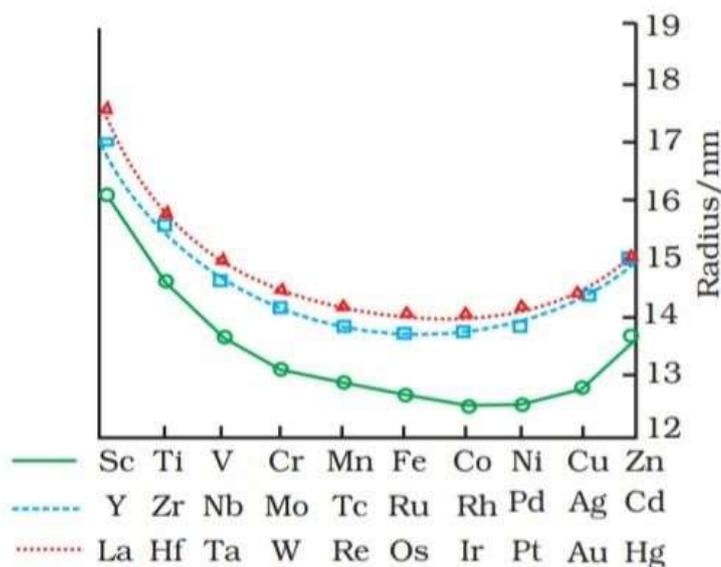


Fig. 8.3: Trends in atomic radii of transition elements

Due to the addition of new electron to a d -orbital each time the effective nuclear charge increases which causes the atomic radii to decrease in a series of transition elements.

However, the atomic size of Fe, Co, Ni is almost the same because the attraction due to increase in nuclear charge is cancelled by the repulsion because of increased in shielding effect.

Atomic size increases from Cu to zinc this is due to addition of electron in the same orbital increases the electron electron repulsion

The size of the $4d$ series elements is almost the same as the size of the $5d$ series elements. This phenomenon is due to lanthanoid contraction.

Lanthanoid contraction

The filling of the $4f$ before the $5d$ orbital results in a regular decrease in size called lanthanoid contraction. This compensates for the expected increase in the atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the $4d$ and $5d$ series elements exhibit similar radii and show similarity in their physical and chemical properties.

Ionization enthalpy

In a particular transition series, there is an increase in ionization enthalpy from left to right which is due to the increase in effective nuclear charge and decrease in size along a series. But the trend is not very regular. The exceptions are chromium and copper which have notably larger ionization enthalpy than their neighbours. These exceptions are due to the extra stability associated with the half-filled and fully-filled set of d -orbitals.

Density

Density of transition metals increases as we go from Ti to Cu because atomic radii decreases at the same time atomic mass increases therefore density increases

Zinc has a lower density because in sync due to electron electron repulsion atomic size increases due to large atomic size zinc has low density

Oxidation States

For example:- Oxidation states of the first row transition metals are:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Why Transition Element show variable Oxidation State?

Because there is very less energy gap between and (n-1)d and ns orbital therefore both the orbitals can participate in Bond formation therefore they have variable Oxidation State.

Why the elements doors those at present in in middle of the series show greater number of Oxidation State?

Because in the middle of transition series metal have maximum number of unpaired electrons.

Note: in the first transition series Mn show Highest Oxidation State which is is + 7 in transition elements , Os show maximum Oxidation State

Magnetic properties

why most of the transition elements are paramagnetic in nature?

Because most of them contain unpaired electron.

Formation of Complexes

- (a) In a transition series the stability of complexes increases with the rise in atomic number.
- (b) The transition metal atom reveals multiple oxidation state; the higher valent ion forms more stable complexes.
- (c) A few examples are: $[\text{Fe}(\text{CN})_6]^{3-}$

Why most of the Transition Element form complexes?

Due to the small size of their metal ion.

Due to The ionic charge and due to availability of the d orbital where ligand can donate its lone pair to the metal.

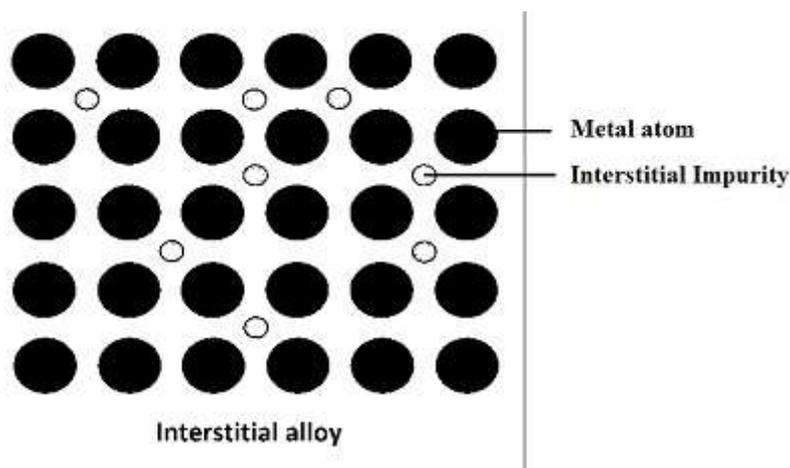
interstitial compound

Formation of Interstitial Compounds

- (d) Transition elements in combination with small atoms like H, B, C, N etc. leads to the formation of interstitial compounds that are non-stoichiometric in composition.

E.g.: $\text{TiH}_{1.3}$, $\text{VH}_{0.54}$

1. The interstitial compounds so formed are chemically inert having higher melting points as compared to pure metals. These compounds are hard and tough and keeps metallic conductivity.



Alloy Formation

- (e) Alloys are homogeneous mixtures of more than one metal that can displace another metal from the crystal lattice due to their comparable sizes. This leads to the formation of alloys.
- (f) The alloys so formed are hard with high melting points. For example, chromium, vanadium, tungsten, manganese, molybdenum are the ferrous alloys.
- (g) Some other examples are brass (alloy of copper + zinc), stainless steel, bronze (alloy of copper + tin), etc.

Example 1.3 which element do not show variable Oxidation State

Ans Scandium (Sc)

Formation of coloured compounds

Transition metals and their compounds show colour. The colour is due to the excitation of electron from one *d* atomic orbital to higher energy *d* atomic orbital in the same subshell. The frequency of the light absorbed generally lies in the visible region. The colour observed is due to the colour of the complementary light. The colour is due to the presence of unpaired electrons.

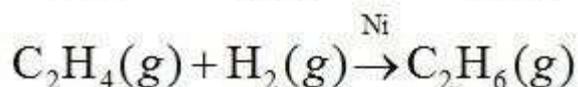
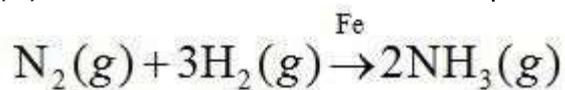
All Zn^{2+} compounds are white. (due to absence of unpaired electron)

Catalytic properties

Most of transition metals are used as catalysts.

This is due to the

- (i) presence of incomplete or empty *d*-orbitals, (ii) large surface area and
 (iii) variable oxidation state. For example Fe, Ni, V_2O_3 , Pt, Mo, Co, etc., are used as catalyst.



Formation of oxides

Transition metals form oxides on reaction with oxygen at elevated temperature. Transition metal form oxide in oxidation state of + 1 (in Ag_2O) to + 7 (Mn_2O_7) to + 8 (in OsO_4). As the oxidation number increases in case of same elements,

- (h) The covalent character of oxides increases.

(i) The acidic strength of the oxides increases.

(j) The oxidizing power of oxides increases.

For example, Cr_2O_3 is amphoteric while CrO is basic and CrO_3 is acidic.

ASSIGNMENT

- Zn^{+2} salts are white while Cu^{+2} salts are coloured. Why?
- What are the transition elements? Write two characteristics of the transition elements.
- (i) E° value for the $\text{Mn}^{+3}/\text{Mn}^{+2}$ couple is positive (+1.5 V) whereas that of $\text{Cr}^{+3}/\text{Cr}^{+2}$ is negative (-0.4 V). Why? ' (ii) Transition metals form coloured compounds. Why?
- (i) MnO is basic whereas Mn_2O_7 is acidic in nature. Why? (ii) Transition metals form alloys. Why?
- (a) Account for the following:
(i) Cu^+ is unstable in an aqueous solution.
(ii) Transition metals form complex compounds
- (a) How would you account for the following:
(i) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7
(ii) Transition metals and their compounds show catalytic properties.
- Assign suitable reasons for the following:
(a) The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.
(b) In the 3d series from Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomization of Zn is the lowest.
(c) Sc^{3+} is colourless in aqueous solution, whereas Ti^{3+} is coloured.
- The enthalpy of atomization is lowest for Zn in 3 d series of the transition elements.?

9. (i) Name the element of 3d transition series which shows maximum number of oxidation states. Why does it show so?
(ii) Which transition metal of 3d series has positive $E^\circ(M^{2+}/M)$ value and why?
(iii) Out of Cr^{3+} and Mn^{3+} , which is a stronger oxidizing agent and why?
10. (a) Which metal in the first transition series (3d series) exhibits +1 oxidation state most frequently and why?
(b) Which of the following cations are coloured in aqueous solutions and why?
 Sc^{3+} , V^{3+} , Ti^{4+} , Mn^{2+}
(At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)
11. How would you account for the following:
(i) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d4) Mn^{3+} is an oxidising agent.
(ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series.
12. Account for the following:
(i) The enthalpies of atomisation of the transition metals are high.
(ii) The lowest oxide of a transition metal is basic, the highest is amphoteric/ acidic.
(iii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised.



Mount Abu Public School

H-Block, Sector-18, Rohini, New Delhi-110085 India

SUBJECT : CHEMISTRY

CLASS XII

Week : 8 February 13 February 2021

CHAPTER 9 : COORDINATION CHEMISTRY

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/53z1EiflKNI>
<https://youtu.be/53z1EiflKNI>
<https://youtu.be/53z1EiflKNI>

Learning outcomes

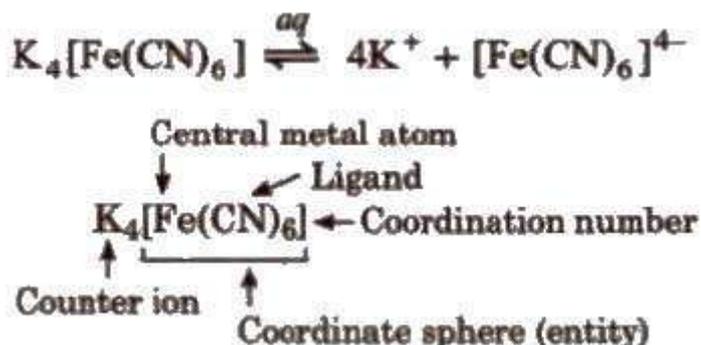
Students will be able to learn about the coordination complexes and various theories related to it

Sub Topics

- Werner's Theory of Coordination Compounds
- Definitions of Some Important Terms Pertaining to Coordination Compounds
- Nomenclature of Coordination Compounds
- Bonding in Coordination Compounds
- Crystal Field Theory

LESSON DEVELOPMENT

Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds, the central metal atom or ion is linked by ions or molecules with coordinate bonds. e.g., Potassium ferrocyanide, $K_4 [Fe(CN)_6]$.



Double Salts

These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr's salt, $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ get dissociated into Fe^{2+} , NH_4^+ and SO_4^{2-} ions.

Terms Related to Coordination Compounds 1. Complex ion or Coordination Entity

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

- (i) **Cationic complex entity** It is the complex ion which carries positive charge. e.g., $[Pt(NH_3)_4]^{2+}$

(ii) **Anionic complex entity** It is the complex ion which carries negative charge. e.g., $[\text{Fe}(\text{CN})_6]^{4-}$

2. Central Atom or Ion

The atom or ion to which a fixed number of ions or groups are bound is called central atom or ion. It is also referred as Lewis acid. e.g., in $[\text{NiCl}_2(\text{H}_2\text{O})_4]$. Ni is central metal atom. It is generally transition element or inner-transition element.

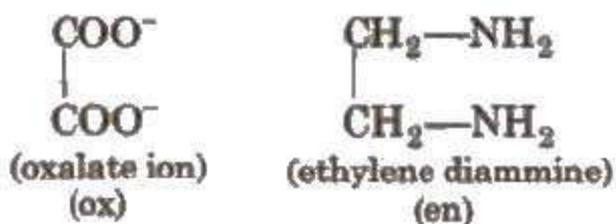
3. Ligands

Ligands is electron donating species (ions or molecules) bound to the Central atom in the coordination entity.

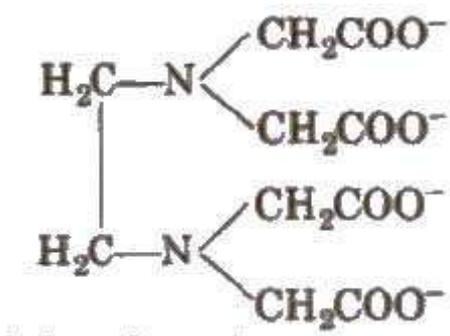
These may be charged or neutral. Ligands are of the following types :

(i) **Unidentate** It is a ligand, which has one donor site, i.e., the ligand bound to a metal ion through a single donor site. e.g., H_2O , NH_3 , etc.

(ii) **Didentate** It is the ligand. which have two donor sites.



(iii) **Polydentate** It is the ligand, which have several donor sites. e.g., $[\text{EDTA}]^{4-}$ is hexadentate ligand.



(iv) **Ambidentate ligands** These are the monodentate ligands which can ligate through two different sites, e.g., NO_2^- , SCN^- , etc.

(v) **Chelating ligands** Di or polydentate ligands cause cyclisation around the metal atom which are known as chelate IS , Such ligands USEs two or more donor atoms to bind a single metal ion and are known as chelating ligands.

More the number of chelate rings, more is the stability of complex.

The stabilisation of coordination compounds due to chelation is known as **chelate effect**.

π – acid ligands are those ligands which can form π – bond and σ -bond by accepting an appreciable amount of π electron density from metal atom to empty π or π^* – orbitals. 4.

Coordination Number

It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

e.g., in $[\text{PtCl}_6]^{2-}$, Pt has coordination number 6.

In case of monodentate ligands,

Coordination number = number of ligands

In polydentate ligands.

Coordination number = number of ligands * denticity

5. Coordination Sphere

The central ion and the ligands attached to it are enclosed in square bracket which is known as coordination sphere. The ionisable group written outside the bracket is known as counter ions.

6. Coordination Polyhedron

The spatial arrangement of the ligands which are directly attached to the central atom or ion, is called coordination polyhedron around the central atom or ion.

7. Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called oxidation number of central atom.

e.g., $[\text{Cu}(\text{CN})_4]^{3-}$, oxidation number of copper is +1, and represented as Cu(I).

Types of Complexes 1. Homoleptic complexes

Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes e.g., $[\text{Co}(\text{NH}_3)_6]^{3+}$

2. Heteroleptic complexes

Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

3. Labile and Inert complexes

Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow, are known as inert complexes.

Effective Atomic Number (EAN)

This concept was proposed by Sidgwick. In a complex, the EAN of metal atom is equal to the total number of electrons present in it.

$$\text{EAN} = Z - \text{ON of metal} + 2 * \text{CN}$$

(where, Z = atomic number of metal atom ON = oxidation number of metal and CN = coordination number of complex)

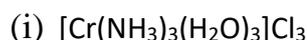
An ion with central metal atom having EAN equal to next inert gas will be more stable.

IUPAC Naming of Complex Compounds

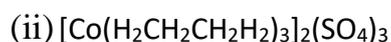
Naming is based on set of rules given by IUPAC.

1. Name of the compound is written in two parts (i) name of cation, and (ii) name of anion.
2. The cation is named first in both positively and negatively charged coordination complexes.
3. The dissimilar ligands are named in an alphabetical order before the name of central metal atom or ion.
4. For more than one similar ligands, the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.
5. If the complex part is anion, the name of the central metal ends with suffix 'ate'.
6. Names of the anionic ligands end in 'o', names of positive ligands end with 'ium' and names of neutral ligands remain as such. But exceptions are there as we use aqua for H₂O, ammine for NH₃, carbonyl for CO and nitrosyl for NO.
7. Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses.
8. The name of the complex part is written as one word.
9. If the complex ion is a cation, the metal is named same as the element.
10. The neutral complex molecule is named similar to that of the complex cation.

Some examples are



triamminetrichlorochromium (III) chloride



tris (ethane-1,2-diamine) cobalt (III) sulphate

(iii) $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$ diamminesilver (I) dicyanoargentate(I)

(iv) $\text{K}_4[\text{Fe}(\text{CN})_6]$

potassium hexacyanoferrate (II)

Bonding in Coordination Compounds

Werner's Theory

Metals exhibit two types of valencies in the formation of complexes.

These are primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.
2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

Valence Bond Theory (VBT)

This theory was proposed by L. Pauling in 1930 s. According to this theory, when a complex is formed, the metal ion/atom provides empty orbitals to the surrounding ligands. Coordination number shows the number of such empty orbitals, i.e., number of empty orbitals is equal to the coordination number. These empty orbitals hybridised before participation in bonding and the nature of hybridisation depends on the nature of metal and on the nature of approaching ligand.

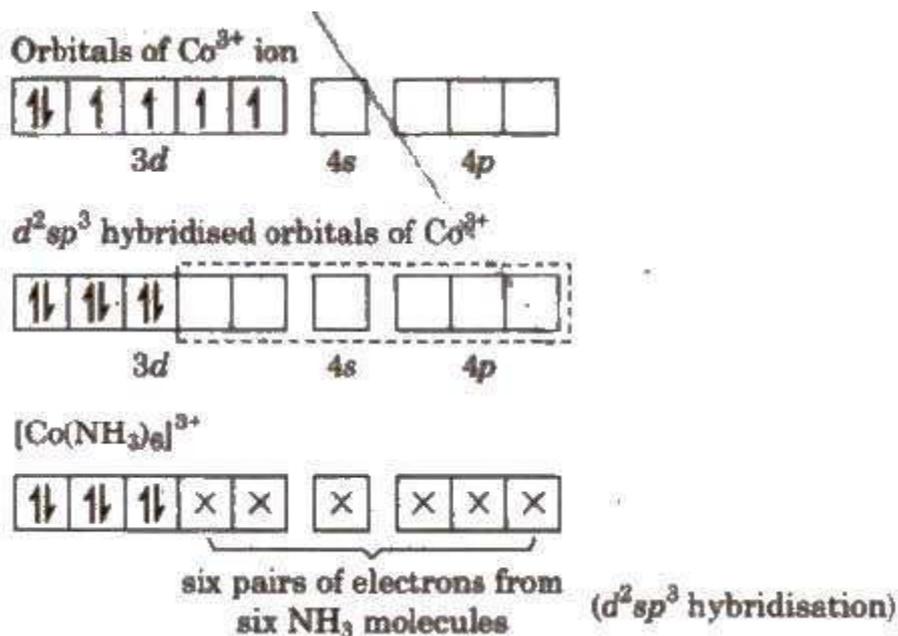
Inner orbital complexes or outer orbital complexes

When outer d-orbitals are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation is sp^3d^2 . They have octahedral shape.

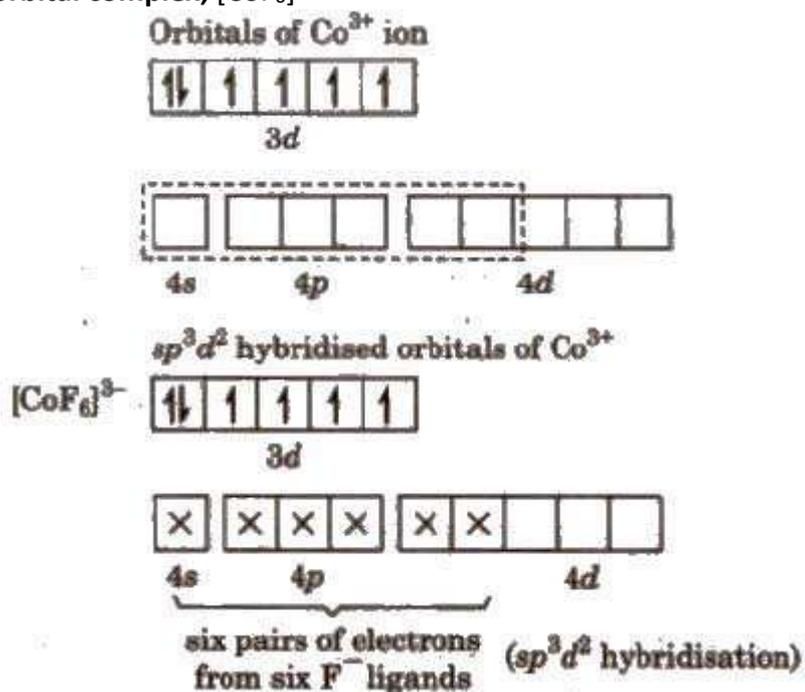
When d-orbitals of $(n - 1)$ shell are used, these are known as inner orbital complex, they are formed due to strong field ligands or low spin ligands and hybridisation is d^2sp^3 . They are also octahedral in shape.

1. **6 – ligands (unidentate), octahedral entity.**

(i) **Inner orbital complex** $[\text{Co}(\text{NH}_3)_6]^{3+}$



All electrons are paired, therefore complex will be diamagnetic in nature. (ii) **Outer orbital complex**, $[\text{CoF}_6]^{3-}$



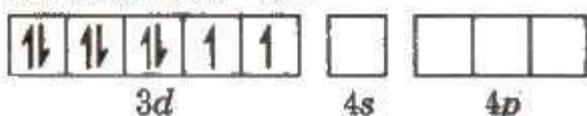
Complex has unpaired electrons, therefore, it will be paramagnetic in nature.

2. **4-ligands** (unidentate) **tetrahedral entity**.

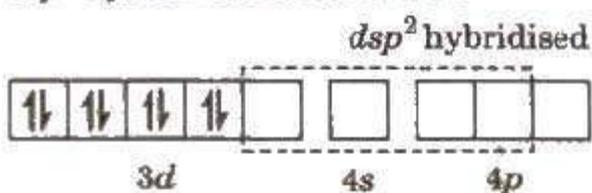
S.No.	Inner orbital complexes	Outer orbital complexes
(a)	Strong field or low spin ligands	Weak field or high spin ligands
(b)	Hybridisation is dsp^2 (where one orbital of $3d$, one orbital of $4s$ and two orbitals of $4p$)	Hybridisation is sp^3 (where one orbital of $4s$ and three orbitals of $4p$)
(c)	Square planar shape	Tetrahedral shape

(i) Inner orbital complex, $[\text{Ni}(\text{CN})_4]^{2-}$

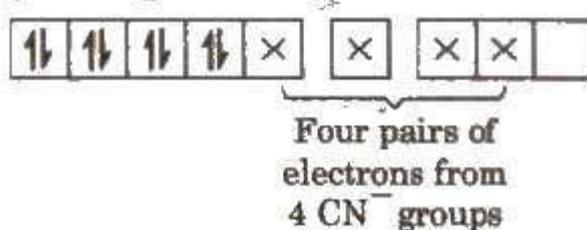
Orbitals of Ni^{2+} ion



dsp^2 hybridised orbitals of Ni^{2+}

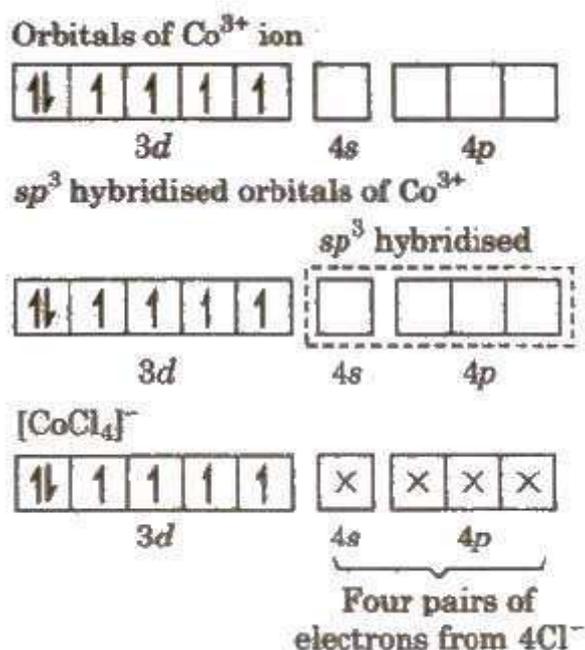


$[\text{Ni}(\text{CN})_4]^{2-}$



All electrons are paired so complex will be diamagnetic in nature.

(ii) Outer orbital complex, $[\text{CoCl}_4]^-$



Since, complex has unpaired electrons. so it will be paramagnetic in nature.

Limitations of VBT

This theory could not explain the quantisation of the magnetic data, existence of inner orbital and outer orbital complex, change of magnetic moment with temperature and colour of complexes.

Crystal Field Theory (CFT)

This theory was proposed by H. Bethe and van Vleck. Orgel. in 1952, applied this theory to coordination compounds. In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

The five d-orbitals are classified as

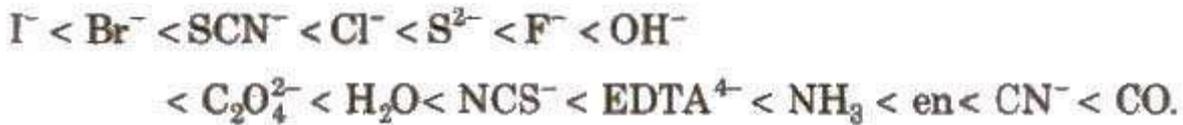
- (i) Three d-orbitals i.e., d_{xy} , d_{yz} and d_{zx} are oriented in between the coordinate axes and are called t_{2g} – orbitals.
- (ii) The other two d-orbitals, i.e., $d_{x^2-y^2}$ and d_{z^2} oriented along the $x - y$ axes are called e_g – orbitals.

Due to approach of ligands, the five degenerate d-orbitals split. Splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between t_{2g} and e_g level is designated by Δ and is called **crystal field splitting energy**.]

By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series



Crystal field splitting in octahedral complexes

In case of octahedral complexes, energy separation is denoted by Δ_o (where subscript 0 is for octahedral).

In octahedral complexes, the six-ligands approach the central metal ion along the axis of $d_{x^2-y^2}$ and d_{z^2} orbitals.

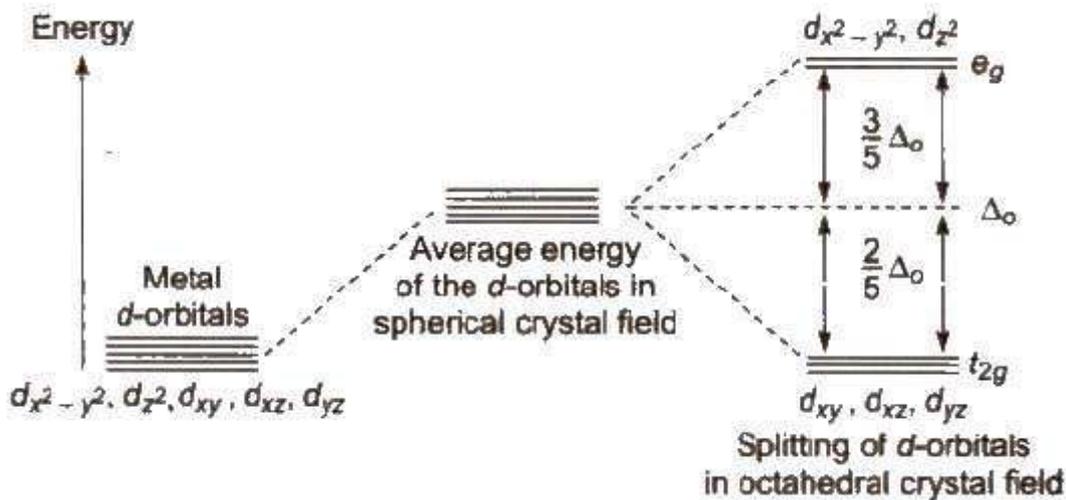
Energy of e_g set of orbitals > energy of t_{2g} set of orbitals.

The energy of e_g orbitals will increase by $(3/5) \Delta_o$ and t_{2g} will decrease by $(2/5) \Delta_o$.

If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.

Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. (where, P = energy required for e^- pairing in an orbital). Ligands which produce this effect are known as strong field ligands and form low spin complexes.



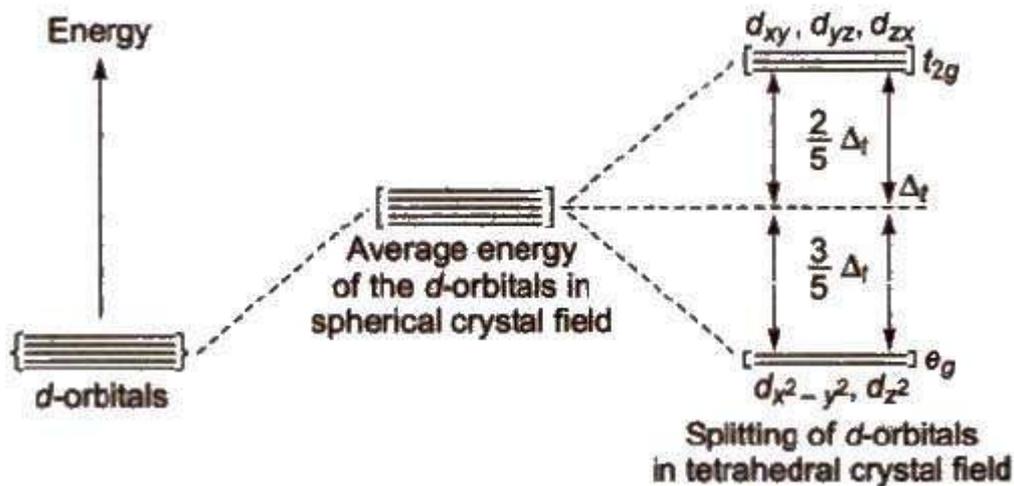
Crystal field splitting in tetrahedral complexes

In tetrahedral complexes, four ligands may be imagined to occupy the alternate corners of the cube and the metal ion at the center of the cube.

Energy of t_{2g} set of orbitals > Energy of e_g set of orbitals.

In such complexes d – orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Orbital splitting energies are so low that pairing of electrons are not possible so these are high spin complexes.



Colour in Coordination Compounds

The crystal field theory attributes the colour of the coordination compounds to the d-d transition of the electron, i.e., electron jump from t_{2g} level to higher e_g level.

In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless.



Limitations of CFT

1. It does not consider the formation of π bonding in complexes.
2. It is also unable to account satisfactorily for the relative strengths of ligands e.g., it does not explain why H_2O is stronger ligand than OH^- .
3. It gives no account of the partly covalent nature of metal-metal bonds.

ASSIGNMENT

- Which of the following is more stable complex and why?
[Co(NH₃)₆]³⁺ and [Co(en)₃]³⁺ (Delhi 2014)
- What is the IUPAC name of the complex [Ni(NH₃)₆]Cl₂? (Comptt. Delhi 2015)
- Why are low spin tetrahedral complexes not formed? (Comptt. Delhi 2017)
- Name the following coordination compounds according to IUPAC system of nomenclature :
(i) [Co(NH₃)₄(H₂O)Cl]Cl₂
(ii) [CrCl₂(en)₂]Cl,
(en = ethane – 1, 2 – diamine) (Delhi 2010)
- Describe the shape and magnetic behaviour of following complexes :
(i) [Co(NH₃)₆]³⁺
(ii) [Ni(CN)₄]²⁻ (At. No. Co = 27, Ni = 28) (Delhi 2010)
- [Fe(H₂O)₆]³⁺ is strongly paramagnetic whereas [Fe(CN)₆]³⁻ is weakly paramagnetic. Explain. (At. no. Fe = 26) (Comptt. All India 2012)
- Explain why [Co(NH₃)₆]³⁺ is an inner orbital complex whereas [Ni(NH₃)₆]²⁺ is an outer orbital complex. (At. no. Co = 27, Ni = 28) (Comptt. All India 2013)
- When a coordination compound CoCl₃.6NH₃ is mixed with AgNO₃, 3 moles of AgCl are precipitated per mole of the compound. Write
(i) Structural formula of the complex
(ii) IUPAC name of the complex (All India 2016)
- For the complex [Fe(en)₂Cl₂], Cl, (en = ethylene diamine), identify
(i) the oxidation number of iron,
(ii) the hybrid orbitals and the shape of the complex,
(iii) the magnetic behaviour of the complex,
(iv) name of the complex. (At. no. of Fe = 26) (Delhi 2009)
- Explain the following cases giving appropriate reasons :
(i) Nickel does not form low spin octahedral complexes.
(ii) The n-complexes are known for the transition metals only. (All India 2010)
- Write the name, stereochemistry and magnetic behaviour of the following : (At. nos. Mn = 25, Co = 27, Ni = 28) (Delhi 2011)
(i) K₄[Mn(CN)₆]
- Give the formula of each of the following coordination entities :
(i) Co³⁺ ion is bound to one Cl⁻, one NH₃ molecule and two bidentate ethylene diamine (en) molecules.
(ii) Ni²⁺ ion is bound to two water molecules and two oxalate ions.
- State a reason for each of the following situations :
(i) Co²⁺ is easily oxidized to Co³⁺ in presence of a strong ligand.
(ii) CO is a stronger complexing reagent than NH₃.
(iii) The molecular shape of [Ni(CO)₄] is not the same as that of [Ni(CN)₄]²⁻ (Delhi 2011)
- What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d⁴ in terms of t_{2g} and e_g in an octahedral field when
(i) Δ₀ > P
(ii) Δ₀ < P (All India 2013)



Mount Abu Public School

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SUBJECT : CHEMISTRY

CLASS XII

Week : 15 February 21 February 2021

CHAPTER 10: HALOALKANES AND HALOARENES

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/LUIEtIdMMRg>

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<https://youtu.be/LUIEtIdMMRg>

Learning outcomes

Students will be able to learn about the haloalkane and haloarenes and its chemical and physical properties

Sub Topics

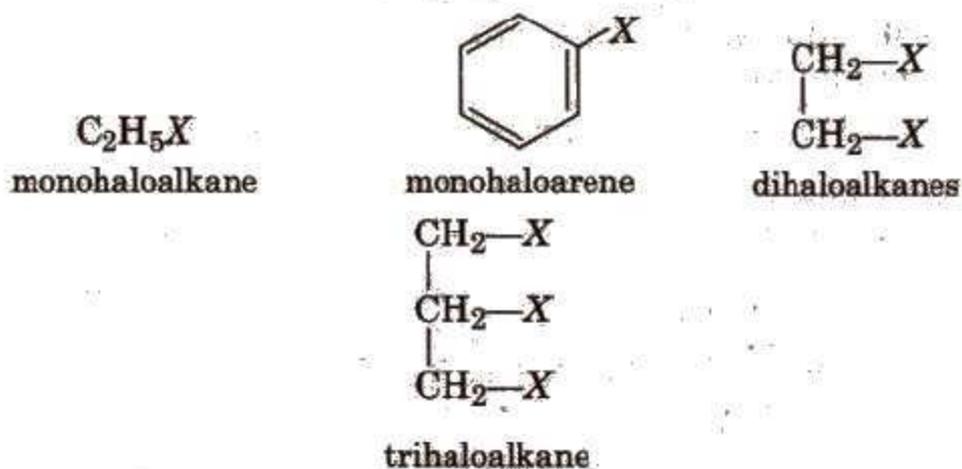
- Classification
- Nomenclature
- Nature of C-X Bond
- Methods of Preparation
- Physical Properties
- Chemical Reaction

LESSON DEVELOPMENT

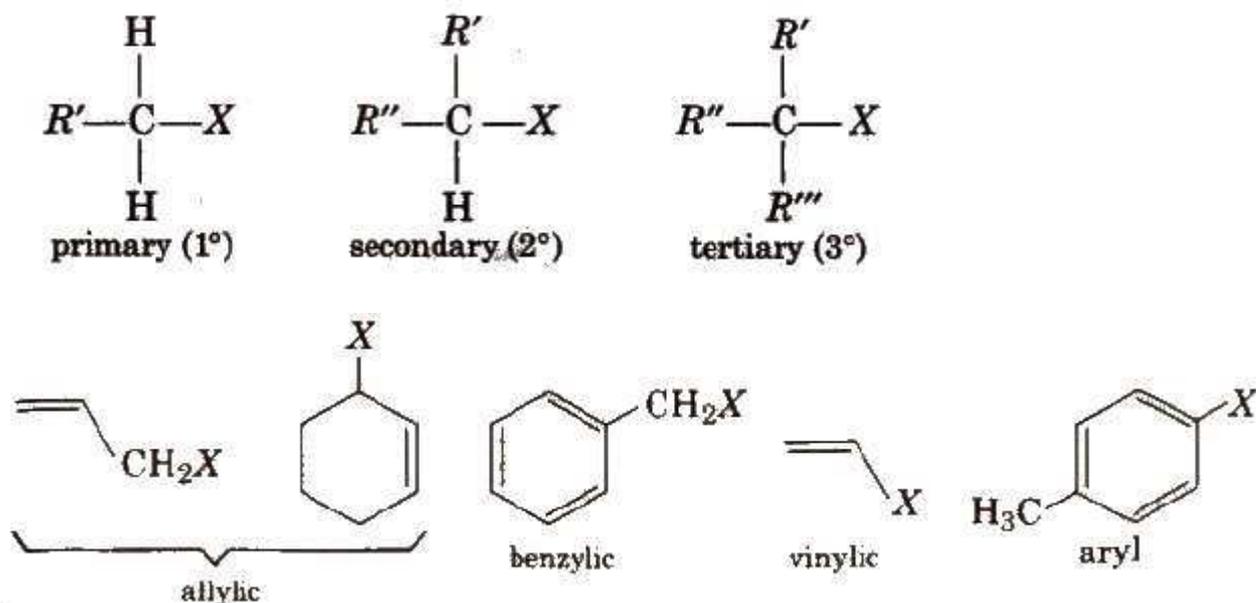
The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Classification of Halogen Derivatives

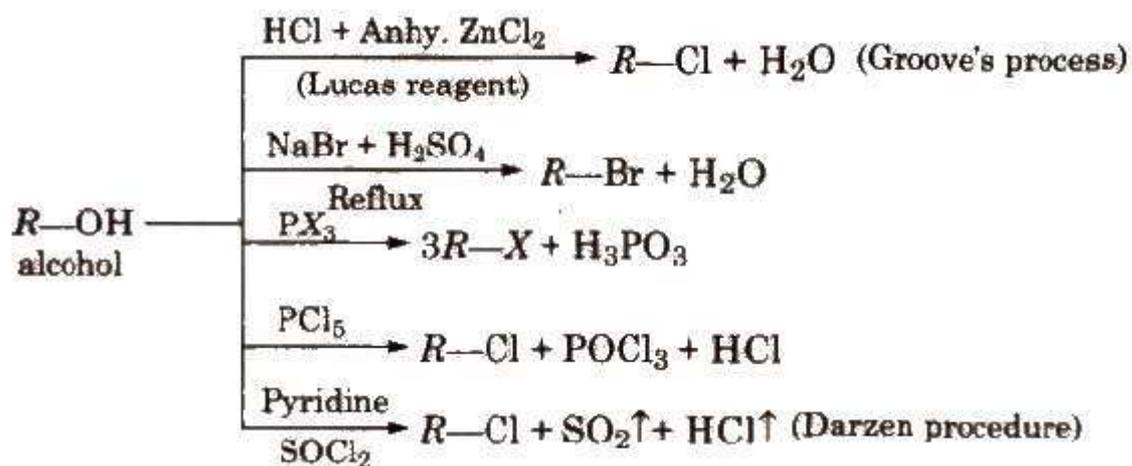
On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,



On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3°, allylic, benzylic, vinylic and aryl derivatives, e.g.,



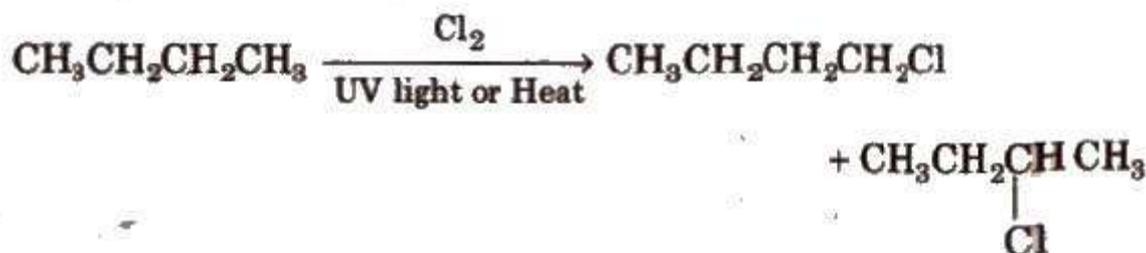
General Methods of Preparation of Haloalkanes 1. From Alcohols



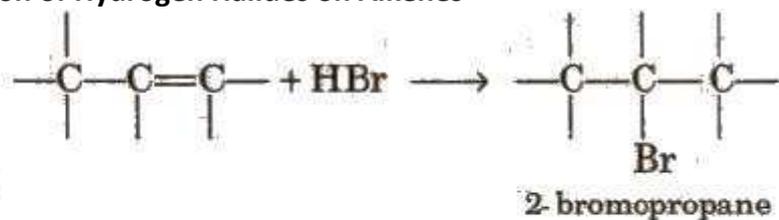
In Groove's method, ZnCl_2 is used to weaken the C-OH bond. In case of 3° alcohols, ZnCl_2 is not required. The reactivity order of halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$.

Darzen procedure is the best method for preparing alkyl halides from alcohols since both the by products (SO_2 and HCl) are gaseous and escape easily.

2. Free Radical Halogenation of Alkanes



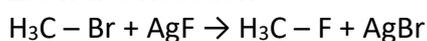
Addition of Hydrogen Halides on Alkenes



1. Finkelstein Reaction

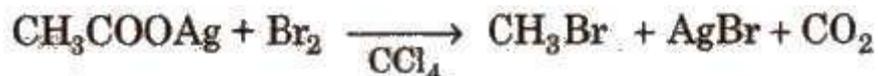


2. Swarts Reaction



Hg₂F₂, COF₂ and SbF₃ can also be used as a reagent for Swarts reaction. **3.**

Hunsdiecker Reaction

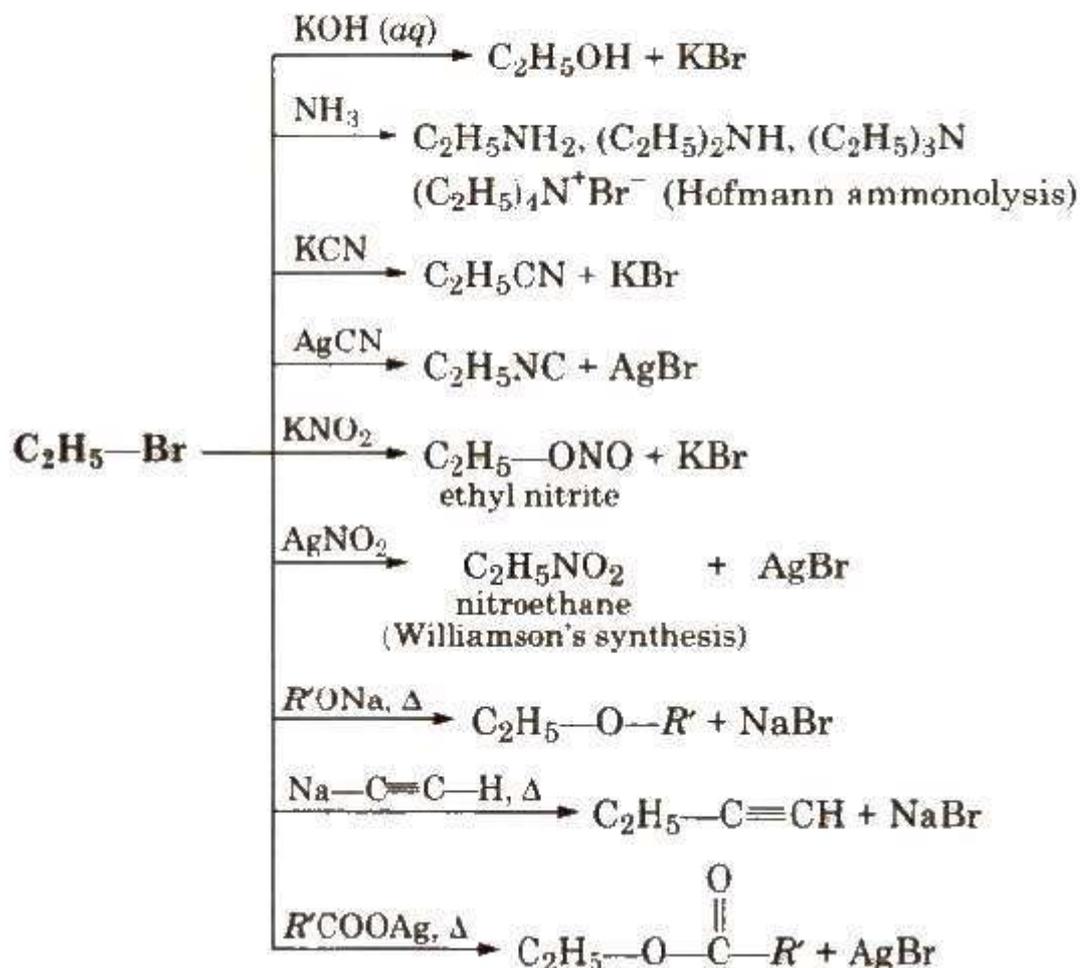
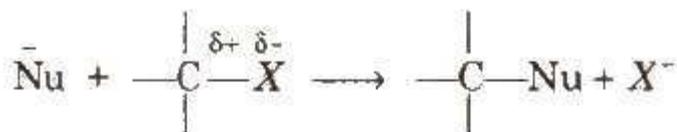


Physical Properties of Haloalkanes 1. Boiling point orders

1. R - I > R - Br > R - Cl > R - F
 2. CH₃ - (CH₂)₂ - CH₂Br > (CH₃)₂ CHCH₂Br > (CH₃)₃CBr
 3. CH₃CH₂CH₂ > CH₃CH₂X > CH₃X
2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is
- $$\text{CH}_3\text{F} > \text{CR}_3\text{Cl} > \text{CR}_3\text{Br} > \text{CH}_3\text{I}$$
3. Dipole moment decreases as the electronegativity of the halogen decreases.
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.
5. Density order is
- $$\text{RI} > \text{RBr} > \text{RCl} > \text{RF} \text{ (For the same alkyl group)}$$
- $$\text{CH}_3\text{I} > \text{C}_2\text{H}_5\text{I} > \text{C}_3\text{H}_7\text{I}$$

Chemical Reactions of Haloalkanes 1. Nucleophilic Substitution Reactions

(S_N reactions)

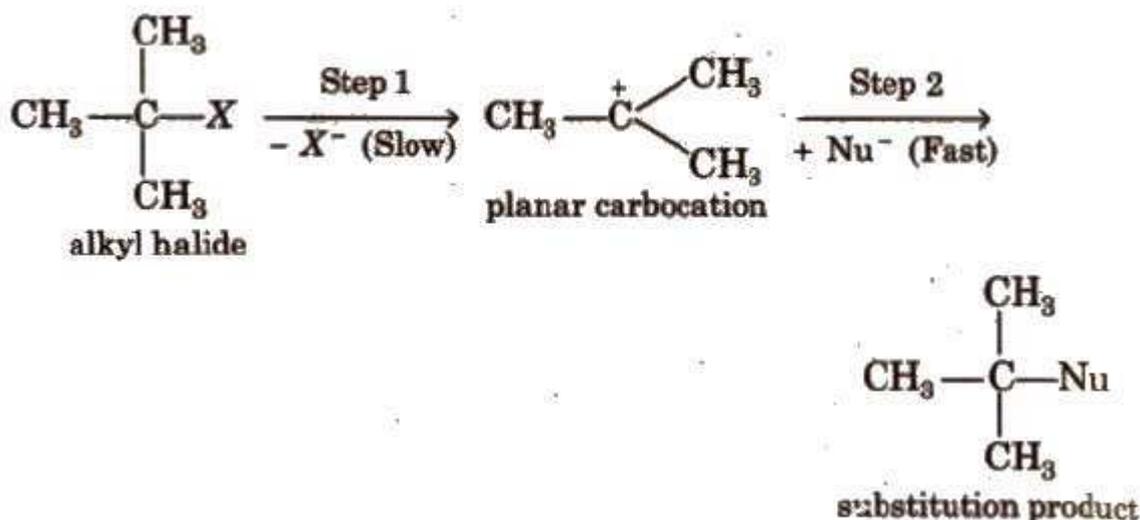


kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO₂ form R-ONO while AgNO₂ produces R-NO₂ as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.

Nucleophilic substitution reactions are of two types

(a) **S_N1 type** (Unimolecular nucleophilic reactions proceed in two steps:



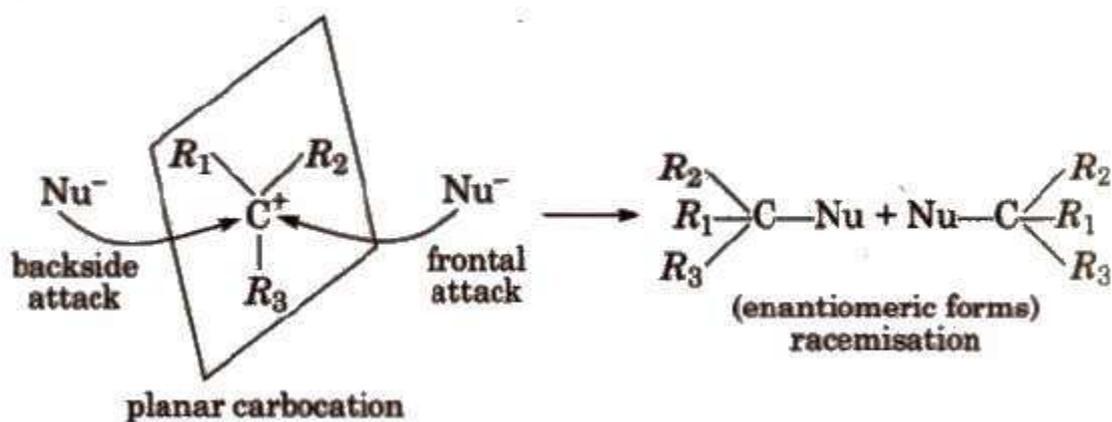
Rate, $r = k [\text{RX}]$. It is a first order reaction.

Reactivity order of alkyl halide towards $\text{S}_{\text{N}}1$ mechanism

$3^\circ > 2^\circ > 1^\circ$

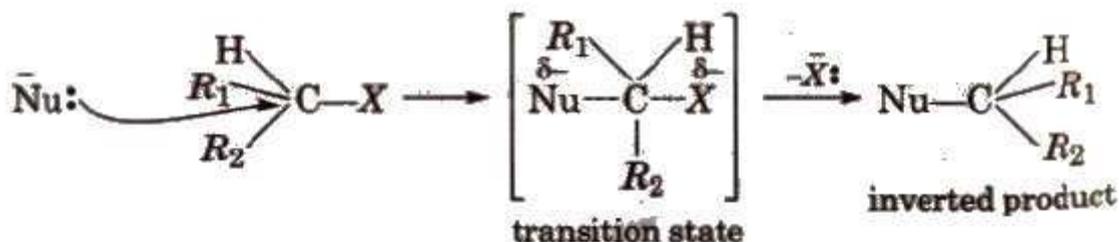
Polar solvents, low concentration of nucleophiles and weak nucleophiles favour $\text{S}_{\text{N}}1$ mechanism.

In $\text{S}_{\text{N}}1$ reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.



(b) $\text{S}_{\text{N}}2$ type (Bimolecular nucleophilic substitution) These reactions proceed in one step and is a second order reaction with $r = k[\text{RX}][\text{Nu}]$.

During $\text{S}_{\text{N}}2$ reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,



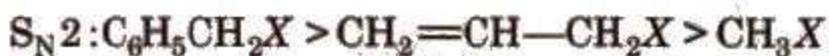
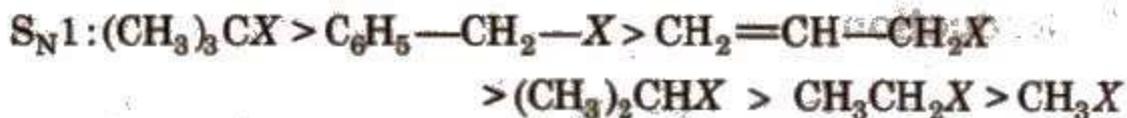
Reactivity of halides towards $\text{S}_{\text{N}}2$ mechanism is

$1^\circ > 2^\circ > 3^\circ$

Rate of reaction in $\text{S}_{\text{N}}2$ mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

$:\text{CN}^- > : \text{I}^- > : \text{OR}^- > : \text{OH}^- > \text{CH}_3\text{COO}^- > \text{H}_2\text{O} > \text{F}^-$

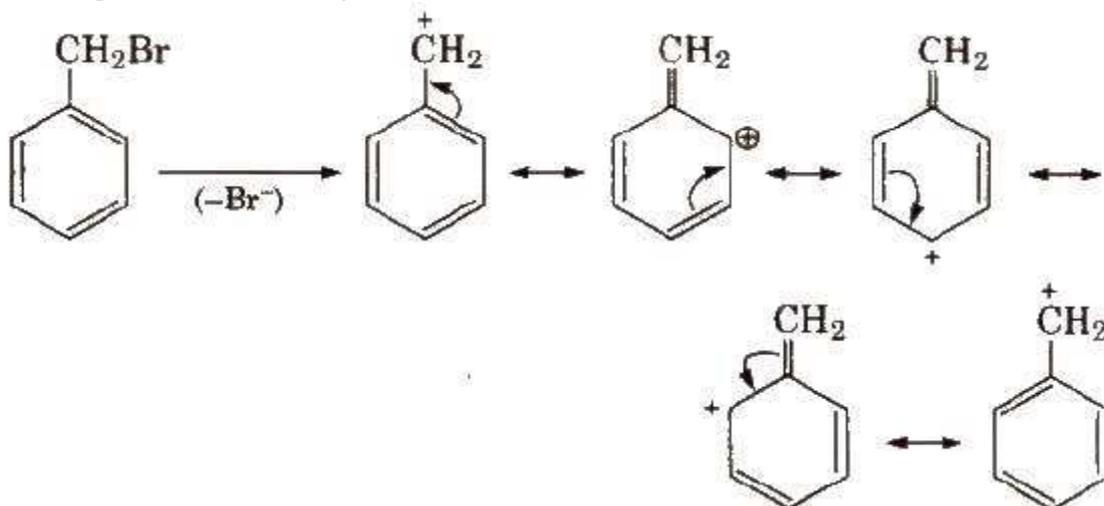
Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour S_N2 mechanism. Relative rates of some alkyl halides in S_N1 and S_N2 reactions are in the order



resonance stabilised



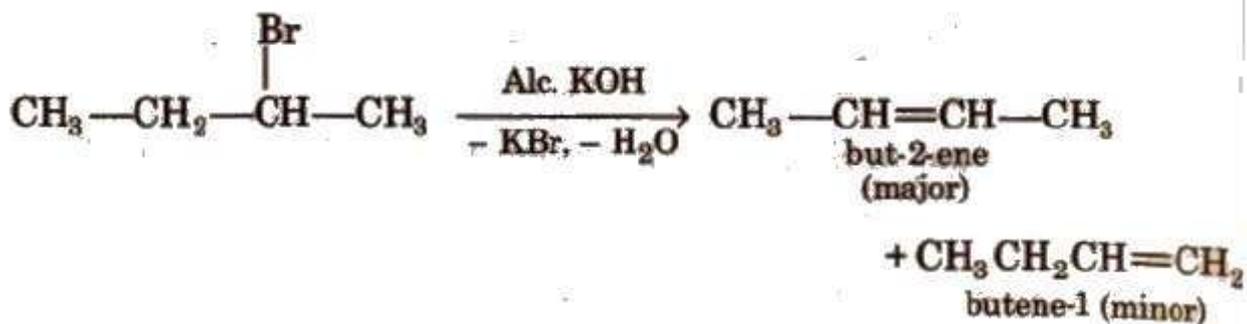
Resonating structure of benzyl carbocations are



Relative reactivity of alkyl halides for same alkyl group is $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$

2. Elimination Reactions

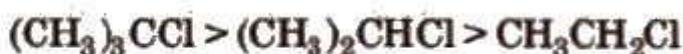
Dehydrohalogenation is a β – elimination reaction in which halogen is from α -carbon atom and the hydrogen from the α -carbon according to Saytzeff rule, e.g.,



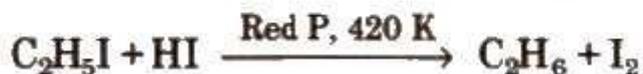
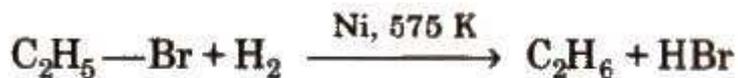
Ease of dehydrohalogenation among halides

$3^\circ > 2^\circ > 1^\circ$

i.e.,

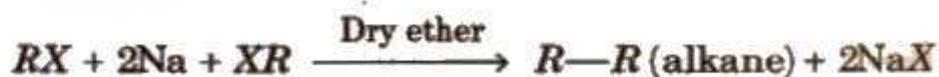


3. Reduction



4. Reaction with Metals

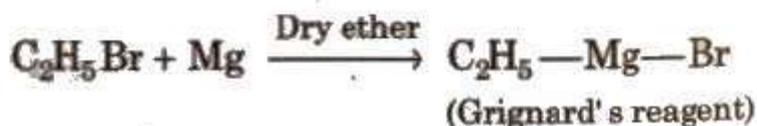
(i) Wurtz reaction



(ii) Wurtz-Fittig reaction

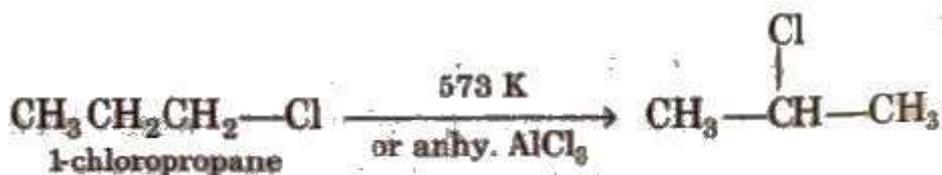


(iii) Reaction with Mg

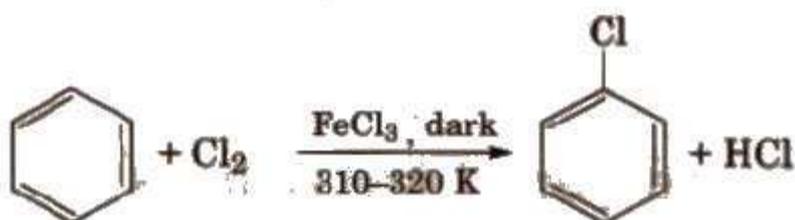


Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used as ethereal solution.

5. Isomerisation

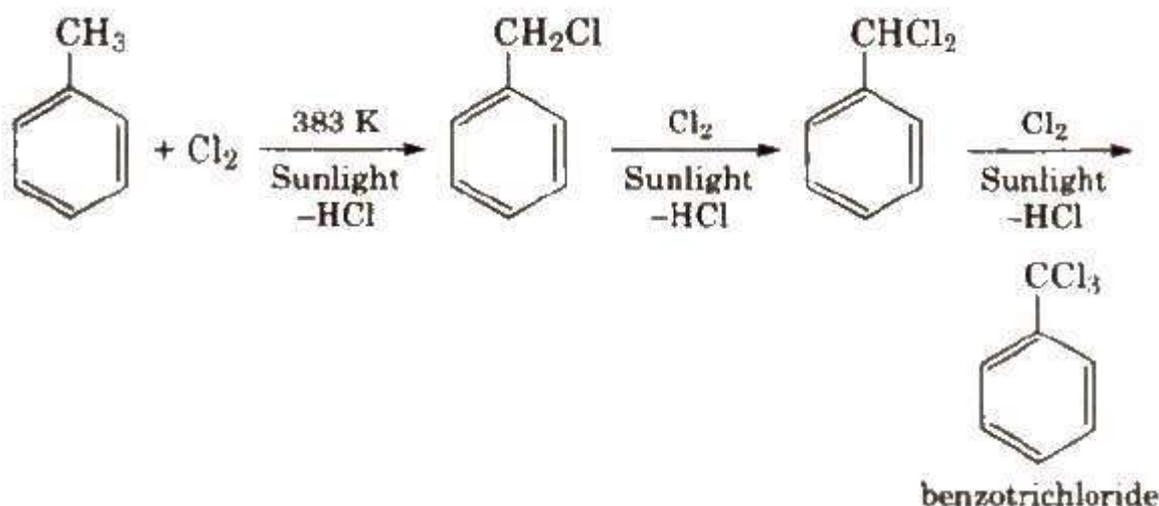


General Methods of Preparation of Aryl Halides 1. By Halogenation of Aromatic Hydrocarbons



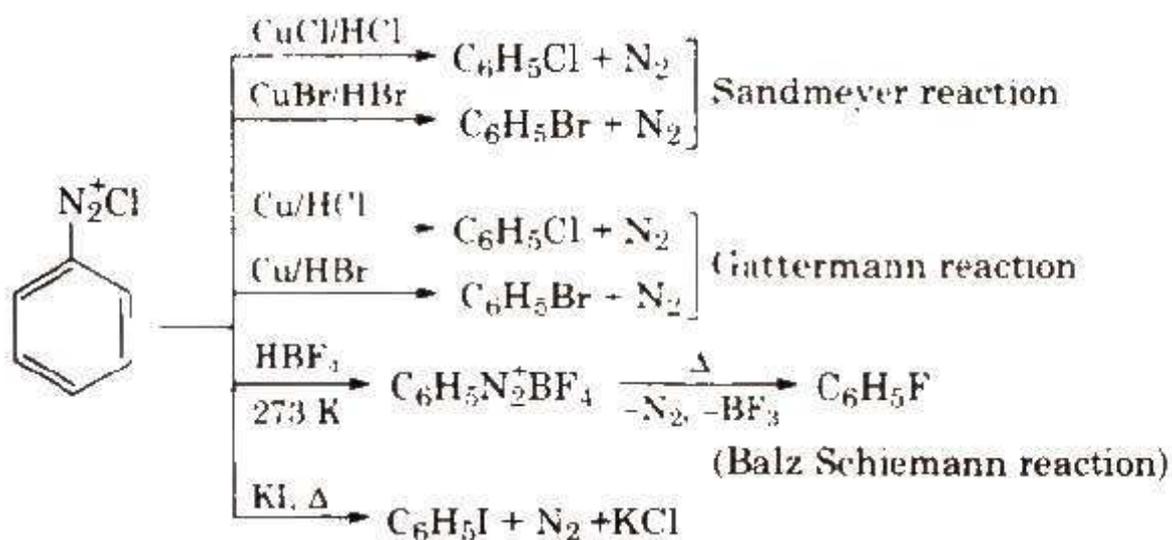
It is an electrophilic substitution reaction.

2. By Side Chain Halogenation

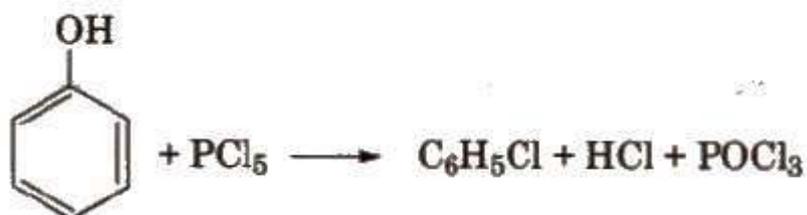


(It involves free radical mechanism.)

3. From Benzene Diazonium Salt



4. From Phenol



Physical Properties of Aryl Halides

1. Aryl halides are colourless liquids or colourless solids with characteristic odour.

2. Boiling point generally increases with increase in the size of aryl group or halogen atom.

Boiling point order

$\text{Ar} - \text{I} > \text{Ar} - \text{Br} > \text{Ar} - \text{Cl} > \text{Ar} - \text{F}$

3. The melting point of p-isomer is more than o- and m-isomer.

This is because of more symmetrical nature of p-isomer.

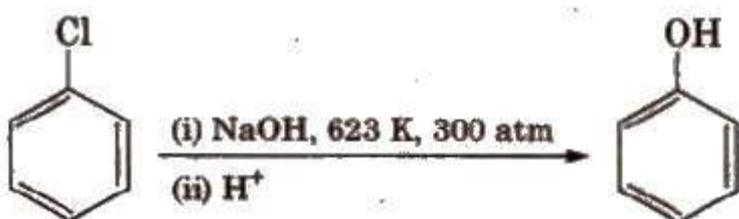
4. Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that of cyclohexylchloride.

Chemical Properties of Aryl Halides 1. Nucleophilic Substitution Reaction

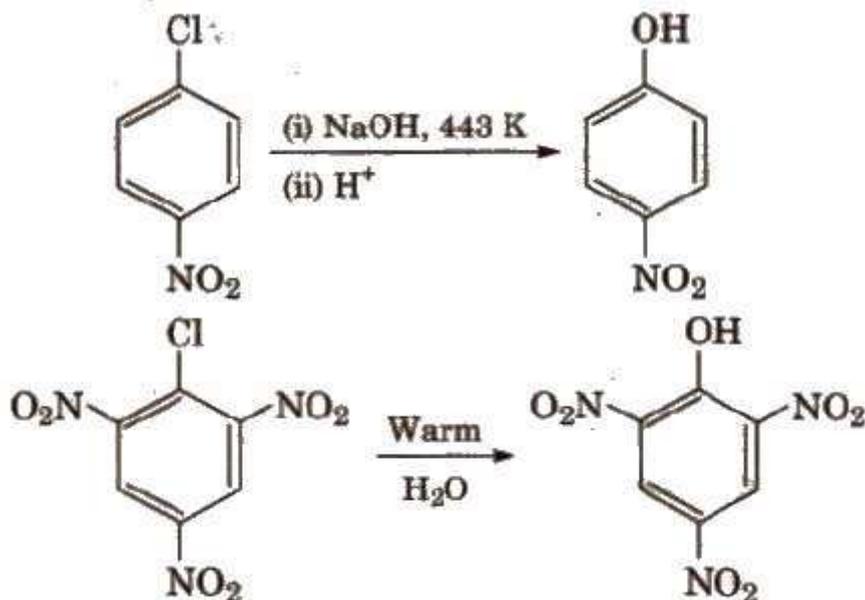
Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

1. Due to resonance, C-X bond has partial double bond character.
2. Stabilisation of the molecule by delocalisation of electrons.
3. (Instability of phenyl carbocation).

However, aryl halides having electron withdrawing groups (like $-\text{NO}_2$, $-\text{SO}_3\text{H}$, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.

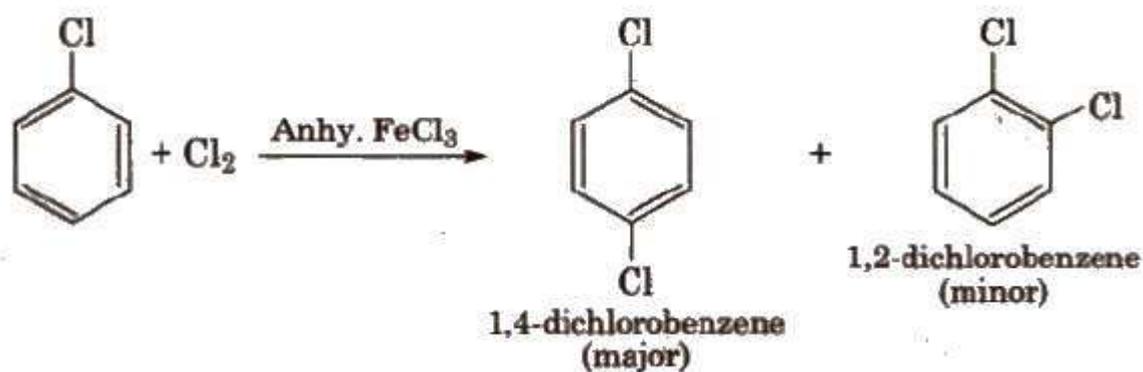


Presence of electron withdrawing group ($-\text{NO}_2$) increases the reactivity.

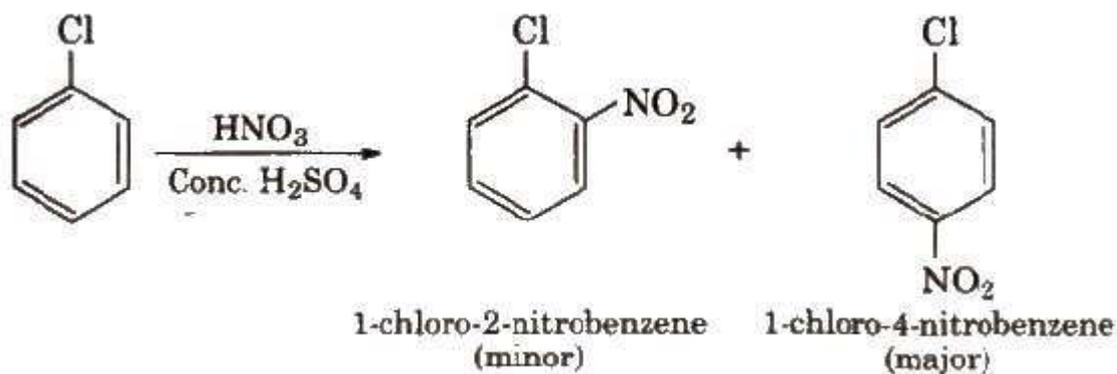


2. Electrophilic Substitution Reactions

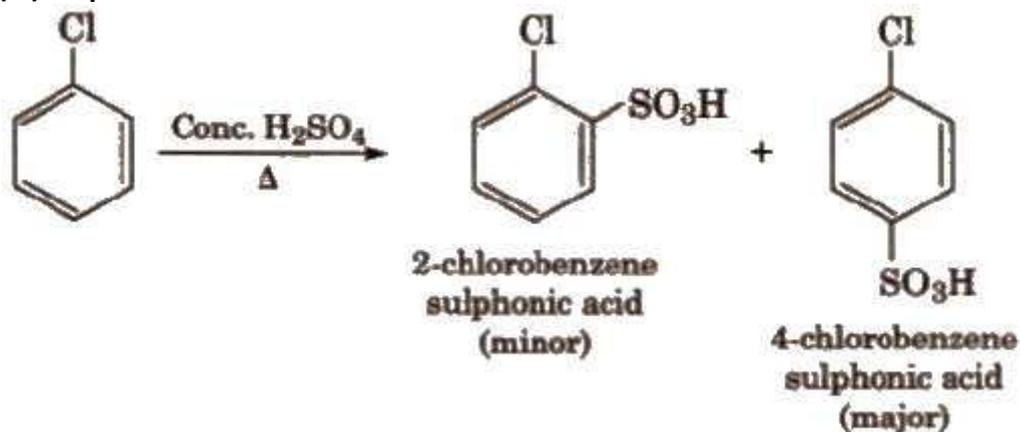
Halogens are deactivating but o, p-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft's reaction give a mixture of o- and p- chloro substituted derivatives. (i) Halogenation



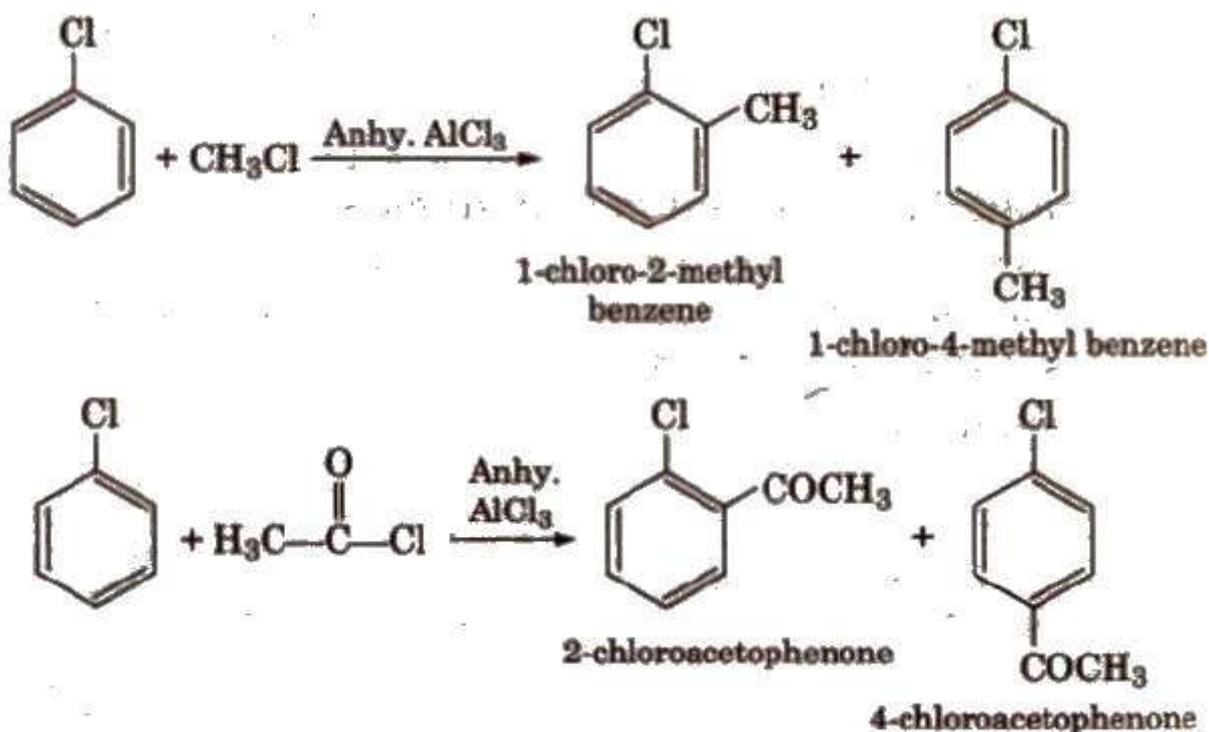
(ii) Nitration



(iii) Sulphonation

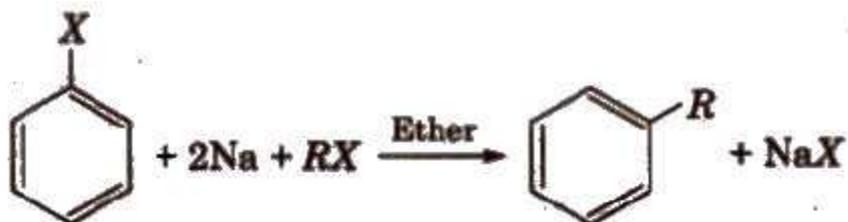


(iv) Friedel-Crafts reaction

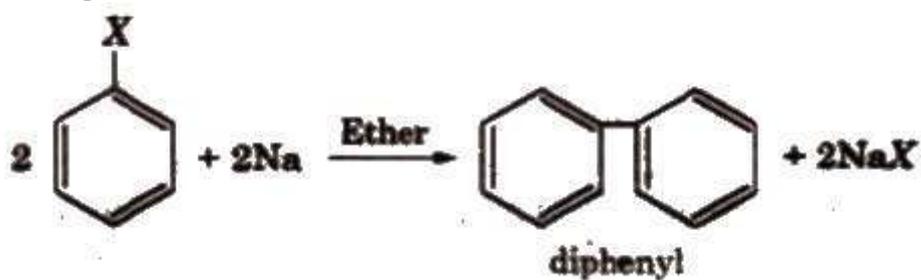


3. Reaction with Metals

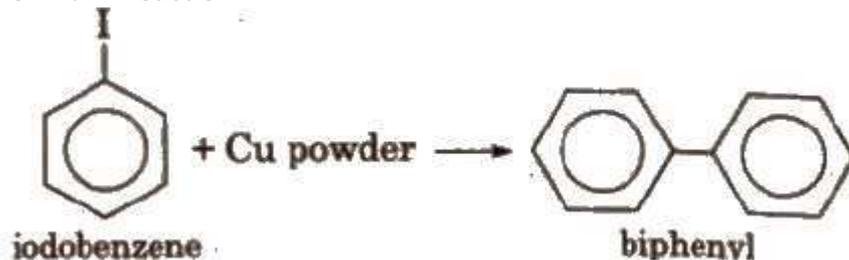
(i) Wurtz Fittig reaction



(ii) Fitting reaction

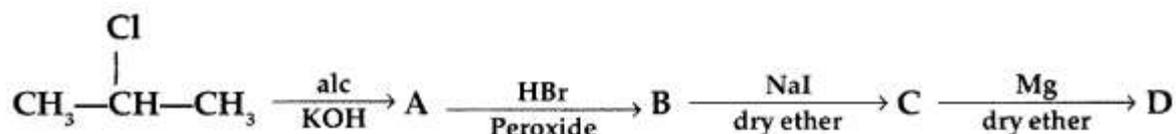


(iii) Ullmann reaction



ASSIGNMENT

2. (a) Write the structural formula of A, B, C and D in the following sequence of reaction: **Delhi 2017**



3. The following compounds are given to you:

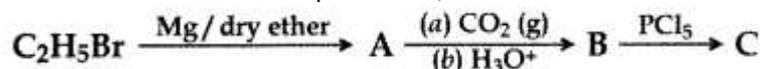
2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards S_N2 reaction.

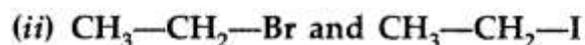
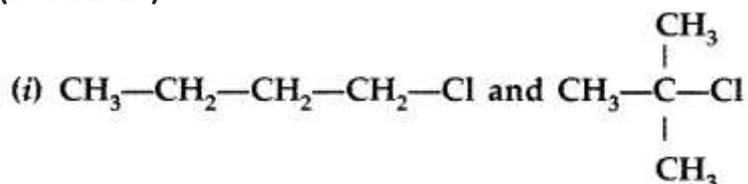
(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards P-elimination reaction. **(All India 2017)**

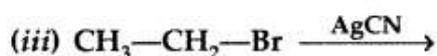
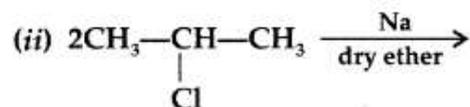
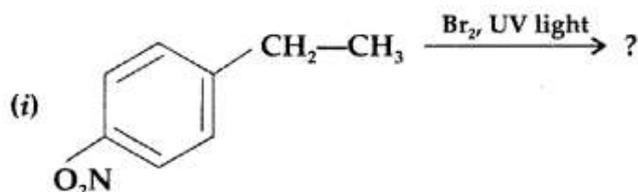
4. Write structures of compounds A, B and C in each of the following reactions: **(Delhi 2017)**



5. In the following pairs of the halogen compounds which compound undergoes faster S_N1 reaction. **(Delhi 2016)**



6. Write the major product(s) in the following: **(All India 2016)**



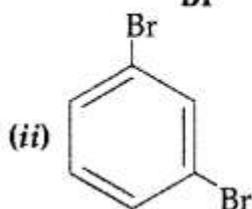
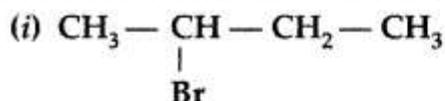
7. How do you convert: **(All India 2016)**

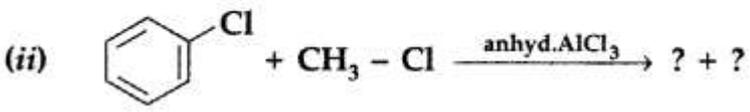
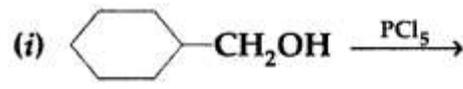
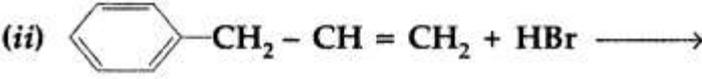
(i) Chlorobenzene to biphenyl

(ii) Propene to 1-iodopropane

(iii) 2-bromobutane to but-2-ene

8. Give the IUPAC names of the following compounds : **(Comptt. All India 2015)**



9. Give reasons: **(Delhi 2016)**
 (i) C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in CH₃—Cl.
 (ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
 (iii) S_N1 reactions are accompanied by racemization in optically active alkyl halides.
10. What happens when
 (i) Chlorobenzene is treated with Cl₂/FeCl₃,
 (ii) Ethyl chloride is treated with AgNO₂,
 (iii) 2-bromopentane is treated with alcoholic KOH?
 Write the chemical equations in support of your answer. **(2015)**
11. How can the following conversions be carried out :
 (i) Aniline to bromobenzene
 (ii) Chlorobenzene to 2-chloroacetophenone
 (iii) Chloroethane to butane **(All India 2015)**
12. Give reasons :
 (a) n-Butyl bromide has higher boiling point than f-butyl bromide.
 (b) Racemic mixture is optically inactive.
 (c) The presence of nitro group (-NO₂) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. **(Delhi 2015)**
13. (a) Which compound in each of the following pairs will react faster in S_N2 reaction with -OH group?
 (i) CH₃Br or CH₃I
 (ii) (CH₃)₃CCl or CH₃Cl
 (b) Write the product of the following reactions: (Comptt. Delhi 2014)
 (i) **CH₃ - Cl + KCN → ?**
- (ii) 
14. (a) Draw the structures of major monohalo products in each of the following reactions :
 (i) 
 (ii) 
- (b) Which halogen compound in each of the following pairs will react faster in S_N2 reaction :
 (i) CH₃Br or CH₃I
 (ii) (CH₃)₃C - Cl or CH₃ - Cl **(All India 2014)**
15. Give reasons for the following :
 (i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.
 (ii) (±) 2-Butanol is optically inactive.
 (iii) C—X bond length in halobenzene is smaller than C—X bond length in CH₃—X. **(All India 2013)**
16. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement :
 (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methyl-butane, 3-Bromo-2-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethyl-propane, 1-Bromo-2-methylbutane (All India 2011)



Mount Abu Public School

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SUBJECT : CHEMISTRY
CLASS XII

Week : 22 February 28 February 2021

CHAPTER 11: ALCOHOL, PHENOLS AND ETHERS

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/qbYXVztddJs>

<https://youtu.be/qbYXVztddJs>

<https://youtu.be/qbYXVztddJs>

Learning outcomes

Students will be able to learn about the alcohols, phenols and ethers and their physical and chemical properties

Sub Topics

- Classification
- Nomenclature
- Structures of Functional groups
- Alcohols and phenols
- Ethers

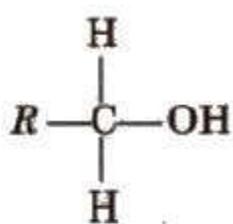
LESSON DEVELOPMENT

Alcohols and Phenols

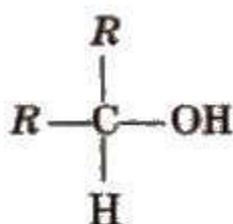
Alcohols and phenols are formed when a hydrogen atom in hydrocarbon, aliphatic and aromatic respectively, is replaced by hydroxyl group (-OR group).

Classification of Alcohols and Phenols

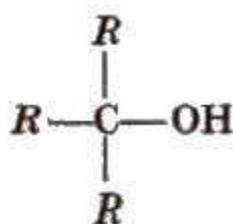
In alcohols, -OR group is attached to sp^3 hybridised carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.



primary (1°)



secondary (2°)



tertiary (3°)

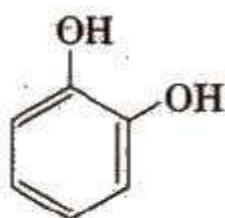
Alcohols may be

- (i) monohydric-containing one -OR group,
- (ii) dihydric-containing two -OR groups and
- (iii) polyhydric-containing three or more -OR groups.

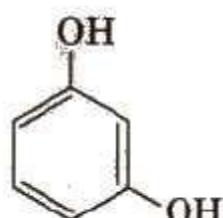
In phenols, -OR group is attached to sp^2 hybridised carbon. These may also be monohydric, dihydric, etc. The dihydric phenol further may be ortho, meta or para derivative.



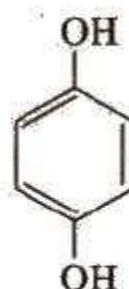
phenol



catechol



resorcinol



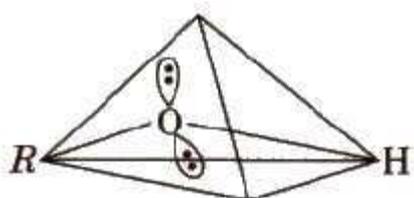
quinol or hydroquinone

In allylic alcohols, – OH group is attached to sp^3 hybridised carbon but next to C=C bond.

e.g., $CH_2 = CH - CH_2OH$, Benzylic alcohol ($C_6H_5CH_2OH$)

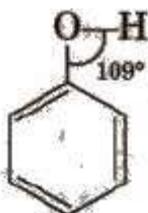
Structure of Alcohols and Phenols

The oxygen atom of alcohols is sp^3 hybridised and they have tetrahedral position of hybrid atomic orbitals .



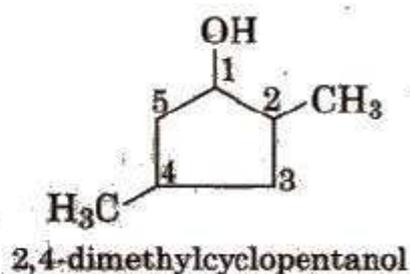
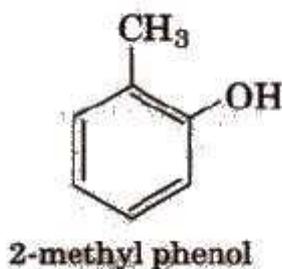
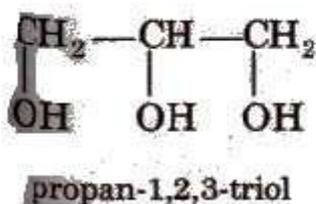
The value of LROH bond angle depends upon the R group. For methyl alcohol, it is ($\angle C - O - H$) 108.9° due to repulsion of lone pairs.

In phenols, the – OH group is attached to sp^2 hybridised carbon and thus, the C – O bond acquires a partial double bond character.



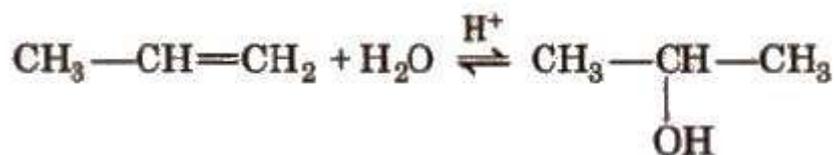
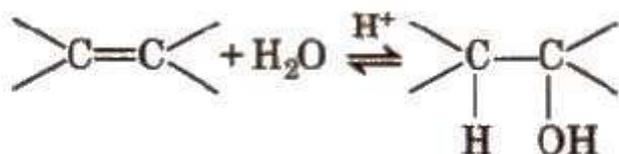
Nomenclature of Alcohols and Phenol

In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g.,



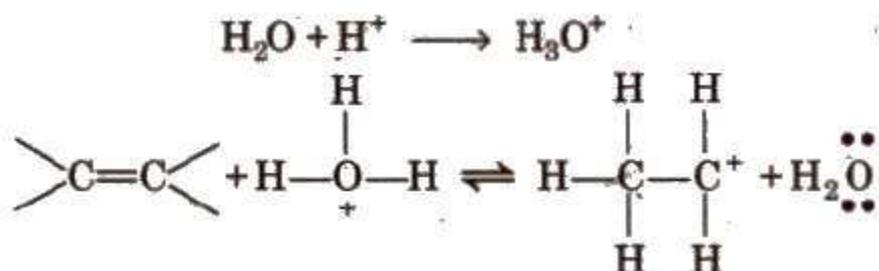
Preparation of Alcohols (i) From alkenes

(a) By acid catalysed hydration in accordance with Markownikoff's rule.

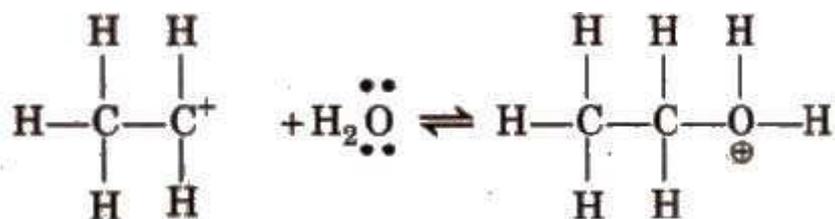


Mechanism

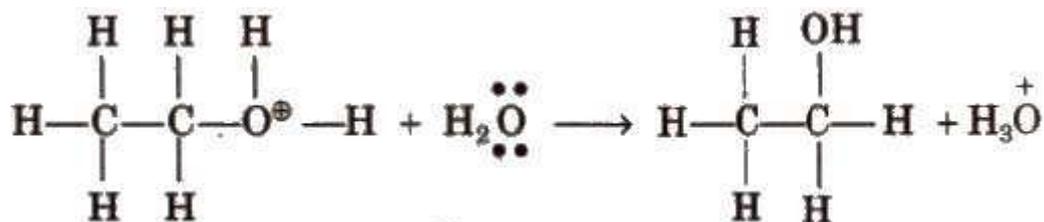
Step I Protonation of alkene by attack of H_3O^+



Step II Nucleophilic attack

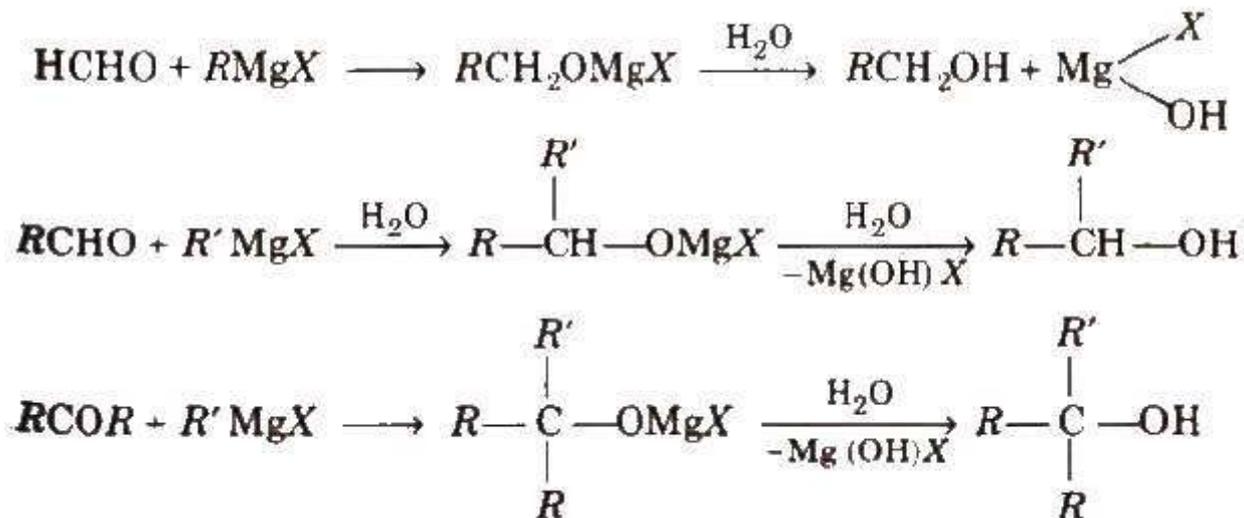


Step III Deprotonation to form an alcohol

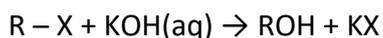


(b) By hydroboration-oxidation

The reaction produces a primary alcohol with methanol, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones

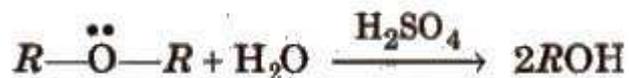


(iv) **Hydrolysis of alkyl halides**

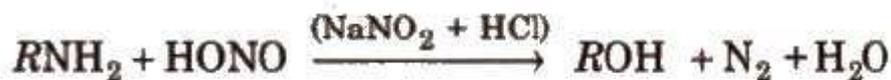


To avoid dehydrohalogenation of RX, mild alkalies like moist

Ease of hydrolysis of alkyl halides $\text{RI} > \text{R-Br} > \text{RCl} > \text{and } \text{t} > \text{s} > \text{p}$ alkyl halides. (v) **Hydrolysis of ethers**

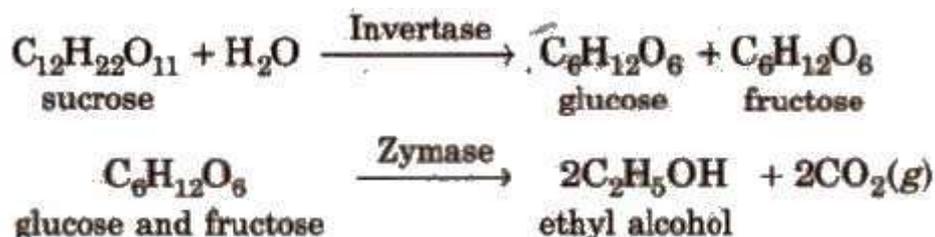


(vi) **From primary amines** By treatment with nitrous acid.

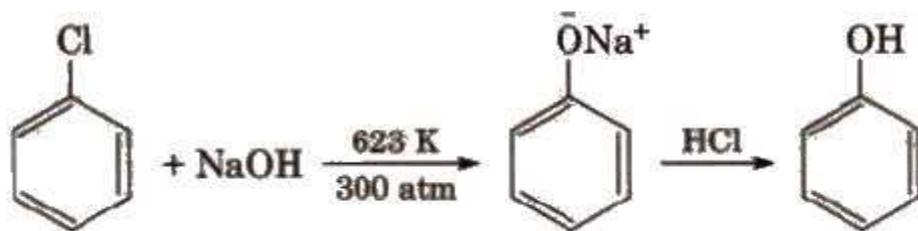


Methylamine does not give methyl alcohol when treated with HNO_2 . It gives CH_3OCH_3 and CH_3ONO .

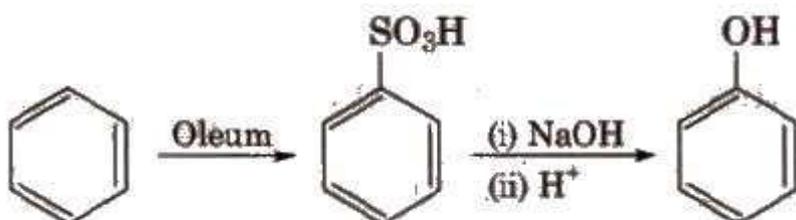
(vii) **By alcoholic fermentation**



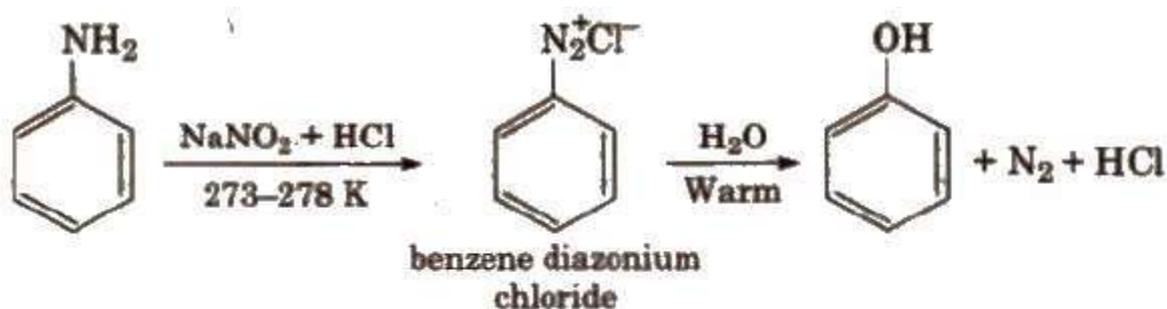
Preparation of Phenols (i) **From haloarenes**



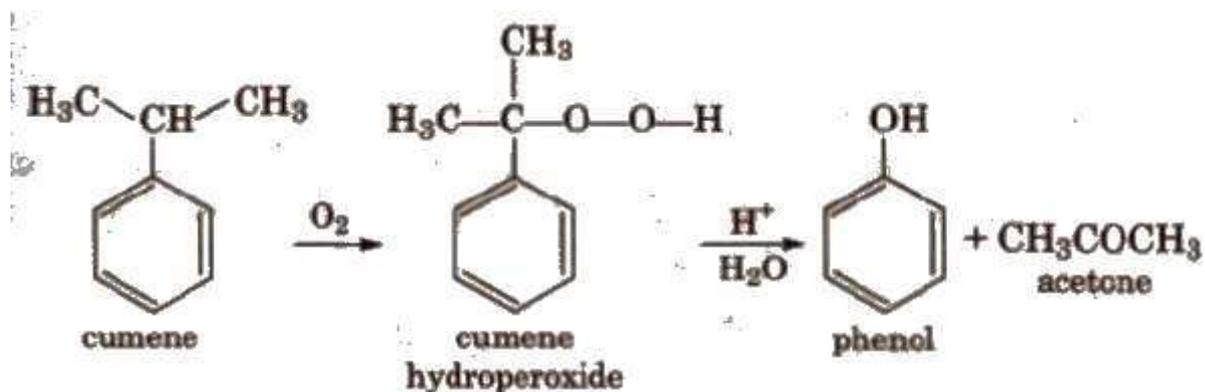
(ii) From benzene sulphonic acid



(iii) From diazonium salts



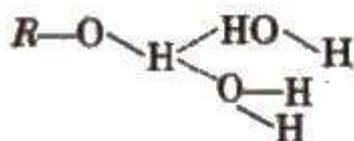
(iv) From cumene



Physical Properties of Alcohols

1. Lower alcohols are colourless liquids, members from C₅ – C₁₁ are oily liquids and higher members are waxy solids.

2. The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass.



3. Boiling points of alkanes are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules.

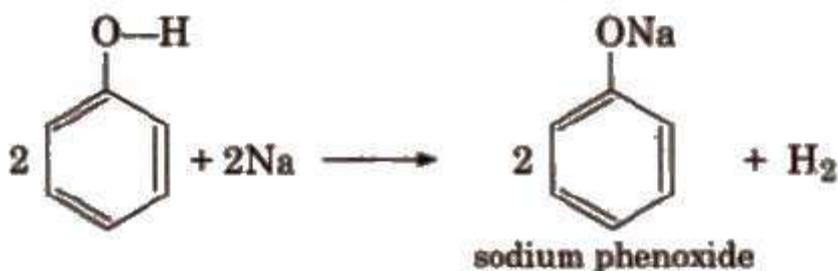
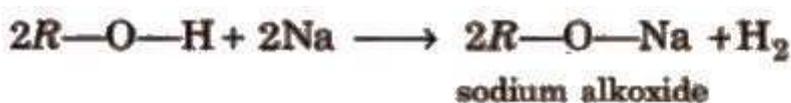
[The boiling point decreases in the order $1^\circ > 2^\circ > 3^\circ$ as the van der Waals' forces of attraction decreases]

Physical Properties of Phenols

1. These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.
2. Phenol is also called carbolic acid.
3. Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

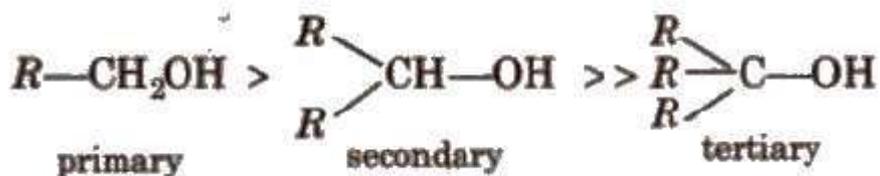
Chemical Reactions of Alcohols and Phenols (i) Reactions involving cleavage of O – H Bond

(a) Acidity of alcohols and phenols



Alcohols are weaker acids than water due to +I group present in alcohols, which decreases the polarity of -O-H bond.

Acid strength of alcohols



Electron releasing group increases electron density on oxygen to decrease the polarity of -OH bond.

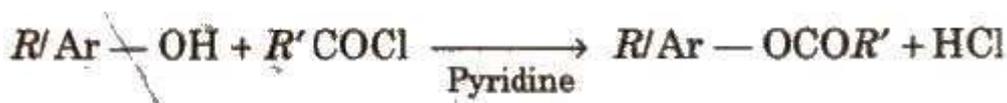
Order of acidity is

$\text{RCOOH} > \text{H}_2\text{CO}_3 > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{R-OH}$.

Phenol is more acidic than alcohols due to stabilisation of phenoxide ion through resonance. Presence of electron withdrawing group increases the acidity of phenol by stabilising phenoxide ion while presence of electron releasing group decreases the acidity of phenol by destabilising phenoxide ion. Thus, increasing acidic strength is o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4, 6-trinitrophenol (picric acid)

Higher K_a and lower $\text{p}K_a$ value corresponds to the stronger acid.

(b) Esterification

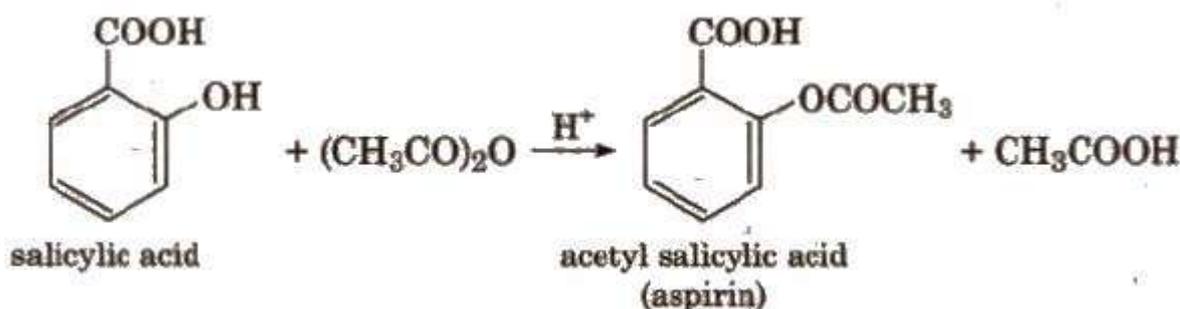


The reaction with $\text{R}'\text{COOH}$ and $(\text{R}'\text{CO})_2\text{O}$ is reversible, so conc. H_2SO_4 is used to remove water.

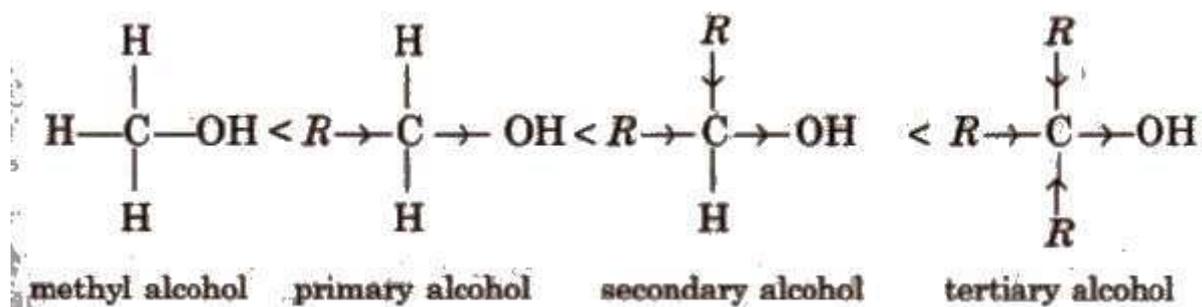
The reaction with $\text{R}'\text{COCl}$ is carried out in the presence of pyridine so as to neutralise HCl which is formed during the reaction.

The introduction of acetyl ($\text{CH}_3\text{CO-}$) group in phenols is known as acetylation.

Acetylation of salicylic acid produces aspirin.



(ii) Reaction involving cleavage of C-O bond in alcohols In these reactions, the reactivity order of different alcohols :

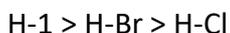


Alkyl group due to +I effect increases the electron density on the carbon and oxygen atom of C-OH bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present, more will be the reactivity of alcohol. Thus, the relative order of reactivity of the alcohols is justified.

(a) **Reaction with halogen acids** Alcohols can be converted into haloalkanes by the action of halogen acids.



For a given alcohol order of reactivity of HX is



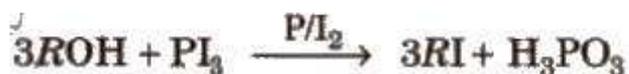
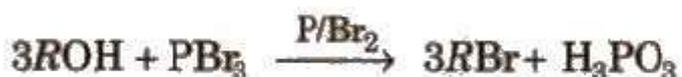
For a given halogen acid order of reactivity of alcohols

Tertiary > Secondary > Primary

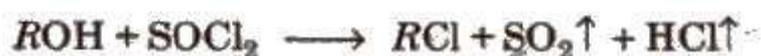
Lucas test

Primary alcohols	Secondary alcohols	Tertiary alcohols
$RCH_2OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$	$R_2CH-OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$	$R_3C-OH \xrightarrow[\text{Anhy. ZnCl}_2]{\text{Conc HCl}}$
No reaction and hence, no white cloudiness or turbidity at room temperature.	R_2CHCl White cloudiness or turbidity appears with in about 5 minutes.	R_3CCl White cloudiness or turbidity appears immediately.

(b) **Reaction with phosphorus halides**

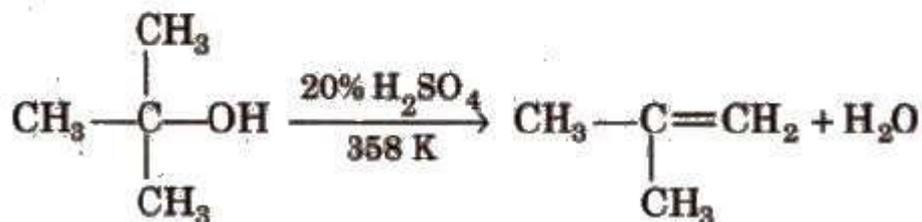
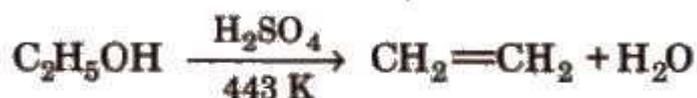


(c) **Reaction with thionyl chloride**



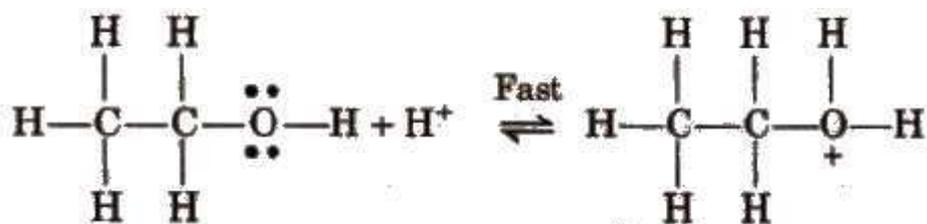
d) **Dehydration of alcohols** It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group.

Since, the rate determining step is the formation of carbocation, the ease of dehydration is

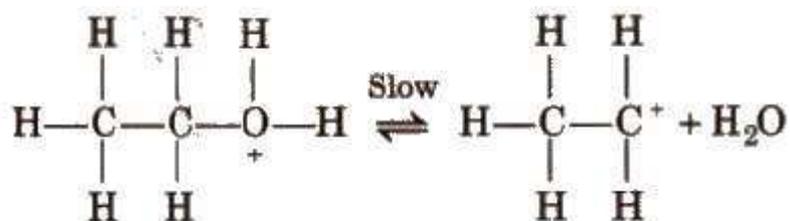


Mechanism

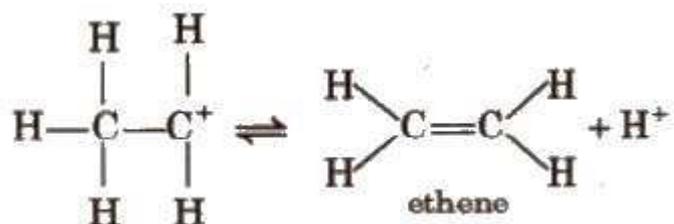
Step I Formation of protonated alcohol



Step II Formation of carbocation



Step III Formation of ethene by elimination of a proton

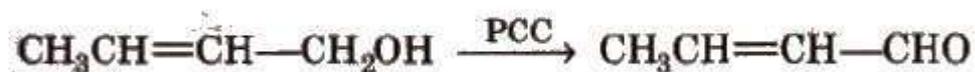


In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product. (Saytzeff's rule).

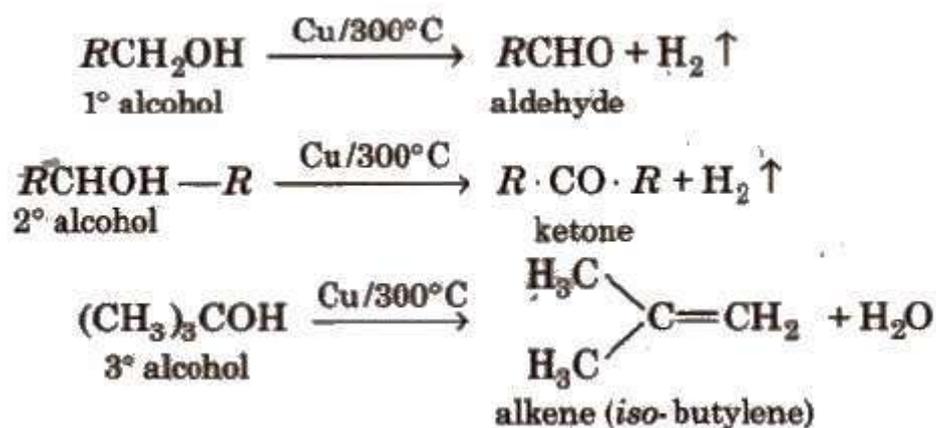
(iii) Oxidation reactions Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline KMnO_4 and acidified $\text{K}_2\text{Cr}_2\text{O}_7$.

Primary alcohols	Secondary alcohols	Tertiary alcohols
$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CHOH}-\text{CH}_3$	$(\text{CH}_3)_3\text{C}-\text{OH}$
$\downarrow[\text{O}]$	$\downarrow[\text{O}]$	$\downarrow[\text{O}]$
CH_3CHO	CH_3COCH_3	$\text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O}$
$\downarrow[\text{O}]$	$\downarrow[\text{O}]$	$\downarrow[\text{O}]$
CH_3COOH	$\text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$	$\text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$

A common reagent that selectively oxidises a primary alcohol to an aldehyde (and no further) is pyridinium chlorochromate (PCC).



(iv) Dehydrogenation

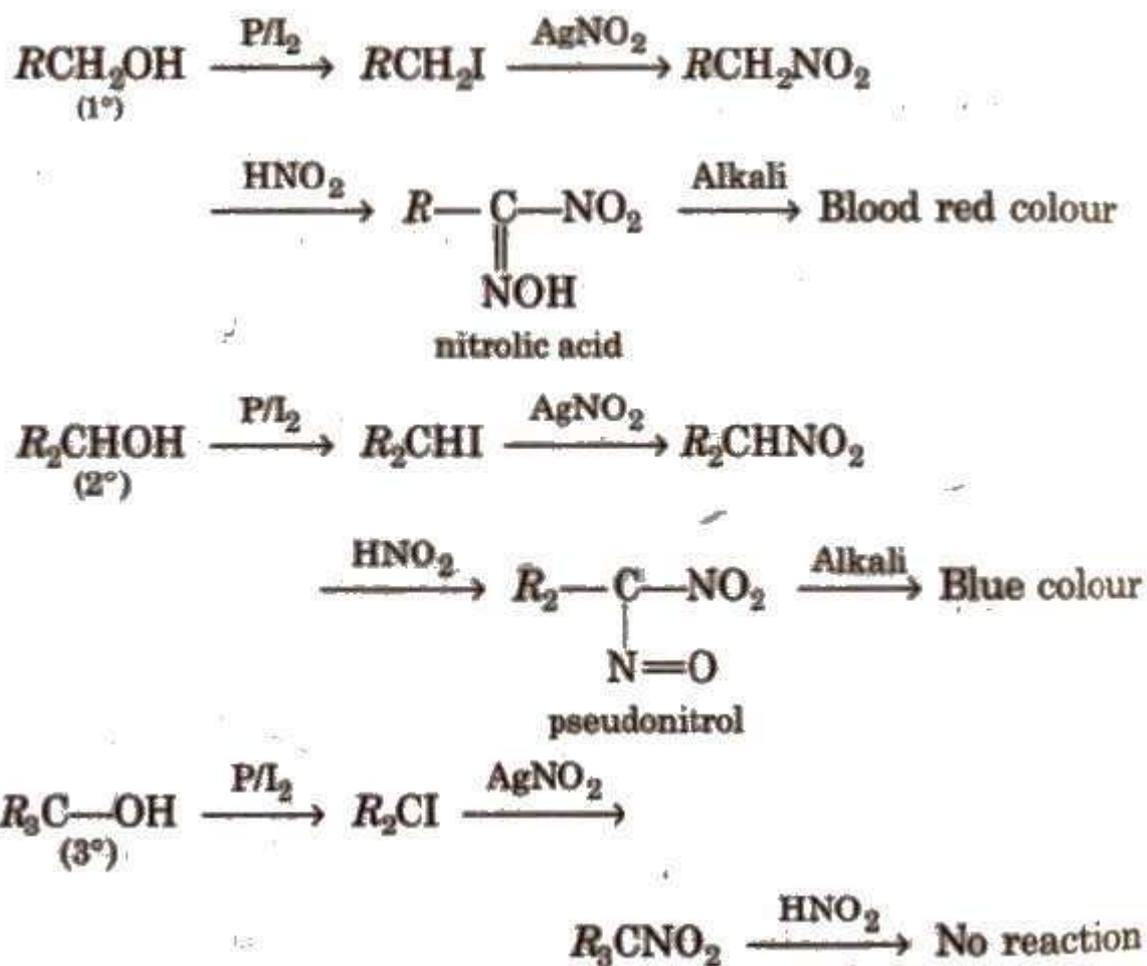


Distinction among 1°, 2° and 3° Alcohols

1°, 2° and 3° alcohols are distinguished by Lucas test, oxidation and reduced copper.

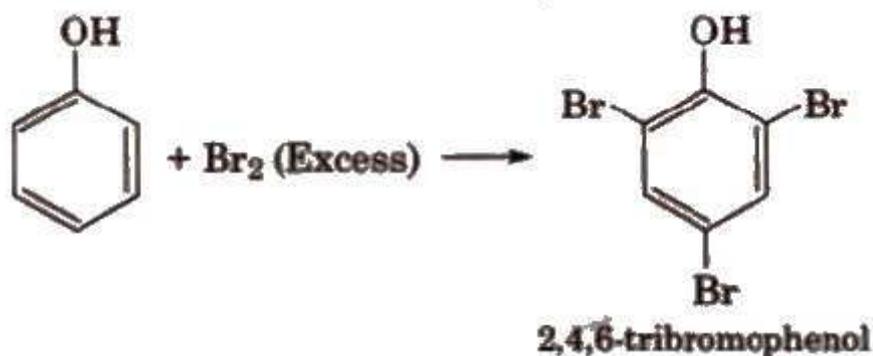
Victor Meyer's test is also used to distinguish them.

In this test, primary (1°) alcohols give red colour, secondary (2°) alcohols give blue colour and tertiary (3°) alcohols give no colouration.

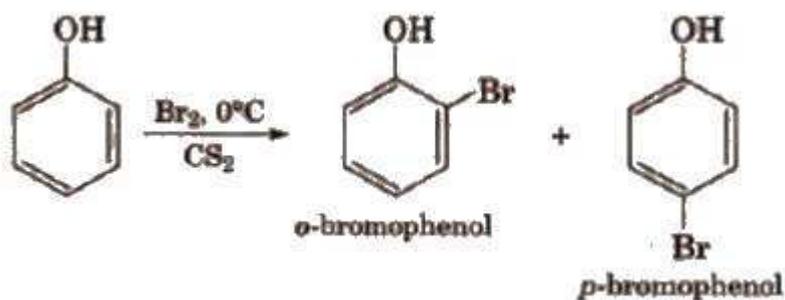


Reactions of Phenols

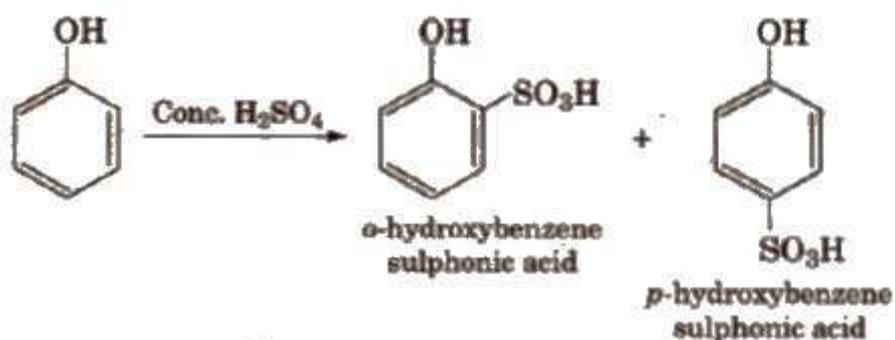
(i) **Electrophilic substitution reactions** The -OH group attached to the benzene ring activates it towards electrophilic substitution at ortho and para positions. (a) **Halogenation**



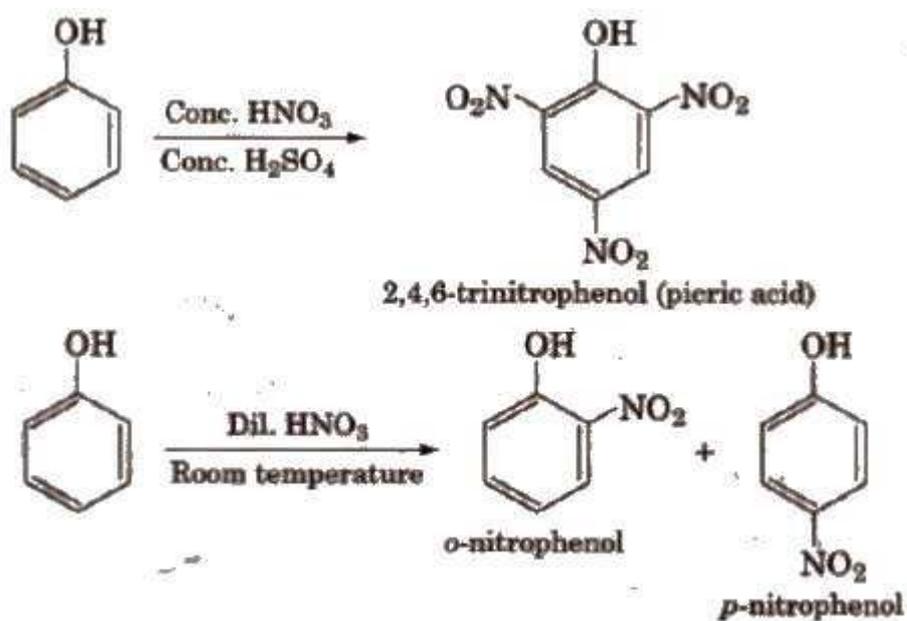
With calculated amount of Br₂ in CS₂ or CHCl₃ it gives ortho and para product.



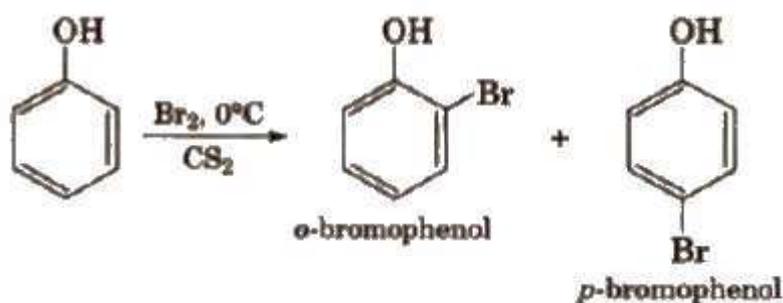
(b) Sulphonation



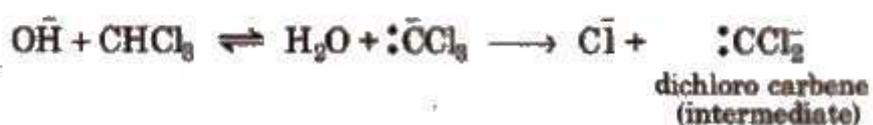
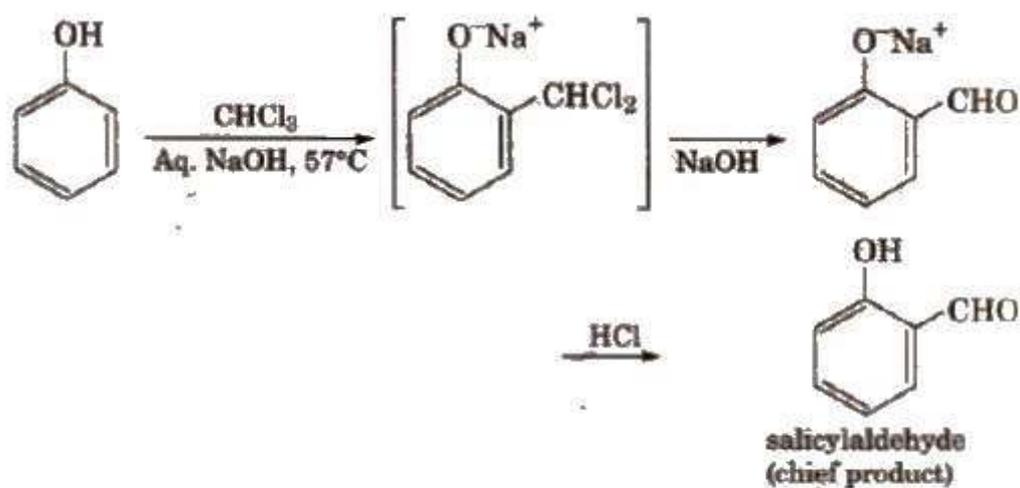
(c) Nitration



The ortho and para isomers can be separated by steam distillation. This is because *o*-nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

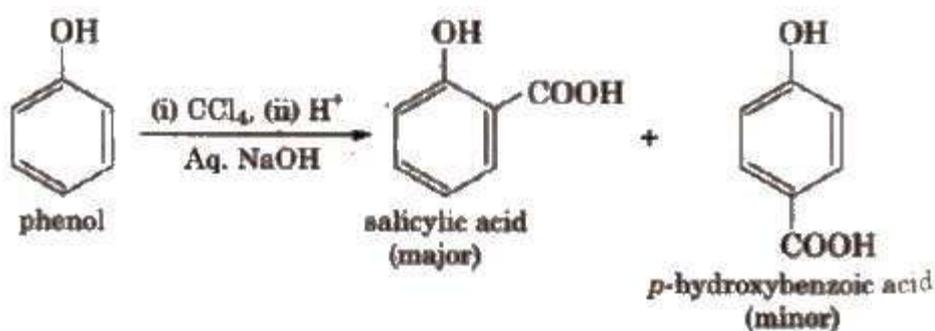


(d) Reimer-Tiemann reaction

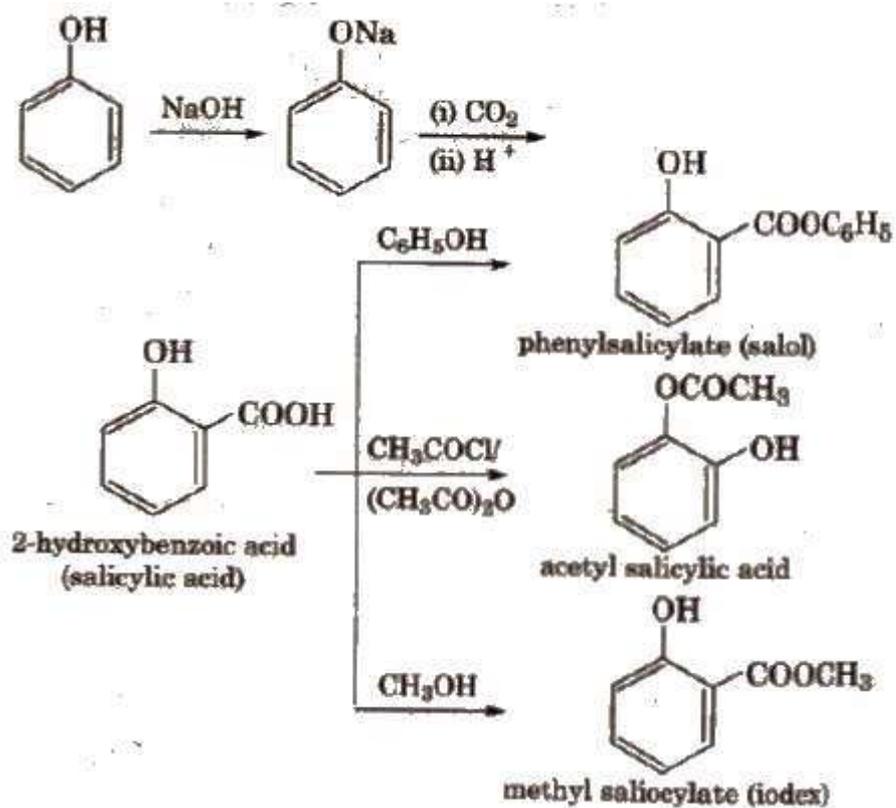


This reaction is an electrophilic substitution reaction and electrophile is dichlorocarbene.

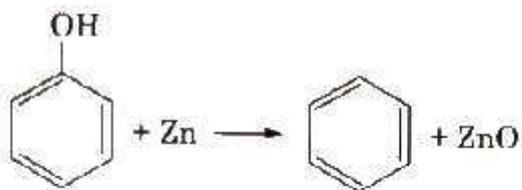
Similarly with carbon tetrachloride and alkali, *c*- and *p*-hydroxybenzoic acid are obtained



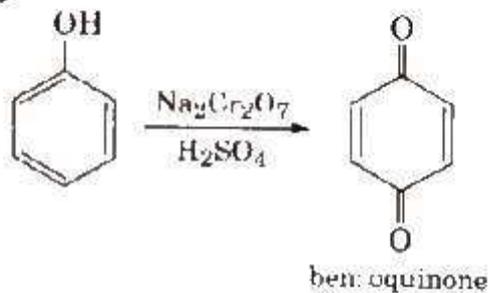
(ii) Kolbe's reaction



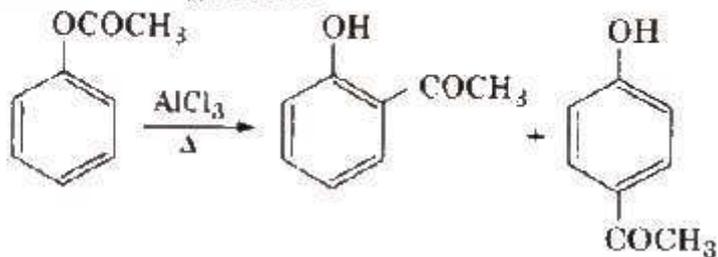
(iii) Reaction with zinc dust



(iv) Oxidation



(v) Fries rearrangement



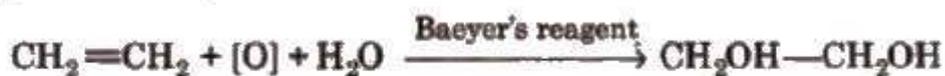
Terms Related to Alcohols

- (a) **Rectified spirit** It contains 95% ethyl alcohol and 45% water. It is an azeotrope (constant boiling mixture) and boils at 74°.
- (b) **Absolute alcohol** Alcohol containing no water, i.e; 100% C₂H₅OH is known as absolute alcohol. It is prepared as follows.
- (i) Quick lime process
- (ii) Azeotropic method
- (c) **Methylated spirit** The rectified spirit rendered poisonous by addition of 4-5% methyl alcohol, traces of pyridine and some copper sulphate and is known as methylated spirit or denatured alcohol.
- (d) **Power alcohol** Alcohol mixed with petrol or fuel and used In internal combustion engines Is known as power alcohol.
- (e) **Wood spirit** Methyl alcohol (CH₃OH) is also called wood spirit. It is obtained by destructive distillation of wood. Pyroligneous add, the product of destructive distillation of wood, contains acetic acid (10%), methyl alcohol (25%) and acetone (05%). Drinking of methanol causes blindness.
- (f) **Grain alcohol** Ethyl alcohol C₂H₅OH is also called grain alcohol. It is used In the preparation of various beverages containing different percentages.

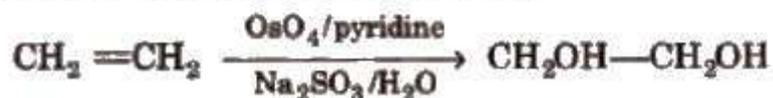
Dihydric Alcohols

These are generally called glycols because of their sweet taste. Ethylene glycol (CH₂OH – CH₂OH) is the first and most important member of dihydric alcohol series. **Methods of Preparation**

(i) From ethylene



(1% alkaline KMnO₄ is called Baeyer's reagent)



(ii) By reduction of glyoxal



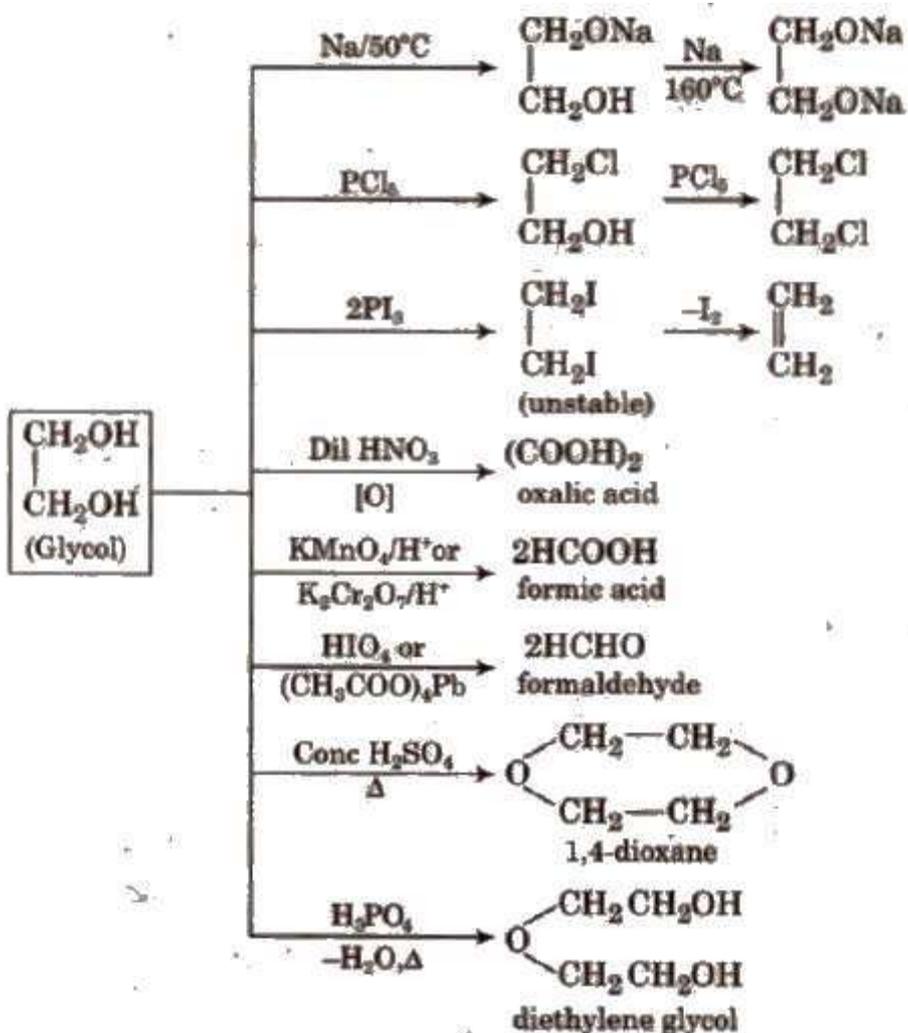
Physical Properties

1. It is a colourless, syrupy liquid with sweet taste.

2. Because of its tendency of formation of H-bonds, it is miscible with H₂O and ethanol but not with ether.

Chemical Properties

It gives all the general reactions of -OH group.



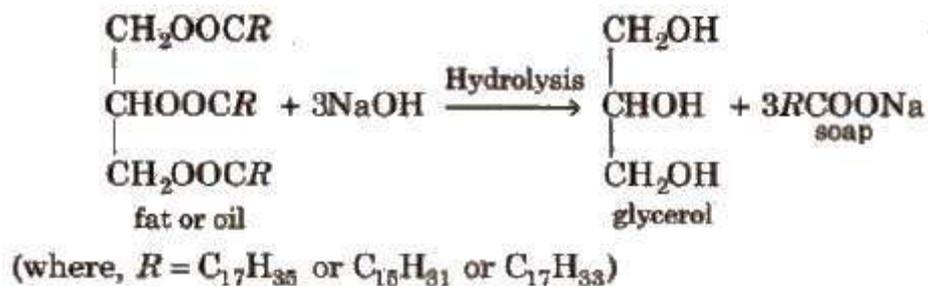
The per-iodic acid cleavage of 1,2-glycols is sometimes called Malaprade reaction.

Trihydric Alcohols

Glycerol or glycerine, CH₂OH – CH(OH) – CH₂OH is the first member of this group. Its IUPAC name is propane-1,2,3-triol.

Method of Preparation

It is obtained as a by product in saponification reaction.



Physical Properties

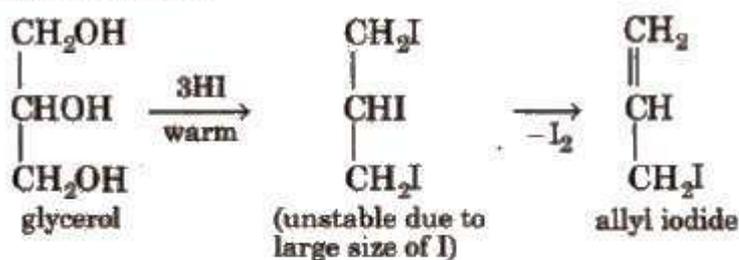
1. It is a colourless, odourless, viscous and hygroscopic liquid.
2. It is sweet in taste and steam volatile.
3. It is soluble in water but insoluble in ether.
4. Due to excessive H-bonding, it is highly viscous and has high boiling point.

Chemical Properties

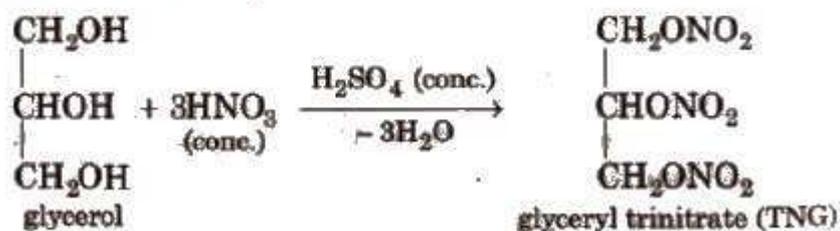
It gives all the general reactions given by -OR group but 2° OR is less reactive as compared to 1°.

Some of its specific reactions are :

(i) Reaction with HI



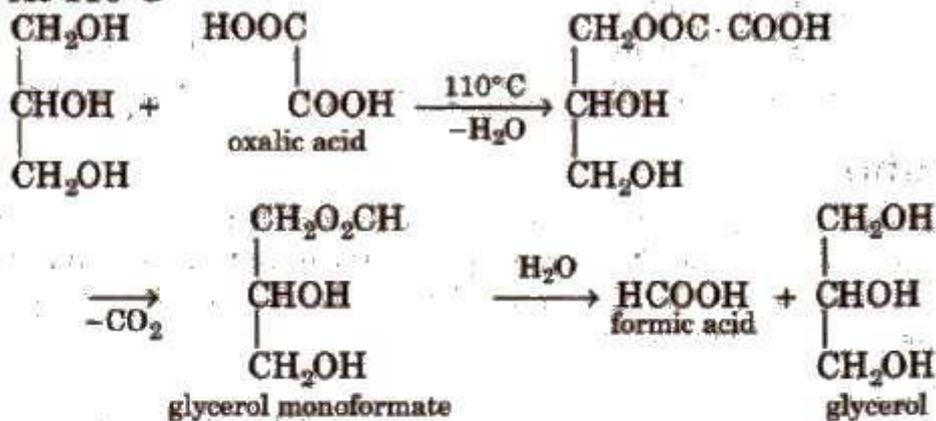
(ii) Reaction with HNO_3



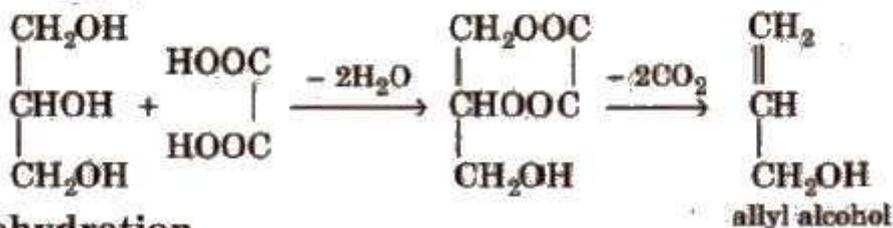
Glyceryl trinitrate or tri nitroglycerine, when adsorbed on Kieselguhr is known as dynamite. Mixture of TNG and cellulose trinitrate is called blasting gelatin.

(iii) Reaction with oxalic acid

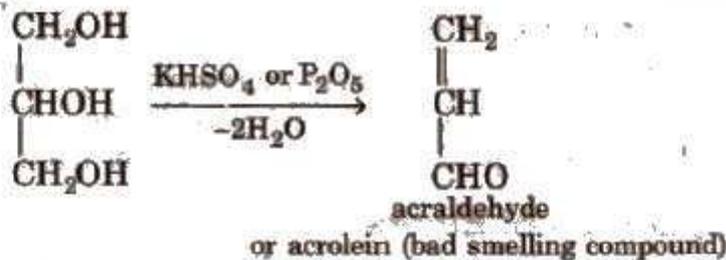
(a) At 110°C



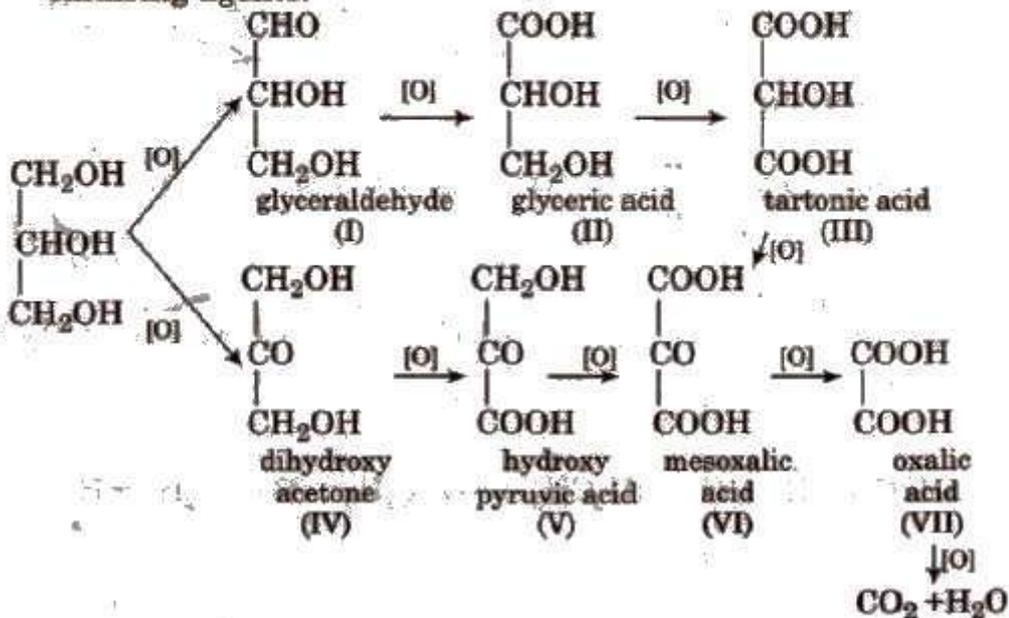
(b) At 260°C



(iv) Dehydration



(v) Oxidation Different products are obtained by different oxidising agents.



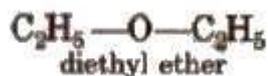
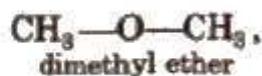
Cone HNO_3 gives II; dil HNO_3 gives II and III; $\text{Bi}(\text{NO}_3)_3$ or NaNO_3 gives VI; Fenton's reagent or NaOBr or Br_2 water in Na_2CO_3 gives a mixture of I and IV.

Solid KMnO_4 oxidises glycerol to VII and CO_2 and H_2O .

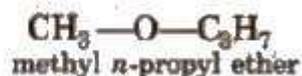
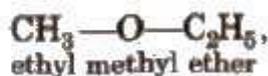
With HIO_4 (periodic acid), glycerol gives HCOOH and HCHO .

Ethers

Ethers are the organic compounds in which two alkyl or aryl groups are attached to a divalent oxygen, known as ethereal oxygen. These are represented by the general formula $\text{R}-\text{O}-\text{R}'$ where R may be alkyl or aryl groups. e.g.,



Mixed ethers



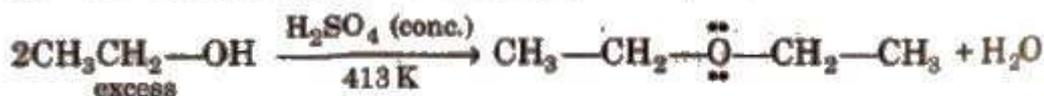
These are the functional isomers of alcohols. These also exhibit chain isomerism and metamerism.

Nomenclature of Ethers

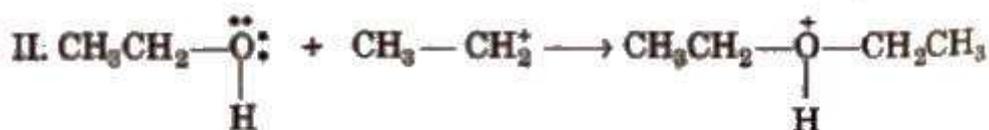
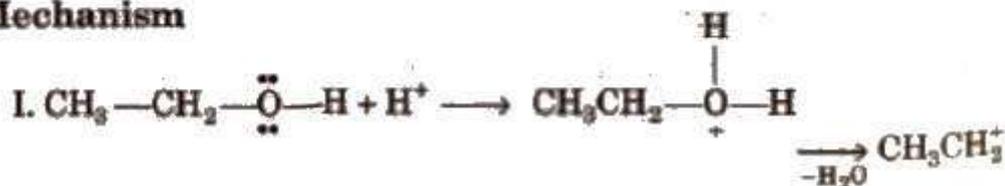
In the IUPAC system, ethers are regarded as 'alkoxy alkanes' in which the ethereal oxygen is taken along with smaller alkyl group while the bigger alkyl group is regarded as a part of the alkane.

Preparation of Ethers

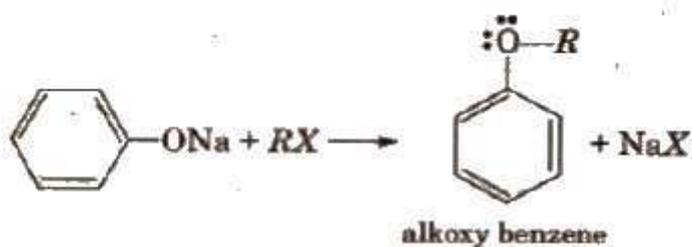
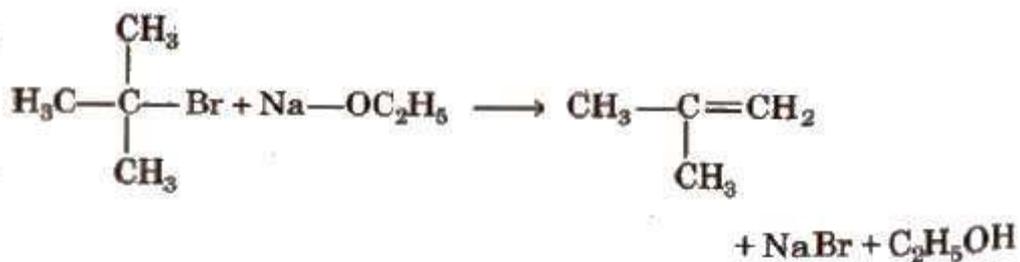
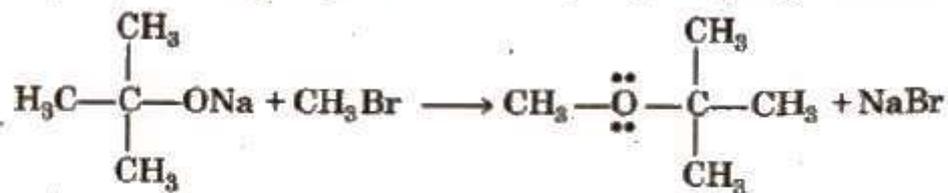
(i) By dehydration of alcohols



Mechanism



(ii) **Williamson's synthesis** Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.

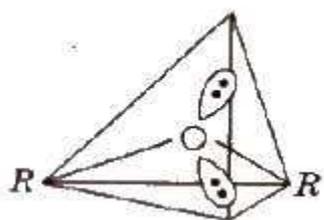


Physical Properties of Ethers

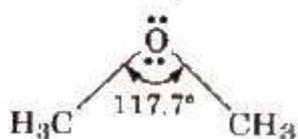
Ethers are polar but insoluble in H_2O and have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

Structure of Ether

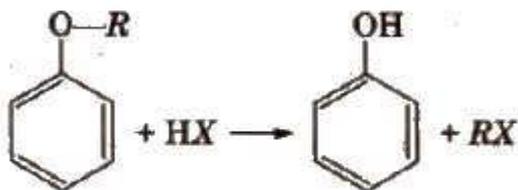
The hybridisation of O atom in ethers is sp^3 (tetrahedral) and its shape is V-shape.



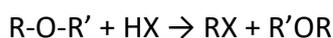
For dimethyl ether



Chemical Reactions of Ether (i) Reaction with HX



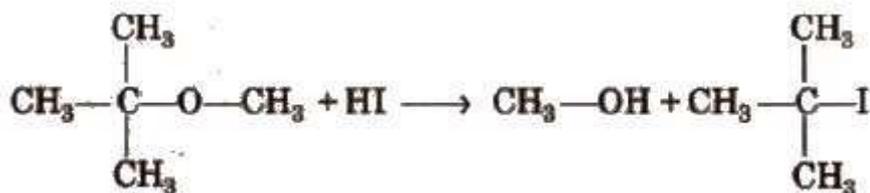
Ethers with two different alkyl groups are also cleaved in the same manner and results in the formation of a primary halide (or smaller and less complex alkyl halide) by S_N^2 mechanism.



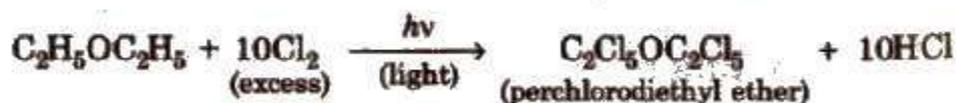
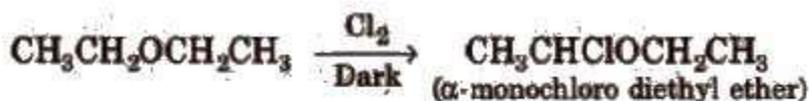
The order of reactivity of hydrogen halides is as follows



In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by S_N^1 mechanism.



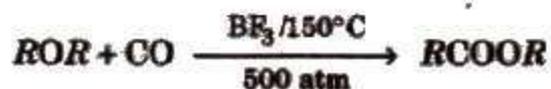
(ii) Halogenation



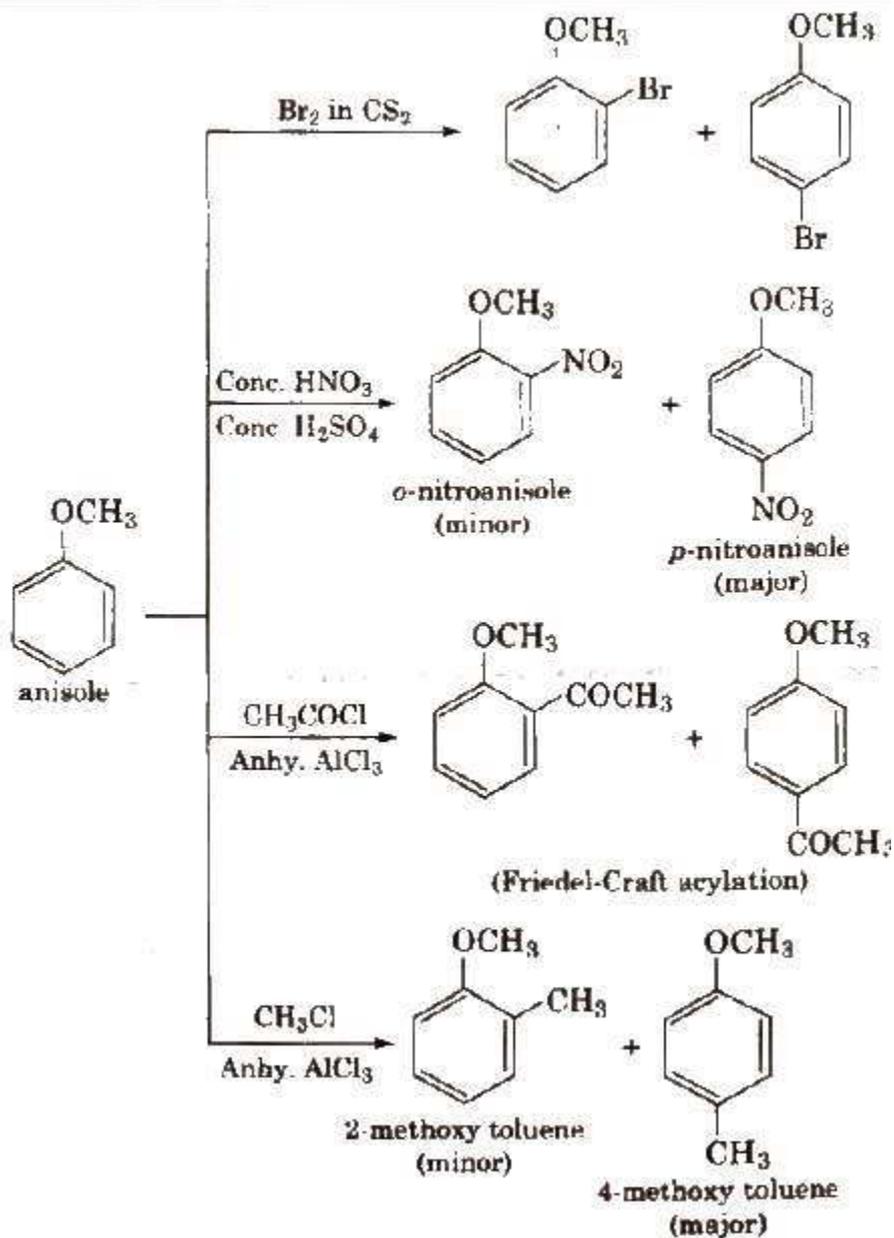
(iii) Reaction with PCl_5



(iv) Reaction with CO



(v) Electrophilic substitution reactions In ethers, -OR is ortho, para directing group and activate. the aromatic ring towards electrophilic substitution reaction.



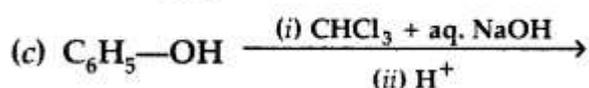
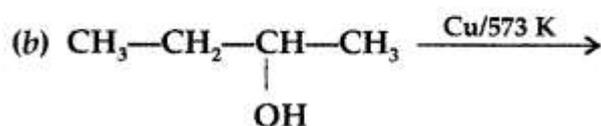
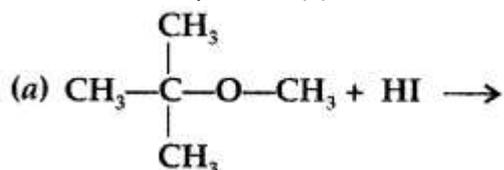
Ethyl phenyl ester $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ is also, known as phenetole.

Uses of Ethers

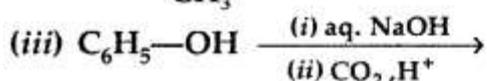
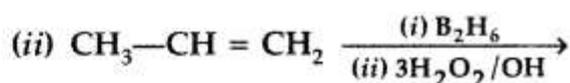
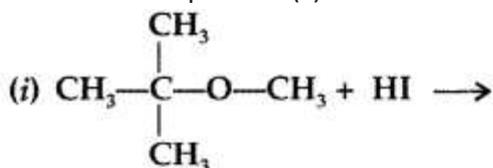
1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
2. Diethyl Ether is used as an anaesthesia in surgery .

ASSIGNMENT

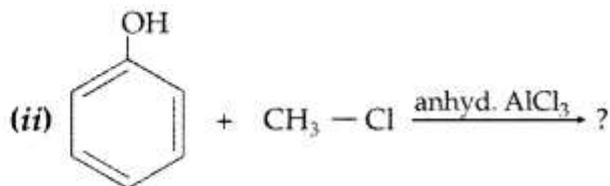
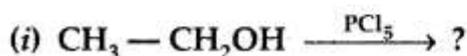
- How are the following conversions carried out?
 - Propene \rightarrow Propan-2-ol
 - Benzyl chloride \rightarrow Benzyl alcohol
 - Ethyl magnesium chloride \rightarrow Propan-1-ol (Comptt. Delhi 2016)
- Write the final product(s) in each of the following reactions: (All India 2016)



- Write the main product(s) in each of the following reactions: (Delhi 2016)

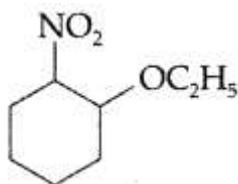


- Write the major product in the following equations : (Comptt. All India 2015)



- How are the following conversions carried out?
 - Propene to propan-2-ol
 - Benzyl chloride to Benzyl alcohol
 - Anisole to p-Bromoanisole (Comptt. Delhi 2015)
- Give reasons for the following :
 - Phenol is more acidic than methanol.
 - The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle ($109^\circ 28'$).
 - $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$ on reaction with HI gives $(\text{CH}_3)_3\text{C}-\text{I}$ and CH_3-OH as the main products and not $(\text{CH}_3)_3\text{C}-\text{OH}$ and CH_3-I . (All India 2015)
- (a) Give chemical tests to distinguish between the following pairs of compounds :
 - Pentan-2-ol and Pentan-3-ol
 - Methanol and Phenol
 (b) o-nitro phenol is more acidic than o-methoxy phenol. Explain why. (Comptt. All India 2013)
- (a) How would you obtain the following :
 - 2-methylpentan-2-ol from 2-methyl-1-pentene
 - Acetophenone from phenol

(b) Write IUPAC name of the following : (Comptt. All India 2012)



9. (a) Give a separate chemical test to distinguish between the following pairs of compounds:
(i) Ethanol and Phenol (ii) 2-Pentanol and 3-Pentanol
(b) Explain Kolbe's reaction with the help of suitable example. (Comptt. Delhi 2012)
10. (a) Illustrate the following name reactions :
(i) Reimer-Tiemann Reaction (ii) Williamson Synthesis.
(b) Give a chemical test to distinguish between 2-propanol and 2-methyl-2-propanol. (Comptt. Delhi 2012)
11. How would you obtain the following ;
(i) Benzoquinone from phenol
(ii) 2-Methylpropan-2-ol from ethylmagnesium chloride
(iii) Propan-2-ol from propene (All India 2010)
12. Explain the following observations :
(i) The boiling point of ethanol is higher than that of methoxymethane.
(ii) Phenol is more acidic than ethanol.
(iii) o- and p-nitrophenols are more acidic than phenol. (All India 2009)
13. Write the structures of the products when Butan-2-ol reacts with the following:
(a) CrO₃
(b) SOCl₂ (All India 2016)
14. (a) Arrange the following compounds in the increasing order of their acid strength: p-cresol, p-nitrophenol, phenol
(b) Write the mechanism (using curved arrow notation) of the following reaction: (All India 2016)
- $$\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{CH}_3 - \text{CH}_2^+ + \text{H}_2\text{O}$$
15. How will you convert:
(i) Propene to propan-2-ol?
(ii) Phenol to 2, 4, 6-trinitrophenol? (Delhi 2013)



Mount Abu Public School

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SUBJECT : CHEMISTRY

CLASS XII

Week : 22 February 28 February 2021

CHAPTER 12: ALDEHYDE, KETONE AND CARBOXYLIC ACID

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/UmbmTSj73K4>

<https://youtu.be/UmbmTSj73K4>

<https://youtu.be/UmbmTSj73K4>

Learning outcomes

Students will be able to learn about the aldehyde, ketone and carboxylic acid and their properties

Sub Topics

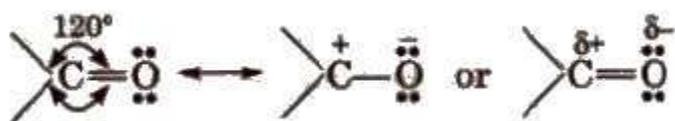
- Nomenclature and Structure of Carbonyl Group
- Preparation of Aldehydes and Ketones
- Physical Properties
- Chemical Reactions
- Uses of Aldehydes and Ketones
- Nomenclature and Structure of Carboxyl Group
- Methods of Preparation of Carboxylic Acids
- Physical Properties
- Chemical Reactions
- Uses of Carboxylic Acids

LESSON DEVELOPMENT

In aldehydes, the carbonyl group ($\text{C}=\text{O}$) is bonded to carbon and hydrogen, while in the ketones, it is bonded to two carbon atoms

Nature of Carbonyl Group

The carbon and oxygen of the carbonyl group are Sp^2 hybridised and the carbonyl double bond contains one σ -bond and one π -bond.



The electronegativity of oxygen is much higher than that of the carbon, so there electron cloud is shifted towards the oxygen. Therefore, C-O bond is polar in nature.

Nomenclature

- (i) **Nomenclature of aldehydes** In IUPAC system, the suffix “e” of alkane is replaced by the suffix “al”. e.g.,

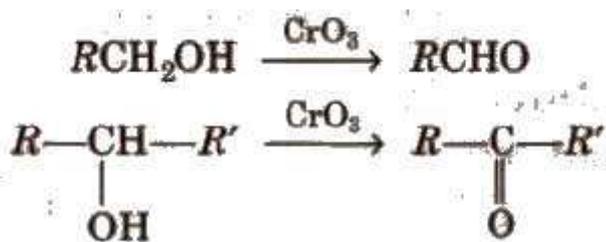
Compound	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal

- (ii) **Nomenclature of ketones** In IUPAC system, the suffix “e” of alkane is replaced by “one”. e.g.,

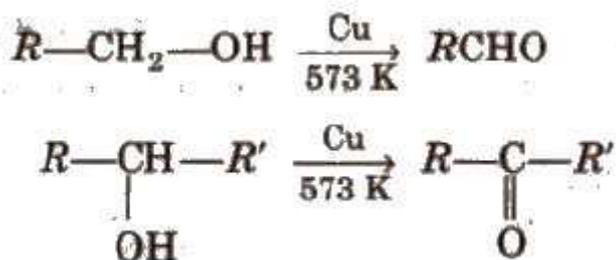
Compound	Common name	IUPAC name
$\text{H}_3\text{C} \cdot \text{COCH}_3$	Dimethyl ketone (acetone)	Propanone
$\text{H}_3\text{C} \cdot \text{COC}_2\text{H}_5$	Ethyl methyl ketone	Butanone

Preparation of Aldehydes and Ketones

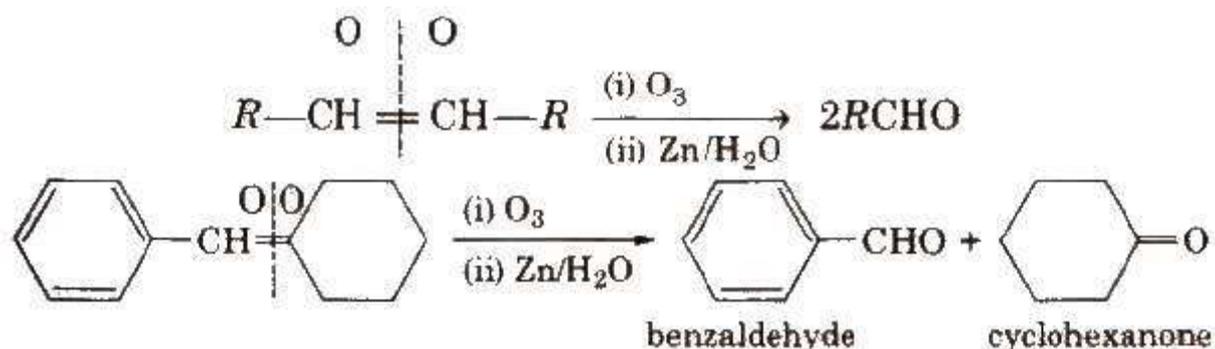
- (i) **By oxidation of alcohols** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.



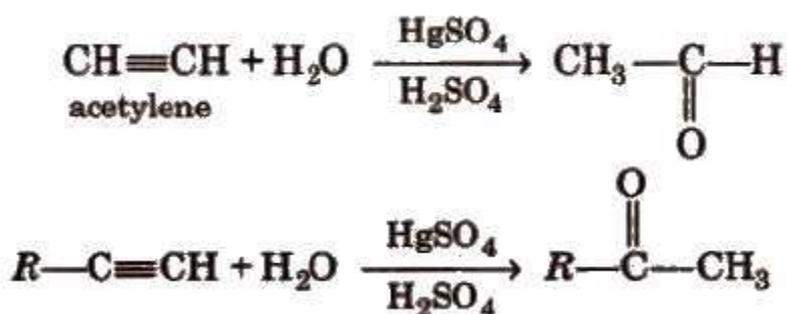
(ii) **By dehydrogenation of alcohols** In this method, alcohol vapours are passed over heavy metal catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones.



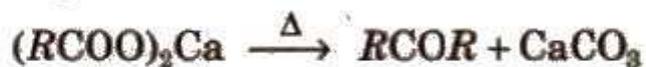
(iii) **By ozonolysis of alkenes**



(iv) **By hydration of alkynes** Acetylene on hydration gives acetaldehyde and other alkynes on hydration give ketones.



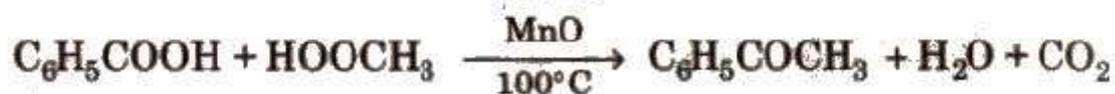
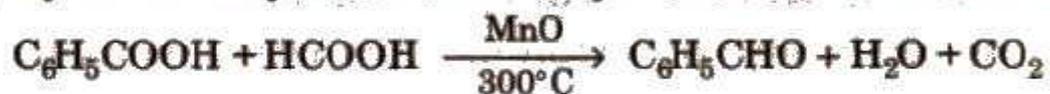
(v) By heating Ca salt of acid



To obtain aldehyde, calcium formate and any other Ca salt of acid are heated.

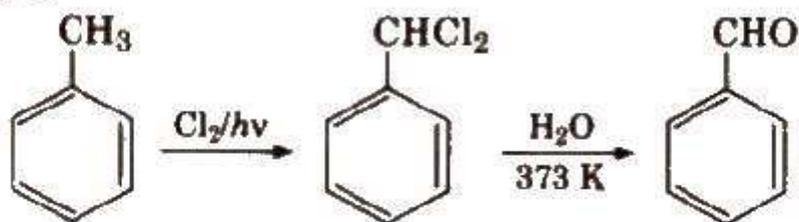


(vi) By decarboxylation and dehydration of aromatic acids

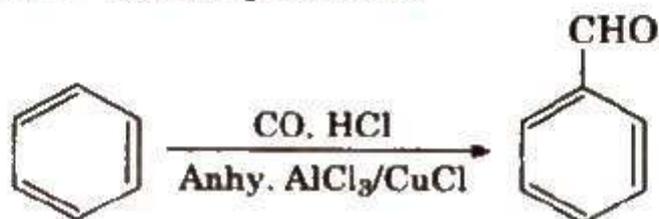


Preparation of Aldehydes

(iv) **Side chain halogenation followed by hydrolysis of toluene**

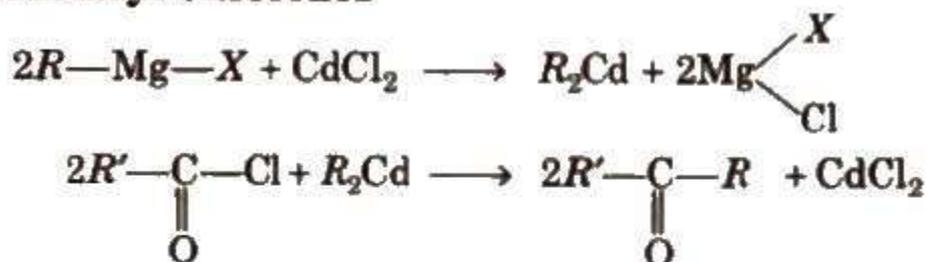


(v) **Gattermann-Koch synthesis**

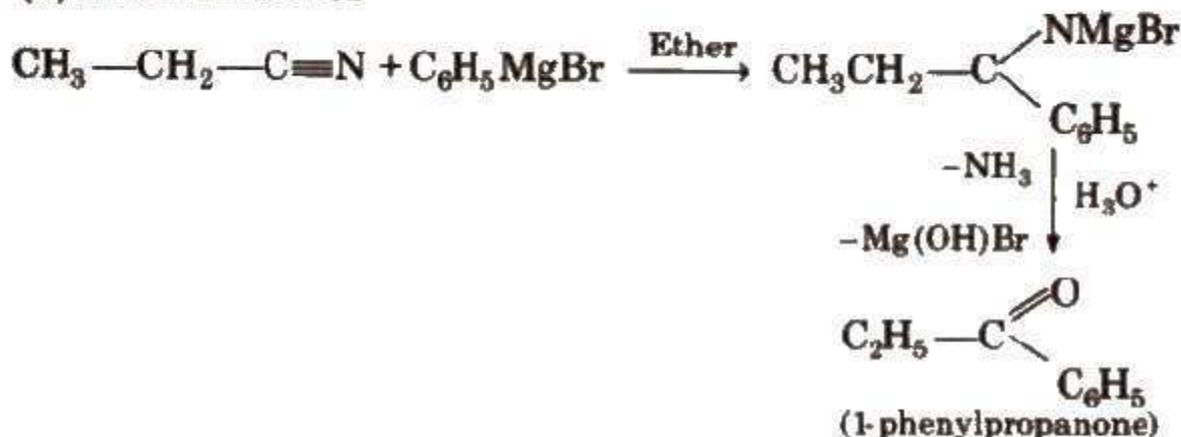


Preparation of Ketones

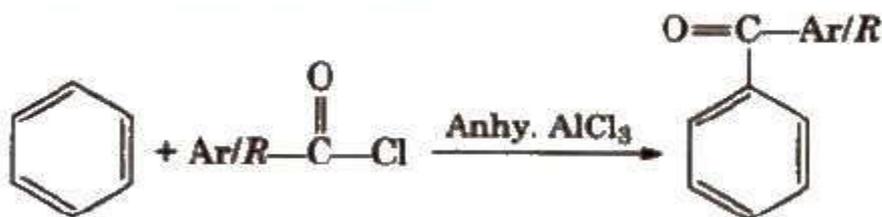
(i) **From acyl chlorides**



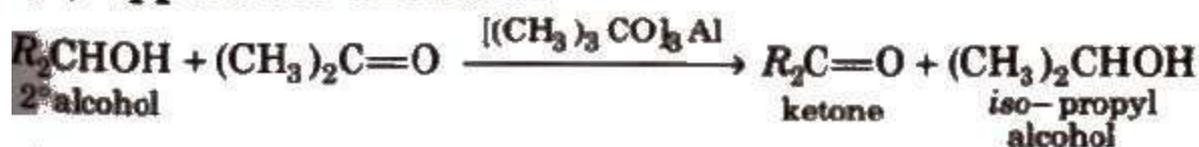
(ii) **From nitriles**



(iii) **Friedel-Crafts acylation**



(iv) **Oppenauer oxidation**



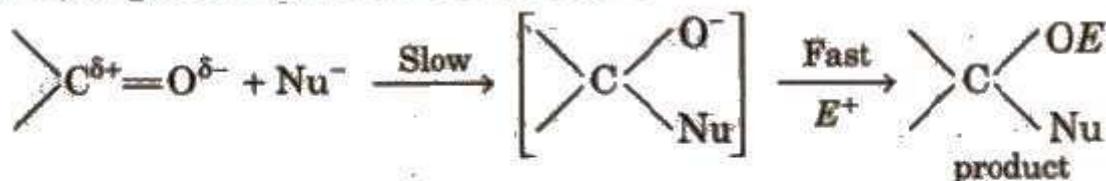
Physical Properties of Aldehydes and Ketones

1. Methanal (HCHO) is a gas at room temperature, and its 40% aqueous solution is known as formalin. It is a reducing agent in silvering of mirrors and decolourising vat dyes.
2. Ethanal (CH₃CHO) is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.
3. The boiling point of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.

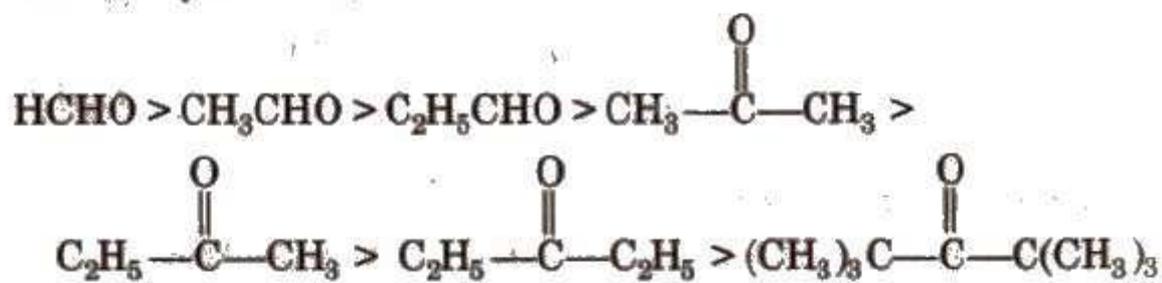
- Aldehydes and ketones have lower boiling point than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
- The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.
- Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.

Chemical Reactions of Aldehydes and Ketones

(i) Nucleophilic addition reactions



Reactivity order is

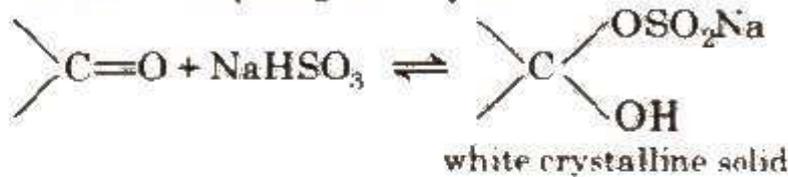


It is due to +I effect of alkyl groups which decreases the positive charge on carbonyl carbon and steric hinderance (The bulky alkyl group hinder the approach of nucleophile).

Addition of hydrogen cyanide

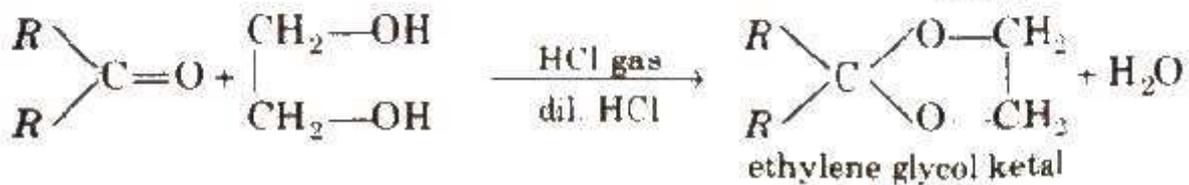
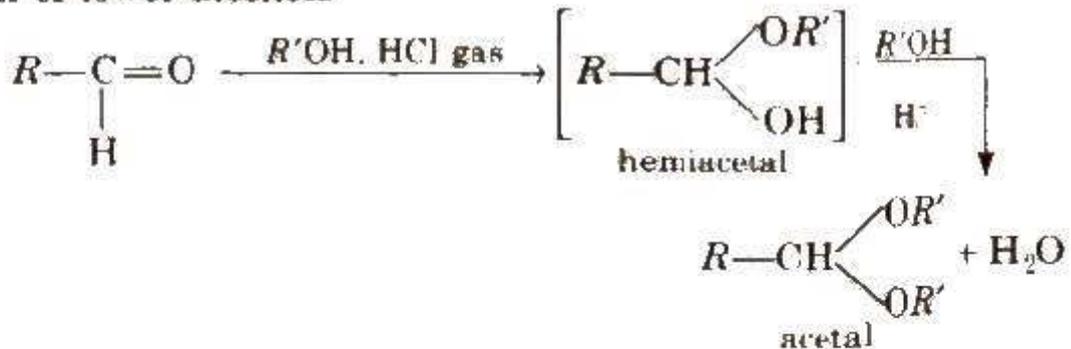


Addition of sodium hydrogen sulphite

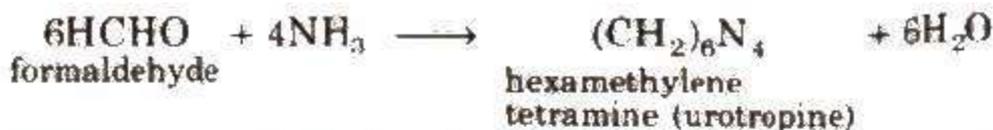


This reaction is used for the separation and purification of aldehydes and ketones. This is because the addition compound formed, is water soluble and can be converted back to the original carbonyl compound by treating with dilute mineral acid or alkali.

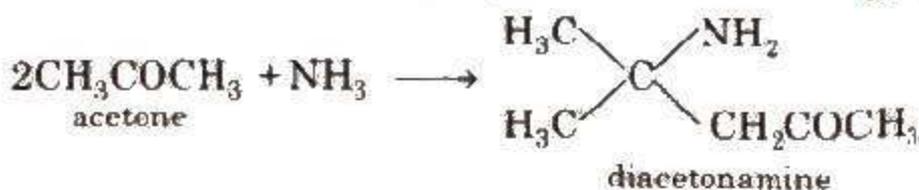
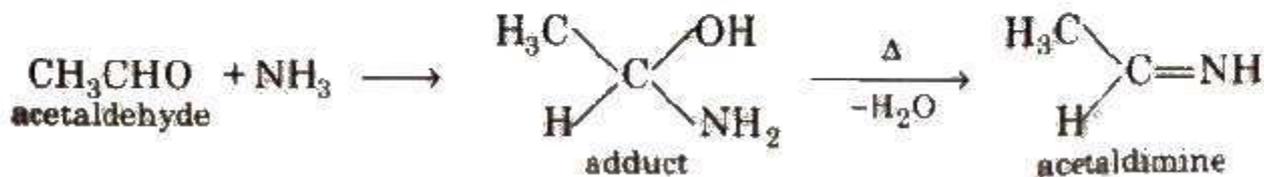
Addition of lower alcohols



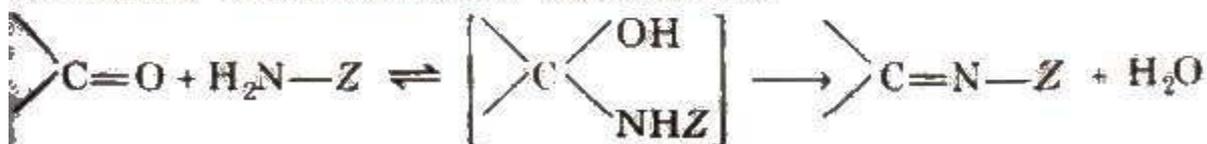
(ii) Addition of ammonia and its derivatives Reaction with ammonia



Urotropine on controlled nitration gives the well known explosive RDX (Research and Development explosive).

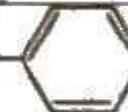
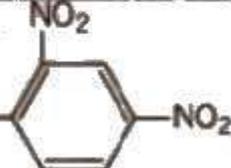
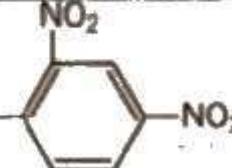
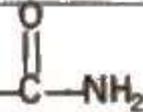
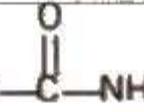


Reaction with ammonia derivatives



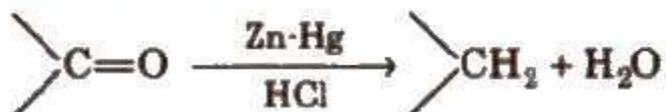
where, Z = alkyl, aryl, -OH, -NH₂, -C₆H₅NH, -NHCONH₂ etc.

Some N-substituted Derivatives of Aldehydes and Ketones

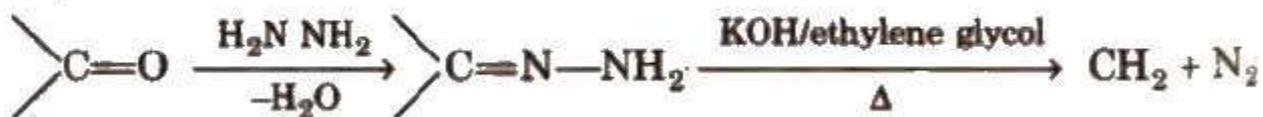
Z	Reagent name	Carbonyl derivative	Product name
—R	Amine	>C=N-R	Substituted imine (Schiff's base)
—OH	Hydroxyl amine	>C=N-OH	oxime
—NH ₂	Hydrazine	>C=N-NH_2	Hydrazone
—NH— 	Phenyl-hydrazine	>C=N-NH- 	Phenylhydrazone
—NH— 	2,4-dinitrophenyl hydrazine	>C=N-NH- 	2,4-dinitrophenyl hydrazone
—NH— 	Semi-carbazide	>C=N-NH- 	Semi-carbazone

- (iii) **Reduction** Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH₄) or lithium aluminium hydride [LiAlH₄].

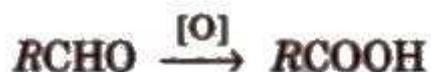
Clemmensen reduction



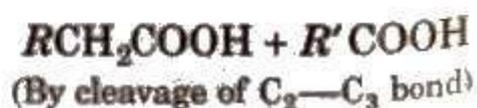
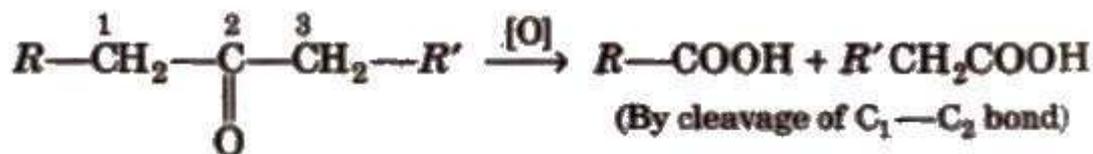
Wolff-Kishner reduction



- (iv) **Oxidation** Aldehydes get easily oxidised to carboxylic acids by HNO₃, KMnO₄, K₂Cr₂O₇, etc., or even by mild oxidising agent.

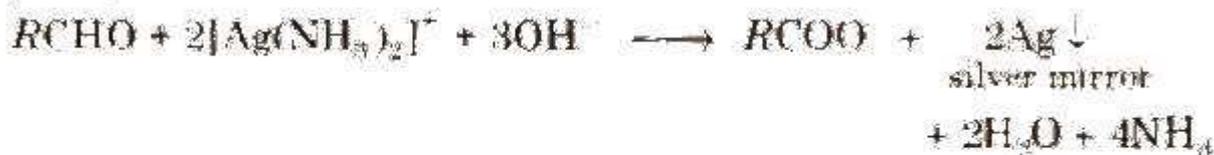


Ketones are generally oxidised under vigorous conditions, *i.e.*, strong oxidising agents and at elevated temperature.



During oxidation of unsymmetrical ketones the point of cleavage is such that keto group stays preferentially with the smaller alkyl group (Popoff's rule).

(a) **Tollen's test** Aldehydes give bright silver mirror with Tollen's reagent (ammoniacal silver nitrate).



(b) **Fehling's test** Fehling solution gives a reddish brown precipitate with aldehydes (except benzaldehyde)

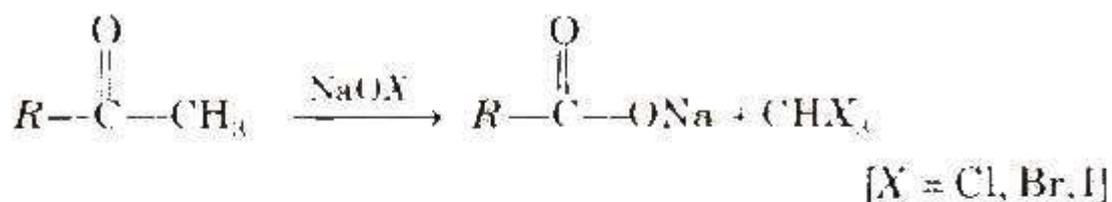


[Fehling solution is a mixture of Fehling solution A and Fehling solution B in 1: 1 ratio. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartrate which is also called, Rochelle salt.]

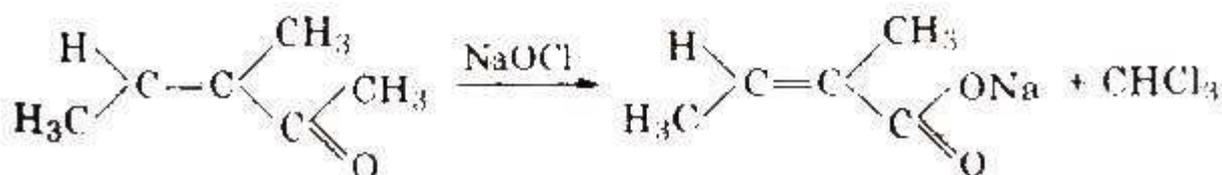
(c) **Benedict solution** With it, aldehydes (except benzaldehyde) also give red ppt. of Cu₂O.

(d) **Schiff's reagent** It is an aqueous solution of magenta or pink coloured rosaniline hydrochloride which has been decolourised by passing SO₂. Aldehydes give pink colour with this reagent but ketones do not.

Haloform reaction Aldehydes and ketones having at least one methyl group [3-α hydrogen] linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypochlorite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform.

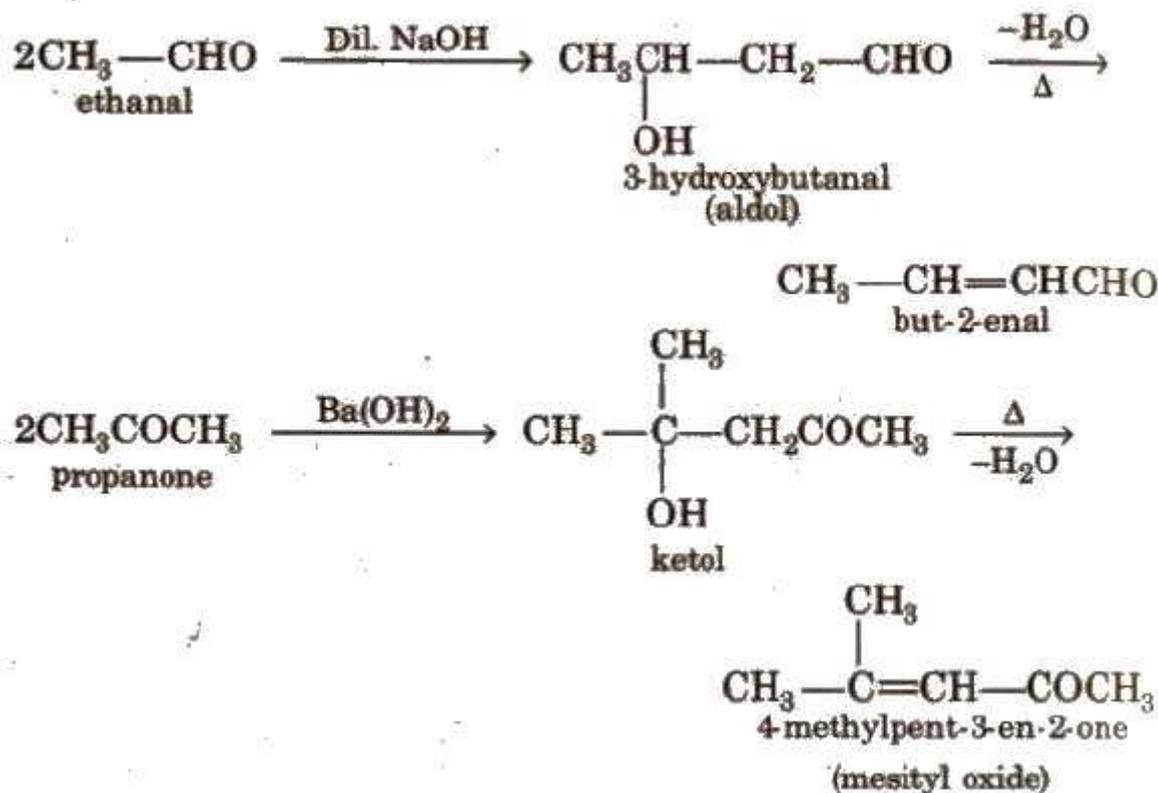


This oxidation does not affect a carbon-carbon double bond, if present in the molecule.



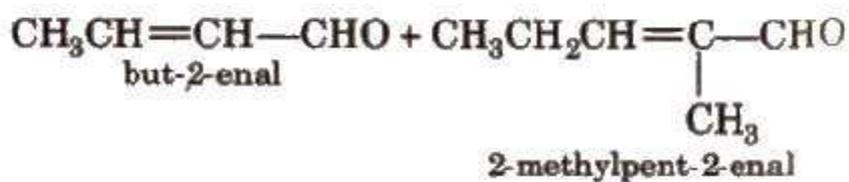
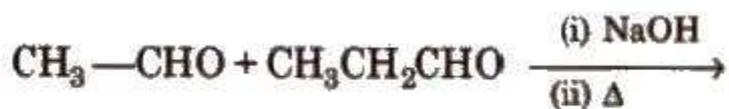
Iodoform reaction with sodium hypiodite is also used for the detection of CH_3- group or $\text{CH}_3\text{CH}(\text{OH})-$ group by producing yellow solid CHI_3 .

(v) Aldol condensation

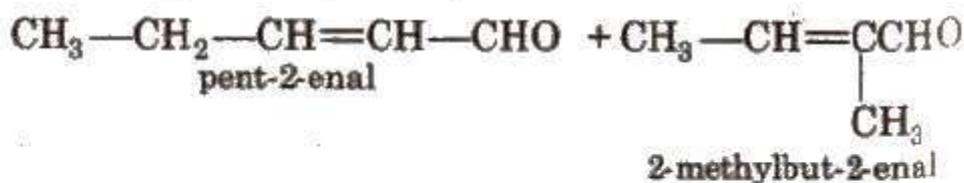


Its further condensation gives phorone,

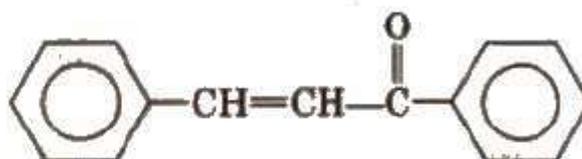
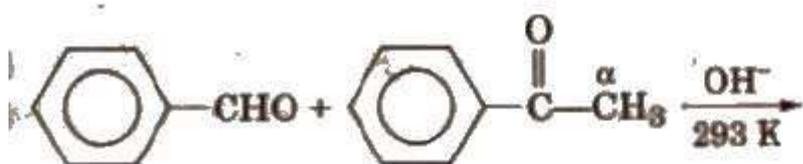
This reaction is exhibited by those aldehydes and ketones which have at least one α -hydrogen. (vi) **Cross aldol condensation** Base catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is called **Claisen-Schmidt condensation** or **Claisen reaction**.



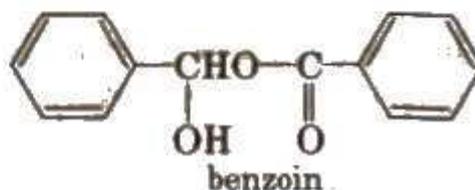
(self aldol products)



(cross aldol product)

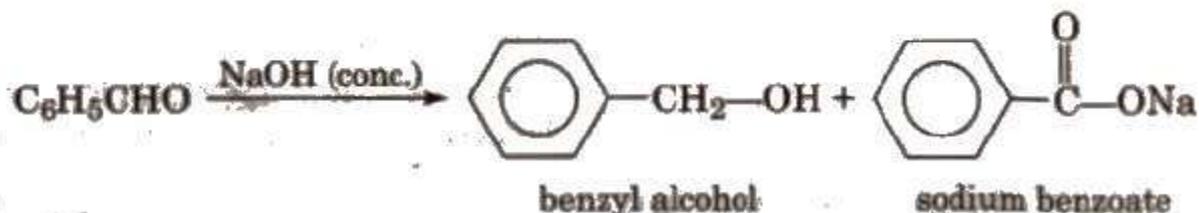
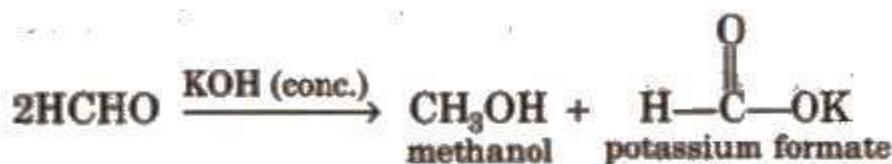


1,3-diphenylprop-2-en-1-one
(benzalacetophenone)
major product

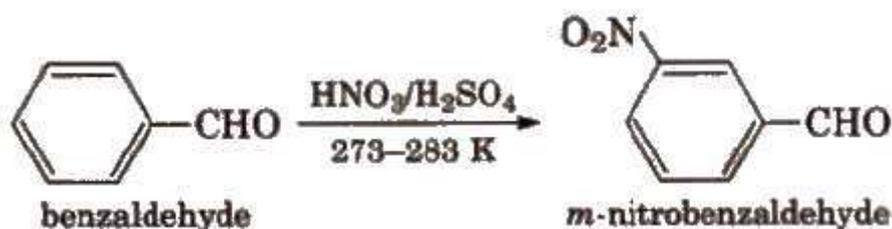


The above reaction is called Benzoin condensation, not the cross aldol condensation.

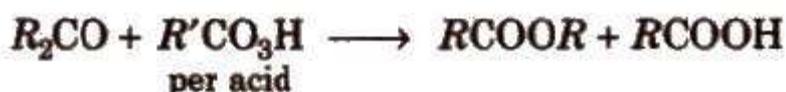
- (vii) **Cannizzaro reaction** Aldehydes which do not have any α – hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.



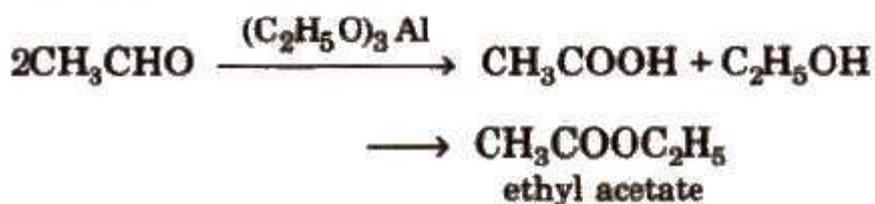
(viii) **Electrophilic substitution reaction** Aromatic aldehydes and ketones undergo electrophilic substitution. Carbonyl group shows + R effect, therefore acts as a deactivating and meta directing group.



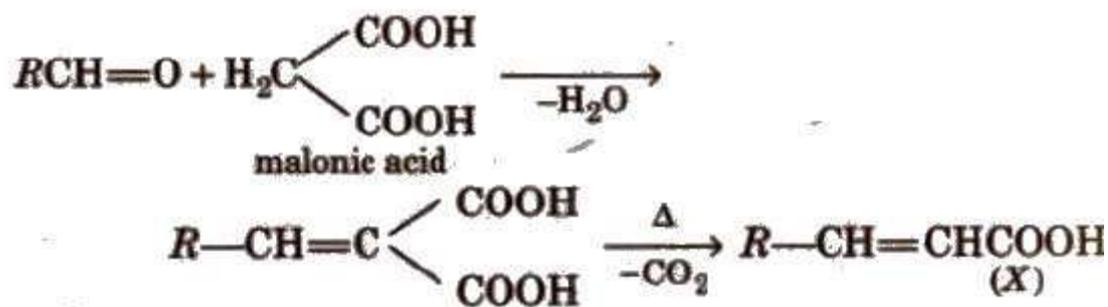
(ix) **Baeyer- Villiger oxidation** With Caro's acid (H_2SO_5) or per benzoic acid ($\text{C}_6\text{H}_5\text{CO}_3\text{H}$) or peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$) aliphatic ketones give ester.



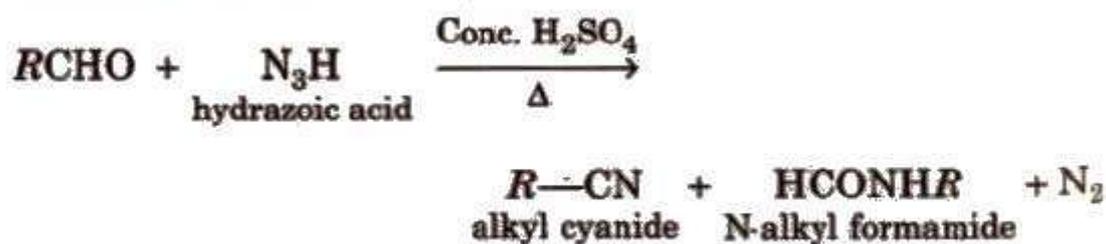
(x) **Tischenko's reaction** It is a modified form of Cannizzaro reaction.



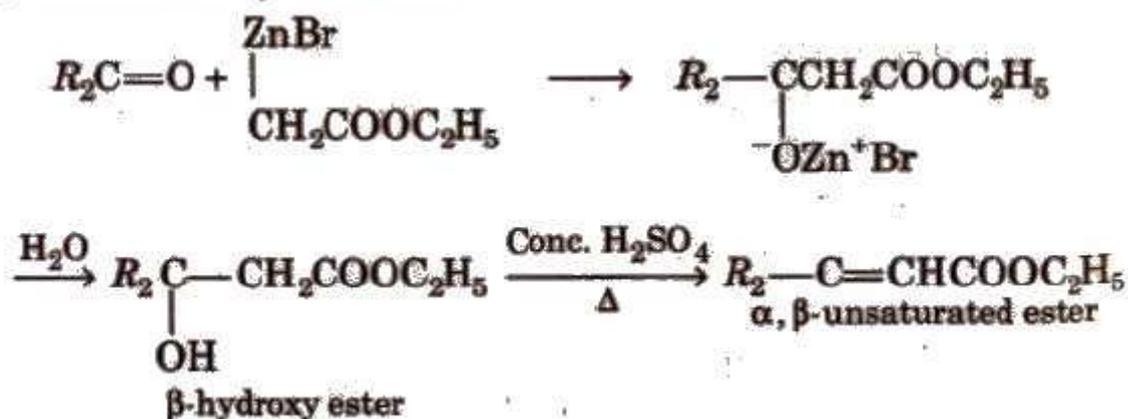
(xi) **Knoevenagel reaction** It involves condensation between active methylene group and carbonyl groups in the presence of base.



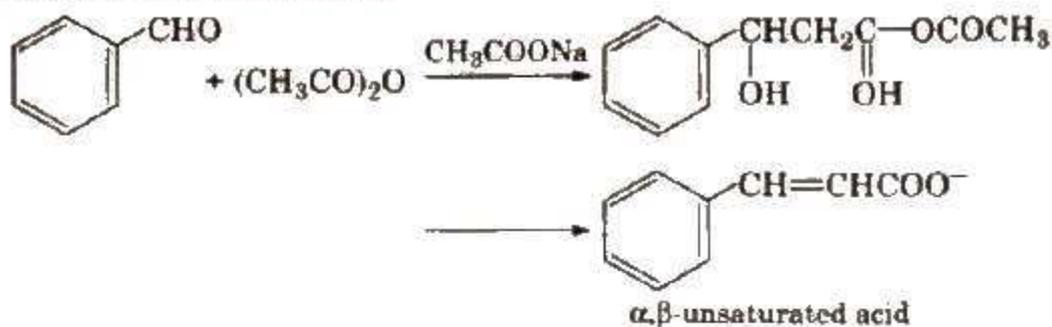
(xii) **Schmidt reaction**



(xiii) **Reformatsky reaction**



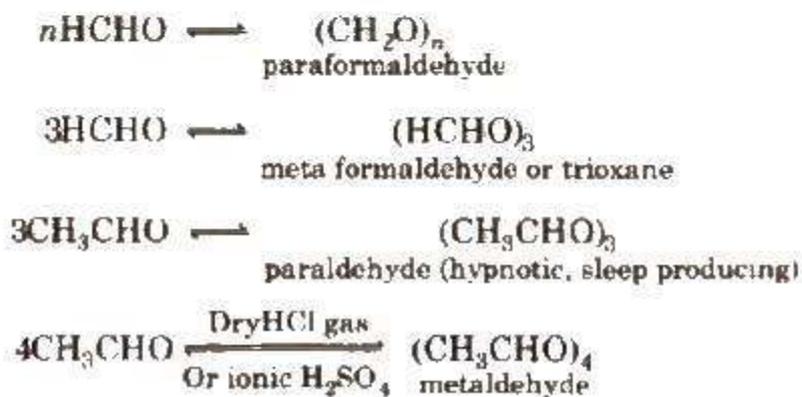
(xiv) **Perkin's reaction**



(xv) **Wittig reaction**



(xvi) **Polymerisation**



Carboxylic Acids

These are the compounds which have $\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---OH} \end{array}$ group [carboxyl group]. The word carboxyl is a combination of two words carbonyl (>C=O) and hydroxyl (---OH).

Classification

Depending upon the number of -COOH groups, they are classified as

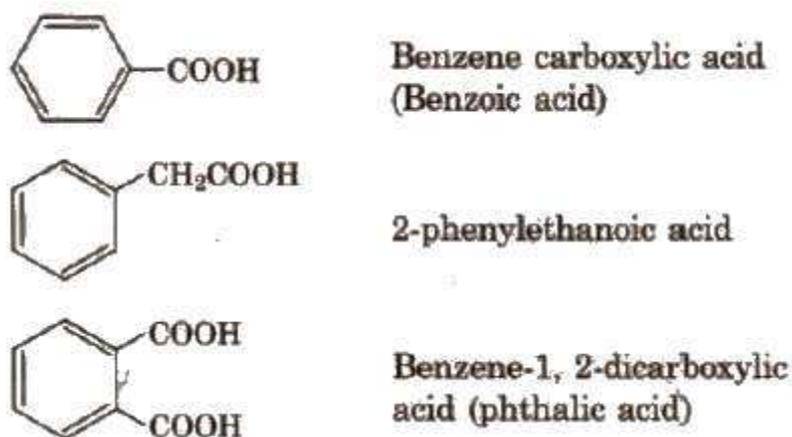
- (i) monocarboxylic acids; containing one -COOH group
- (ii) dicarboxylic acids: containing two -COOH groups.

Sources of carboxylic acids

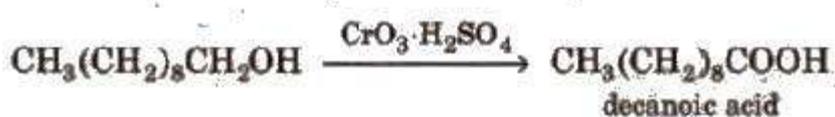
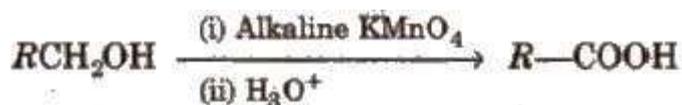
Formula	Common name	Source
HCOOH	Formic acid	Red ant (formica)
CH ₃ COOH	Acetic acid	Vineger (acetum)
C ₃ H ₇ COOH	Butyric acid	Butter (butyrum)

Nomenclature

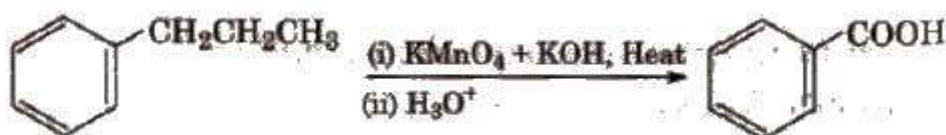
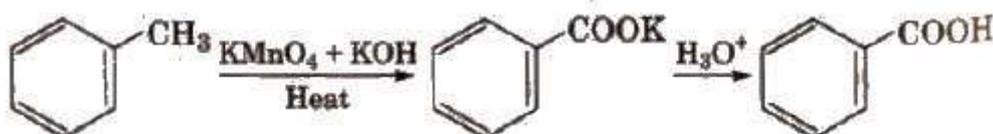
Their IUPAC names have been derived from the corresponding alkanes by replacing the letter „li of the alkane with „oic“ and adding suffix „acid“ at the end, Thus, monocarboxylic acids are called alkanic acids.



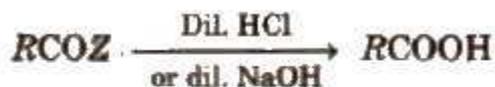
Methods of Preparation of Monocarboxylic Acids (i) From primary alcohols and aldehydes



(ii) **From alkyl benzenes** Alkyl benzene when treated with strong oxidising agent like H₂CrO₄ (chromic acid), acidic or alkaline KMnO₄ gives benzoic acid.



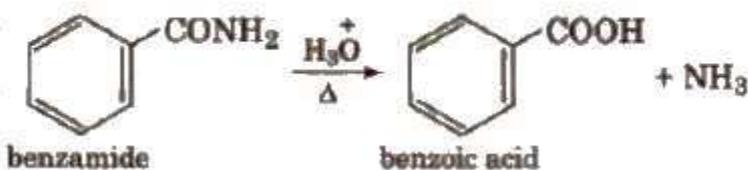
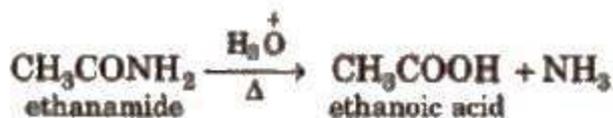
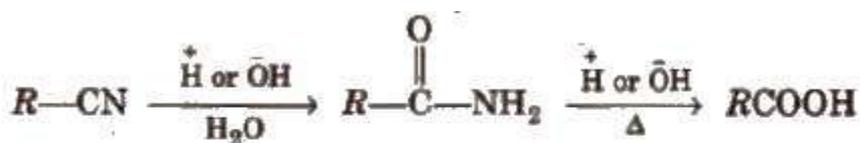
- (iii) **From acid derivatives** All acid derivatives like amides (RCONH_2), acid halides (RCOCl), esters (RCOOR'), acid anhydrides (RCO-O-COR) on hydrolysis give carboxylic acids. All acid derivatives break from RCO^+ .



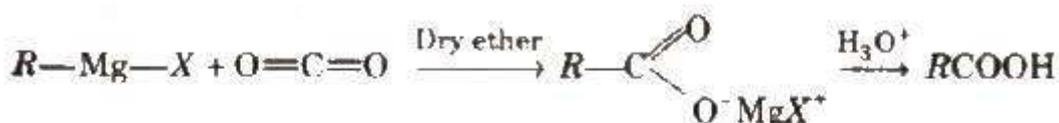
$Z = -\text{NH}_2, -\text{X} (\text{X} = \text{Cl, Br, I}), \text{OR}', \text{RCOO}-$ etc.

Ease of hydrolysis : $\text{RCOCl} > (\text{RCO})_2\text{O} > \text{RCOOR}' > \text{RCONH}_2$

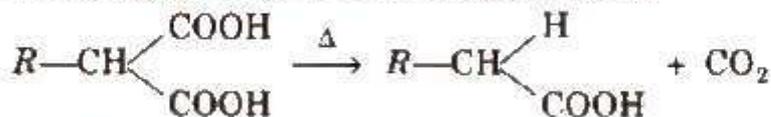
- (iv) **From nitriles and amides** Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.



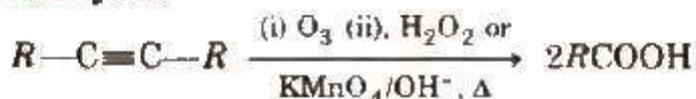
- (v) **From Grignard reagents** Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid



(vi) **By heating geminal dicarboxylic acids**



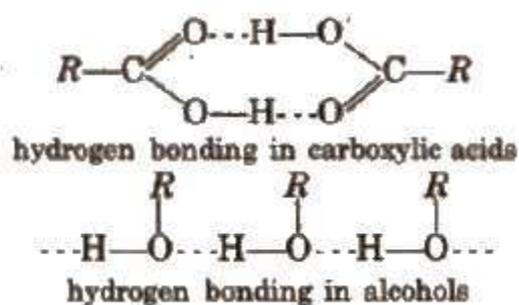
(vii) **From alkynes**



Physical Properties of Carboxylic Acids

- Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids.

- The lower carboxylic acids are freely miscible with water due to the presence of intermolecular hydrogen bonding with H₂O molecules. However, the solubility in water decreases gradually due to increase in the size of alkyl group.
- Monocarboxylic acids have higher boiling points as compared to the alcohols of comparable molecular masses due to the presence of stronger intermolecular hydrogen bonding as shown below.

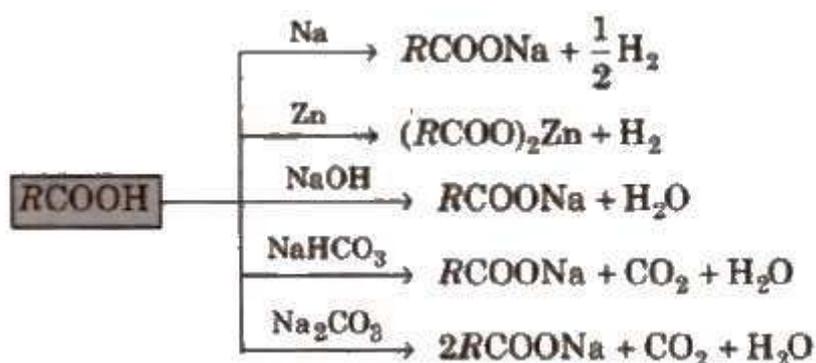


- Melting points of aliphatic monocarboxylic acids shows alternation or oscillation effect, i.e., the m.p. of an acid with even number of carbon atoms is higher than the next lower and next higher homologue containing odd number of carbon atoms. This is because, in case of acids with even number of carbon atoms, the terminal -CH₃ and -COOH groups lie on the opposite sides of the zig-zag chain. As a result, they get closely packed in the crystal lattice.
- Glacial acetic acid is completely pure acetic acid and represents the solid state of acetic acid. Below 16.6°C temperature pure acetic acid is converted into ice like solid hence it is called glacial acetic acid.

Chemical Properties of Carboxylic Acids

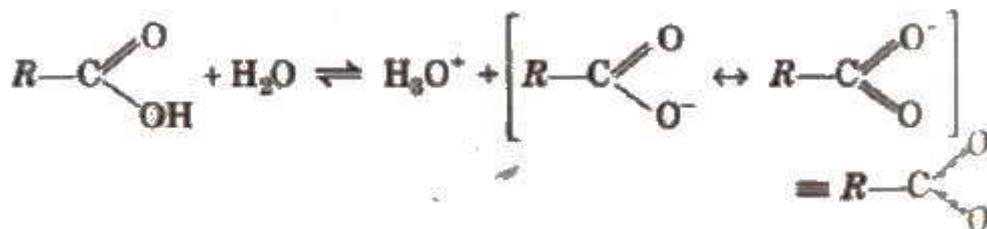
Carboxylic acids do not give reactions of carbonyl groups as it enters into resonance with lone pair of O of -OH group.

(i) Acidity



Above reactions are used to detect the presence of carboxyl group in an organic compound.

Carboxylic acids dissociate in water to give resonance stabilised carboxylate anions and hydronium ion.

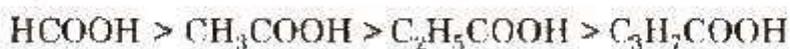


The strength of the acid is expressed in terms of the dissociation constant (K_a), also called acidity constant. A stronger acid has higher K_a but lesser pK_a value ($pK_a = -\log K_a$).

The electron releasing substituents (+1 effect) decrease the acidic strength of the carboxylic acids by destabilising the carboxylate ion.

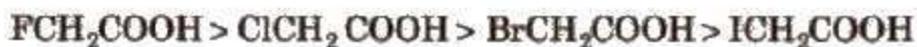
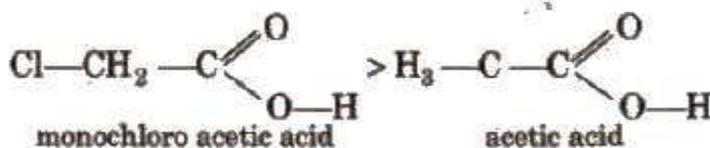
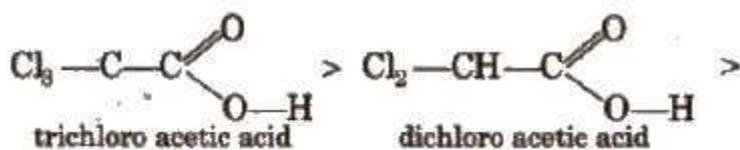
Order of + I effect : $-H < -CH_3 < -C_2H_5 < -C_3H_7$

Therefore, the order of acidic strength is

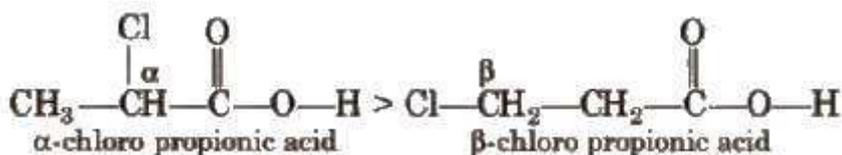


The electron withdrawing substituents (-1 effect) such as halogen atoms (X), nitro (NO_2) group increase the acidic strength by decreasing the magnitude of the negative charge on the carboxylate anion and thus stabilising it. The release of H^+ ion becomes easy.

Acidic strength order



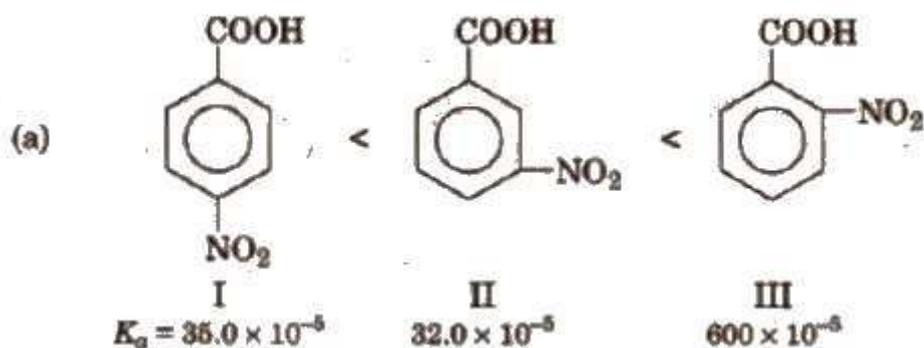
This is because -1 effect decreases in the order : $F > Cl > Br > I$.



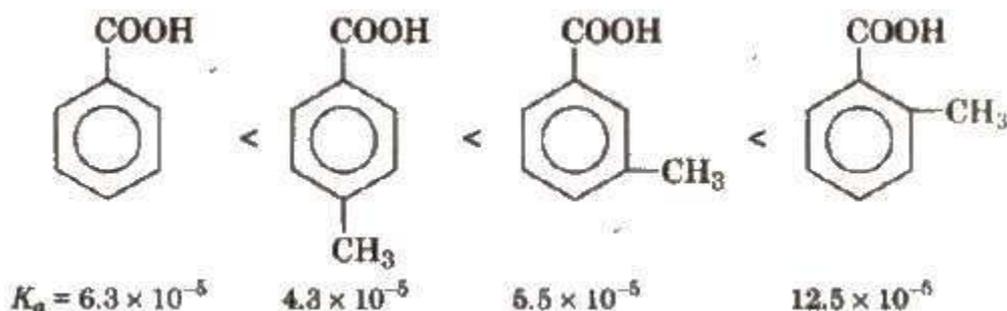
This is because - I effect decreases with distance.

Per acetic acid (CH_3COOH) is a weaker acid than acetic acid as acetate ion is stabilised by resonance.

Acidic strength of aromatic acids The parent member of the family benzoic acid which is a weaker acid ($K_a = 6.3 \times 10^{-5}$) than acid ($K_a = 17.7 \times 10^{-5}$) but stronger than acetic acid. **Some order of acidity are**

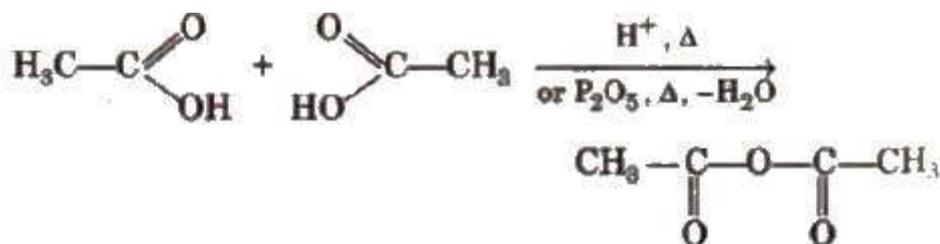


(b) Similarly, K_a values of methyl substituted (toluic acids) at 298 K are as follows:

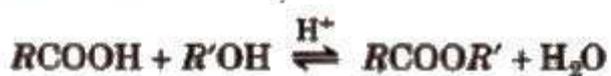


From the K_a values, it is evident that with the exception of o-isomer, both p and m-toluic acids are weaker acids than benzoic acid whereas the three isomeric nitro benzoic acids are stronger acids than benzoic acid.

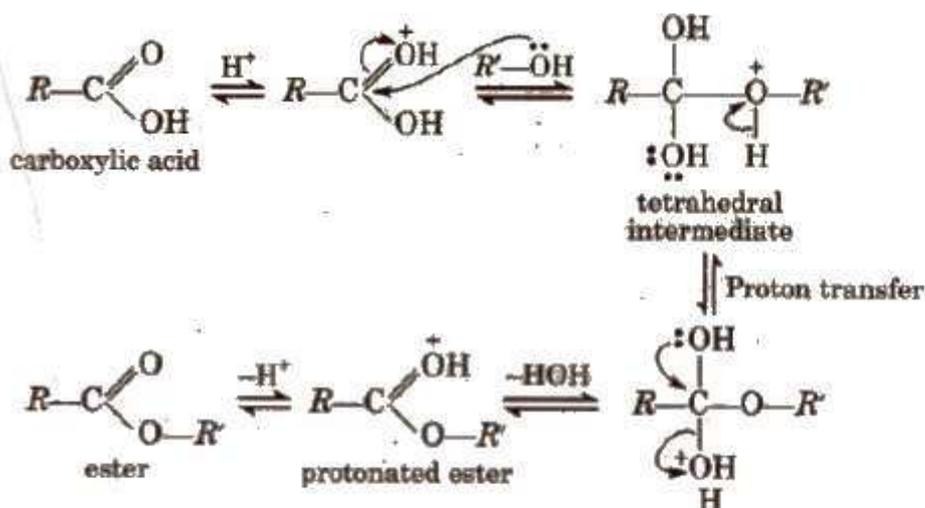
(ii) Reactions involving cleavage of C-O-H bond (a) Formation of anhydride



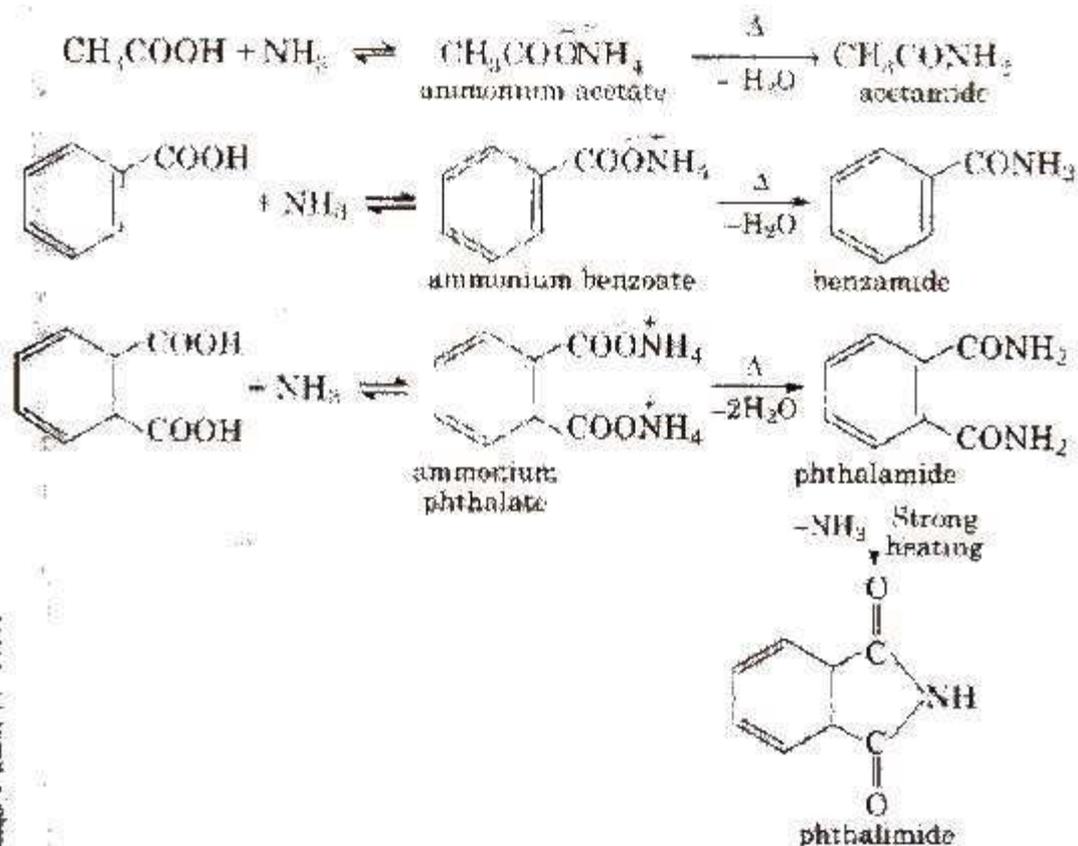
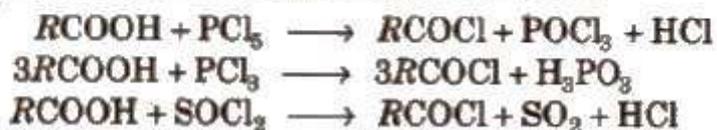
(b) Esterification



Mechanism

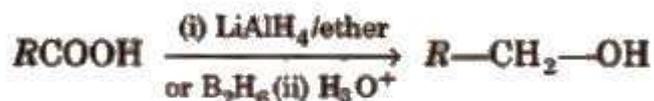


(c) Reactions with PCl_5 , PCl_3 and $SOCl_2$



(iii) Chemical reactions involving -COOH group

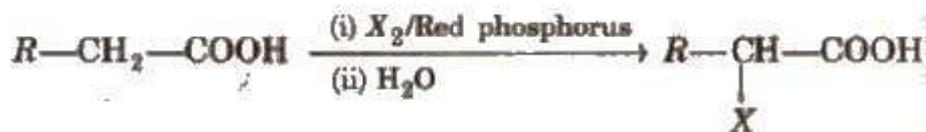
(a) **Reduction**



(b) **Decarboxylation**



- (iv) **Substitution reactions in the hydrocarbon part** α -hydrogen atoms in carboxylic acids are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction

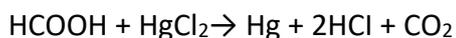


The reaction is known as Hell-Volhard-Zelinsky reaction.

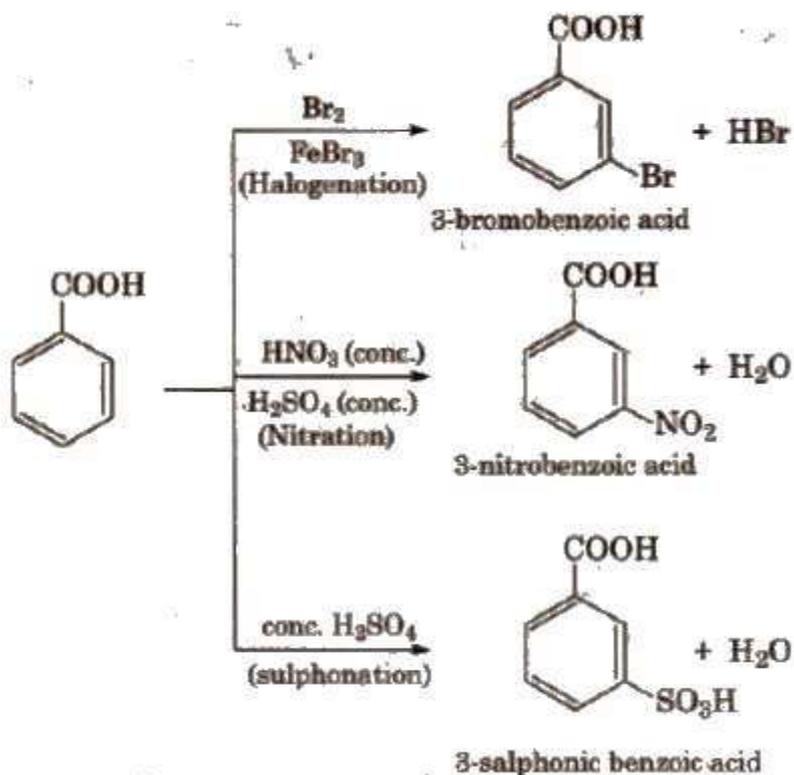
- (v) **Arndt-Eistert reaction** It is method of converting lower carboxylic acids to their higher homologues



- (vi) **Reducing property** Among carboxylic acids, formic acid is the only acid that acts as reducing agent. It reduces, acidified KMnO_4 to MnSO_4 , HgCl_2 to Hg , Tollen's reagent to silver mirror and Fehling's solution to red ppt. and itself gets oxidised to CO_2 and H_2O .



- (vii) **Electrophilic substitution reactions of aromatic acids** $-\text{COOH}$ group shows $-\text{R}$ effect, therefore, acts as a deactivating and meta-directing group. Carboxylic acids do not undergo Friedel-Craft's reaction because the carboxylic group is deactivating and the catalyst AlCl_3 (anhy.) gets bonded to the carboxyl group.

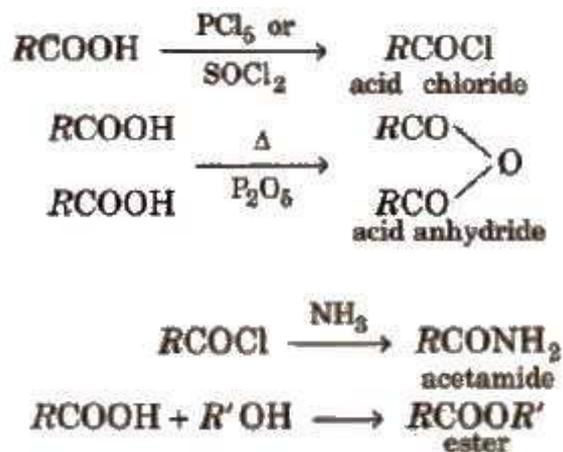


Uses

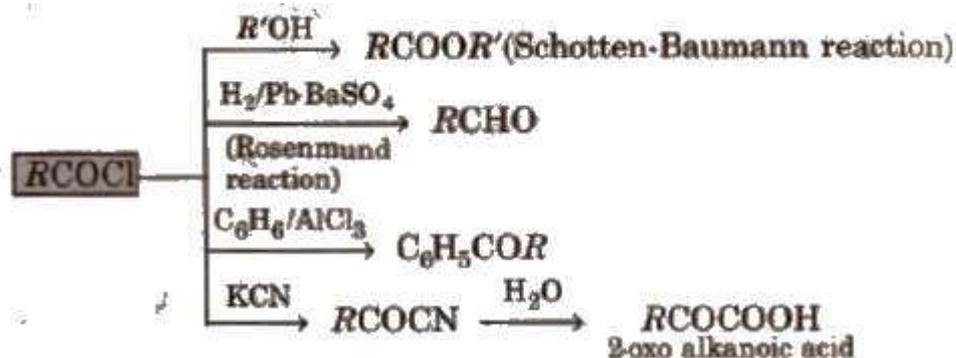
1. Formic acid is used in leather tanning, textile dyeing and finishing.
2. Acetic acid is used in the manufacture of rayon and in plastics, in rubber and silk industries, in cooking and in vinegar (a 8-10% solution of acetic acid).
3. Benzoic acid and its salts are used as urinary antiseptics.
4. Formic acid can act as a reducing agent.

Derivatives of Carboxylic acids

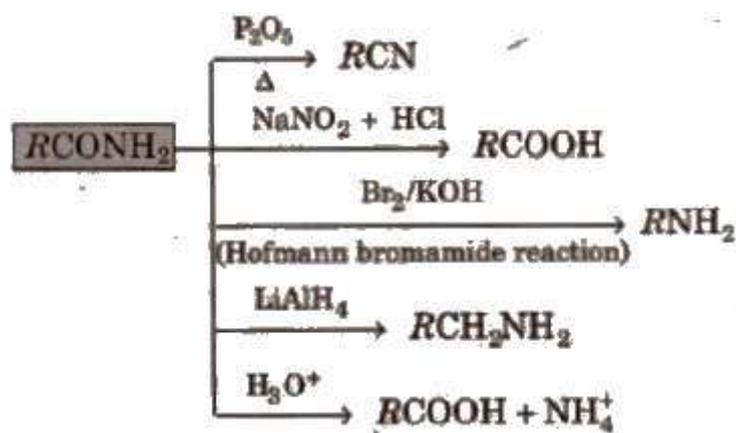
These are obtained when -OH group of carboxylic acids is replaced by Cl, NH₂, OR and OCOR and are called respectively acid chloride, acid amide, ester and acid anhydride.



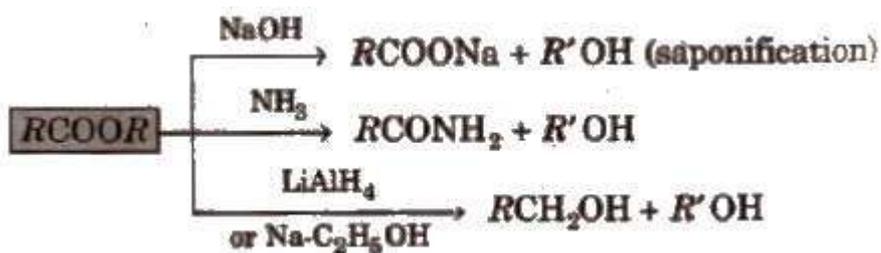
Properties of Acid Derivatives 1. Chemical reactions of acid halides



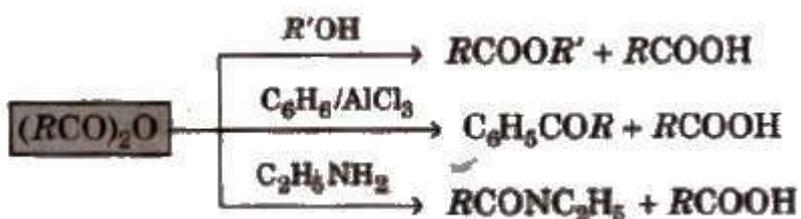
Chemical reactions of acid amides



Chemical reactions of ester

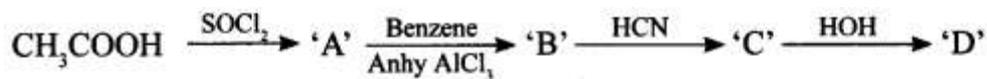


Chemical reactions of anhydrides

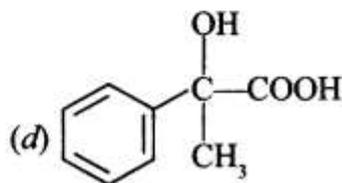
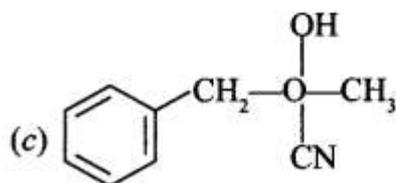
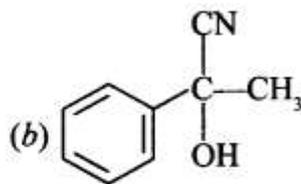
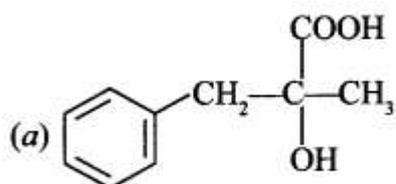


ASSIGNMENT

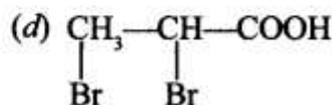
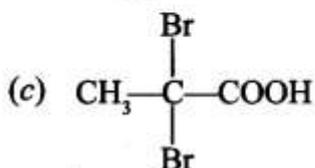
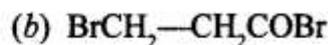
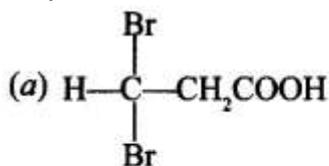
1.



The product 'D' is:



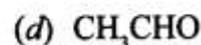
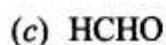
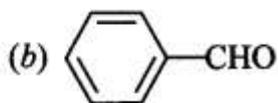
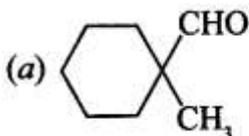
2. Propanoic acid with Br_2/P_4 yields a dibromo product. The structure will be



3. CH_3CHO and $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ can be distinguished chemically by

- Benedict's test
- Iodoform test
- Tollen's reagent test
- Fehling's solution test

4. Cannizaro's reaction is not given by _____.



5. Write Chemical equation for the following reactions :

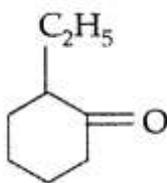
- Propanone is treated with dilute $\text{Ba}(\text{OH})_2$.
- Acetophenone is treated with $\text{Zn}(\text{Hg})/\text{Conc. HCl}$

6. How do you convert the following?

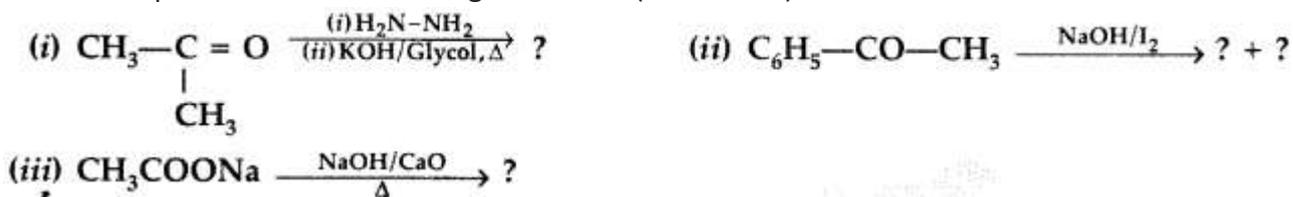
- Ethanal to Propanone
- Toluene to Benzoic acid

7. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula $\text{C}_4\text{H}_8\text{O}$. Isomers (A) and (C) give positive Tollen's test whereas isomer (B) does not give Tollen's test but gives positive Iodoform test. Isomers (A) and (B) on reduction with $\text{Zn}(\text{Hg})/\text{conc.}$

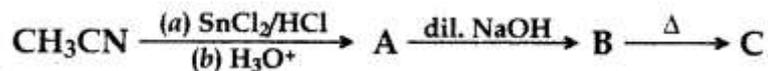
- HCl give the same product (D). a. Write the structures of (A), (B), (C) and (D). b. Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN?
8. Primary and secondary amines cannot be distinguished by
 (a) Schiff's reagent
 (b) Carbylamine reaction
 (c) Hoffmann's bromamide reaction
 (d) Iodoform test
9. How do you convert the following?
 a. Ethanal to Propanone
 b. Toluene to Benzoic acid
10. Give a chemical test to distinguish between benzoic acid and phenol. (Comptt. Delhi 2013)
11. Write IUPAC name of the following : (Comptt. All India 2013)



12. Arrange the following compounds in increasing order of their property as indicated :
 (i) CH_3COCH_3 , $\text{C}_6\text{H}_5\text{COCH}_3$, CH_3CHO
 (reactivity towards nucleophilic addition reaction)
 (ii) $\text{Cl}-\text{CH}_2-\text{COOH}$, $\text{F}-\text{CH}_2-\text{COOH}$, CH_3-COOH (acidic character) (All India 2015)
13. Predict the products of the following reactions : (Delhi 2015)



14. Write structures of compounds A, B and C in each of the following reactions: (Delhi 2017)



15. Do the following conversions in not more than two steps:
 (i) Benzoic acid to benzaldehyde
 (ii) Ethyl benzene to Benzoic acid
 (iii) Propanone to Propene



Mount Abu Public School

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SUBJECT : CHEMISTRY
CLASS XII

Week : 22 February 28 February 2021

CHAPTER 13: AMINES

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/p3jtsiyEmHc>

<https://youtu.be/p3jtsiyEmHc>

<https://youtu.be/p3jtsiyEmHc>

Learning outcomes

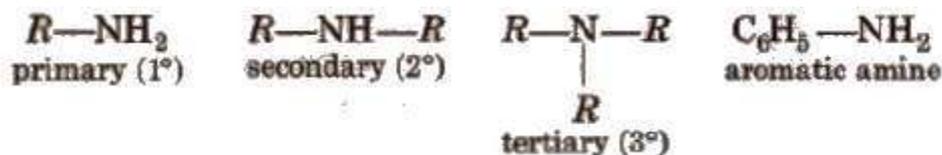
Students will be able to learn about the amines and its physical and chemical properties

Sub Topics

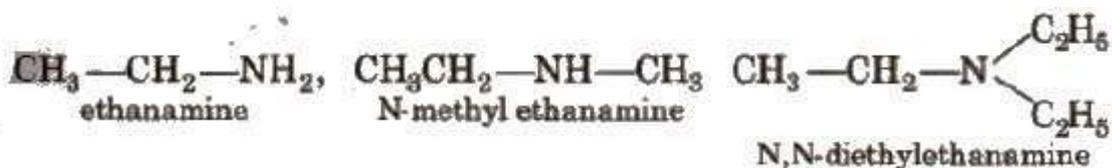
- Structure of Amines
- Classification
- Nomenclature
- Preparation of Amines
- Physical Properties
- Chemical Reactions
- Methods of preparation of Diazonium Salts
- Physical Properties
- Chemical reactions

LESSON DEVELOPMENT

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of NH_3 molecule by alkyl/aryl group(s).

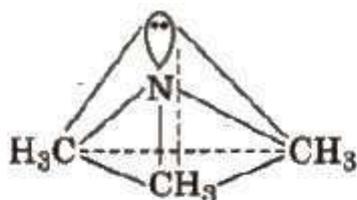


In the IUPAC system, the amines are regarded as alkanamines, e.g.,

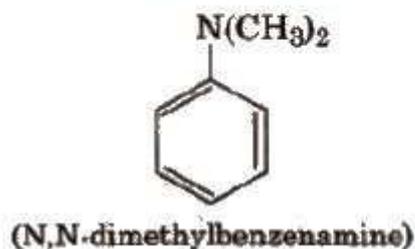
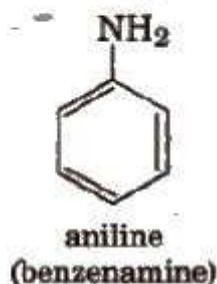


Structure

The nitrogen atom in amine is sp^3 -hybridised. The three hybrid orbitals are involved in bond formation and one hybrid atomic orbital contains the lone pair of electrons, giving the pyramidal geometry of amines.

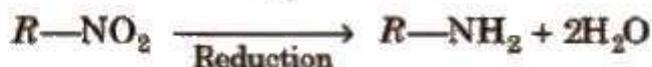


In arylamines, $-\text{NH}_2$ group is directly attached to the benzene ring.

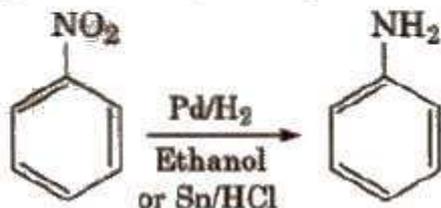


Methods of Preparation of Amines

(i) Reduction of nitro compounds

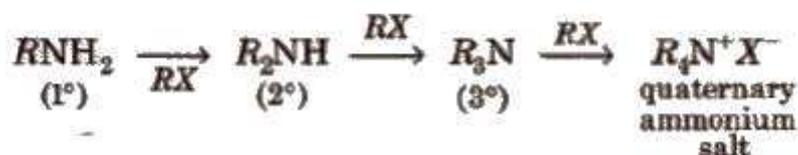
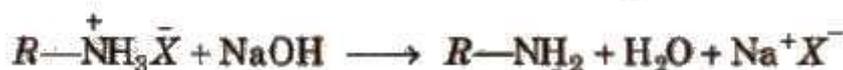
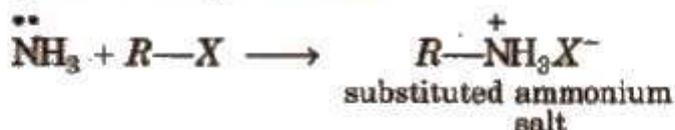


Reduction can take place by Sn/HCl, Ni/H₂, Zn/NaOH, Pd/H₂.



The reduction of nitroalkane or nitrobenzene in neutral medium gives hydroxyl amines.

(ii) Ammonolysis of alkyl halides



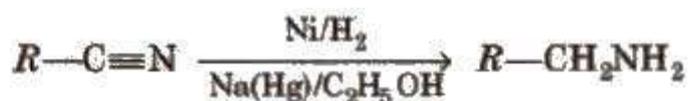
Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt.

However, primary amine is obtained as a major product by taking large excess of NH₃.

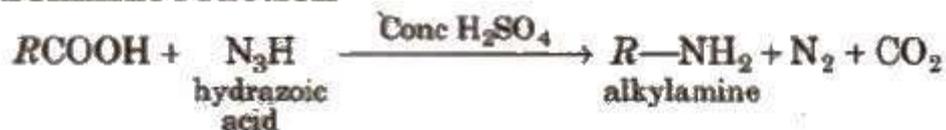
Order of reactivity of halides with amines is RI > RBr > RCl.

Aromatic amines could not be prepared since aryl halides are much less reactive towards nucleophilic substitution reactions.

(iii) Reduction of nitriles or cyanides

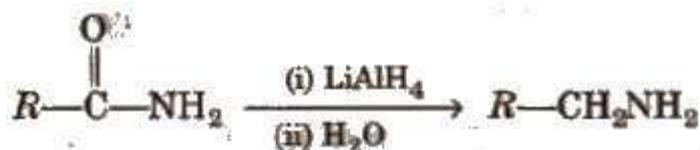


(iv) Schmidt reaction

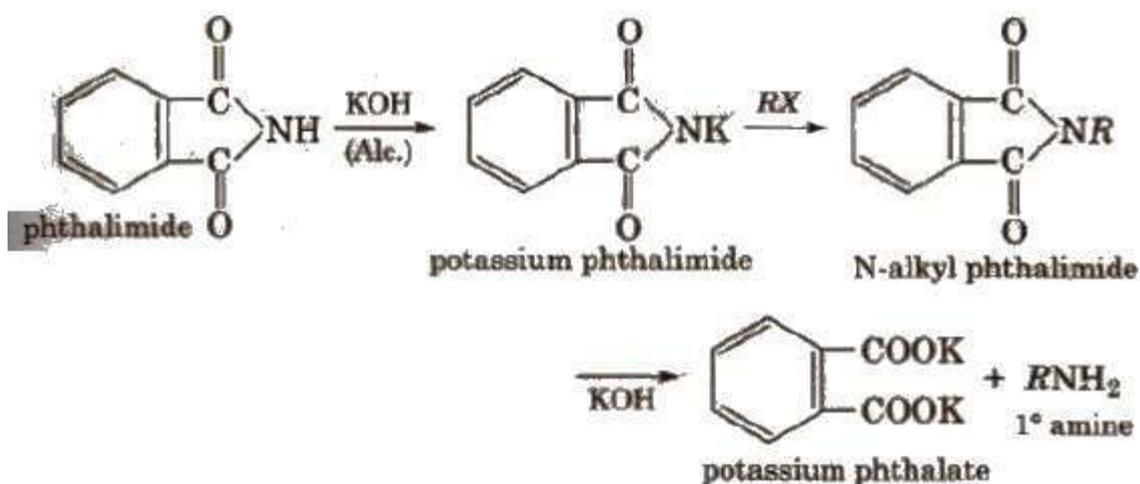


It is a modification of Curtius degradation.

(v) Reduction of amides

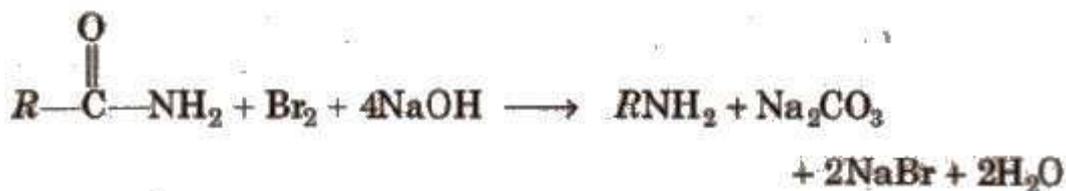


(vi) Gabriel's phthalimide reaction



It only produces 1° amines. This method is not suitable for 1° arylamine because aryl halide does not give nucleophilic substitution reaction.

(viii) Hofmann bromamide degradation reaction



In Hofmann degradation reaction, the amine formed has one carbon less than the parent amide. To obtain primary amine with same number of carbon atoms from primary amide, reduction is done with LiAlH₄/ether.

Physical Properties of Amines

1. The lower aliphatic amines are gases with fishy smell.
2. Primary amines with three or more carbon atoms are liquid and higher members are all solids.
3. Lower aliphatic amines are water soluble because they can form hydrogen bonds with water molecules, however the solubility decreases with increase in hydrophobic alkyl group.
4. Boiling points order primary > secondary > tertiary
5. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

Basic Strength of Amines

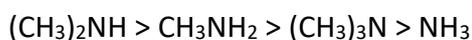
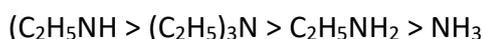
Amines act as Lewis bases due to the presence of lone pair of electrons on the nitrogen atom.

More the K_b (dissociation constant of base), higher is the basicity of amines.

Lesser the pK_b' higher is the basicity of amines.

Aliphatic amines (CH_3NH_2) are stronger bases than NH_3 due to the electron releasing +/ effect of the alkyl group.

Among aliphatic methyl amines, the order of basic strength in aqueous solution is as follows



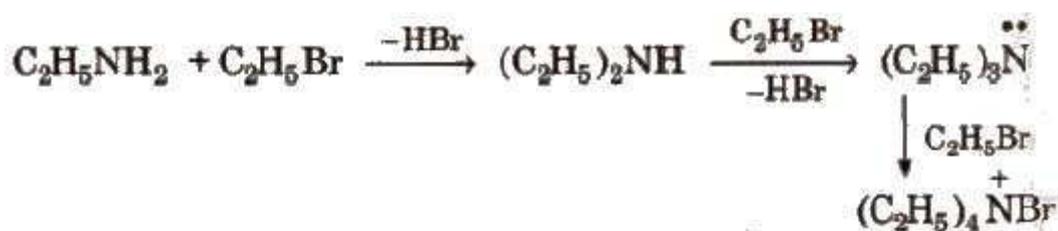
Aromatic amines are weaker bases than aliphatic amines and NH_3 , due to the fact that the electron pair on the nitrogen atom is involved in resonance with the π -electron pairs of the ring.

Electron releasing groups (e.g., $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{NH}_2$ etc.) increase the basic strength of aromatic amines while electron withdrawing groups (like $-\text{NO}_2$, $-\text{X}$, $-\text{CN}$ etc.) tend to decrease the same.

o-substituted aromatic amines are usually weaker bases than aniline irrespective of the nature of substituent whether electron releasing or electron withdrawing. This is called ortho effect and is probably due to steric and electronic factors.

chemical Properties of Amines

(i) Alkylation All the three types of amines react with alkyl halides to form quaternary ammonium salt as the final product provided alkyl halide is present in excess.

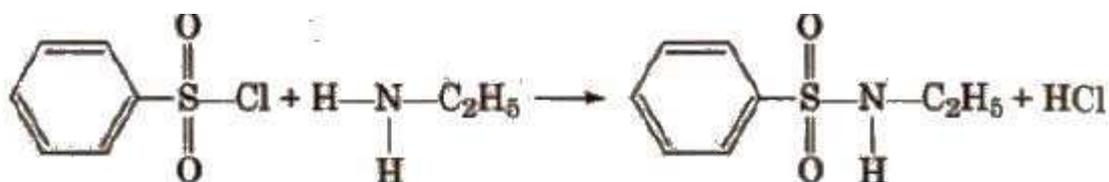


Aromatic amines also undergo alkylation as given below.

But secondary and tertiary amines react with nitrous acid in different manner.

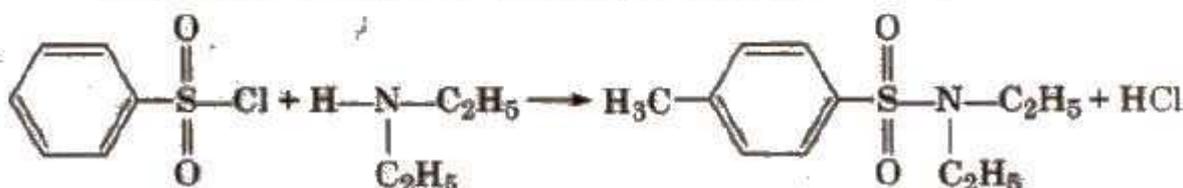
Methyl amine give dimethyl ether with HNO_2 .

(vi) **Reaction with aryl sulphonyl chloride** [Hinsberg reagent] The reaction of benzenesulphonyl chloride with primary amine yield N-ethyl benzenesulphonyl amide.



(soluble in alkali)

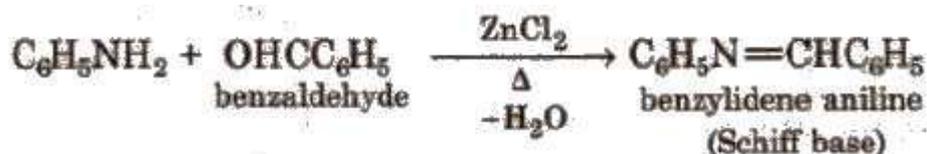
The reaction of benzenesulphonyl chloride with secondary amine yields N,N-diethyl benzene sulphonamide.



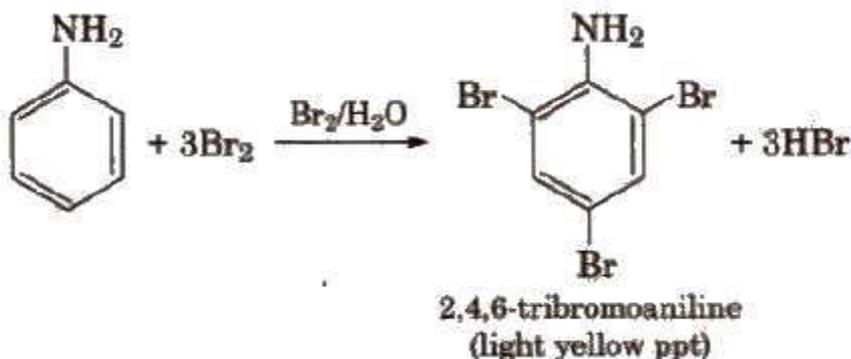
(insoluble in alkali)

Tertiary amines does not react with benzenesulphonyl chloride.

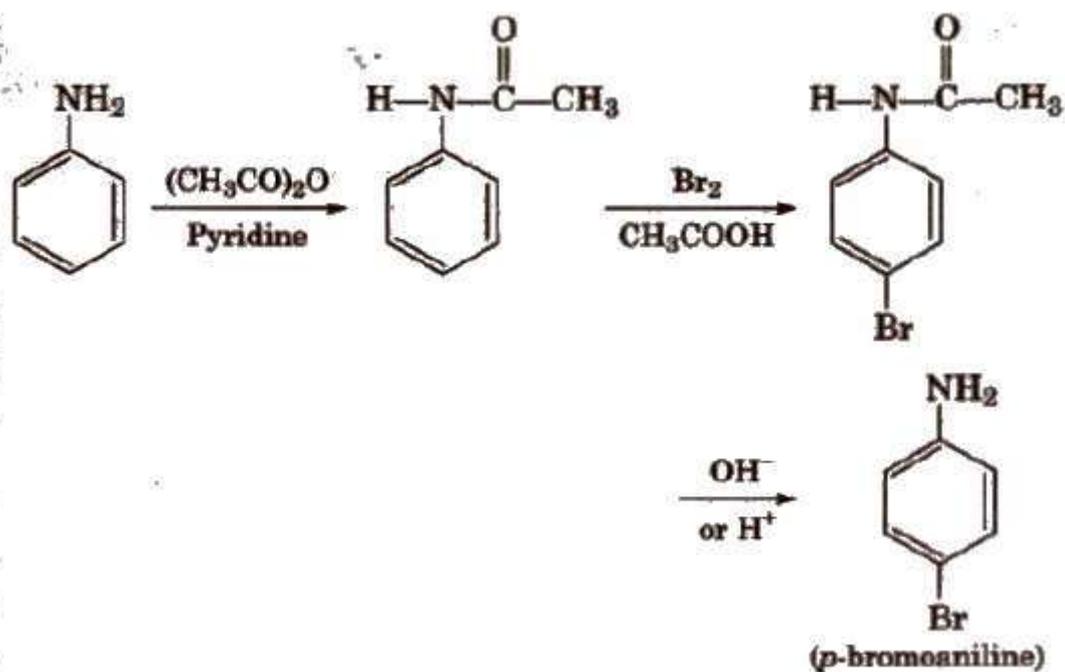
(vii) **Reaction with aldehydes** Schiff base is obtained.



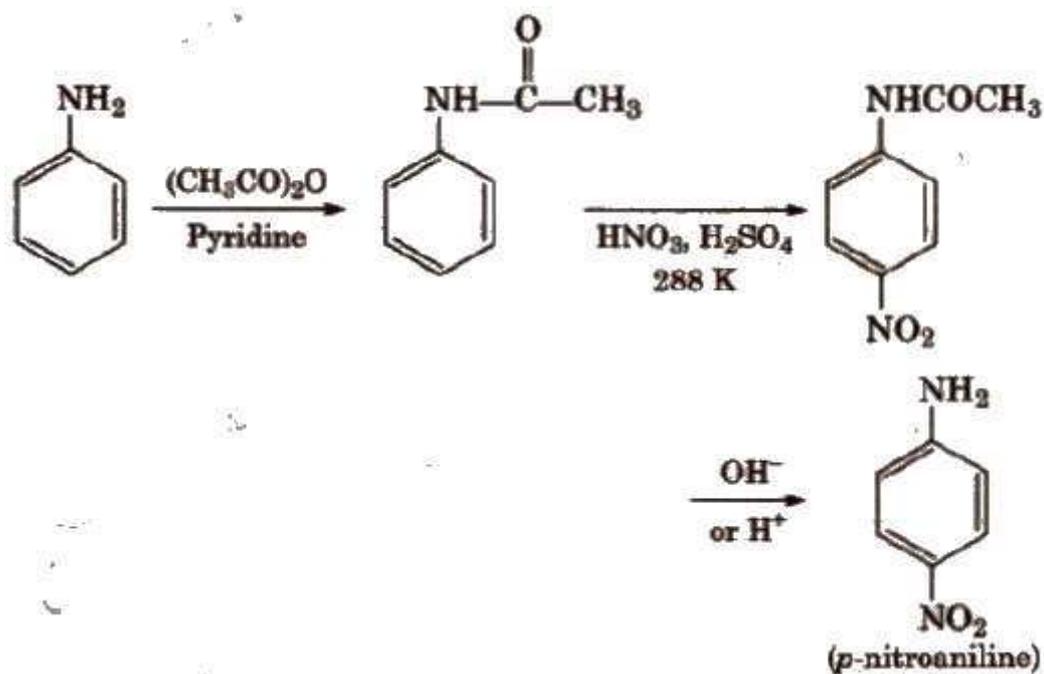
(viii) **Electrophilic substitution reactions** Aniline is ortho and para directing towards electrophilic substitution reaction due to high electron density at ortho and para-positions.



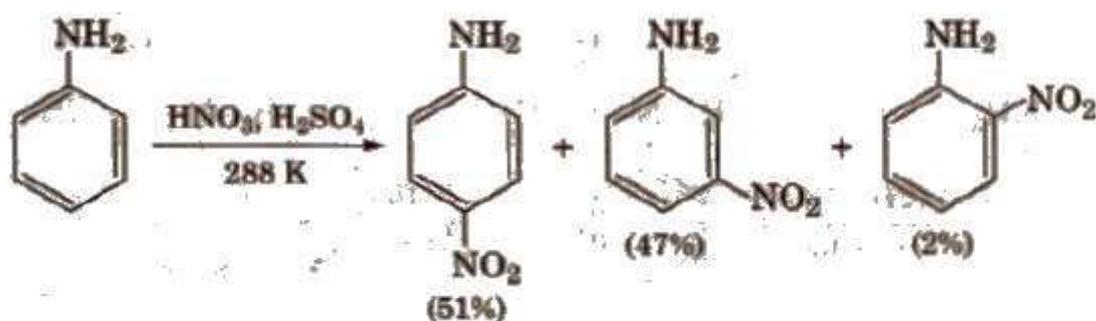
To prepare monosubstituted derivative, activating effect of -NH₂ group must be controlled. It can be done by protecting the -NH₂ group by acetylation with acetic anhydride.



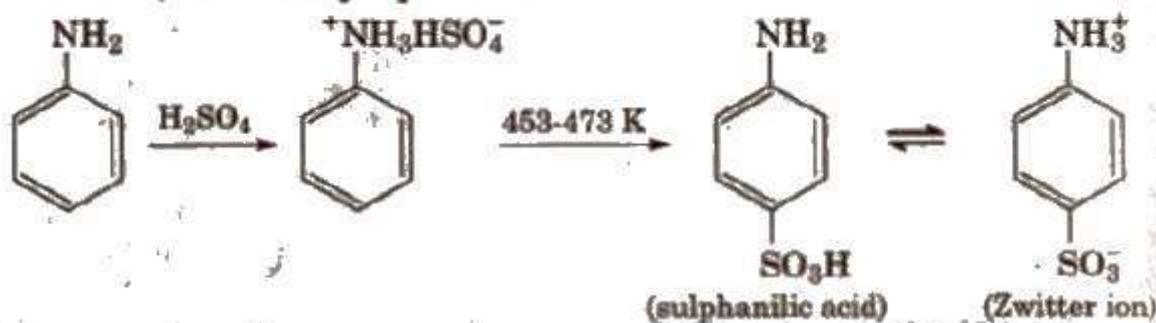
(b) Nitration Direct nitration of aniline is not possible as it is susceptible to oxidation, thus amino group is first protected by acetylation.



In strongly acidic medium, aniline is protonated as anilinium ion which is meta directing so it gives meta product also.



(c) **Sulphonation** On sulphonation, aniline gives sulphanilic acid, as the major product.



(d) Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence behave like a strong deactivating group for further chemical reaction.

(ix) **Oxidation** Use of different oxidising agents gives different products. e.g.,

Oxidising agent	Product
Acidified KMnO_4 (or $\text{Na}_2\text{C}_2\text{O}_7 + \text{CuSO}_4 + \text{dil acid}$)	Aniline black (a dye)
Chromic acid ($\text{Na}_2\text{C}_2\text{O}_7 + \text{Conc H}_2\text{SO}_4$)	<i>p</i> -benzoquinone
Caro's acid (H_2SO_5)	nitrobenzene and nitrosobenzene
Conc. nitric acid	decomposes

Separation of Mixture of Amines (1° , 2° and 3°)

(a) **Fractional distillation** This method is based on the boiling points of amines and is used satisfactorily in industry.

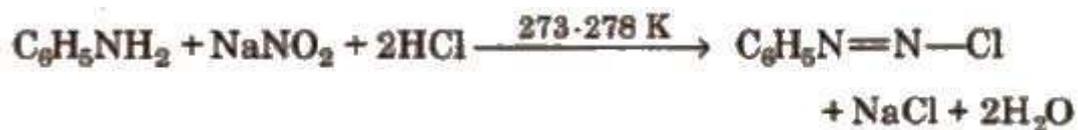
(b) **Hofmann's method** Diethyl oxalate is called Hofmann's reagent with which mixture of amines is treated.

- 1° amine forms solid dialkyl oxamide $(\text{CONHR})_2$
- 2° amine forms liquid dialkyl oxamic ester $(\text{CONR}_2\text{-COOC}_2\text{H}_5)$ \square 3° amines do not react

(c) **Hinsberg's method** see chemical reactions.

Benzene Diazonium Chloride ($C_6H_5N_2^+;Cl^-$)

Preparation (Diazotisation reaction)



The excess acid in diazotisation reaction is necessary to maintain proper acidic medium for the reaction and to prevent combination of diazonium salt formed with the undiazotised amine.

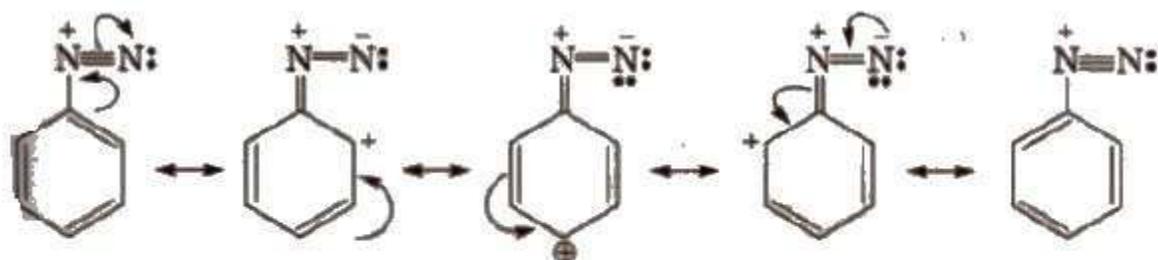
Diazonium salts are prepared and used in aqueous solutions because in solid state, they explode.

Properties

It is a colourless crystalline solid, soluble in water. It has tendency to explode when dry.

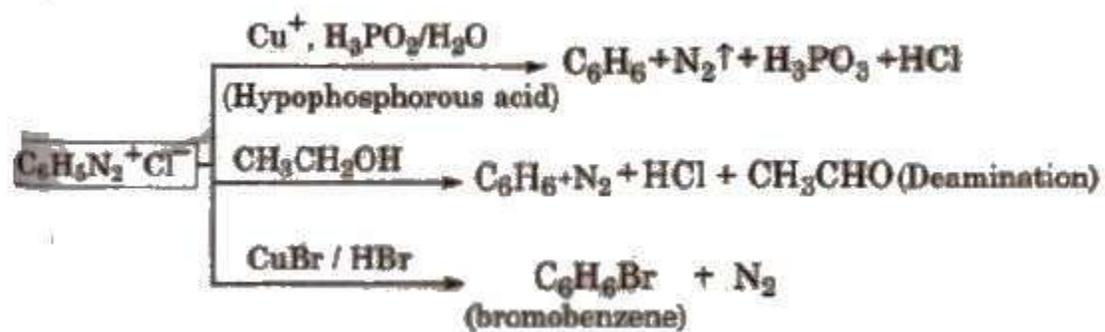
Stability of Arenediazonium salts

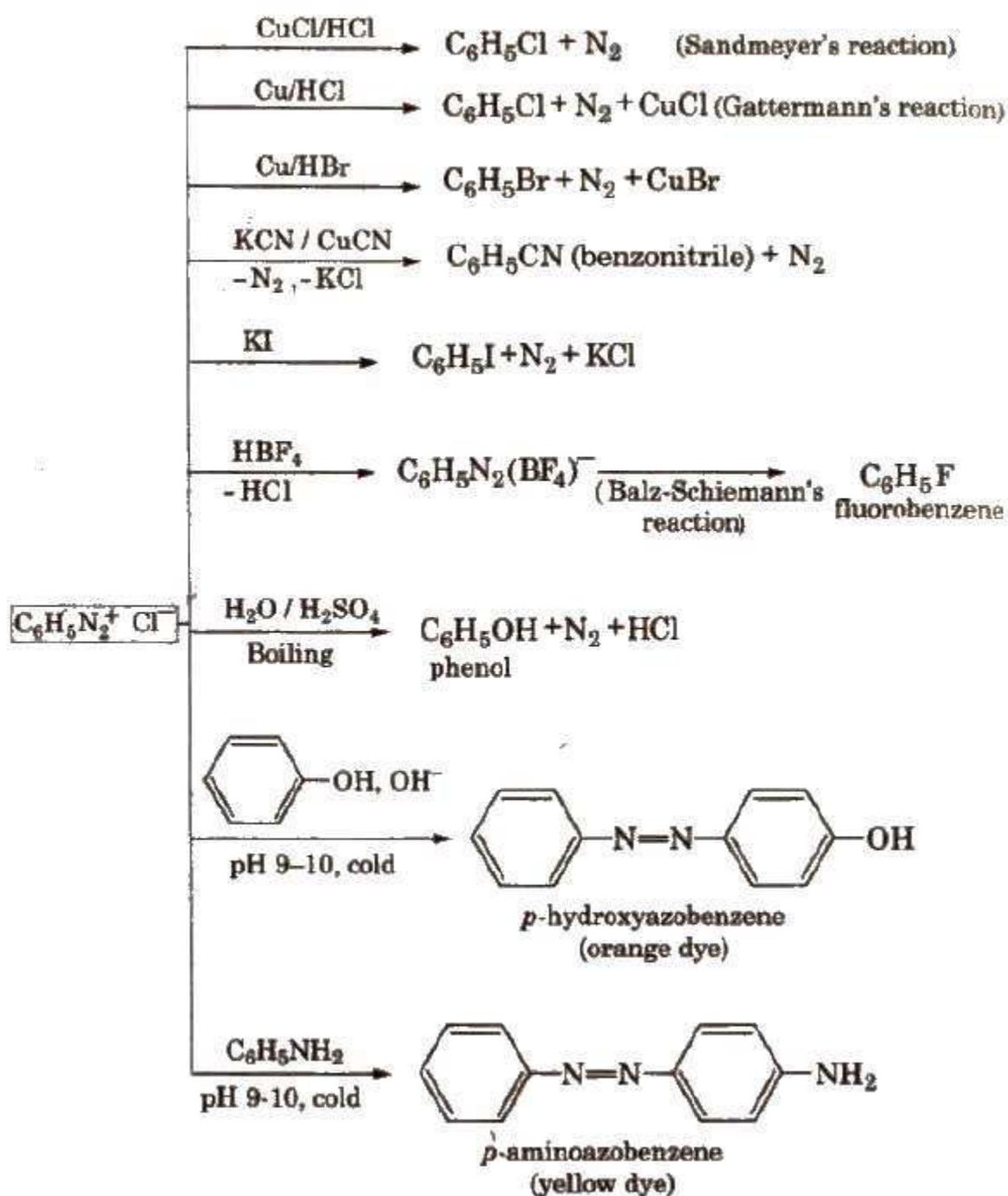
It is relatively more stable than the alkyldiazonium salt. The arenediazonium ion is resonance stabilised as is indicated by the following resonating structures:



Various resonating structures of arenediazonium ion

Chemical Reactions

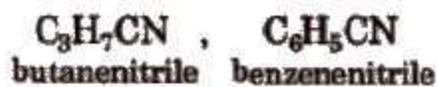




Alkyl Cyanides'

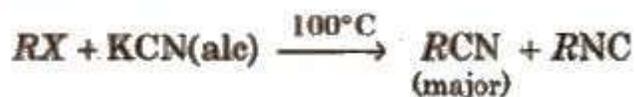
These compound have formula RCN. These are the derivatives of RCN.

According to IUPAC system, cyanides are named as 'alkane nitrile', e.g.,

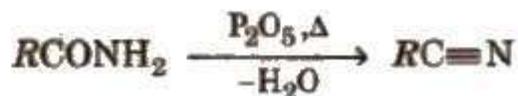


Methods of Preparation

(i) From alkyl halides



(ii) From acid amides

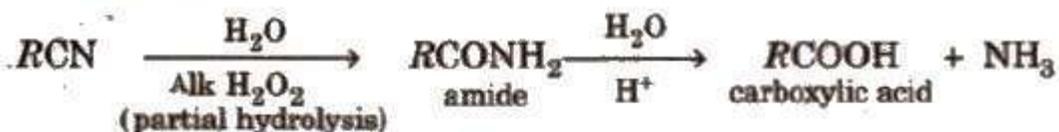


Physical properties

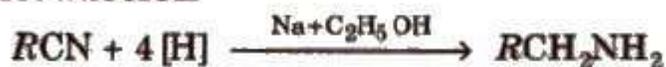
1. These are neutral compound with pleasant odour, similar to bitter almonds.
2. These are soluble in water as well as organic solvents.
3. These are poisonous but less than HCN.

Chemical Properties

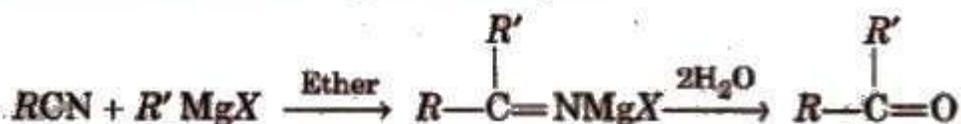
(i) Hydrolysis



(ii) Reduction



(iii) Reaction with Grignard reagent



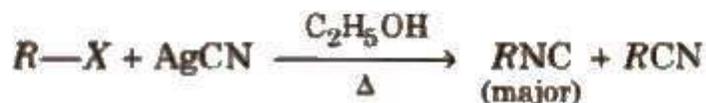
Alkyl isocyanides (RNC)

According to IUPAC system, these are named as 'alkane isonitrile'

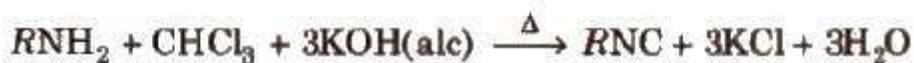
e.g., CH_3NC methyl isonitrile

C_6H_5NC benzene isonitrile

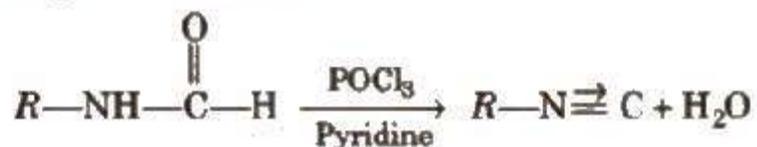
Methods of Preparation (a) From alkyl halides



(b) **Carbylamine reaction**



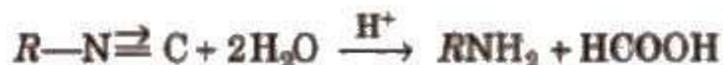
(c) **From N-alkyl formamide**



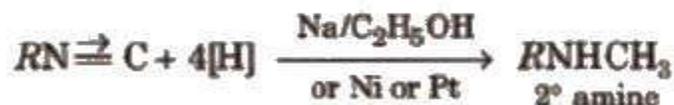
Physical Properties

1. These are colourless unpleasant smelling liquids.
2. These are soluble in organic solvents but insoluble in water.

Chemical Properties (i) Hydrolysis



(ii) **Reduction**



(iii) **Addition reaction** Due to the presence of unshared pair of electrons on C atom, alkyl isocyanides give addition reaction.



(iv) **Isomerisation** At 250°C, it isomerises to nitrile.



Nitro Compounds

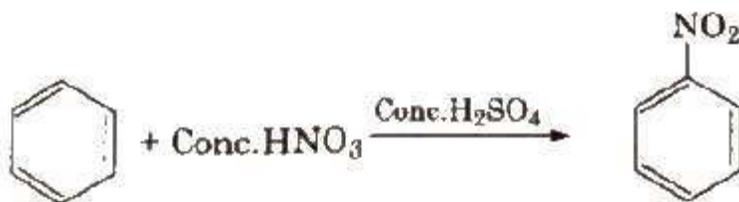
These are obtained by replacing one H of hydrocarbon by -NO₂ group.

These are named according to IUPAC system as 'nitro alkane'.

Methods of Preparation (i) From alkyl halides



(ii) **Nitration** Nitrating mixture is conc HNO_3 + conc H_2SO_4 .



Physical Properties

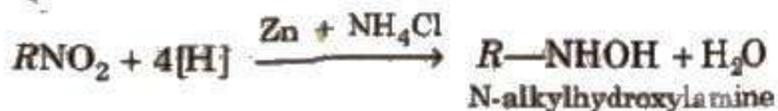
1. These are colourless pleasant smelling liquids.
2. Their boiling point are much higher than isomeric alkyl nitriles.
3. These are less soluble in water but readily soluble in organic solvents.

Chemical Properties

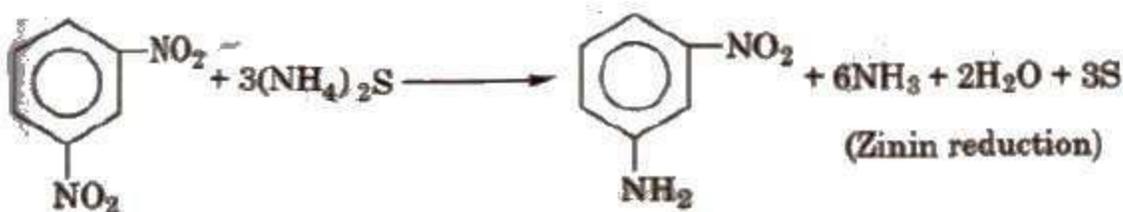
(i) **Reduction** With Sn/HCl or catalytic hydrogenation, nitroalkanes are reduced to amines.



If neutral reducing agent like Zn dust + NH_4Cl is used, hydroxylamines are obtained as major product.



In the presence of $(NH_4)_2S$ or Na_2S , selective reduction takes place.

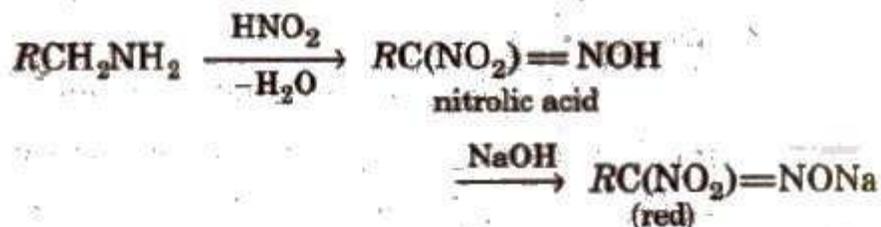


Nitrobenzene gives different products with different reagents and in different mediums.

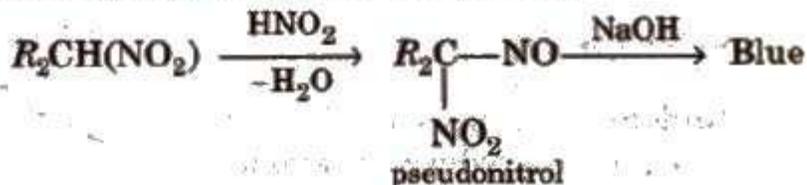
Medium	Reagent	Product
Acid	Sn/HCl	aniline
Neutral	$\text{Zn/NH}_4\text{Cl}$	N-phenyl hydroxylamine
Alkaline	$\text{Na}_3\text{AsO}_3/\text{NaOH}$	azoxybenzene ($\text{C}_6\text{H}_5\text{N}=\overset{\text{O}}{\text{N}}\text{C}_6\text{H}_5$)
	$\text{Zn/NaOH, CH}_3\text{OH}$	azobenzene
Metallic hydride	$\text{Zn/NaOH, C}_2\text{H}_5\text{OH}$	hydrazobenzene
Electrolytic	LiAlH_4	aniline
	dil H_2SO_4	p-aminophenol

(ii) Action of HNO_2

1° nitroalkane gives nitrolic acid which gives red colour with NaOH.

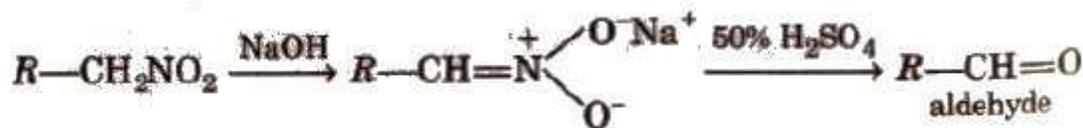


2° nitroalkanes give pseudonitrol with HNO_2 .

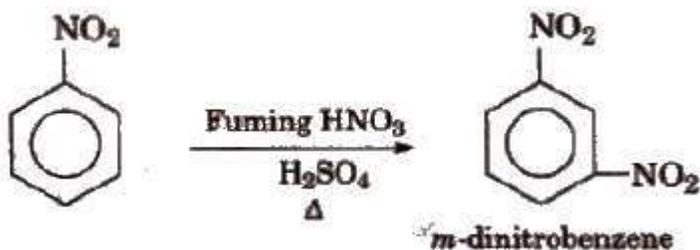


3° nitroalkanes does not react with HNO_2

(iii) **Nef carbonyl synthesis** Na or K salt of 1° or 2° nitroalkanes give carbonyl compounds on acidification with 50% H_2SO_4 at room temperature. This reaction is called Nef carbonyl synthesis.

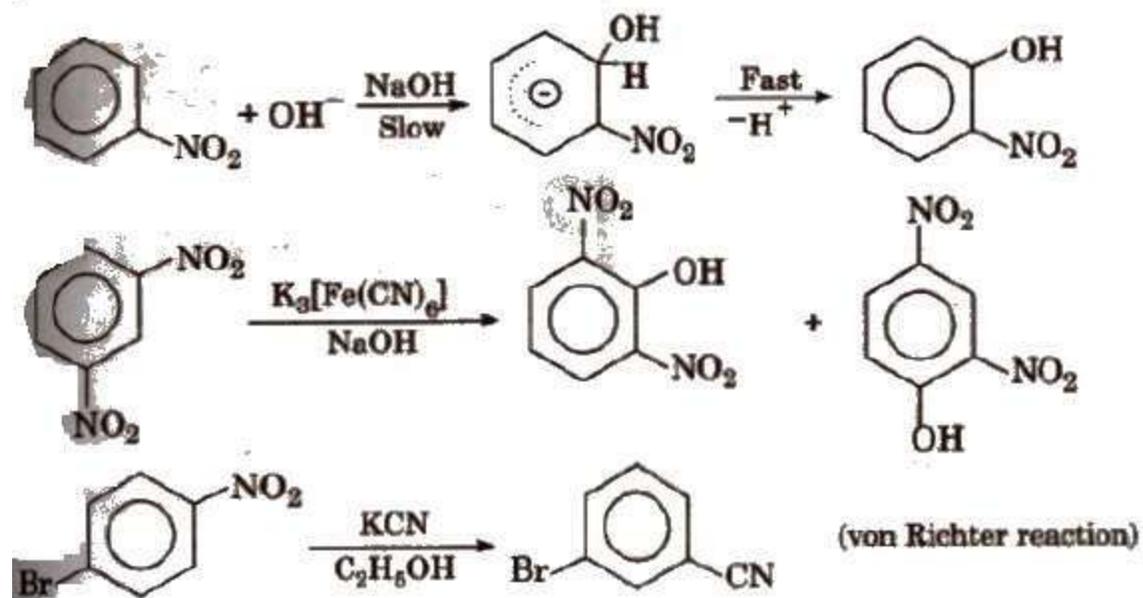


(iv) **Electrophilic substitution** On nitration, nitrobenzene gives m-dinitrobenzene (as $-\text{NO}_2$ is a m-directing group and strongly deactivating).



It does not give Friedel-Craft's alkylation.

(v) **Nucleophilic substitution** reaction -NO₂ group activates the ring towards nucleophilic substitution.

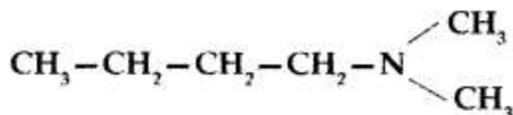


ASSIGNMENT

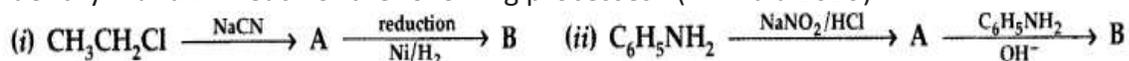
1. Give a chemical test to distinguish between ethylamine and aniline
2. Arrange the following in the decreasing order of their basic strength in aqueous solutions: CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$ and NH_3 (Delhi 2012)
3. Write the structure of 2-aminotoluene. (All India 2013)
4. (i) Arrange the following compounds in an increasing order of basic strength : $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2
(ii) Arrange the following compounds in a decreasing order of pK_b values : $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}$ (Comptt. Delhi 2014)
5. Give reasons :
(i) Electrophilic substitution in aromatic amines takes place more readily than benzene.
(ii) CH_3CONH_2 is weaker base than $\text{CH}_3\text{CH}_2\text{NH}_2$.
6. Write the IUPAC name of the given compound: (Delhi 2016)



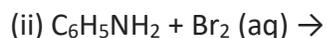
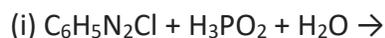
7. Write IUPAC name of the following compound : (Comptt. All India 2017)



8. Identify A and B in each of the following processes : (All India 2010)



9. Complete the following reaction equations : (All India 2012)





Mount Abu Public School

H-Block, Sector-18, Rohini, New Delhi-110085 India

SUBJECT : CHEMISTRY

CLASS XII

Week : 22 February 28 February 2021

CHAPTER BIOMOLECULES

Guidelines

- Refer to the content given below and view the links
- These notes will help you to understand the concept and complete the assignment that follows
- The assignment is to be done in the chemistry notebook
- Please read the science NCERT book before you begin answering

Instructional Aids / Resources

NCERT Link is given below :

<https://youtu.be/MkqtHP9MhDs>

<https://youtu.be/AUVfliEcrIq>

<https://youtu.be/AUVfliEcrIq>

Learning outcomes

Students will able to learn about the biomolecules

Sub Topics

- Carbohydrates
- Proteins
- Vitamins
- Nucleic acid

Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds.

Some common examples of carbohydrates are cane sugar, glucose, starch, etc. Most of them have a general formula, $C_x (H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived.

For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6 (H_2O)_6$.

But all the compounds which fit into this formula may not be classified as carbohydrates.

For example acetic acid (CH_3COOH) fits into this general formula, $C_2 (H_2O)_2$ but is not a carbohydrate.

Chemically, the carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.

Some of the carbohydrates, which are sweet in taste, are also called sugars. The most common sugar, used in our homes is named as sucrose whereas the sugar present in milk is known as lactose. Carbohydrates are also called saccharides

Carbohydrates are classified on the basis of their behaviour on hydrolysis. They have been broadly divided into following three groups. (i) **Monosaccharides**: A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. About 20 monosaccharides are known to occur in nature. Some common examples are glucose, fructose, ribose, etc.

(ii) **Oligosaccharides**: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis.

For example, one molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose gives two molecules of only glucose.

(iii) **Polysaccharides**: Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc.

Polysaccharides are not sweet in taste, hence they are also called non-sugars.

The carbohydrates may also be classified as either reducing or nonreducing sugars.

All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars.

All monosaccharides whether aldose or ketose are reducing sugars.

Monosaccharides are further classified on the basis of number of carbon atoms and the functional group present in them.

If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose.

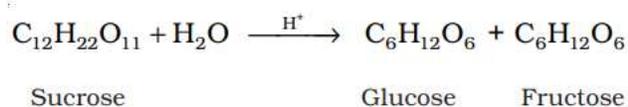
Carbon atoms	General term	Aldehyde	Ketone
3	Triose	Aldotriose	Ketotriose
4	Tetrose	Aldotetrose	Ketotetrose
5	Pentose	Aldopentose	Ketopentose
6	Hexose	Aldohexose	Ketohexose
7	Heptose	Aldoheptose	Ketoheptose

GLUCOSE :

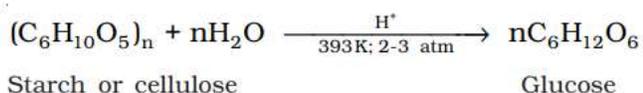
Different Types of Monosaccharides Glucose occurs freely in nature as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts.

It is prepared as follows:

1. From sucrose (Cane sugar): If sucrose is boiled with dilute HCl or H₂SO₄ in alcoholic solution, glucose and fructose are obtained in equal amounts.

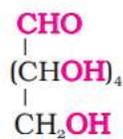


2. From starch: Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute H₂SO₄ at 393 K under pressure.



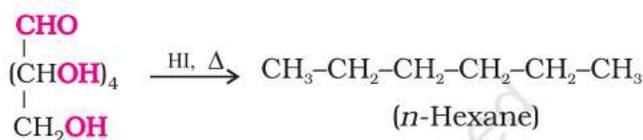
STRUCTURE OF GLUCOSE :

1. Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. It is probably the most abundant organic compound on earth.
2. It was assigned the structure given below on the basis of the following evidences:

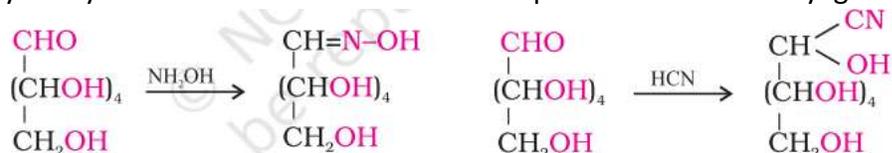


Glucose

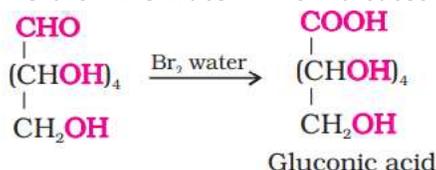
3. Its molecular formula was found to be C₆H₁₂O₆.
4. On prolonged heating with HI, it forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.



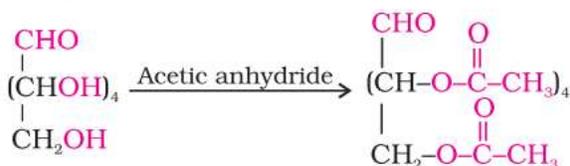
5. Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a carbonyl group (>C = O) in glucose.



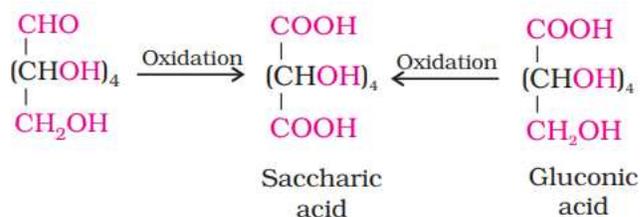
6. Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group.



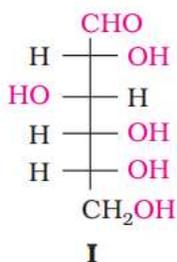
7. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five -OH groups. Since it exists as a stable compound, five -OH groups should be attached to different carbon atoms.



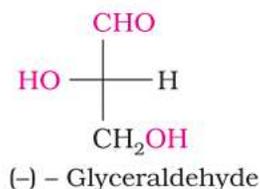
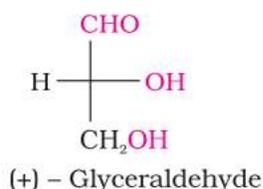
8. On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (-OH) group in glucose.



9. The exact spatial arrangement of different -OH groups was given by Fischer after studying many other properties.



10. Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule.

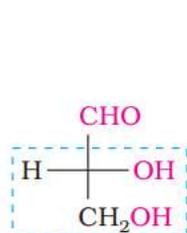


11. Glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms .

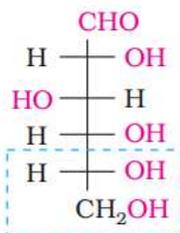
12. (+) Isomer of glyceraldehyde has 'D' configuration.

the -OH group lies on right hand side in the structure. All those compounds which can be chemically correlated to D (+) isomer of glyceraldehyde are said to have D configuration

13. whereas those which can be correlated to 'L' (-) isomer of glyceraldehyde are said to have L— configuration. In L (-) isomer -OH group is on left hand side as you can see in the structure.



D- (+) - Glyceraldehyde



D-(+) - Glucose

CYCLIC STRUCTURE OF GLUCOSE

1. The structure (I) of glucose explained most of its properties but the following reactions and facts could not be explained by this structure.

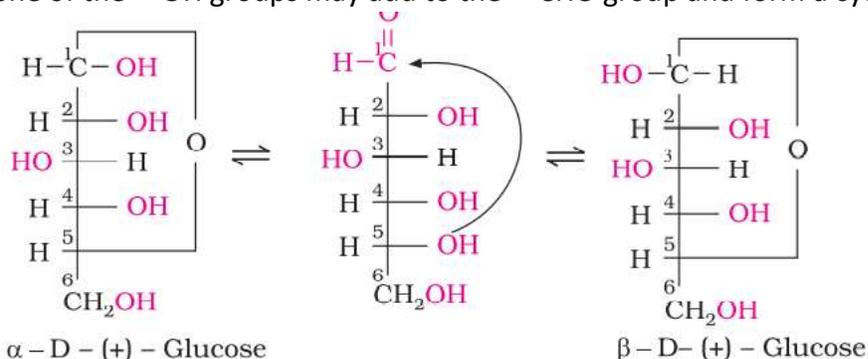
1. Despite having the aldehyde group, glucose does not give Schiff's test and it does not form the hydrogensulphite addition product with NaHSO₃ .

2. The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free — CHO group.

3. Glucose is found to exist in two different crystalline forms which are named as α and β.

The α-form of glucose (m.p. 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K while the β-form (m.p. 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

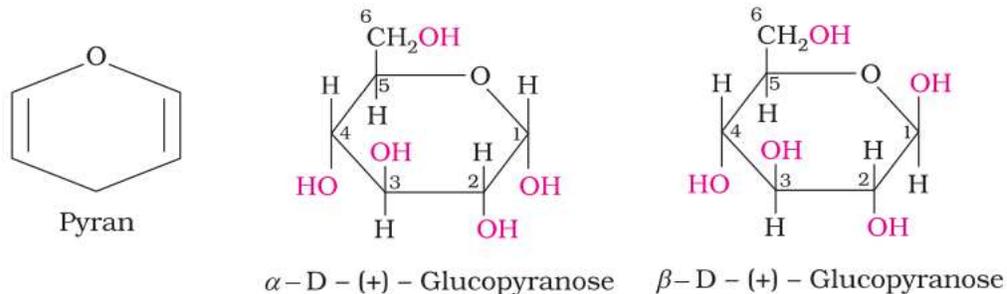
This behaviour could not be explained by the open chain structure (I) for glucose. It was proposed that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure.



These two cyclic forms exist in equilibrium with open chain structure. The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called **anomeric carbon** Cyclic

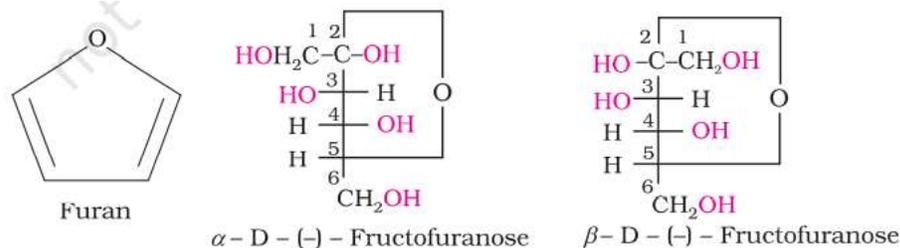
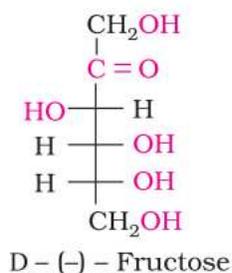
Structure of Glucose (the aldehyde carbon before cyclisation). **Such isomers, i.e., α -form and β -form, are called anomers.**

The six membered cyclic structure of glucose is called pyranose structure (α - or β -), in analogy with pyran. Pyran is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.

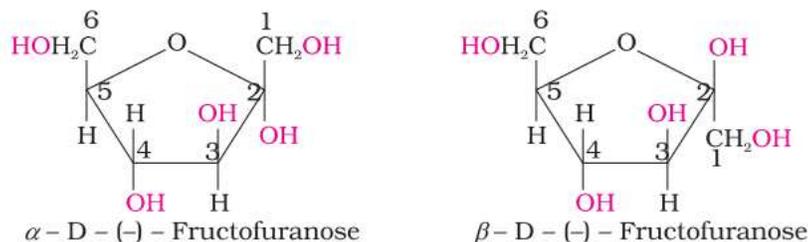


FRUCTOSE

Fructose is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose. It is a natural monosaccharide found in fruits, honey and vegetables. In its pure form it is used as a sweetener. It is also an important ketohexose. Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2



The cyclic structures of two anomers of fructose are represented by Haworth structures as given.



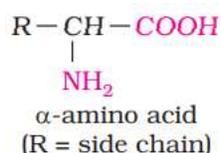
FRUCTOSE is a laevorotatory compound. It is appropriately written as D-(-)-fructose.

- **Proteins** -Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins.
- **Nucleic Acids:** DNA and RNA.

Proteins are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc. They occur in every part of the body and form the fundamental basis of structure and functions of life. They are also required for growth and maintenance of body.

All proteins are polymers of α -amino acids. Amino acids contain amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) functional groups.

Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α , β , γ , δ and so on. Only α -amino acids are obtained on hydrolysis of proteins.



Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule.

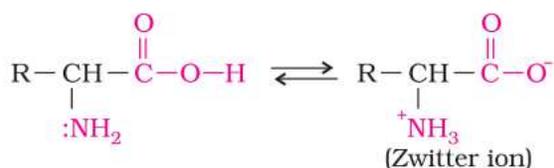
1. Equal number of amino and carboxyl groups makes it neutral;
2. more number of amino than carboxyl groups makes it basic and
3. more carboxyl groups as compared to amino groups makes it acidic.

A) The amino acids, which can be synthesised in the body, are known as nonessential amino acids.

B) On the other hand, those which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids

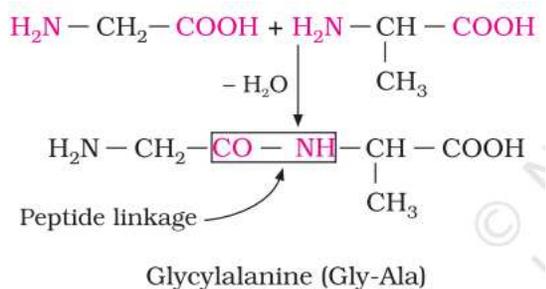
Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule.

In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known **as zwitter ion**. This is neutral but contains both positive and negative charges.



In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases. Except glycine, all other naturally occurring α -amino acids are optically active, since the α -carbon atom is asymmetric. These exist both in 'D' and 'L' forms. Most naturally occurring amino acids have L-configuration. L-Aminoacids are represented by writing the $-\text{NH}_2$ group on left hand side.

proteins are the polymers of α -amino acids and they are connected to each other by peptide bond or peptide linkage. Chemically, **peptide linkage** is an amide formed between $-\text{COOH}$ group and $-\text{NH}_2$ group.



The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond $-\text{CO}-\text{NH}-$. The product of the reaction is called a dipeptide because it is made up of two amino acids.

For example, when carboxyl group of glycine combines with the amino group of alanine we get a dipeptide, glycylalanine.

If a third amino acid combines to a dipeptide, the product is called a tripeptide. A tripeptide contains three amino acids linked by two peptide linkages

. Similarly when four, five or six amino acids are linked, the respective products are known as tetrapeptide, pentapeptide or hexapeptide, respectively.

When the number of such amino acids is more than ten, then the products are called polypeptides.

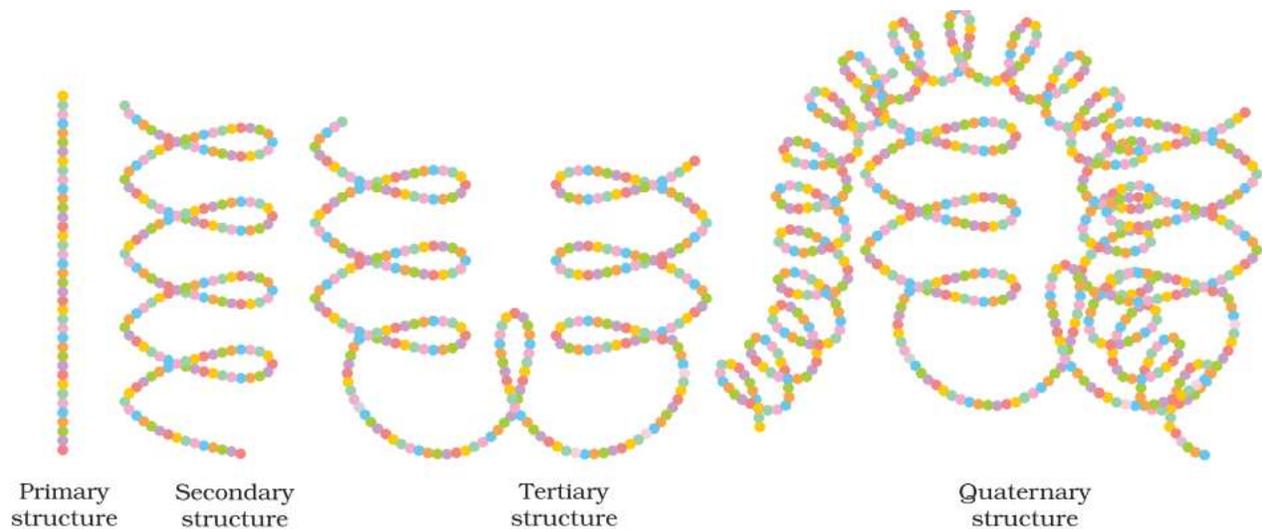
A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein.

Proteins can be classified into two types on the basis of their molecular shape.

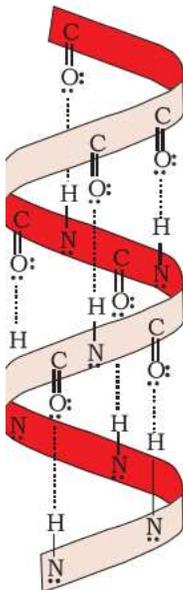
(a) Fibrous proteins When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common examples are keratin (present in hair, wool, silk) and myosin (present in muscles), etc.

(b) Globular proteins This structure results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

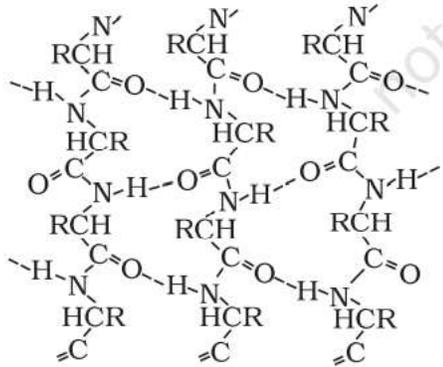
Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary,



- (i) **Primary structure of proteins:** Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.
- (ii) **Secondary structure of proteins:** The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two different types of structures viz. α -helix and β -pleated sheet structure. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between and -NH- groups of the peptide bond.
- (iii) α -Helix is one of the most common ways in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the -NH group of each amino acid residue hydrogen bonded to the C O of an adjacent turn of the helix.



- (iv) In β -pleated sheet structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β -pleated sheet.



- (v) **Tertiary structure of proteins:** The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilise the 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
- (vi) **Quaternary structure of proteins:** Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.
- (vii) **Primary, secondary, tertiary and quaternary structures of haemoglobin**

DENATURATION OF PROTEIN

Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. During denaturation secondary and tertiary structures are destroyed but primary structure remains intact. The coagulation of egg white on boiling is a common example of denaturation. Another example is curdling of milk which is caused due to the formation of lactic acid by the bacteria present in milk.

ASSIGNMENT

1. Write the structure of the product obtained when glucose is oxidised with nitric acid. (All India 2012)
2. Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain. (All India 2012)
3. What are three types of RNA molecules which perform different functions? (Delhi 2013)
4. Mention one important function of nucleic acids in our body. (Comptt. All India 2013)
5. Explain what is meant by (Delhi 2009)
 - (i) a peptide linkage
6. What are essential and non-essential amino acids in human food? Give one example of each type. (Delhi 2009)
7. State clearly what are known as nucleosides and nucleotides. (Delhi 2009)
8. What is essentially the difference between a-form of glucose and p-form of glucose? Explain. (Delhi 2009)
9. Describe what you understand by primary structure and secondary structure of proteins. (Delhi 2009)
10. Name the bases present in RNA. Which one of these is not present in DNA? (Delhi 2009)
11. Write such reactions and facts about glucose
12. which cannot be explained by its open chain structure. (All India 2009) Write down the structures and names of the products formed when D-glucose is treated with
 - (i) Hydroxylamine
 - (ii) Acetic anhydride. (Comptt. All India 2012)
13. Write down the structures and names of the products formed when D-glucose is treated with
 - (i) Bromine water
 - (ii) Hydrogen Iodide (Prolonged heating). (Comptt. All India 2012)
14. Amino acids may be acidic, alkaline or neutral. How does this happen? What are essential and non-essential amino acids? Name one of each type.
15. Differentiate between fibrous proteins and globular proteins. What is meant by the denaturation of a protein? (All India 2010)