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UNIT - 3

S.SHANMUGAM *P - BLOCK ELEMENTS - II* **St.John's M.H.S.S porur Ch -116**

1. What is inert pair effect?

In heavier post-transition metals, the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding, which is known as inert pair effect. This effect is also observed in groups 14, 15 and 16.

2. Chalcogens belongs to p-block. Give reason.

i) The chalcogens are the first group in the p block to have no stable metallic elements.

ii) All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can even be described as a semimetal.

iii) As in groups 14 and 15, the lightest element of group 16, oxygen, is found in nature as the free element.

3. Explain why fluorine always exhibit an oxidation state of -1?

1.fluorine the most electronegative element, also behaves quiet differently compared to the rest of the members of group

2. Absence of d orbitals in their valance shell

3. The fluorine is the strongest oxidising agent and the most reactive element among the halogens.

4. Give the oxidation state of halogen in the following.

a) OF_2 **b) O_2F_2** **c) Cl_2O_3** **d) I_2O_4**

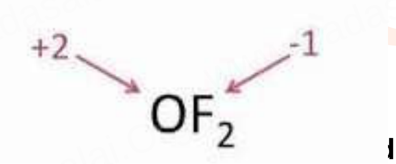
Fluorine shows only -1 oxidation state

a) OF_2

$2 + 2x = 0$

$2x = -2$

$x = -1$



b) O_2F_2

$2(1) + 2x = 0$

$2 - 2x = 0$

$2x = -2$, $X = -1$

c) Cl_2O_3

$2x + 3(-2) = 0$

$2x - 6 = 0$

$2x = 6$

$X = 3$

Oxidation state of Cl is +3

d) I_2O_4

$2x + 4(-2) = 0$

$2x - 8 = 0$

$2x = 8$

$X = 4$

Oxidation state of I is +4

5. What are interhalogen compounds? Give examples.

Each halogen combines with other halogens to form a series of compounds called inter halogen compounds.

A is less electronegative than B.

AB type - ClF, BrF

AB_3 type -BrF_3

AB_5 type - IF_5

AB_7 type - IF_7

6 Why fluorine is more reactive than other halogens?

Fluorine is more reactive.

Due to very small size of F there is inter electronic repulsion in F_2

This is due to the low value of F-F bond dissociation energy.

Fluorine wants to get to a stable 10 electrons to be like Neon.

This is because the valence/bonding electrons are closer to the nucleus in Fluorine than they are Chlorine and others and thus more strongly attracted

Fluorine is most electronegative, thus it is most reactive.

7. Give the uses of helium.

i). Helium is used to provide inert atmosphere in electric arc welding of metals

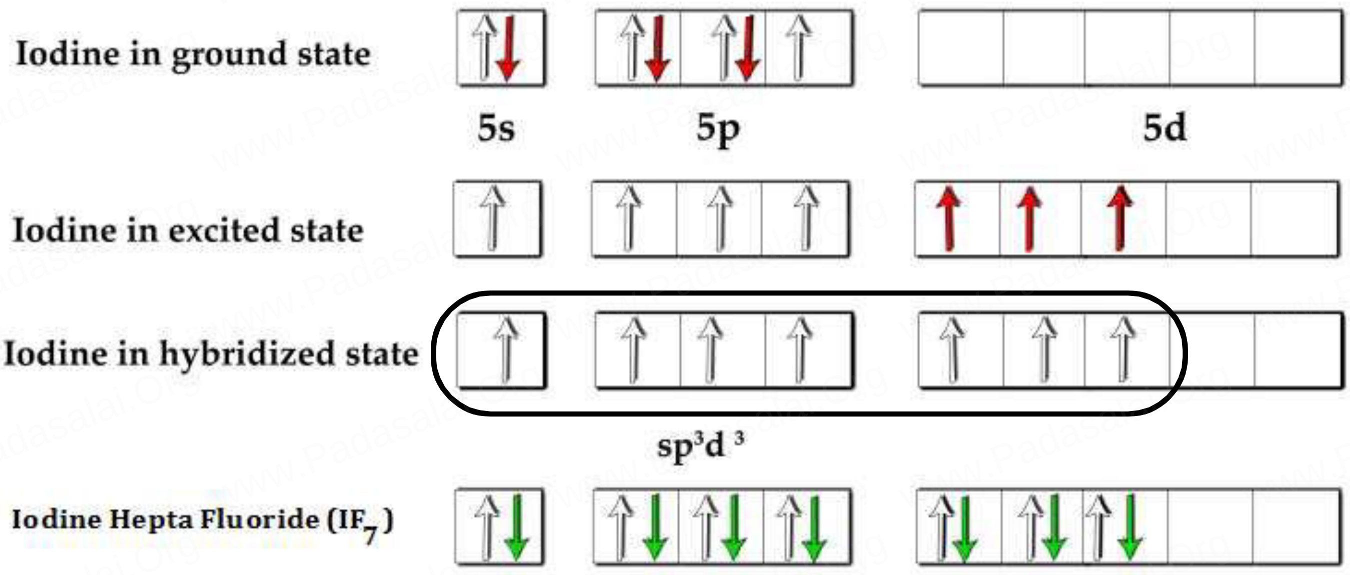
ii). Helium has lowest boiling point hence used in cryogenics (low temperature science).

iii) It is much less denser than air and hence used for filling air balloons

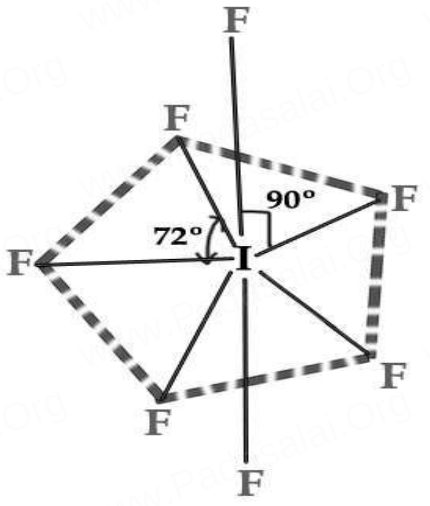
8. What is the hybridisation of iodine in IF_7? Give its structure.

Iodine atom undergoes sp^3d^3 hybridization to give 7 half filled sp^3d^3 hybrid orbitals in pentagonal bipyramidal symmetry. shape of IF_7 is pentagonal bipyramidal.

F - I - F bond angles in the pentagonal plane are equal to 72°



Geomentry of IF_7 is pentagonal bipyramidal.



9 Give the balanced equation for the reaction between chlorine with cold NaOH and hot NaOH.

i) Cold dilute alkali to give chloride and hypochlorite

$$2NaOH_{(aq)} + Cl_2 \rightarrow NaCl_{(aq)} + NaOCl + H_2O$$

ii) hot concentrated alkali to give chlorides and chlorates are formed.

$$6NaOH_{(aq)} + 3Cl_2 \rightarrow 5\,NaCl_{(aq)} + NaClO_3\,(aq) + 3H_2O\,(l)$$

10. How will you prepare chlorine in the laboratory?

Chlorine can also be prepared by dripping concentrated hydrochloric acid on $KMnO_4$ crystals:

$$2KMnO_4 + 16HCl \rightarrow 2\,KCl + 2\,MnCl_2 + 8H_2O + 5Cl_2$$

11. Give the uses of sulphuric acid.

1. Sulphuric acid is used in the manufacture of fertilisers, ammonium sulphate and super phosphates and other chemicals such as hydrochloric acid, nitric acid etc...
2. It is used as a drying agent and also used in the preparation of pigments, explosives etc..

12. Give a reason to support that sulphuric acid is a dehydrating agent.

i) It is highly soluble in water and has strong affinity towards water and hence it can be used as a dehydrating agent .

ii) When dissolved in water, it forms mono ($H_2SO_4.H_2O$) and dihydrates ($H_2SO_4.2H_2O$) and the reaction is exothermic

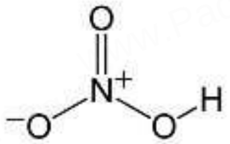
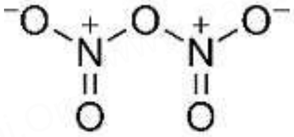
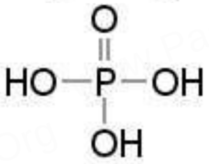
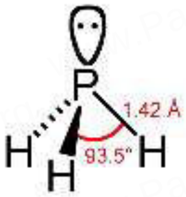
Example : $C_{12}H_{22}O11 + H_2SO_4 \rightarrow 12C + H_2SO_4.11H_2O$

13. Write the reason for the anamolous behaviour of Nitrogen.

i) Small size of N atom.
ii) High value of electronegativity of N atom and high ionization energy.
iii) Absence of d-orbitals in the valency shell.
iv) Tendency of form multipole bonds.
v) As a result the catenation tendency is weaker in nitrogen

14. Write the molecular formula and structural formula for the following molecules.

a) Nitric acid b) dinitrogen pentoxide c) phosphoric acid d) phosphine

Name	Molecular Formula	Structure
a) Nitric acid	HNO_3	
b) dinitrogen pentoxide	N_2O_5	
c) phosphoric acid	H_3PO_4	
d) phosphine	PH_3	

15. Give the uses of argon.

Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs

16. Write the valence shell electronic configuration of group-15 elements.

The general valence shell electronic set up of group fifteen elements is **ns^2, np^{1-6}**

17. Give two equations to illustrate the chemical behaviour of phosphine.

Basic nature: Phosphine is weakly basic and forms phosphonium salts with halogen acids.

$$PH_3 + HI \rightarrow PH_4I$$

Reducing property : Phosphine precipitates some metal from their salt solutions.

$$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$$

18. Give a reaction between nitric acid and a basic oxide.

Nitric acid react with zinc oxide to produce zinc nitrate and water.

$$2HNO_3 + ZnO \rightarrow Zn(NO_3)_2 + H_2O$$

Magnesium react with nitric acid to produce nitrate magnesium and water.

$$MgO + 2HNO_3 \rightarrow Mg((NO_3)_2 + H_2O$$

19. What happens when PCl_5 is heated?

$$PCl_{5(g)} \xrightarrow{\Delta} PCl_{3(g)} + Cl_{2(g)}$$

20. Suggest a reason why HF is a weak acid, whereas binary acids of the all other halogens are strong acids.

HF is the weakest acid because of it's strong H-F bond.
Fluorine being small in size overlaps better with 1s orbital of hydrogen leading to a strong bond.
Hence can not give proton easily.Here bond strength overweighs the electronegativity of F

21. Deduce the oxidation number of oxygen in hypofluorous acid – HOF.

H - O - F **+1 + x - 1= 0 , x =0**

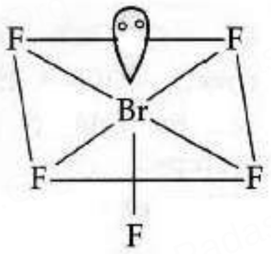
The oxidation state of the oxygen in hypofluorites is 0.
It is also the only hypohalous acid that can be isolated as a solid.

22. What type of hybridisation occur in a) BrF_5 b) BrF_3

b) BrF_5
Valence electron 7+ bonding electron 5 = 12

$$X = \frac{12}{2} = 6$$

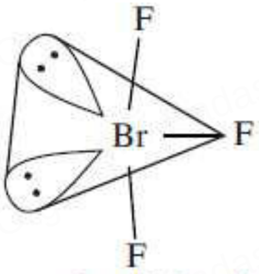
Hybridization : sp^3d^2
Geometry: Square Pyramidal



b) BrF3
Valence electron 7+ bonding electron 3 = 10

$$X = \frac{10}{2} = 5$$

Hybridization: sp^3d
Geometry: Trigonal Bipyramidal
Shape - T-shaped
lone pair - 2 **bond pair - 3**



Bent T–shaped

S.SHANMUGAM ,St.John's M.H.S.S porur Chennai -116 Mob: 9841945665

23. Complete the following reactions.

1. $NaCl + MnO_2 + H_2SO_4 \longrightarrow$
2. $NaNO_2 + HCl \longrightarrow$
3. $IO_3^- + I^- + H^+ \longrightarrow$
4. $I_2 + S_2O_3^{2-} \longrightarrow$
5. $P_4 + NaOH + H_2O \longrightarrow$
6. $AgNO_3 + PH_3 \longrightarrow$
7. $Mg + HNO_3 \longrightarrow$
8. $KClO_3 \xrightarrow{\Delta}$
9. $\underset{\text{Hot conc}}{Cu + H_2SO_4} \longrightarrow$
10. $Sb + Cl_2 \longrightarrow$
11. $HBr + H_2SO_4 \longrightarrow$
12. $XeF_6 + H_2O \longrightarrow$
13. $XeO_6^{4-} + Mn^{2+} + H^+ \longrightarrow$
14. $XeOF_4 + SiO_2 \longrightarrow$
15. $Xe + F_2 \xrightarrow[400^0C]{Ni / 200\ atm}$

Ans:

1. $4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow Cl_2 + MnCl_2 + 4NaHSO_4 + 2H_2O$
2. $NaNO_2 + HCl \longrightarrow NaCl + HNO_2$
3. $IO^{3-} + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$
4. $I_2 + 2\ S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$
5. $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$
6. $3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$
7. $4Mg + 10\ HNO_3 \longrightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

   If the acid is diluted we get N_2O

   $4Mg + 10\ HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O_5 + 5H_2O$
8. $2\ KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$
9. $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

   (Hot Conc.)
10. $2Sb + 3Cl_2 \longrightarrow 2SbCl_3$
11. $2HBr + H_2SO_4 \longrightarrow 2H_2O + Br_2 + SO_2$
12. $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
13. $5XeO_6^{4-} + 2\ Mn^{2+} + 14H^+ \longrightarrow 2MnO_4^- + 5XeO_3 + 7H_2O$
14. $2\ XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$
15. $Xe + F_2 \xrightarrow[400°C]{Ni /200\ atm} XeF_2$

TRANSITION AND INNER TRANSITION ELEMENTS

1. What are transition metals? Give four examples.

Transition elements that have incompletely filled d sub shell in the neutral or cationic state are called transition metals

Four examples.

First	**(3d) :**	**Ti , V , Cr , Fe**	**Second :**	**(4d)**	**Mo , Ru , Rh, pd**
Third	**(5d) :**	**W, Os ,Ir, Pt,**	**Fourth :**	**(6d)**	**Db , Sg, Bh, Ds**

2. Explain the oxidation states of 4d series elements.

al At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable

b) The oxidation states of **4d series elements** vary from

+3 for Y and + 2 to +8 for Ru , Cd for +2.

c) The highest oxidation state of **4d elements** are found in their compounds with the higher electronegative elements like O, F and Cl. for example: RuO_4, .

d) Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.

3. What are inner transition elements?

The last electron enters into (n - 2) f - orbital which is inner to the penultimate shell,they are also called inner transition elements.

In the inner transition elements there are two series of elements.

1) Lanthanoids (previously called lanthanides (57-71))

2) Actinoids (previously called actinides (89-103))

4. Justify the position of lanthanides and actinides in the periodic table.

The actual position of Lanthanoids in the periodic table is at group number 3 and period number 6. However, in the sixth period after lanthanum,

The electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties.

Therefore these elements are grouped together and placed at the bottom of the periodic table. This position can be justified as follows.

1. Lanthanoids have general electronic configuration [Xe] $4f^{1-14}$ $5d^{0-1}6s^2$
2. The common oxidation state of lanthanoides is +3
3. All these elements have similar physical and chemical properties.

5. What are actinides? Give three examples.

The fourteen elements following actinium ,i.e., from thorium (Th) to lawrentium (Lr) are called actinoids

Actinide - These are elements with atomic numbers from 90 to 103

Examples.

The 15 elements include: Actinium (Ac), Thorium (Th), Protactinium (Pa), Uranium (U),

6 Why Gd $^{3+}$ is colourless?

The At.No of Gd is 64. EC is (Xe) $4f^7\ 5d^1\ 6s^2$. In Gd $^{+3}$, they have exactly half filled f-orbitals

Hence (Xe) $4f^7 5d^0\ 6s^0$. Due to this it is colourless.

7. Explain why compounds of Cu^{2+} are coloured but those of Zn^{2+} are colourless.

1) Zn^{2+} ion has all paired electrons (configuration [Ar] $3d^{10}$)

Cu^{2+} ion has an **unpaired electron** (its configuration is [Ar] $3d^9$)

2) i) In case of Zn^{2+} ion **fully filled** d orbital is present therefore no d-d transition can be possible in this case and it is colorless.

ii) In case of Cu^{2+} ion because of d-d transition electrons emits light in the visible range and hence they are colored compounds

8. Describe the preparation of potassium dichromate.

Potassium dichromate is prepared from chromate ore. The ore is concentrated by gravity separation

i) Conversion of Chromate ore into Sodium chromate

$$4FeCr_2O_3 + 8Na_2CO_3 + 7O_2 \xrightarrow{900\text{-}1000^oC} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

ii) Conversion of Sodium chromate into Sodium di chromate

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

iii) Conversion of Sodium di chromate into Potassium dichromate

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$$

9. What is lanthanide contraction and what are the effects of lanthanide contraction?

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increse in atomic number. This decrese in ionic size is called lanthanoid contraction.

A. Basicity differences

As we from Ce^{3+} to Lu^{3+} , the basic character of Ln^{3+} ions decrease. Due to the decrease in the size of Ln^{3+} ions, the ionic character of Ln - OH bond decreases (covalent character increases) which results in the decrease in the basicity.

B. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

10. complete the following

a) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

b) $C_6H_5CH_3 \xrightarrow{KMnO_4/H^+} C_6H_5\text{-}COOH$

c) $MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \rightarrow Mn^{2+} + 5\,Fe^{3+} + 4H_2O$

d) $KMnO_4 \xrightarrow{\text{Red hot}\,/\,\Delta} K_2MnO_4 + MnO_2 + O_2$

e) $Cr_2O_7^{2-} + 6\,I^- + 14\,H^+ \rightarrow 2Cr^{3+} + 3\,I_2 + 7H_2O$

f) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2\,NaCl$

11. What are interstitial compounds?

An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen carbon or nitrogen are trapped in the interstitial holes in a metal lattice .

Example :TiC, $ZrH_{1.92}$, Mn_4N etc

12. Calculate the number of unpaired electrons in Ti^{3+} , Mn^{2+} and calculate the spin only magnetic moment.

ion	configuration	n	$\mu_s = \sqrt{n(n+2)}\ \mu_B$	μ_s (observed)
Ti^{3+}	d^1	1	$\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73\ \mu_B$	paramagnetic
Mn^{2+}	d^5	5	$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.91\ \mu_B$	paramagnetic

13. Write the electronic configuration of Ce^{4+} and Co^{2+}.

i) **configuration of** Ce^{4+} $[Xe_{54}]\ 4f^0\ 5d^0\ 6s^0$

ii) **configuration of** Co^{2+} $[Ar_{18}]\ 3d^7 4s^0$

14. Explain briefly how +2 states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

i) All the metals display +2 oxidation states except Sc.

ii) On moving from the Sc to the Mn, the atomic numbers increase from 21 to the 25.

iii) It means the number of electrons in the 3d-orbital also increases from 1 to 5.

Sc (+2) = d^1,

Ti (+2) = d^2,

V (+2) = d^3,

Cr (+2) = d^4

and Mn (+2) = d^5.

iv) The +2 oxidation state is achieved by loss of the two 4s electrons by the metals.Since the number of d electrons in (+2) state also increases from Ti(+2) to Mn(+2), the stability of +2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has d^5 electrons

15. Which is more stable? Fe3+ or Fe2+ - explain.

Fe^{3+} ion is more stable due to its half-filled 3d5 electron configuration.

As half filled and completely filled shells are more stable Fe^{3+} ion is more stable.

While Fe^{2+} ion is partially filled d sub shell ($3d^6$) in not stable.Hence, Fe^{3+} is more stable than Fe^{2+}.

16. Explain the variation in $E^o_{M3+/\ M2+}$ /3d series.

ii) In 3d series as we move from Ti to Zn, the standard reduction potential **($E^o_{M3+/\ M2+}$**) value is approaching towards less negative value and copper has a positive reduction potential.ie elemental copper is more stable than Cu^{2+}.

ii) In the general trend, **($E^\circ_{M3+/\,M2+}$)**

The value for manganese and zinc are more negative than the regular trend. It is due to extra stability which arises due to the half filled d^5 configuration in $Mn^{2+}$and completely filled d^{10} configurationin Zn^{2+}.

iii) Transition metals in their high oxidation states tend to be oxidizing . For example, Fe^{3+} is moderately a strong oxidant, and it oxidises copper to Cu^{2+} ions.

The feasibility of the reaction is predicted from the following standard electrode potential values.

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}$ $E^0 = 0.77\ V$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^0 = +0.34\ V$

iv) The standard electrode potential for the **($E^\circ_{M3+/\,M2+}$**) half-cell gives the relative stability between M^{3+} and M^{2+}.

i) $Ti^{3+} + e^- \rightarrow Ti^{2+}$ Standard reduction potential = - 0.37 V

ii) $V^{3+} + e^- \rightarrow V^{2+}$ Standard reduction potential = - 0.26 V

iii) $Cr^{3+} + e^- \rightarrow Cr^{2+}$ Standard reduction potential = - 0.41 V

v) The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred. If we want to reduce such a stable Cr^{3+} ion, strong reducing agent which has high negative value for reduction potential like metallic zinc . (E^0= -0.76 V) is required.

eg) The high reduction potential of **M3+/ M2+** indicates Mn^{2+} is more stable than Mn^{3+}.

$Mn^{2+} + 2e^- \rightarrow Mn$ $E^\circ_{Mn^{2+}/Mn} = -1.18\ V$

$Mn^{3+} + e^- \rightarrow Mn^{2+}$ $E^\circ_{Mn^{3+}/Mn^{2+}} = +1.51\ V$

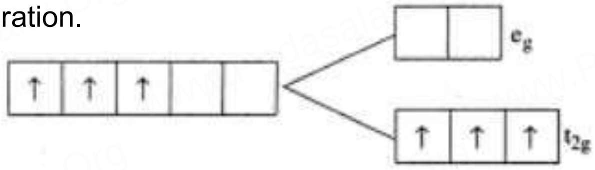
Mn^{3+} has a $3d^4$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a half filled d sub shell makes the reduction of Mn^{3+} very feasible (E^0 = +1.51V). .

17. Compare lanthanides and actinides.

1 Differentiating electron eneters in 4f orbital	Differentiating electron eneters in 5f orbital
2 Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3 They show less tendency to form complexes	They show greater tendency to form complexes
4 Most of the lanthanoids are colourless	Most of the actinoids are coloured. eg) U^{3+}(red),U^{4+}(green) ,UO_2^{2+} (yellow)
5 They do not form oxo cations	They do form oxo cations such as UO_2^{2+} O_2^{2+},etc

18. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

Cr^{2+} is strongly reducing in nature. It has a d4configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3configuration can be written as $t_{2}g^3$ configuration, which is a more stable configuration.



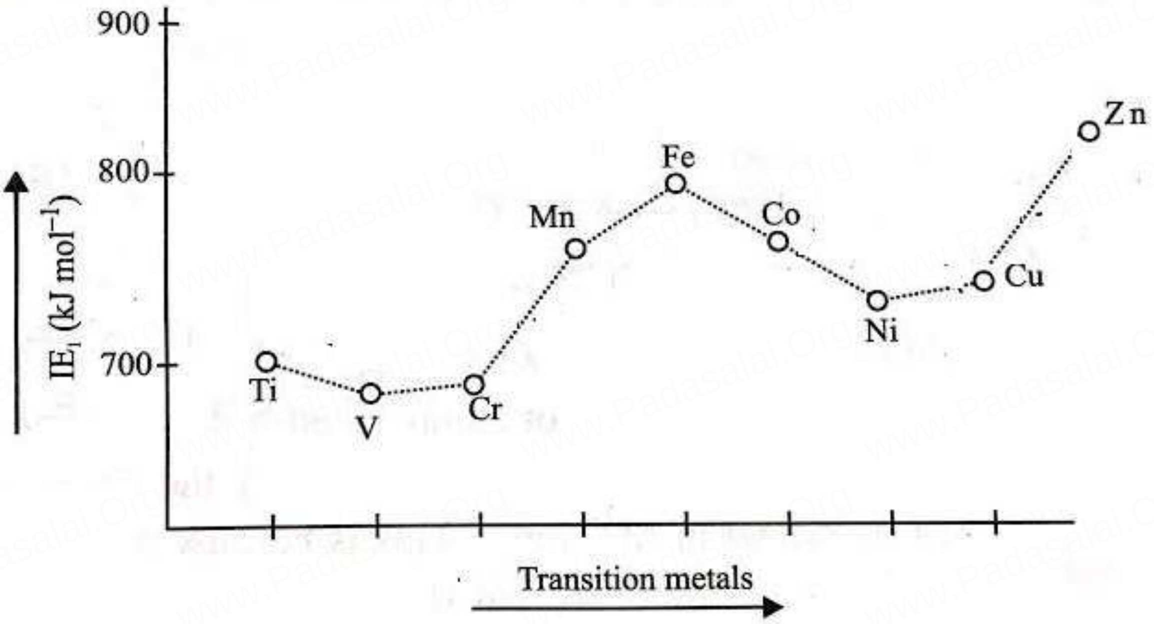
In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d-orbital and has an extra-stability.

19. **Compare the ionization enthalpies of first series of the transition elements.**

1) As we move from left to right in a transition metal series, the ionization enthalpy increases as expected. This is due to increase in nuclear charge corresponding to the filling of d electrons.

2) The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.

3) The added electron enters (n-1)d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values



4) Chromium has low first ionization enthalpy because lose one electron gives stable configuration ($3d^5$)

While Zinc has very high ionization enthalpy because electron has to be removed from 4s orbitals.

20. **Actinoid contraction is greater from element to element than the lanthanoid contraction, why?**

i) In actinoids, 5f orbitals are filled. These 5f orbitals have a poorer shielding effect than 4f orbitals (in lanthanoids).

ii) Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more that than experienced by lanthanoids.

iii) Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

21. Out of $Lu(OH)_3$ and $La(OH)_3$ which is more basic and why?

$La(OH)_3$ is most basic and $Lu(OH)_3$ is least basic. Due to lanthanide contraction. As the size of lanthanide ions decreses from La^{3+} to Lu^{3+} , the covalent character of the hydroxides increases and hence the basic strength decreases.

22. Why europium (II) is more stable than Cerium (II)?

i) Europium (II) is more stable trhan Cerium (II) As we from left to right, effective nuclear charge increases due to which lanthanide contraction takes place. The inert pair effect becomes more dominative.

ii) In Eu^{2+}, 4f sub shell is half filled and Ce^{2+}, 4f and 5d sub shells are partially filled.so, Eu(II) more stable than Ce(II)

23. Why do zirconium and Hafnium exhibit similar properties?

Zr and Hf exhibit similar properties due to lanthanoid contraction.

Electrons present in f subshell didn't do good shielding due to which with the increasing atomic number or increasing effective nuclear charge size gets constricted .

The size of Halfenium and Zirconium becomes almost equal.

4d series	**Zr**	**145 pm**
5d Series	**Hf**	**144 pm**

24. Which is stronger reducing agent Cr^{2+} or Fe^{2+}?

Cr^{2+} is a stronger reducing agent than Fe^{2+}.

This can be explained on the basis of the standard electrode potential values

$$E^\circ(Cr^{3+}/Cr^{2+} = -0.41\ V) \quad \text{and} \quad E^\circ\ (Fe^{3+}/Fe^{2+} = +\ 0.77\ V).$$

Thus Cr^{2+} is easily oxidised to Cr^{3+} but Fe^{2+} cannot be as readily oxidised to Fe^{3+}.

25. The $E^0_{M2+\ /M}$ value for copper is positive. Suggest a possible reason for this.

1. Sublimation energy:
The energy needed to convert one mole of atoms from a solid state to gaseous state.

2. Ionization energy:

The energy supplied to remove electrons from one mole of atoms, which are in the gaseous state.

3. Hydration energy:

The energy emitted to hydrate one mole of ions.

Now,Copper has a high energy of atomization and low hydration energy. Hence, the $E^0(M^{2+}/M)$ value for copper is positive.

26. predict which of the following will be coloured in aqueous solution Ti^{2+} , V^{3+} , Cu^+ ,Sc^{3+}, Fe^{3+}, Ni^{2+} and Co^{3+}

A transition metal ion in coloured if it has one or more unpaired electron in (n-1)d orbitals i.e. 3d orbitals in case of first transition series.When such species are exposed to visible radiation, d-d transition can take place.

(It does not contain unpaired electron in 3d orbitals so it is colourless)

ion	**configuration**	**colour**
Ti^{2+}	$3d^1 4s^0$	Violet
V^{3+}	$3d^2 4s^0$	Green
Cu+	$3d^{10}\ 4s^0$	colourless
Sc^{3+}	$3d^0 4s^0$	colourless
Fe^{3+}	$3d^5 4s^0$	brown to yellow
Ni^{2+}	$3d^8 4s^0$	green
Co^{3+}	$3d^6 4s^0$	blue

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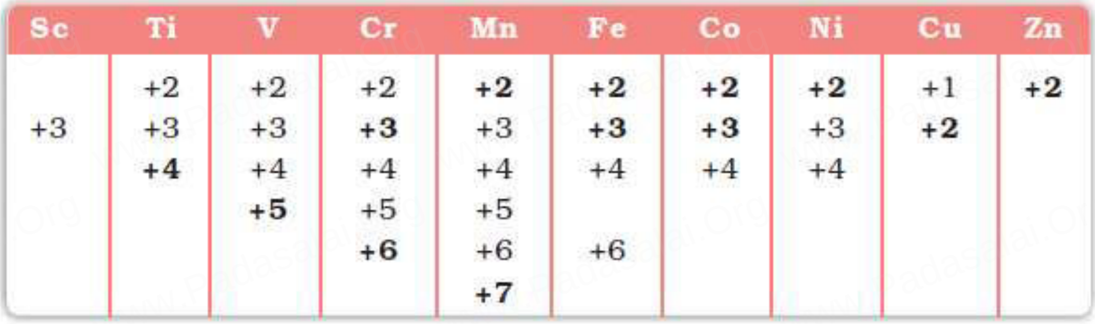
27. Describe the variable oxidation state of 3d series elements.

The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small .

At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable

For example, the first element Sc has only one oxidation state +3; the middle element Mn has six different oxidation states from +2 to +7. The last element Cu shows +1 and +2 oxidation states only.

Oxidation States of the first row Transition Metals
(the most common ones are in bold types)



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					

The relative stability of different oxidation states of 3d metals is correlated with the extra stability of half filled and fully filled electronic configurations. Example: Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^4$)

28. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

Cu is the only metal in the first transition series (3d series) which shows +1 oxidation state most frequently. This is because the electronic configuration of Cu is 3d10 4s1 and after losing one electron it acquires a stable 3d10 configuration.

29. Why first ionization enthalpy of chromium is lower than that of zinc?

The electronic configuration of Zn and Cr is given below :

Cr = [Ar] $3d^5 4s^1$ Zn = [Ar] $3d^{10} 4s^2$.

First ionisation enthalpy of Cr is lower than that of Zinc because in case of zinc first electron has to be remove from fulfilled orbital and full filled electronic configuration is most stable so it require high energy to remove electron from it. While in case of Chromium electron is easily removed from half filled orbital with less amount of energy.

30. Transition metals show high melting points why?

a) The melting-points of the transition metals are high due to the 3d electrons being available for metallic bonding.

b) This strength of the bond is due to the presence of unpaired or delocalized electrons in the outermost shell of the atom

c)The enthalpies of atomization and the densities of transition elements are also high that leads to high boiling and melting points.

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UNIT- 5
COORDINATION CHEMISTRY

1. Write the IUPAC names for the following complexes.

i) $Na_2[Ni(EDTA)]$ ii) $[Ag(CN)_2]^-$ iii) $[Co(en)_3]_2(SO_4)_3$
iv)$[Co(ONO)(NH_3)_5]^{2+}$ v) $[Pt(NH_3)_2Cl(NO_2)]$

Ans:

i) $Na_2[Ni(EDTA)]$ - Sodium 2,2',2'',2'''-(ethane-1,2- diamminetetraacetate)nickelate(II)

ii) $[Ag(CN)_2]^-$ - Dicyanidoargentate(I) ion

iii) $[Co(en)_3]_2(SO_4)_3$ - tris (ethylenediamine)cobalt(III)sulphate.

iv) $[Co(ONO)(NH_3)_5]^{2+}$ - pentaammine (nitrito κ -O) cabalt (III) sulphate

v) $[Pt(NH_3)_2Cl(NO_2)]$ - diamminechloridonitrito κ -N- platinum(II)

2. Write the formula for the following coordination compounds.

a) potassiumhexacyanidoferrate(II) - $K_4[Fe(CN)_6]$

b) pentacarbonyliron(0) - $[Fe(CO)_5]$

c) pentaamminenitrito -N-cobalt(III)ion - $[Co(NH_3)_5NO_2]^{2+}$

d) hexaamminecobalt(III)sulphate - $[Co(NH_3)_6]_2(SO_4)_3$

e) sodiumtetrafluoridodihydroxidochromate(III) - $Na_3[Cr(F)_4(OH)_2]$

3. Arrange the following in order of increasing molar conductivity

i) $Mg\,[Cr(NH_3)(Cl)_5]$ ii) $[\,Cr(NH_3)Cl\,]_3[CoF_6]_2$ iii) $[\,Cr(NH_3)_3Cl_3\,]$

i) $Mg\,[Cr(NH_3)(Cl)_5] \rightarrow Mg^{2+} + [Cr(NH_3)(Cl)_5]^{2-}$ Total no of ions = 2

ii) $[\,Cr(NH_3)Cl\,]_3[CoF_6]_2 \rightarrow 3[Cr(NH_3)_5Cl]^{2+} + 2[CoF_6]^{3-}$ Total no of ions = 5

iii) $[\,Cr(NH_3)_3Cl_3\,] \rightarrow$ no dissociation occurs Total no of ions = 0

More the number of ions given out by the complex on dissociation and their molar conductivity also increases

increasing order of molar conductivity

$[\,Cr(NH_3)_3Cl_3\,] < Mg\,[Cr(NH_3)(Cl)_5] < [\,Cr(NH_3)Cl\,]_3[CoF_6]_2$

4. Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction

Addition of an alcoholic solution of dimethylglyoxime to an ammoniacal solution of Ni(II) gives a rose-red precipitate, abbreviated **$Ni(dmg)_2$:**

$$[Ni(NH_3)_6]^{2+}{}_{(aq)} + 2(CH_3CNOH)_2(alc) \rightleftharpoons \mathbf{Ni[ONC(CH_3)C(CH_3)NOH]_2}(s) + 2NH_4^+{}_{(aq)} + 4NH_{3\,(aq)}$$

5. $[CuCl_4]^{2-}$ exists while $[Cu\,I_4]^{2-}$ does not exist why?

Both the species contains Cu^{2+} ions but only iodide ion (not chloride ion) reduces Cu^{2+} to cuprous iodide and I_2. Hence, $[CuI_4]^{2-}$ does not exist.

In [CuI4]2-complex iodide ion reduces Cu2+ to Cu+ therefore the complex is unstable.

so , $2CuI_2 \rightarrow Cu_2I_2 + I_2$

6 **Calculate the ratio of $\frac{[Ag^+]}{[Ag(NH_3)_2]^+}$ in 0.2 M solution of NH_3. If the stability constant for the complex $[Ag(NH_3)_2]^+$ is 1.7 x10^7**

$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ **(β)** = 1.7 x10^7 , $[NH_3]$= 0.2M

i) (β) = $\frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$, $\frac{[Ag(NH_3)_2]^+}{[Ag^+]} = \beta \times [NH_3]^2 = 1.7\times10^7\ (0.2)^2 = 6.8\times10^5$

ii) $\frac{[Ag^+]}{[Ag(NH_3)_2]^+} = \frac{1}{\beta\,[NH_3]^2} = \frac{1}{6.8\times10^5} = 1.47\times10^{-5}$ **ratio =** 1.47×10^{-5}

7. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

Used in medicine

(1) Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning

(2) Cis-platin is used as an antitumor drug in cancer treatment.

Biologically important coordination compounds.

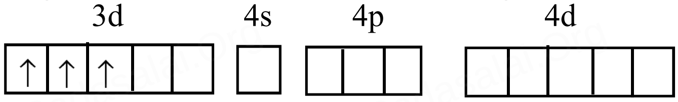
i) (RBC) is composed of heme group, which is Fe^{2+}- Porphyrin complex It plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.

ii) Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein

8. Based on VB theory explain why $[Cr(NH_3)_3]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ diamagnetic.

i) Cr is in the +3 oxidation state i.e., d^3 configuration. Also,

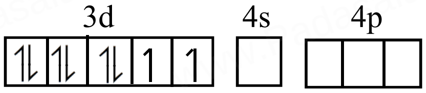
NH_3 is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.



Therefore, it undergoes d^2sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, **it is paramagnetic in nature.**

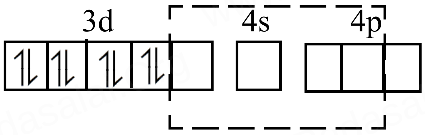
ii) In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state i.e., d^8 configuration.

Ni^{2+} ion



CN^- is a strong field ligand. It causes the pairing of the 3d orbital electrons.

Then, Ni^{2+} under goes dsp^2 hybridization.



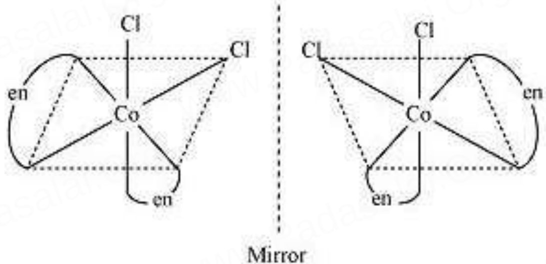
As there are **no unpaired electrons, it is diamagnetic.**

9. Draw all possible geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ and identify the optically active isomer.

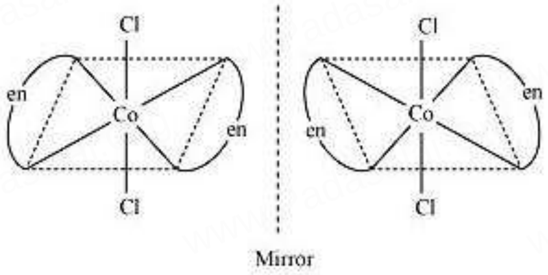
Cis - $[Co(en)_2Cl_2]^+$ is shows both geometrical as well as optical isomerism.

Its cis form is unsymmetrical,

cis- $[CoCl_2(en)_2]^+$



Cis-$[Co(en)_2Cl_2]^+$ - **optically active** [Non - superimposable mirror image]



trans- $[CoCl_2(en)_2]^+$

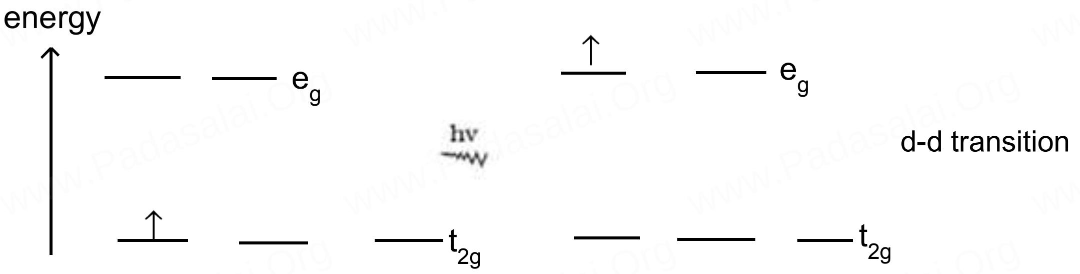
trans-$[Co(en)_2Cl_2]^+$ is symmetrical because it contains a **plane of symmetry**

Hence,***optically in active***

In total , Three isomers are possible

10. $[Ti(H_2O)_6]^{3+}$ is coloured, while $[Sc(H_2O)_6]^{3+}$ is colourless- explain .

i) $[Ti(H_2O)_6]^{3+}$ is coloured because of configuration is Ti^{3+} - $3d^1$ $\boxed{\uparrow}\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$



has one unpaired electron for d-d transition, hence it is coloured

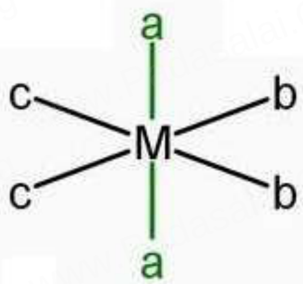
i) **$[Sc(H_2O)_6]^{3+}$ is colourless because of** configuration is Configuration Sc^{3+} - $3d^0$ $\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }\boxed{\ }$

No unpaired electron, so d-d transition is not possible hence it is not coloured

11. Give an example for complex of the type [$Ma_2b_2c_2$] where a, b, c are monodentate ligands and give the possible isomers.

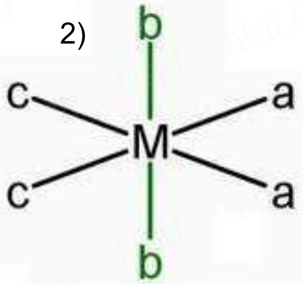
The combination are as follows for **[$Ma_2b_2c_2$] are (a,a)(b,b),(c,c)** - this means in the octahedral structure of the compound a lies directly opposite of **a** ,and **b** lies opposite of **b** , same followed for **c**. these are the five possible combination e**g) [$Cr((NH_3)_2(H_2O)_2(Br)_2]^+$**

1)



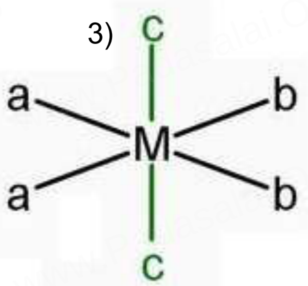
a-a trans

2)



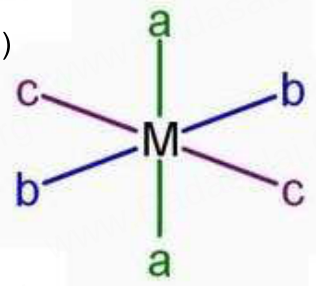
b-b trans

3)



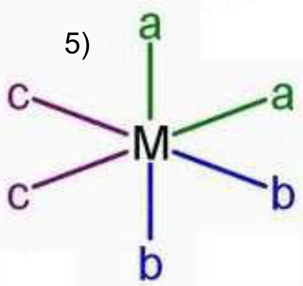
c-c trans

4)



all trans

5)



all cis

[$Ma_2b_2c_2$]
5 - Geometrical isomers

1. (a,a)(b,c)(b,c) -trans **2. (b,b) (a,c) (a,c) -trans** **3. (c,c) (a,b) (a,b)- trans**
4.(a,a)(b,b),(c,c) -all trans **5. (a,c)(a,b) (b,c) - all cis**

(5th , isomer - shows optical isomerism d and l form)

7- isomers out of which 5 are geometrical and 2 are optical isomers.

12. Give one test to differentiate [$Co(NH_3)_5Cl]SO_4$ and [$Co(NH_3)_5SO_4]Cl$.

This can be tested by using $AgNO_3$solution and $BaCl_2$

Barium chloride test

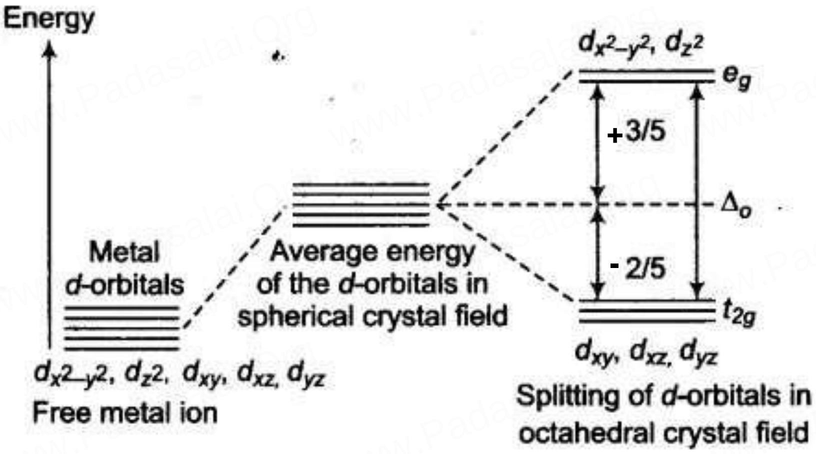
i) $[Co(NH_3)_5Cl]SO_{4(aq)} + BaCl_{2(aq)} \rightarrow BaSO_{4(ppt)}$ **ii)** $[Co(NH_3)_5(SO_4)]Cl_{(aq)} + BaCl_{2(aq)} \rightarrow$ no reaction

Silver nitrate test

i)$[Co(NH_3)_5Cl]SO_{4(aq)} + AgNO_{3(aq)} \rightarrow$ no reaction **ii)**$[Co(NH3)5(SO4)]Cl_{(aq)} + AgNO3_{(aq)} \rightarrow AgCl_{(ppt)}$

Hence they give different precipitates with different solutions. Thus they are ionisation isomers.

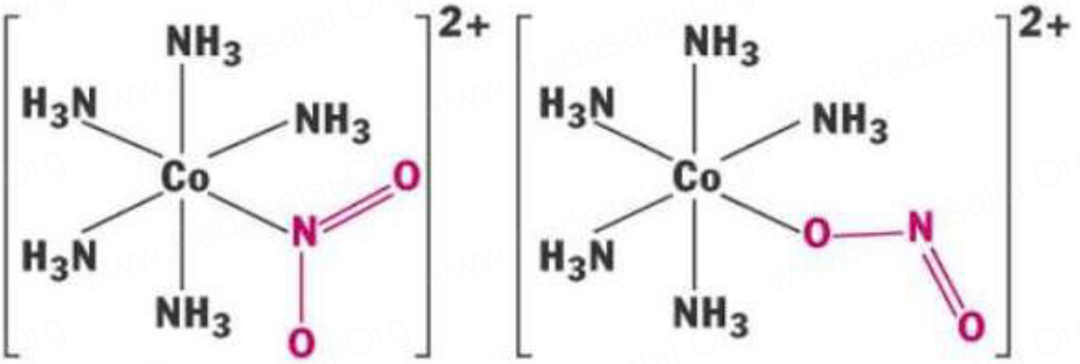
13. In an octahedral crystal field, draw the figure to show splitting of d orbitals.



14. What is linkage isomerism? Explain with an example.

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.

Example - $[Co(NH_3)_5(NO_2)]^{2+}$



Nitro Nitrito

15. Write briefly about the applications of coordination compounds in volumetric analysis.

a) Colour Tests :

Since many complexes are highly coloured they can be used as colourimetric reagents

e.g. formation of red 2,2'-bipyridyl and 1,10-phenanthroline complexes as a test for Fe^{2+}

b) Gravimetric Analysis : Here chelating ligands are often used to form insoluble complexes

e.g. $Ni(DMG)_2$ and $Al(oxine)_3$.

c) Complexometric Titrations and Masking Agents :

An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution,

e.g. Zn^{2+}, Pb^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+}.

Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

16. Classify the following ligand based on the number of donor atoms.

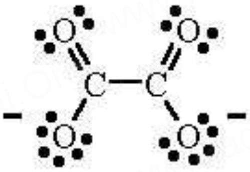
a) NH_3 b) en c) ox^{2-} d) triaminotriethylamine e) pyridine

a) $\ddot{N}H_3$ **- Monodentate** : The ligands which have only one donor atom.

b) en **- Bidentate ligands :** $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ **ethane-1,2-diamine**

Bidentate ligands have two lone pairs and both of which can bond to the central metal ion. Bidentate ligands may be neutral molecules or anions

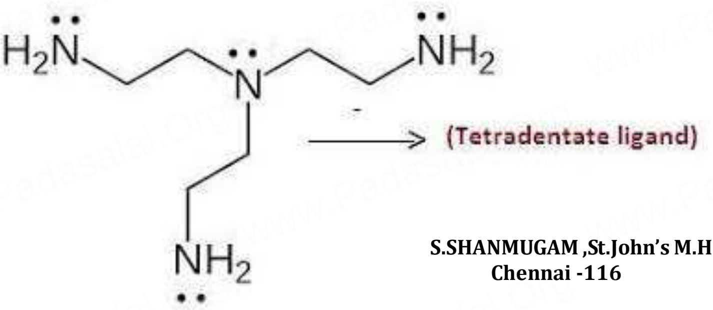
c) ox^{2-} **- Bidentate ligands**



oxalato

d) triaminotriethylamine - Tetradentate ligands :

Tetradentate ligands have two lone pairs and the four lone pair can bond to the central metal ion.



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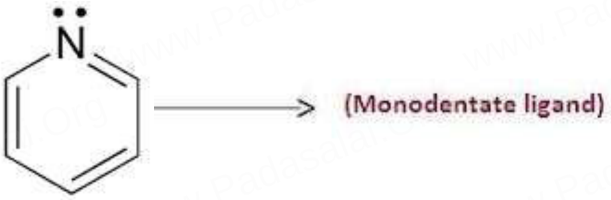
e) pyridine



17. Give the difference between double salts and coordination compounds.

i) **Double salts** are molecular compounds which are formed by the evoporation of solution containing 2 or more salts in stoichiometric proportions. They dissociate into their constituent ions in solution

eg: $K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$

ii) **A complex compound** is a compound formed from a lewis acid and a lewis base.

They do not dissociate into its constituent ions in solutions

eg: $Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$

$K_4[Fe(CN)_6]$ on dissociation gives $4K^+ + [Fe(CN)_6]^{4-}$ In $K_4[Fe(CN)_6]$ the individual components lose their identity. The metal of the complex ion is not free in solution unlike the metal in double salt solution.

18. Write the postulates of Werner's theory.

i) Most of the elements exhibit, two types of valence namely primary valence and secondary valence

ii) primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.

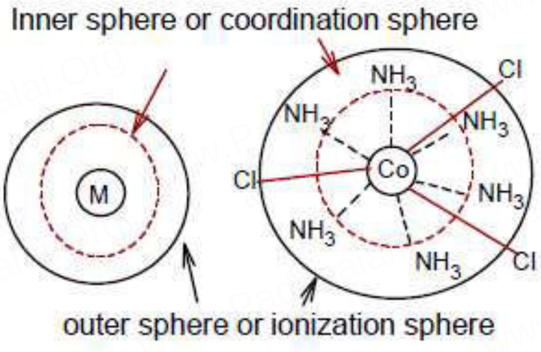
iii) The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions.

iv) The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these.

v) Two spheres of attraction around a metal atom/ion in a complex.

1) The inner sphere is known as coordination sphere

2) The outer sphere is called ionisation sphere.



two sphere of attraction of metal

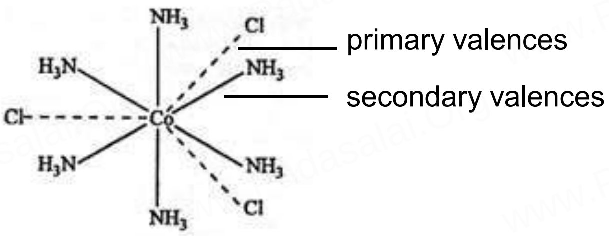
vi) i)The primary valences - non-directional

ii) Secondary valences - directional

vii) The geometry of the complex is determined by the spacial arrangement of the groups which satisfy the secondary valence.

6 - octahedral geometry. 4 -either tetrahedral or square planar geometry.

Werner's representation



CoCl₃.6NH₃ Complex

19. **$[Ni(CN)_4]^{2-}$ is diamagnetic, while $[Ni(Cl)_4]^{2-}$ is paramagnetic using crystal field theory?**

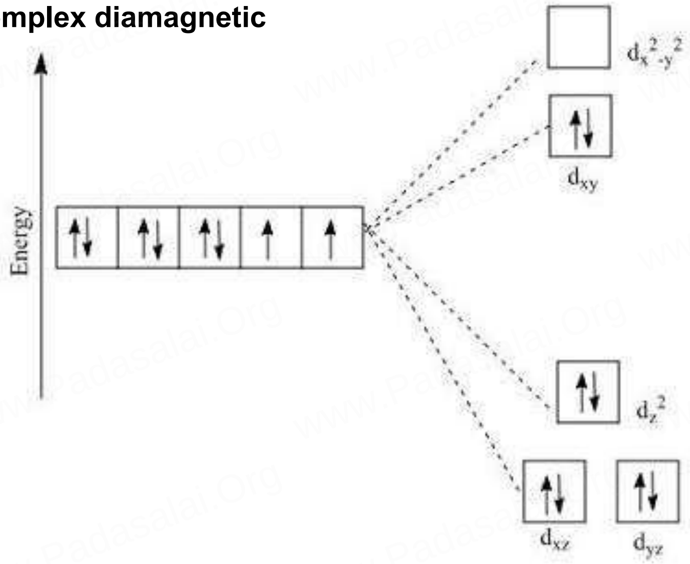
The $[Ni(CN)_4]^{2-}$ is a low-spin square planar complex, since it contains the strong-field CN– ligand in it.

The oxidation state number of Ni in the complex +2 and the electronic configuration of $Ni^{2+}$is $3d^8$.

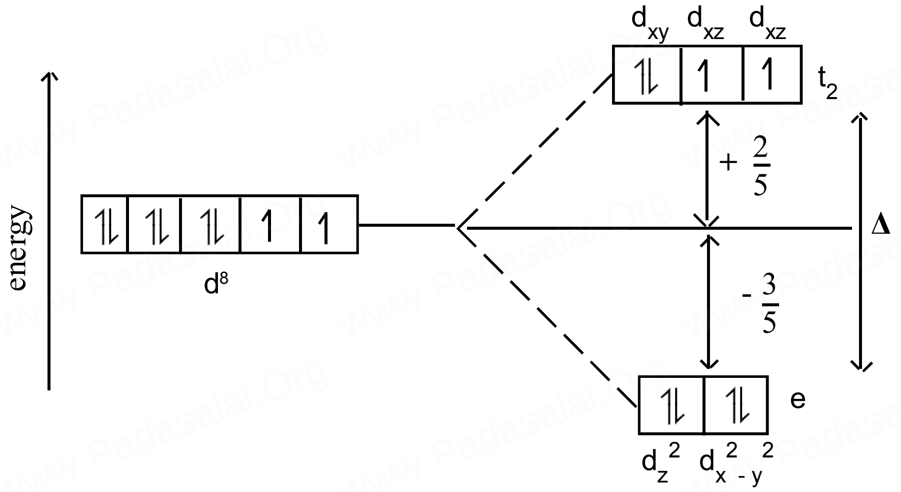
In the splitting pattern for a square-planar complex, the orbital possess the highest energy, followed by the dxy and orbitals. **The dxz and dyz are symmetrically equivalent.**

All the eight electrons will enter these five orbitals, such that no electron remains unpaired.

This makes the complex diamagnetic



[NiCl4]2-: Splitting in the tetrahedral field



8 electrons, but instead, high spin.
The d orbitals fill with

So, the dz^2 and dx^2-y^2 fill with one electron each, then the dxy, dxz, and dyz with one electron each, and then pairing occurs only after that, filling the dz^2, dx^2-y^2, and dxy completely. This leaves two unpaired electrons in the t2 orbitals, and thus this complex is **paramagnetic** with two unpaired electrons, as expected

20. Why tetrahedral complexes do not exhibit geometrical isomerism.

In tetrahedral complex metal atom or ion is at the Centre of a tetrahedron and four ligands are at four corners of tetrahedron this type of complex does not exhibit geometrical isomerism since all four ligands are at the equidistance having bond angle $109^o28'$

OR

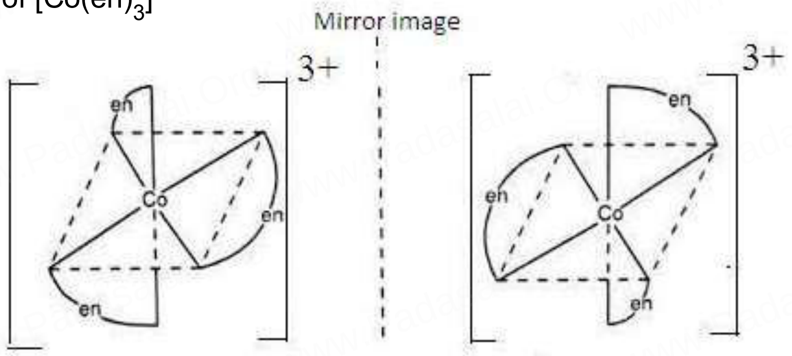
Tetrahedral complexes do not show geometrical isomerism because the relative positions of unidentate ligands attached to the central atom are same with respect to each other

21. Explain optical isomerism in coordination compounds with an example.

The pair of two optically active isomers which are mirror images of each other are called enantiomers. Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called 'd' (dextro rotatory) and 'l' (levo rotatory) forms respectively .

Examples:

The optical isomers of $[Co(en)_3]^{3+}$



l-form *d*-form

The octahedral complexes of type $[M(xx)_3]^{n\pm}$, $[M(xx)_2AB]^{n\pm}$ and $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism

22. What are hydrate isomers? Explain with an example.

The exchange water molecules in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called hydrate isomers.

For example

$[Cr(H_2O)_6]Cl_3$ - is a violet colour compound and gives $3Cl^-$ ions in solution

$[CrCl(H_2O)_5]Cl_2.H_2O$ - is a pale green colour compound and gives $2Cl^-$ ions in solution

$[CrCl_2(H_2O)_4]Cl.2H_2O$ is a dark green colour compound and gives one Cl^- ion in solution

23. What is crystal field splitting energy?

The degenerate d-orbitals (in a spherical field environment) split into two levels i.e., e_g and t_{2g} in the presence of ligands. The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting while the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy. It is denoted by Δo.

24. What is crystal field stabilization energy (CFSE) ?

The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand filed (E_{LF}) and the isotropic field/barycentre (E_{iso}).

$$CFSE\ (\Delta E_o) = \{E_{LF}\} - \{E_{iso}\}$$

$$= \{ [\, nt_{2g}(-0.4) + n_{eg}\,(0.6)]\, \Delta o + n_pP\} - \{n'_p\, P\}$$

nt_{2g} - is the number of electrons in t_{2g} orbitals

n_{eg} - is number of electrons in eg orbitals

n_p is number of electron pairs in the ligand field

n'_p is the number of electron pairs in the isotropic field (barycentre).

25. A solution of $[Ni(H_2O)_6]^{2+}$ is green, whereas a solution of $[Ni(CN)_4]^{2-}$ is colorless – Explain.

in $[Ni(H_2O)_6]^{2+}$, Ni is +2 state with the configuration is $3d^8$ i.e it has two unpaired electrons which do not pair up in the presence of the week H_2O ligand. Hence, it is coloured, For d-d transition, red is absorbed and complementary light emitted is green

In case **$[Ni(CN)_4]^{2-}$** Ni is again in + 2 state with with the configuration is $3d^8$ but in the presence of the strong CN- ligand , the two unpaired electrons in the 3d orbitals pair up.Thus, there is no unpaired electron present. Hence, it is colourlesss (no d-d transition)

26. Discuss briefly the nature of bonding in metal carbonyls.

The metal-carbon bonds in metal carbonyls have both **σ** and **π** characters.

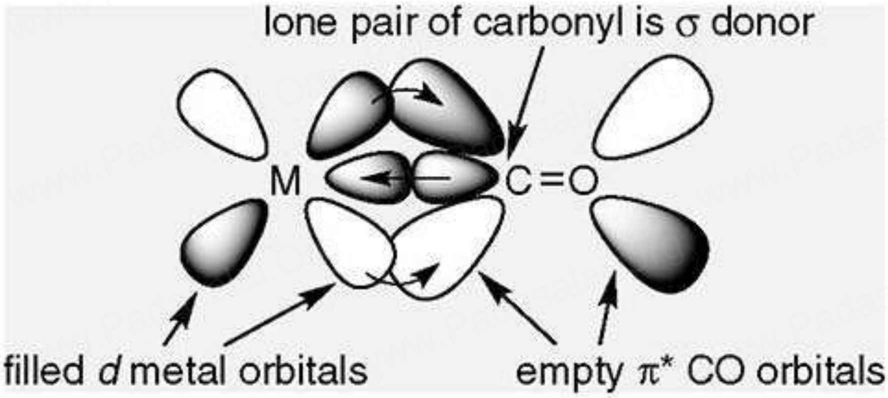
A **σ** bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal.

A π bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti- bonding **π** orbital (also known as back bonding of the carbonyl group).

The **σ** bond strengthens the **π** bond and vice-versa.

Thus, a synergic effect is created due to this metal-ligand bonding.

This synergic effect strengthens the bond between CO and the metal.



27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution of copper sulphate?

When excess of liquid ammonia is added to an aqueous solution of copper sulphate it gives tetraammine copper (II) sulphate.

$$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$$

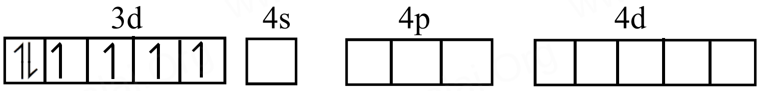
Thus, the coordination entity formed in the process is $[Cu(NH_3)_4]SO_4$ is a very stable complex, which does not ionize to give Cu^{2+} ions when added to water

28. On the basis of VB theory explain the nature of bonding in $[Co(C_2O_4)_3]^{3-}$

$[Co(C_2O_4)_3]^{3-}$

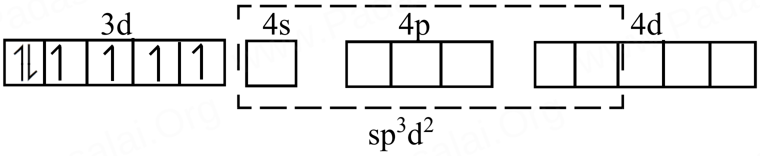
Cobalt exists in the +3 oxidation state in the given complex.

Orbitals of Co^{3+} ion

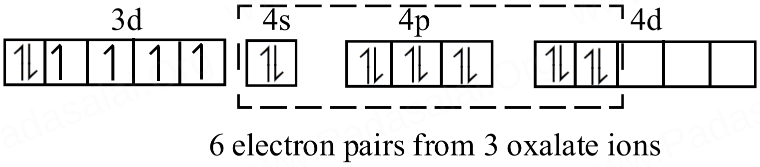


Oxalate is a weak field ligand. Therefore, it cannot cause the pairing of the 3d orbital electrons. As there are 6 ligands, hybridization has to be either sp^3d^2 or d^2sp^3 hybridization.

sp^3d^2 hybridization of Co^{3+}:



The 6 electron pairs from the 3 oxalate ions (oxalate anion is a bidentate ligand) occupy these sp^3d^2 orbitals.



Hence, the geometry of the complex is found to be octahedral.

29. What are the limitations of VB theory?

1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal.

30. Write the oxidation state, coordination number , nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex $K_4[Mn(CN)_6]$

$K_4[Mn(CN)_6]$ - Potassium hexacyanomanganate(II)

Oxidation state of manganese = +2 { 4(+1) + x + 6(-1) = 0; x = +2 }

Coordination number - 6

Nature of ligand - CN^- Monodentate ligand

Magnetic property : Paramagnetic

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}$$
$$= \sqrt{1(1+2)}$$
$$= \sqrt{3}$$
$$= 1.732 \text{ BM}$$

Electronic configuration - d5$^+$: $t_{2g}^{\ 5}$

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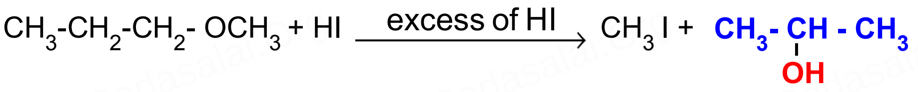
UNIT - 11
HYDROXY COMPOUNDS AND ETHERS

1. **Identify the product (s) is / are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction**

   The carbon-oxygen bond is ethers can be cleaved by heating with HI to form an alcohol and an alkyl halide at 373K.In case of unsymmetrical ethers which contains two different alyl groups,the site of cleavege is such that the halide is formed from the alkyl group which is smaller in size.

   Thus the products formed in this case are iodomethane and Propan-2-ol



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OCH_3 + HI \xrightarrow{\text{excess of HI}} CH_3I + CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_3$$

   i) **Name the mechanism involved in the reaction** - S_N1 reaction.

   In the presence of conc.HI I think $(CH_3)_2CH\text{-}OH$ changes to $(CH_3)_2CH$ - I. Also since a secondary carbon is present SN_1 mechanism may occur then the products are different (CH_3OH and $(CH_3)_2CH\text{-}I$).

2. **Draw the major product formed when 1-ethoxyprop-1-ene is heated with one equivalent of HI**

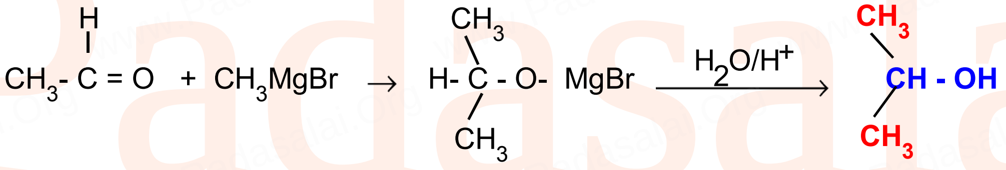
   1-Ethoxyprop-1-ene reacts with HI to form iodoethane and prop-1-en-1-ol.

$$C_2H_5\text{-}OCH = CH - CH_3 + HI \xrightarrow{\text{one equivalent of HI}} C_2H_5\text{- I} + HO - CH = CH\text{- }CH_3$$

   Not easy to break this bond as it is enaged in resonance so

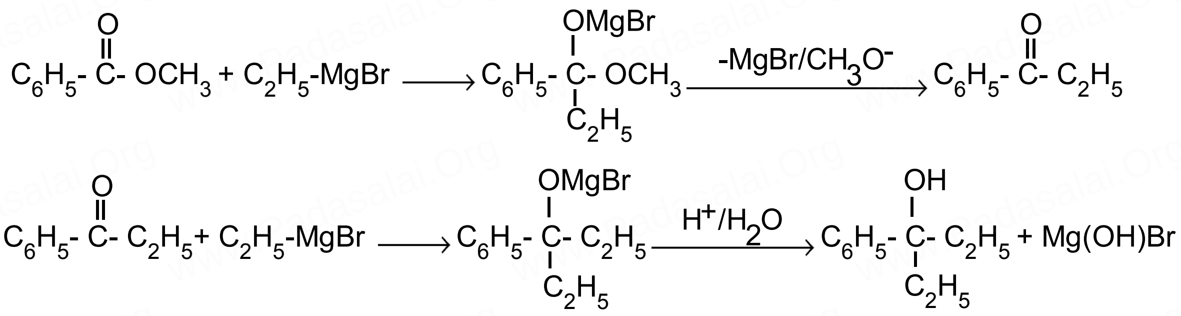
$$HO - CH = CH\text{- }CH_3 \xleftrightarrow{\text{Tautomerism}} O = CH - CH_2\text{- }CH_3 \text{ (aldehyde)}$$

3. **Suggest a suitable reagent to prepare secondary alcohol with identical group using Grignard reagent.**



$$CH_3\text{-}\overset{H}{\overset{|}{C}} = O + CH_3MgBr \rightarrow H\text{-}C(CH_3)_2\text{-}O\text{-}MgBr \xrightarrow{H_2O/H^+} (CH_3)_2CH\text{-}OH$$

4. **What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.**



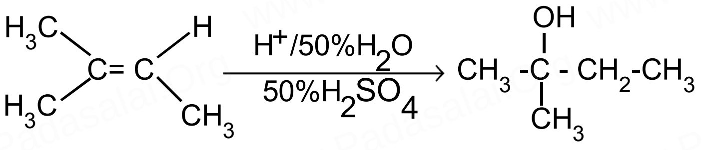
$$C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3 + C_2H_5\text{-}MgBr \longrightarrow C_6H_5\text{-}\overset{OMgBr}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}\text{-}OCH_3 \xrightarrow{-MgBr/CH_3O^-} C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_2H_5$$

$$C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_2H_5 + C_2H_5\text{-}MgBr \longrightarrow C_6H_5\text{-}\overset{OMgBr}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}\text{-}C_2H_5 \xrightarrow{H^+/H_2O} C_6H_5\text{-}\overset{OH}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}\text{-}C_2H_5 + Mg(OH)Br$$

3-phenyl-pentan-3-ol

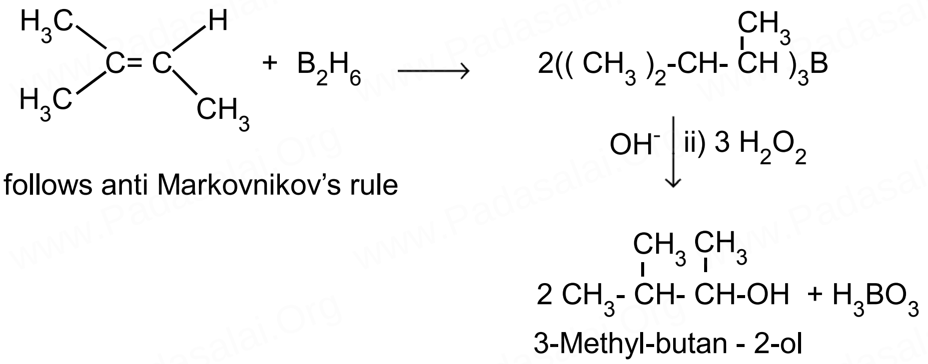
5. **Predict the major product, when 2-methyl but -2-ene is converted into an alcohol in each of the following methods.**
   (i.) Acid catalysed hydration (ii.) Hydroboration (iii.) Hydroxylation using bayers reagent

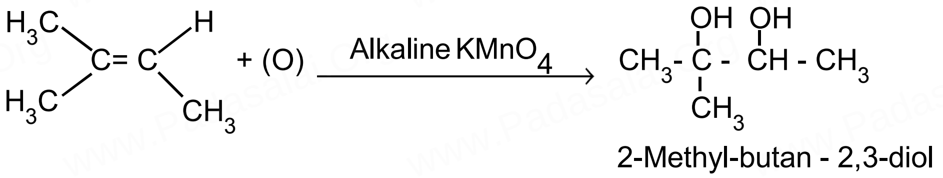
   i) 2-methyl but -2-ene is converted into an alcohol in Acid catalysed hydration



follows Markovnikov's rule 2-Methyl-butan - 2-ol

ii)2-methyl but -2-ene is converted into an alcohol in Hydroboration





iii) 2-methyl but -2-ene is converted into an alcohol in Hydroxylation using bayers reagent

6. Arrange the following in the increasing order of their boiling point and give a reason for your ordering

(i) Butan – 2- ol, Butan -1-ol, 2 –methylpropan -2-ol

(ii) Propan -1-ol, propan -1,2,3-triol, propan -1,3 – diol, propan -2-ol

a) Among isomeric alcohols primary alcohols have higher boiling point and the tertiarly alcohols have lower boiling points

b) The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surfacearea).

i) increasing order of their boiling point

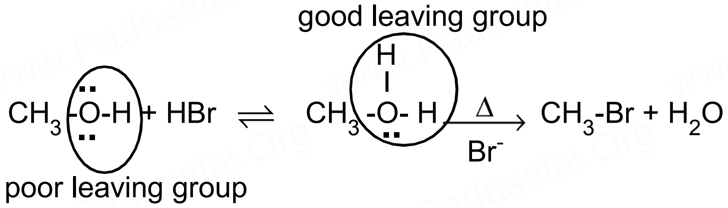
2 –methyl propan -2-ol < Butan – 2- ol < Butan -1-ol

ii) increasing order of their boiling point

propan -2-ol < Propan -1-ol < propan -1,3 – diol < propan -1,2,3-triol

7. Can we use nucelophiles such as NH_3 ,CH_3O^- for the Nucleophilic substitution of alcohols

Because the OH group of the alcohol must be protonated before it can be displaced by a nucleo-phile, only weakly basic nucleophiles (I^-, Br^-, Cl^-) can be used in the substitution reaction.Moderately and strongly basic nucleophiles (NH_3, RNH_2, and CH_3O^-) cannot be used because theytoo would be protonated in the acidic solution and, once protonated, would no longer be nucleo-philes (+ NH_4^+,RNH_3^+) or would be poor nucleophiles (CH_3OH).



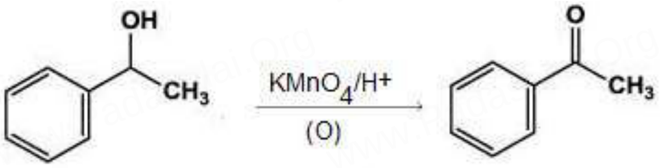
8. Is it possible to oxidise t- butyl alcohol using acidified dichromate to form a carbonyl compound.

i) Tertiary alcohol does not allow for their oxidation because of **absence α- hydrogen** atom.

ii) This is why tertiary alcohols are said to be resistant to oxidation

But at elevated temperatures **it possible to oxidise**, under strong oxidising agent like acidified $K_2Cr_2O_7 / H^+$ cleavage of C –C bond takes place to give a mixture of carboxylic acid like formic acid and acetic acid

9. What happens when 1-phenyl ethanol is treated with acidified $KMnO_4$.



Acetophenone

10. Write the mechanism of acid catalysed dehydration of ethanol to give ethene.

The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

Primary alcohols undergo dehydration by E_2 mechanism

Step 1: Protonation of ethanol to form ethyl oxonium ion:

$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + H^+ \rightleftharpoons CH_3-CH_2-\overset{H}{\underset{\oplus}{\ddot{O}}}-H$$

Step 2:Formation of carbocation (rate determining step):

$$CH_3-CH_2-\ddot{O}^{\oplus}\begin{smallmatrix}H\\H\end{smallmatrix} \xrightarrow{Slow} CH_3-\overset{\oplus}{CH_2} + H_2O$$

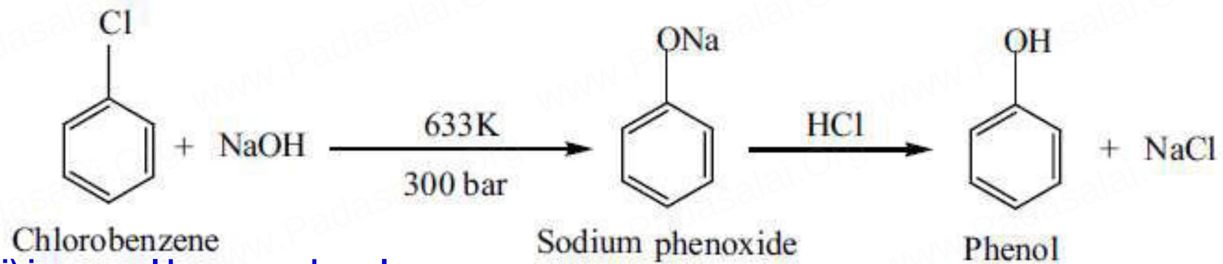
Step 3:Elimination of a proton to form ethene:

$$H-CH_2-\overset{\oplus}{CH_2} \rightleftharpoons CH_2=CH_2 + H^+$$

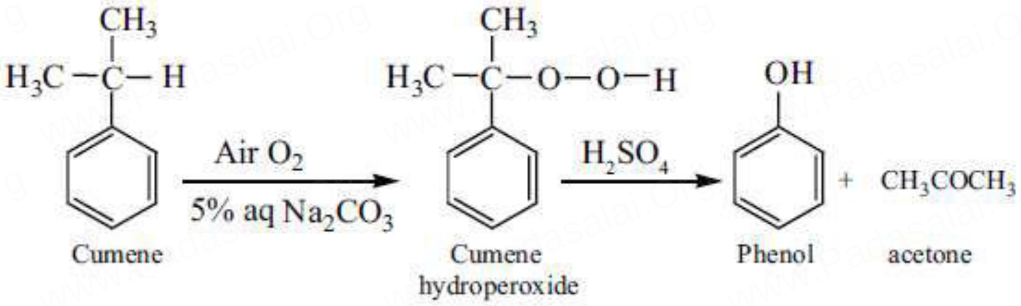
11. **How is phenol prepared form**

i) chloro benzene ii) isopropyl benzene

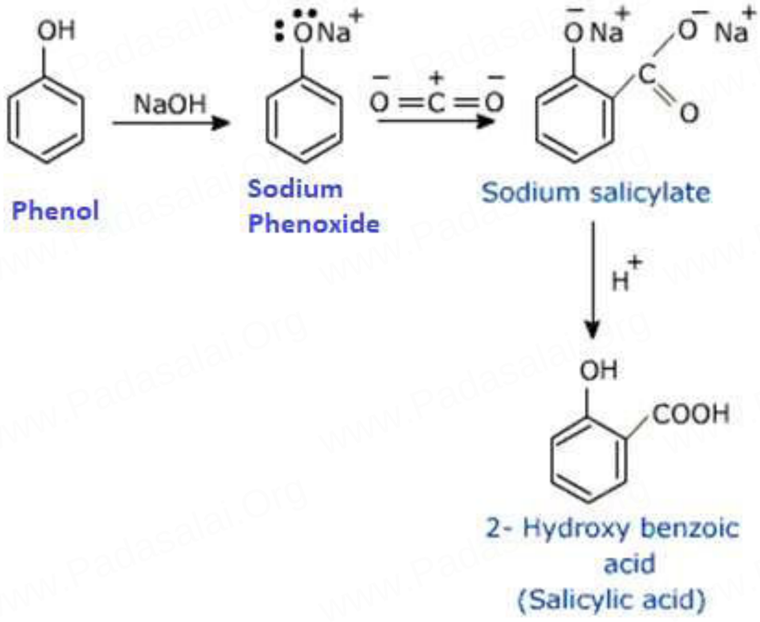
i) chloro benzene to phenol



ii) isopropyl benzene phenol



12. Explain Kolbe’s reaction

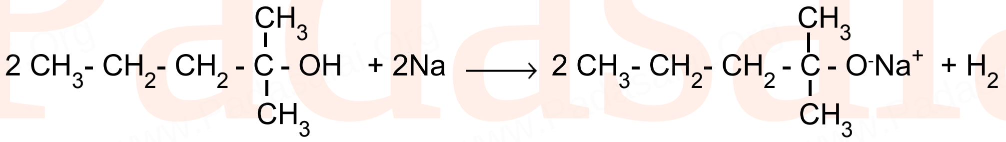


13. Write the chemical equation for Williamson synthesis of 2-ethoxy – 2- methyl pentane starting from ethanol and 2 – methyl pentan -2-ol

Step 1 : alcohol into alkylhalide

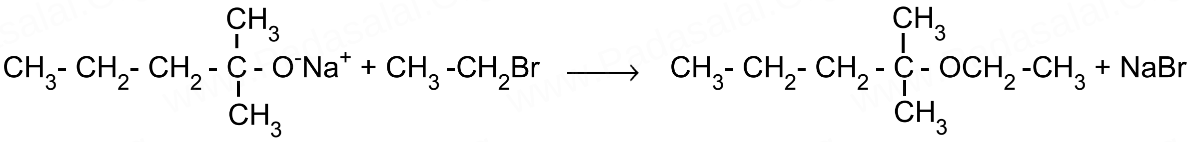
$$CH_3-CH_2-OH + HBr \xrightarrow{\Delta} CH_3-CH_2-Br + H_2O$$

Step 2 : 2 – methyl pentan -2-ol into sodium alkoxide



$$2\,CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH + 2Na \longrightarrow 2\,CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-O^-Na^+ + H_2$$

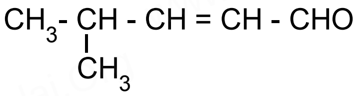
Step 3 : sodium alkoxide into 2-ethoxy – 2- methyl pentane



$$CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-O^-Na^+ + CH_3-CH_2Br \longrightarrow CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OCH_2-CH_3 + NaBr$$

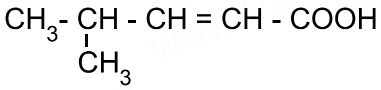
14. Write the structure of the aldehyde, carboxylic acid and ester that yield 4- methylpent-2-en-1-ol.

i) aldehyde yield 4- methylpent-2-en-1-ol



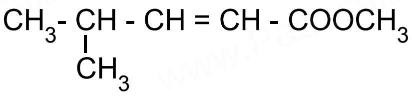
$$CH_3-\underset{CH_3}{CH}-CH=CH-CHO$$

ii) carboxylic acid yield 4- methylpent-2-en-1-ol



$$CH_3-\underset{CH_3}{CH}-CH=CH-COOH$$

iii) ester yield 4- methylpent-2-en-1-ol



$$CH_3-\underset{CH_3}{CH}-CH=CH-COOCH_3$$

aldehyde, carboxylic acid and ester undergoes reduction that yield 4- methylpent-2-en-1-ol

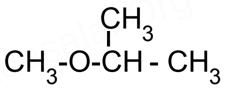
$$CH_3-\underset{CH_3}{CH}-CH=CH-CH_2OH$$

15. What is metamerism? Give the structure and IUPAC name of metamers of 2-methyoxy propane

Metamerism :

It is a special isomerism in which molecules with same formula, same functional group, differing only in the nature of the alkyl group attached to oxygen.

For example an ether having molecular formula $C_4H_{10}O$ exhibits following **metamers**

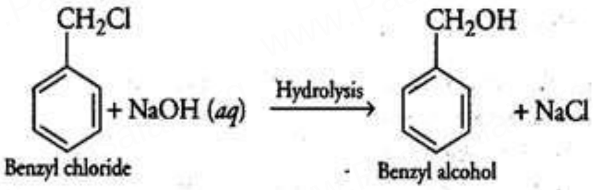
	Comman Name	**IUPAC name**
 $CH_3\text{-}O\text{-}\overset{CH_3}{\overset{\mid}{C}H}\text{-}CH_3$	Methyl isopropyl ether	2- methoxy propane
$CH_3CH_2\text{-}O\text{-}CH_2CH_3$	dietyl ether	ethoxy ethane
$CH_3\text{-}O\text{-}CH_2CH_2CH_3$	methyl propyl ether	1 - methoxy propane

Ethoxy ethane and 1 - methoxy propane are metamers 2- methoxy propane

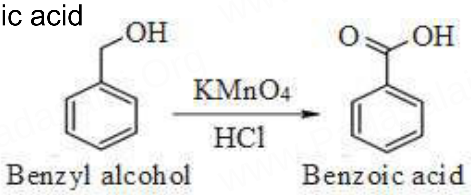
16. How are the following conversions effected

i) benzylchloride to benzylalcohol ii) benzyl alcohol to benzoic acid

i) benzylchloride to benzylalcohol :



ii) benzyl alcohol to benzoic acid



17. Complete the following reactions

i) $CH_3\text{-}CH_2\text{-}OH \xrightarrow{PBr_3} A \xrightarrow{(aq)NaOH} B \xrightarrow{Na} C$

$$\mathbf{CH_3\text{-}CH_2\text{-}OH \xrightarrow{PBr_3} CH_3\text{-}CH_2\text{-}Br \xrightarrow{(aq)NaOH} CH_3\text{-}CH_2\text{-}OH \xrightarrow{Na} CH_3\text{-}CH_2\text{-}ONa + \frac{1}{2}H_2}$$

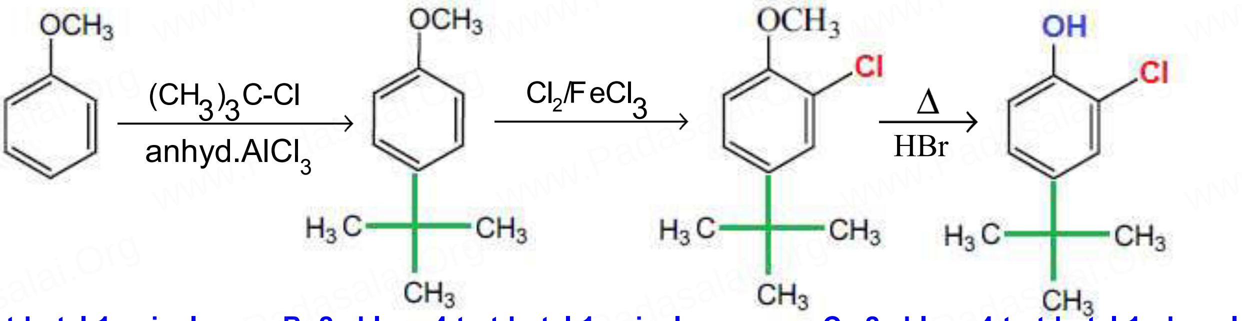
A - ethyl bromide B - ethanol C - Sodium ethoxide

i) $C_6H_5\text{-}OH \xrightarrow{Zn} A \xrightarrow{CH_3Cl/anhydrous\ AlCl_3} B \xrightarrow{KMnO_4/H^+} C$

$$\mathbf{C_6H_5\text{-}OH \xrightarrow{Zn} C_6H_6 \xrightarrow{CH_3Cl} C_6H_5\text{-}CH_3 \xrightarrow{KMnO_4/H^+} C_6H_5\text{-}COOH}$$

A - benzene B - Toluene C - Benzoic acid

iii) Anisole $\xrightarrow{t\text{-}butylchloride/AlCl_3} A \xrightarrow{Cl_2/FeCl_3} B \xrightarrow{HBr} C$



A - 4-tert-butyl-1-anisole B - 2-chloro-4-tert-butyl-1-anisole C - 2-chloro-4-tert-butyl-1-phenol

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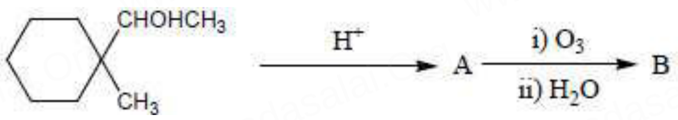
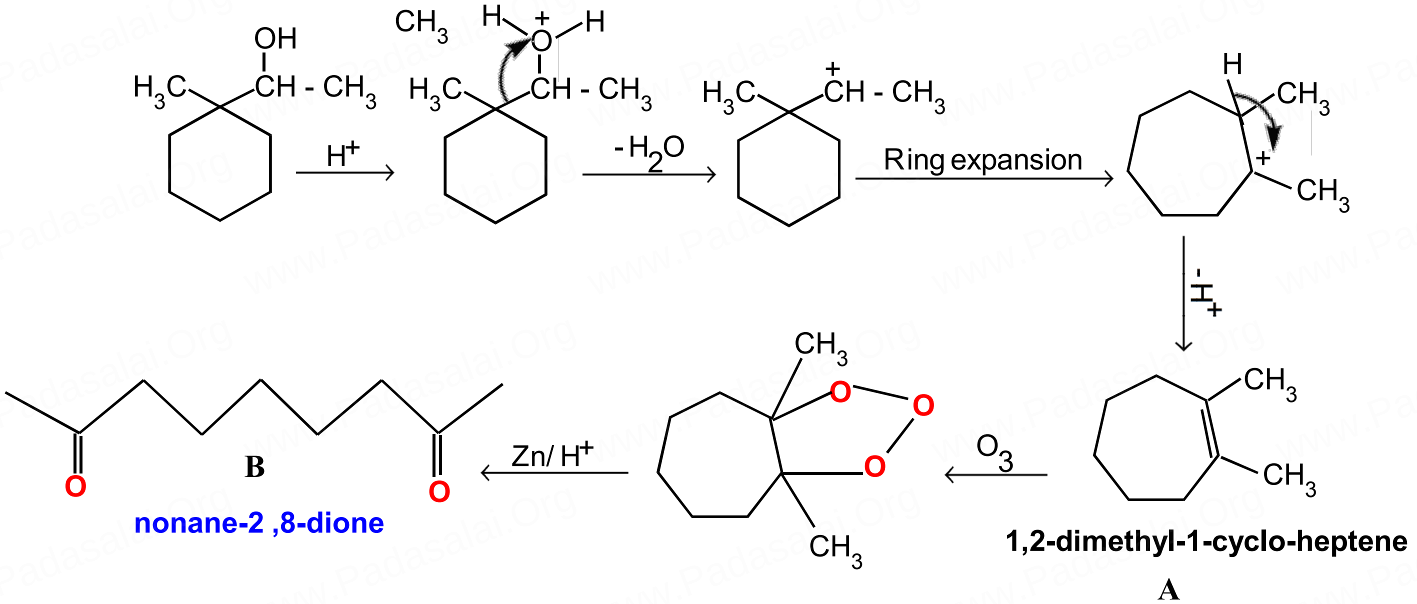
iv) 

1-(1-methyl-cyclohexyl)-ethanol to nonane-2,8 -dione



18. 0.44g of a monohydric alcohol when added to methyl magnesium iodide in ether liberates at STP 112 cm^3 of methane with PCC the same alcohol form a carbonyl compound that answers silver mirror test. Identify the compound.

$$\text{Monohydric alcohol} + CH_3MgI \xrightarrow{\text{Ethers}} CH_4$$

$$\text{Monohydric alcohol} \xrightarrow{\text{PCC}} \text{Carbonyl compound} \longrightarrow + \text{ ve silver mirror test}$$

Monohydric alcohol means a alcohol which contains one hydroxyl group.PCC is an oxidising agent which convert alcohols to aldehyde or ketones. Aldehydes show silver mirror test not ketones. So, aldehyde is formed and primary alcohols give aldehyde on oxidation. Secondary alcohols give ketones.Consider the formula of monohydric alcohol is $C_nH_{2n+1}OH$. Alcohols react with grignard reagent form alkyl magnesium halide with the evolution of alkane.

$$CnH_{2n+1}OH + CH_3MgI \longrightarrow CH_4 + C_nH_{2n+1}OMgI$$

112 cm^3 of methane is produced from 0.44 g of alcohol

22400 cm3 of methane is produced from = $\frac{22400 \times 0.44}{112} = 88$ g

This is the molar mass of alcohol as 1 mole of alcohol which is equivalent to molar mass produces 22400 cm^3 of gas at STP.

Molar mass of alcohol = 81 g

Subtract the mass of hydroxyl group from it = 88 - (16 + 1) = 71 g

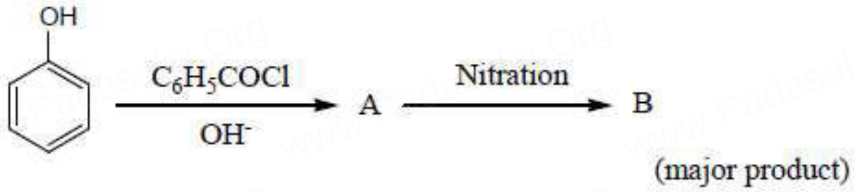
$C_nH_{2n+1} = 71$ g

Number of carbon can be possible with this molar mass is 5 which comprises mass 60 g and the rest mass is the mass of hydrogen.

So, the formula of alcohol is $C_5H_{11}OH$.

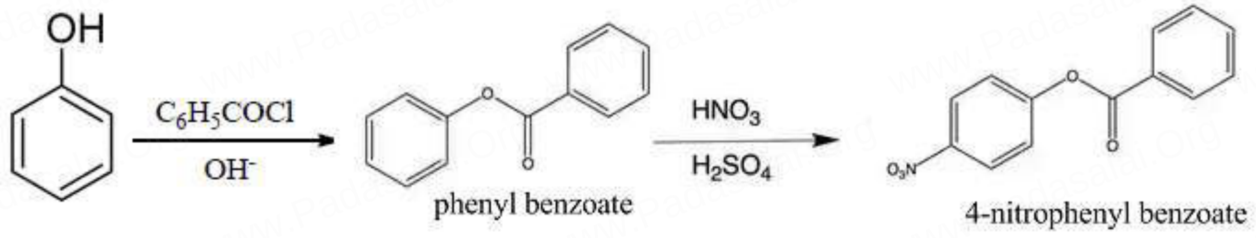
19. Complete the following reactions

i)



ii) C_6H_5-CHCH(OH)CH$(CH_3)_2 \xrightarrow{ConH_2SO_4}$

i) Phenol on treatment with acid chlorides gives esters.The acetylation and benzoylation of phenol are called **Schotten-Baumann reaction.**



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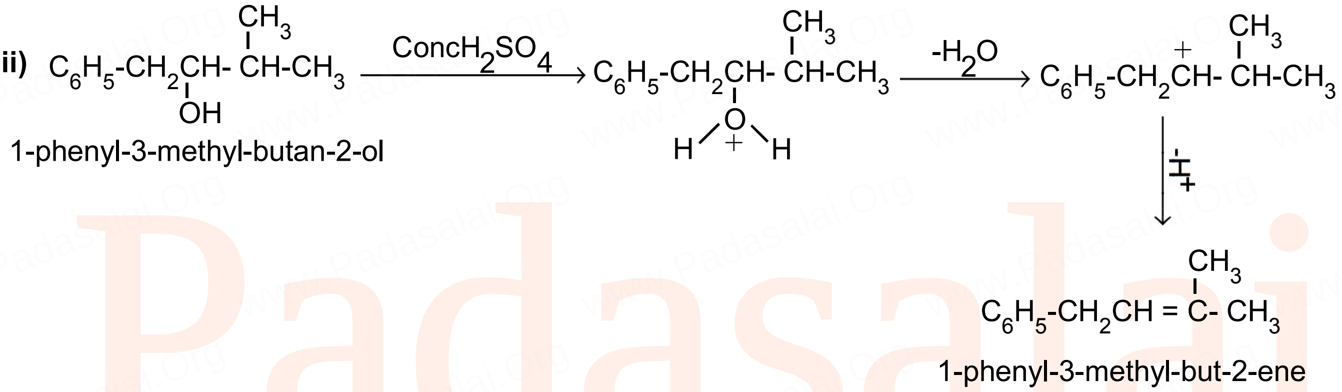
ii)



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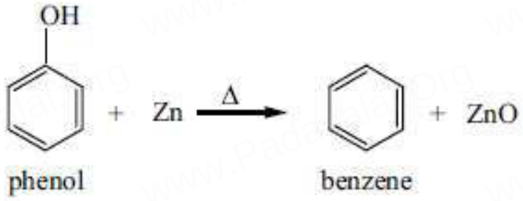
20. Phenol is distilled with Zn dust followed by friedel – crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (c) Identify A,B and C.

i) Phenol to benzene

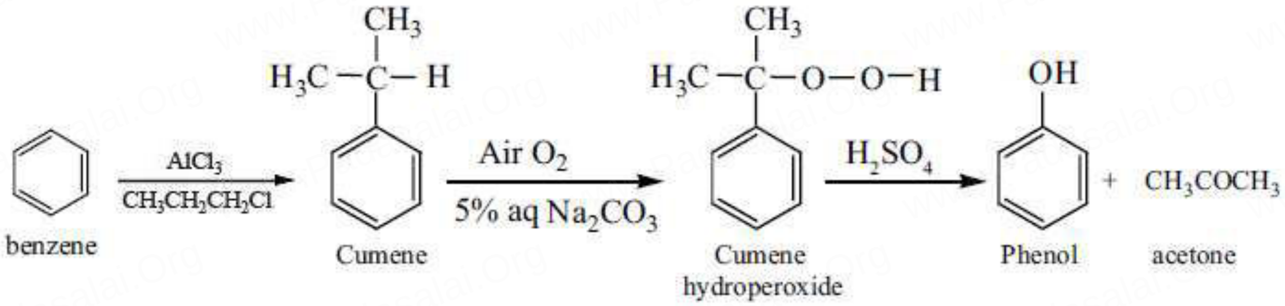


A- benzene

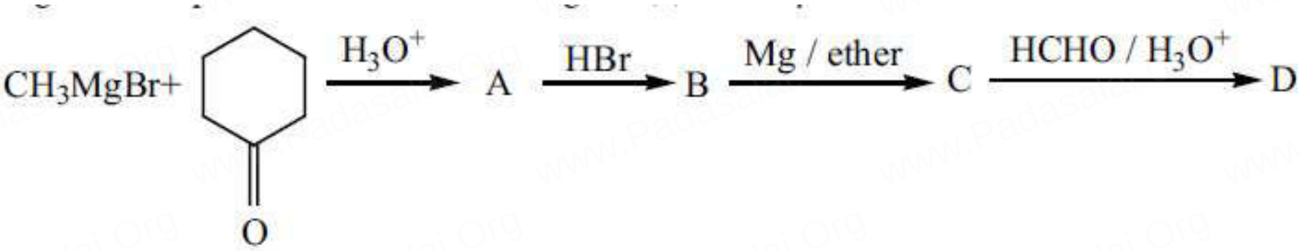
B- Cumene

C- Cumene hydro peroxide

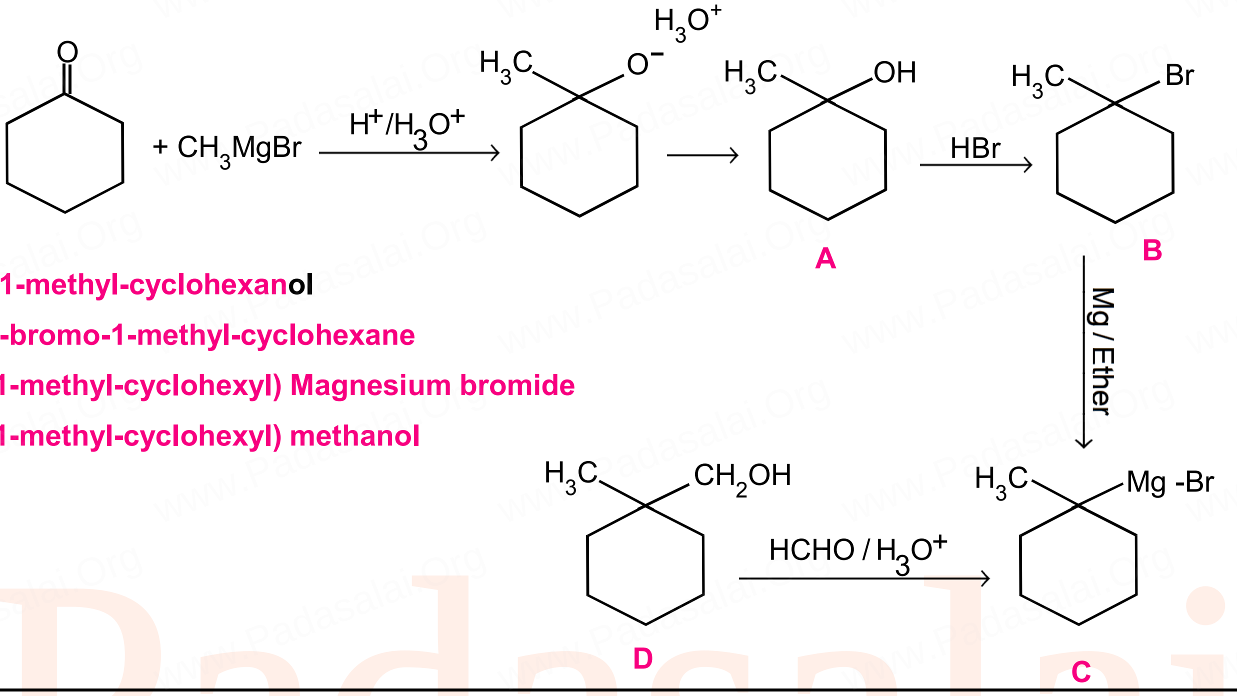
ii) benzene to phenol



21.



Identify A,B,C,D and write the complete equation



A- 1-methyl-cyclohexanol

B-1-bromo-1-methyl-cyclohexane

C-(1-methyl-cyclohexyl) Magnesium bromide

D-(1-methyl-cyclohexyl) methanol

---

22. What will be the product (X and A)for the following reaction

acetylchloride $\xrightarrow[\text{ii) } H_3O^+]{\text{i) } CH_3MgBr} X \xrightarrow{\text{acid } K_2Cr_2O_7} A$

$CH_3\text{-}COCl \xrightarrow[\text{ii) } H_3O^+]{\text{i) } CH_3MgBr} CH_3\text{-}COCH_3 \xrightarrow{\text{acid } K_2Cr_2O_7} CH_3\text{-}COOH + H\text{-}COOH$

X - Acetone **A- Acetic acid**

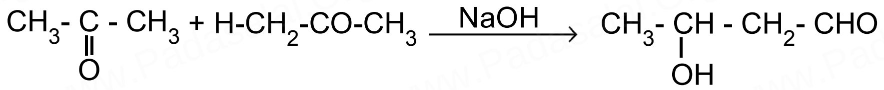
---

23. How will you convert acetylene into n-butyl alcohol.

step -1 : $H\text{-}C\equiv C\text{-}H \xrightarrow{42\%\ H_2SO_4\ /\ 1\%Hg^{2+}} CH_3\text{-}COCH_3$

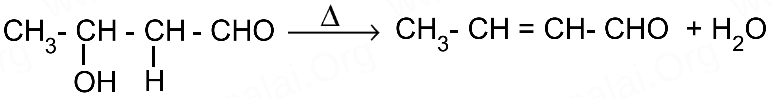
Aldol condesation

step-2 :



$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 + H\text{-}CH_2\text{-}CO\text{-}CH_3 \xrightarrow{NaOH} CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2\text{-}CHO$ **aldol**

step- 3 :

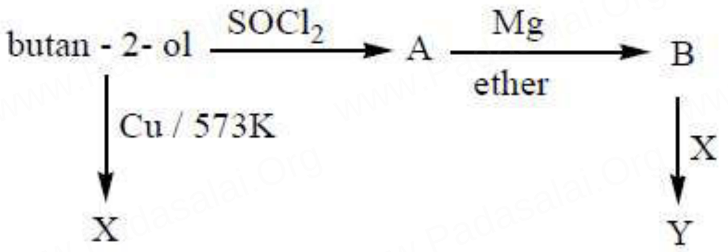


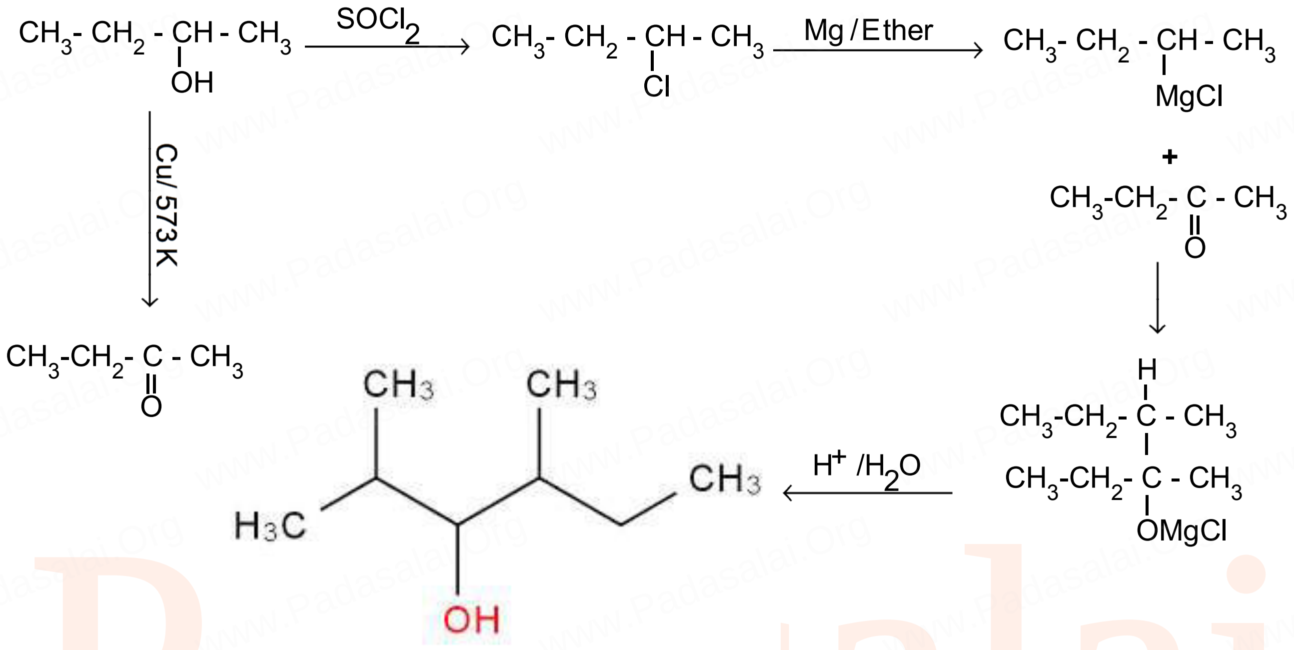
$CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}\underset{\underset{H}{|}}{CH}\text{-}CHO \xrightarrow{\Delta} CH_3\text{-}CH = CH\text{-}CHO + H_2O$

step-4 Reduction of crotonaldehyde to n-butyl alcohol.

$CH_3\text{-}CH = CH\text{-}CHO \xrightarrow{H_2/Ni} CH_3\text{-}CH_2\ CH_2\text{-}COOH$

24. Predict the product A,B,X and Y in the following sequence of reaction



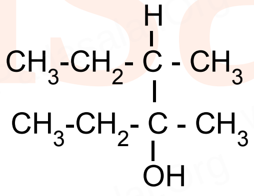


Compound- A : **2- chloro - butane**

Compound- B : **2- butanone**

Compound- X : **2- butanone**

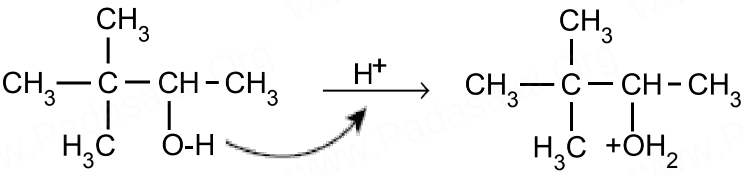
Compound- Y : **3, 4-dimethyl-hexan-3-ol**



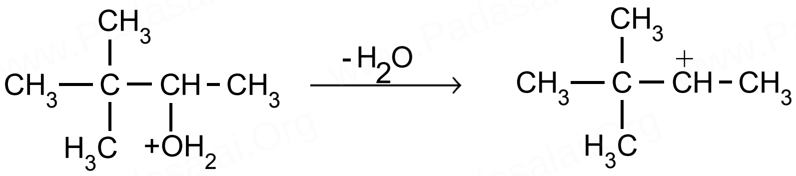
25. 3,3 – dimethylbutan-2-ol on treatment with conc. H_2SO_4 to give tetramethyl ethylene as a major product. Suggest a suitable mechanism

The mechanism is as follows:

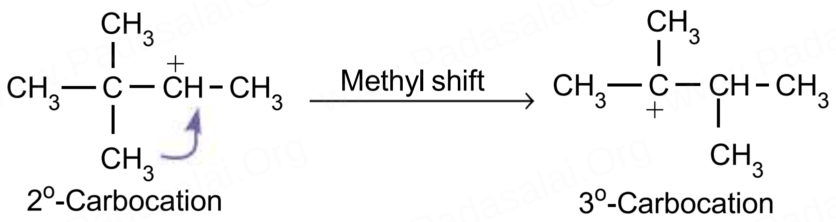
Step-1: protonation of 3,3-dimethylbutan-2-ol



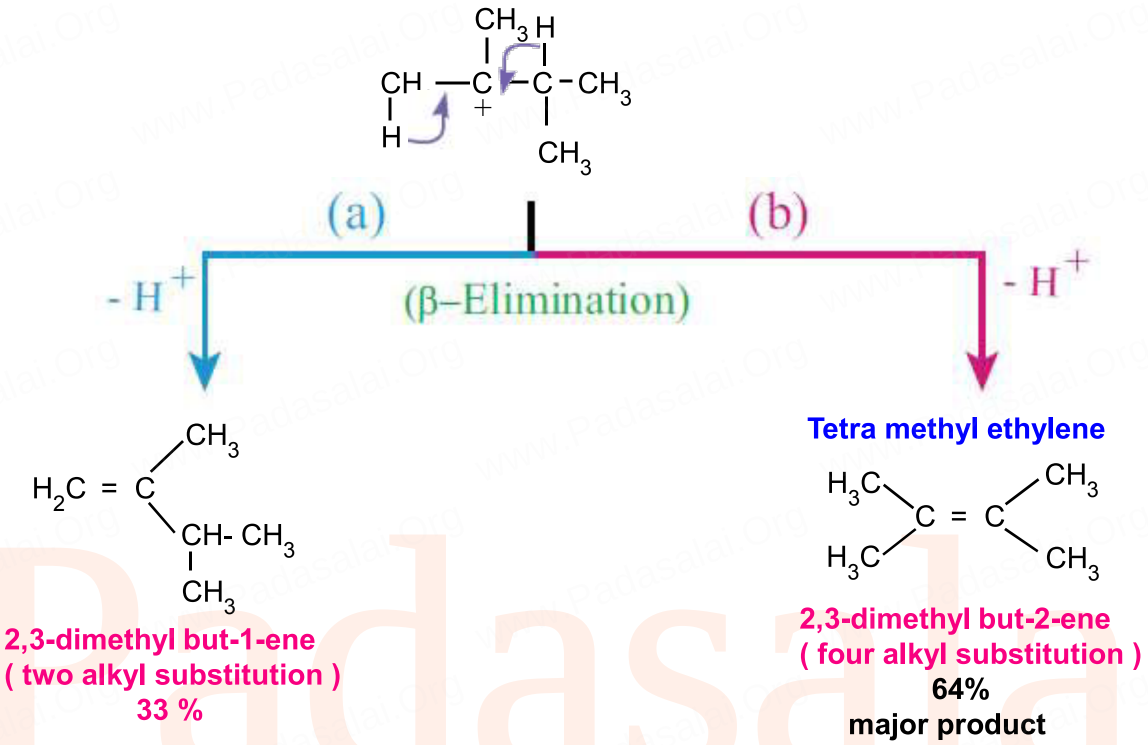
2) Removal of a water molecule from the carbonium ion formed above



3) Conversion of 2 degree carbonium to 3 degree carbonium by methyl shift:



4) Removal of H^+ ion to form a double bond:



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UNIT - 13

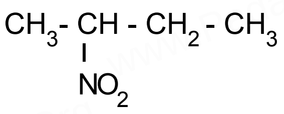
ORGANIC NITROGEN COMPOUNDS

1. Write down the possible isomers of the $C_4H_9NO_2$ give their IUPAC names

i) $CH_3-CH_2-CH_2-CH_2-NO_2$

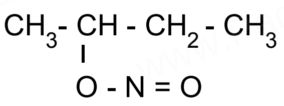
ii) $CH_3-CH_2-CH_2-CH_2-O-N=O$

iii)



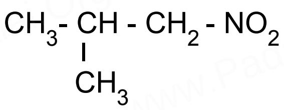
$CH_3-\underset{NO_2}{\underset{|}{CH}}-CH_2-CH_3$

iv)



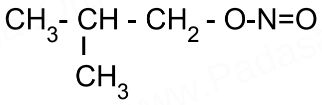
$CH_3-\underset{O-N=O}{\underset{|}{CH}}-CH_2-CH_3$

v)



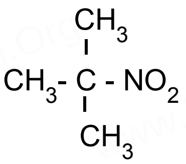
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-NO_2$

vi)



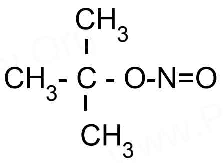
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-N=O$

vii)



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-NO_2$

viii)



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-O-N=O$

i) 1- nitro butane

ii) 1-nitrosooxybutane

iii) 2 - nitro butane

iv) 2- nitroso oxy butane

v) 2- methyl - 1- nitro propane

vi) 2 - methyl -1-nitroso oxy propane

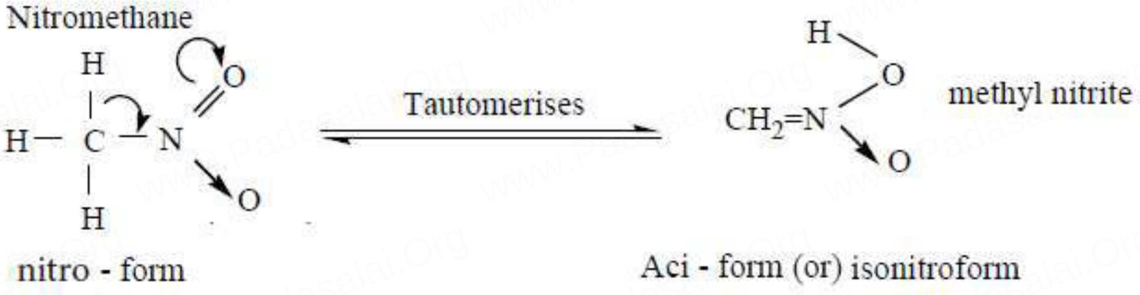
vii) 2- methy-2-nitro propane

viii) 2-methyl-2-nitroso oxy propane

2. There are two isomers with the formula CH_3NO_2 How will you distinguish between them?

Tautomerism:

Primary and secondary nitroalkanes, having α-H , also show an equilibrium mixture of two tautomers namely nitro and aci- form



Distinguish between two form

S.No.	Nitro form	Aci – form
1.	Less acidic	More acidic and also called pseudoacids (or) nitronic acids
2.	Dissolves in NaOH slowly	Dissolves in NaOH instantly
3.	Decolourises $FeCl_3$ solution	With $FeCl_3$ gives reddish brown colour
4.	Electrical conductivity is low	Electrical conductivity is high

3. What happends when

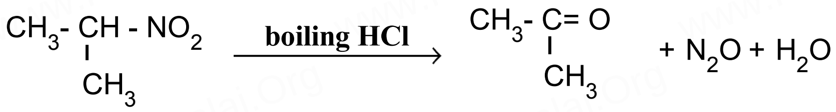
i. 2 - Nitropropane boiled with HCl

ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.

iii. Oxidation of tert - butylamine with $KMnO_4$

iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.

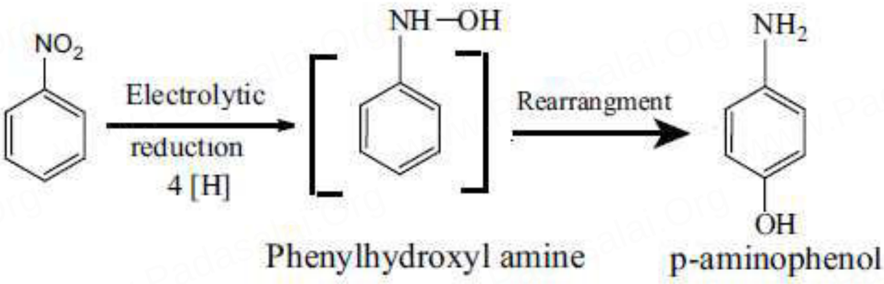
i. 2 - Nitropropane boiled with HCl



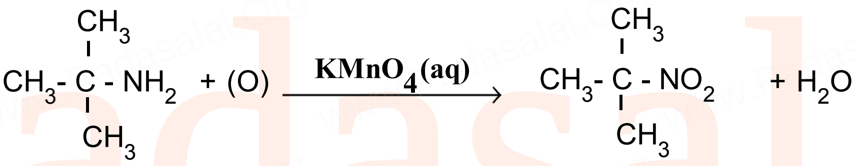
$$CH_3-\underset{CH_3}{CH}-NO_2 \xrightarrow{\text{boiling HCl}} CH_3-\underset{CH_3}{C}=O + N_2O + H_2O$$

Acetone

ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.



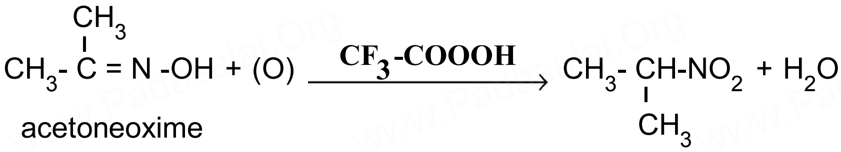
ii) Oxidation of tert - butylamine with $KMnO_4$



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-NH_2 + (O) \xrightarrow{KMnO_4(aq)} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-NO_2 + H_2O$$

iv. Oxidation of acetoneoxime with trifluoro peroxy acetic acid.

Oxidation of acetoneoxime with trifluoroperoxy acetic acid gives 2 - nitropropane (2^0) respectively.



$$CH_3-\overset{CH_3}{C}=N-OH + (O) \xrightarrow{CF_3-COOOH} CH_3-\underset{CH_3}{CH}-NO_2 + H_2O$$

acetoneoxime

2 - nitropropane (2^0)

4. How will you convert nitrobenzene into

i. 1,3,5 - trinitrobenzene

ii. o and p- nitrophenol

iii. m - nitro aniline

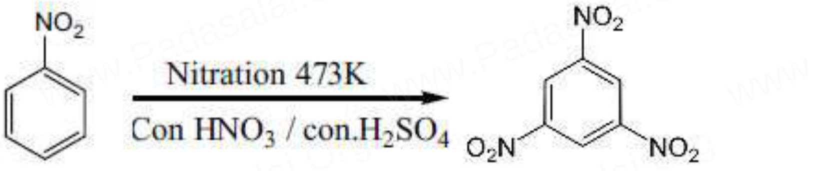
iv. azoxybenzene

v. hydrozobenzene

vi. N - phenylhydroxylamine

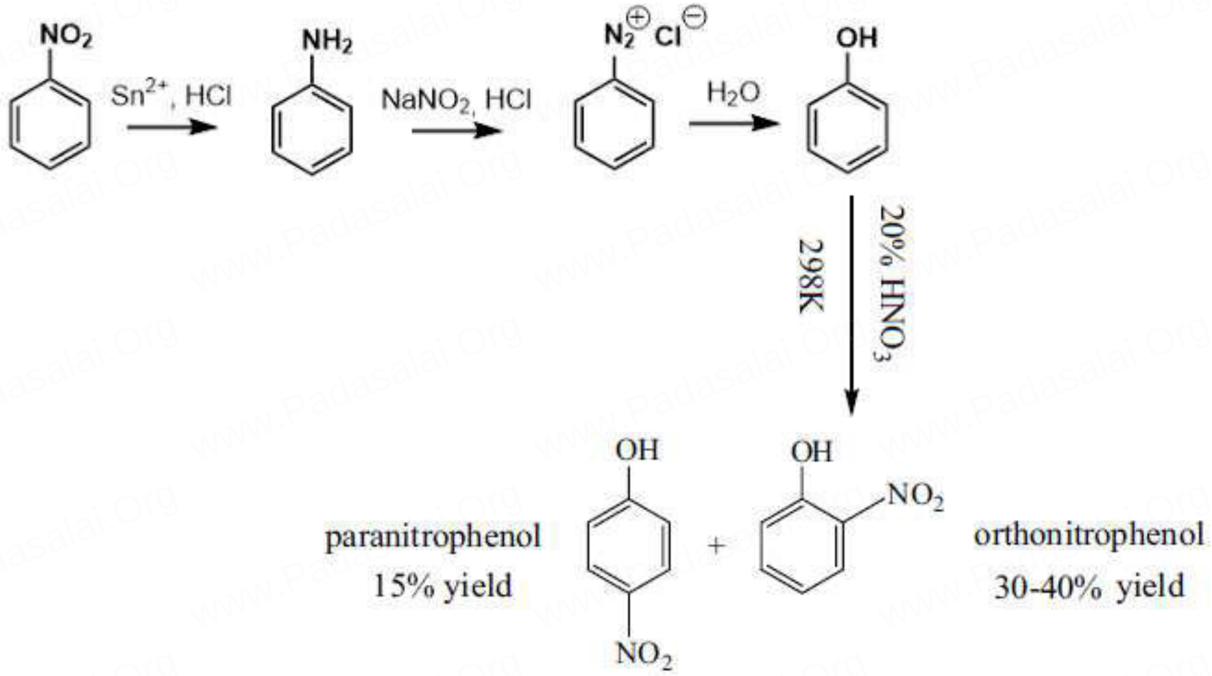
vii. aniline

i) Conversion of nitrobenzene into 1,3,5 - trinitrobenzene

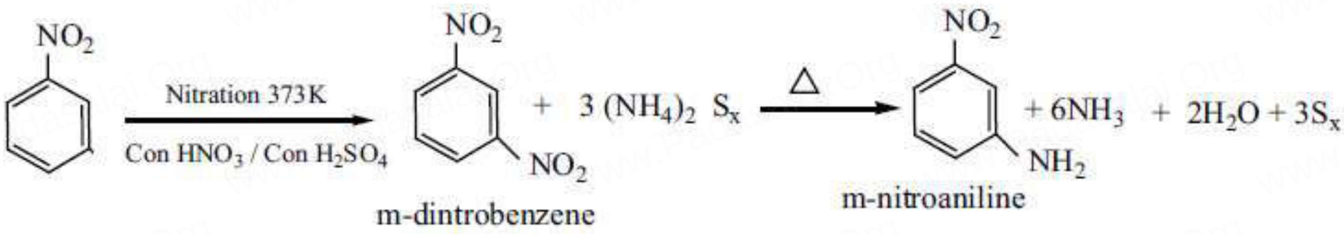


1,3,5 - trinitrobenzene (TNB)

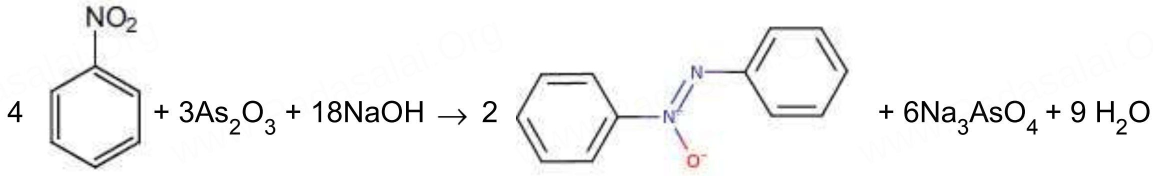
ii Conversion of nitrobenzene into o and p- nitrophenol



iii) Conversion of nitrobenzene into m - nitro aniline



iv) Conversion of nitrobenzene into azoxybenzene hydrozobenzene



iv) Conversion of nitrobenzene into hydrozobenzene

$$C_6H_5\text{-}NO_2 \xrightarrow[\text{basic medium}]{\text{Zn / NaOH}} [C_6H_5\text{-}N{=}N\text{-}C_6H_5] \xrightarrow{2[H]} C_6H_5\text{-}NH{=}NH\text{-}C_6H_5$$

iv) Conversion of nitrobenzene into N - phenylhydroxylamineaniline

$$C_6H_5\text{-}NO_2 + 2[H] \xrightarrow[\text{Neutral medium}]{\text{Zn /}NH_4Cl} C_6H_5\text{-}NH\text{-}OH + ZnO$$

iv) Conversion of nitrobenzene into aniline

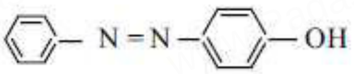
$$C_6H_5\text{-}NO_2 + 6[H] \xrightarrow[\text{Acid medium}]{\text{Sn / HCl]}} C_6H_5\text{-}NH_2$$

5. Identify compounds A,B and C in the following sequence of reactions.

i) $C_6H_5\text{-}NO_2 \xrightarrow{Fe\ /\ HCl} A \xrightarrow{HNO_2/273K} B \xrightarrow{C_6H_5OH} C$

Ans: $C_6H_5\text{-}NO_2 \xrightarrow{Fe\ /\ HCl} C_6H_5\text{-}NO_2 \xrightarrow{HNO_2/273K} C_6H_5\text{-}N_2Cl$

$\xrightarrow[\text{Coupling reaction}]{C_6H_5OH}$



p- hydroxy azobenzene

A- Aniline **B - Benzene diazonium chloride** **C - p - hydroxy azobenzene**

---

ii) $C_6H_5\text{-}N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[288\ K]{NH_3} C$

Ans: $C_6H_5\text{-}N_2Cl \xrightarrow{CuCN} C_6H_5\text{-}CN \xrightarrow{H_2O/H^+} C_6H_5\text{-}COOH \xrightarrow[288\ K]{NH_3} C_6H_5\text{-}CONH_2$

A- Cyanobenzene **B - Benzoic acid** **C - Benzamide**

---

iii) $CH_3\text{-}CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

Ans: $CH_3\text{-}CH_2I \xrightarrow{NaCN} CH_3\text{-}CH_2CN \xrightarrow[\text{partial hydrolysis}]{OH^-} CH_3\text{-}CH_2CONH_2 \xrightarrow[\text{Hoffmann bromamide reaction}]{NaOH + Br_2} CH_3\text{-}NH_2$

A- Ethyl cyanide **B - Acetamide** **C - Methyl amine**

---

iv) $CH_3\text{-}NH_2 \xrightarrow{CH_3Br} A \xrightarrow{CH_3COCl} B \xrightarrow{B_2H_6} C$

Ans: $CH_3\text{-}NH_2 \xrightarrow{CH_3Br} (CH_3)_2NH \xrightarrow{CH_3COCl} (CH_3)_2N\text{-}CO\text{-}CH_3$

$\xrightarrow{B_2H_6} (CH_3)_2N\text{-}CH(OH)\text{-}CH_3$

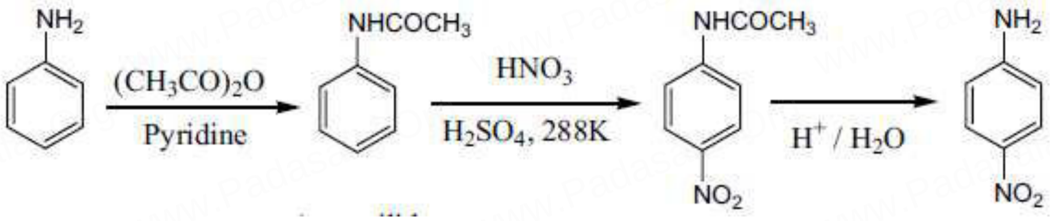
A- N,N dimethyl amine **B - N,N-dimethyl acetamide**

C - N,N-dimethyl 2- hydroxy ethan amine

---

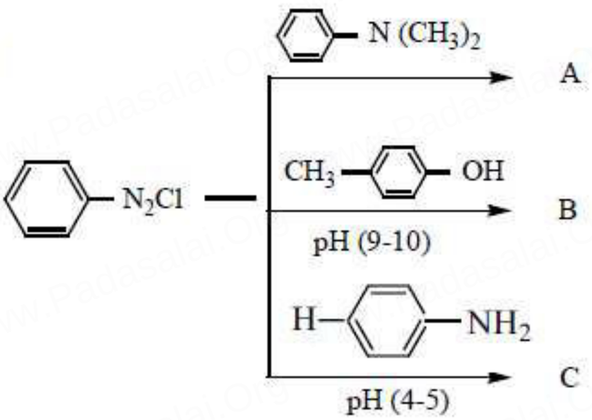
v) $C_6H_5\text{-}NH_2 \xrightarrow{(CH_3CO)_2O/\ pyridine} A \xrightarrow{HNO_3/H_2SO_4} B \xrightarrow{H_2O/H^+} C$

Ans:

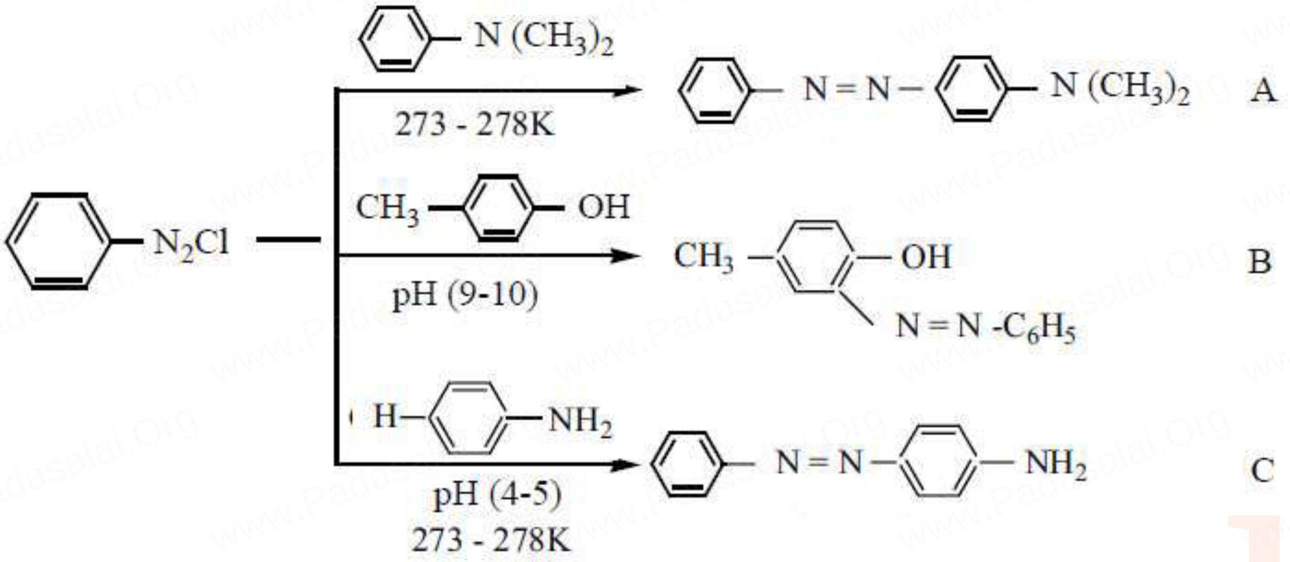


A - Acetanilide **B - p- nitroacetanilide** **C- p- nitro aniline**

vi)



Ans:



A- **p-N,N - dimethyl amino azobenzene**

B - **2 - phenylazo - 4 -Methyl phenol**

C - **p - amino azobenzene (Yellow dye)**

---

vii) $CH_3\text{-}CH_2\text{-}NC \xrightarrow{HgO} A \xrightarrow{H_2O} B \xrightarrow[ii)\ H_2O]{i)\ NaNO_2\ /HCl} C$

Ans : $CH_3\text{-}CH_2\text{-}NC \xrightarrow{HgO} CH_3\text{-}CH_2\text{-}N = C = O \xrightarrow{H_2O} CH_3\text{-}CH_2\text{-}NH_2$

$\xrightarrow{i)NaNO_2\ /HCl} \underset{\text{unstable}}{[C_2H_5N_2Cl]} \xrightarrow{ii)\ H_2O} CH_3\text{-}CH_2OH + N_2$

A- **Ethyl iso cyanate** B- **Ethyl amine** C- **Ethanol**

---

6. **Write short notes on the following**

i. Hofmann's bromide reaction
ii. Ammonolysis
iii. Gabriel phthalimide synthesis
iv. Schotten - Baumann reaction
v. Carbylamine reaction
vi. Mustard oil reaction
vii. Coupling reaction
viii. Diazotisation
ix. Gomberg reaction

i. Hofmann's bromide reaction

When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

$$CH_3\text{-}CONH_2 \xrightarrow{Br_2/KOH} CH_3\text{--}NH_2 + K_2CO_3 + KBr + H_2O$$

ii. Ammonolysis

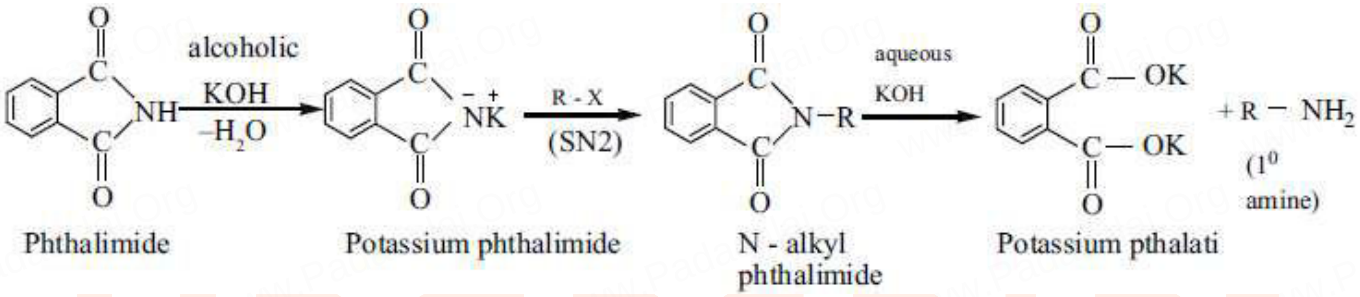
When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1^0, 2^0 and 3^0 amines and quaternary ammonium salts are obtained

$$\underset{}{CH_3\text{-}Br} \xrightarrow{NH_3/\Delta} \underset{1^o\ amine}{CH_3\text{--}NH_2} \xrightarrow{CH_3Br} \underset{2^o\ amine}{(CH_3)_2\text{-}NH} \xrightarrow{CH_3Br} \underset{3^o\ amine}{CH_3)_3\text{-}N}$$

$$\xrightarrow{CH_3Br} CH_3)_4\text{-}N^+Br^- \ \textbf{Quarternary ammonium bromide}$$

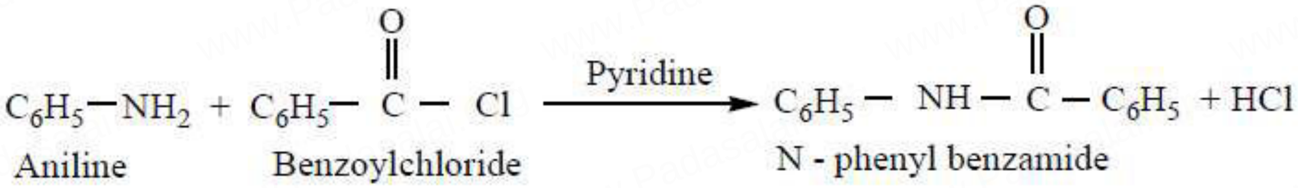
iii. Gabriel phthalimide synthesis

Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide



iv. Schotten - Baumann reaction

Aniline reacts with benzoylchloride (C_6H_5COCl) in the presence of NaOH to give N-phenyl benzamide. This reaction is known as Schotten - Baumann reaction



$$\underset{Aniline}{C_6H_5-NH_2} + \underset{Benzoylchloride}{C_6H_5-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow{Pyridine} \underset{N\text{ - phenyl benzamide}}{C_6H_5-NH-\overset{\overset{O}{\|}}{C}-C_6H_5} + HCl$$

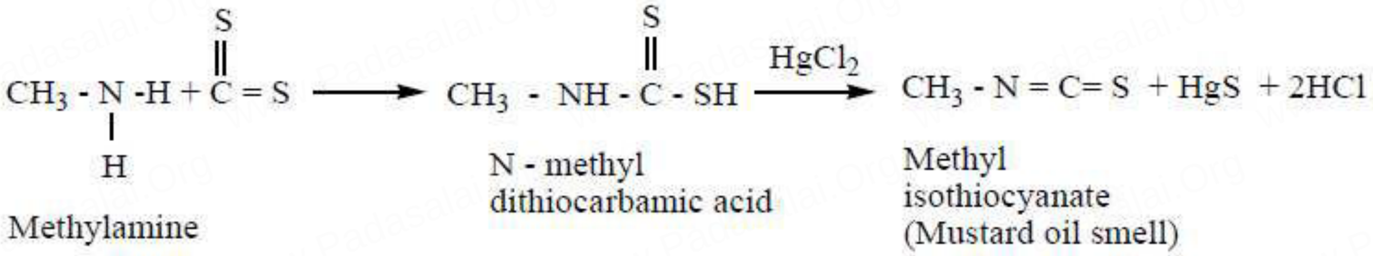
v. Carbylamine reaction

Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamines test.
This test used to identify the primary amines

$$C_2H_5\text{-}NH_2 + 3KOH + CHCl_3 \xrightarrow{Br_2/KOH} \underset{carbylamines}{C_2H_5\text{-}NC} + 3\ KCl + 3H_2O$$

vi. Mustard oil reaction

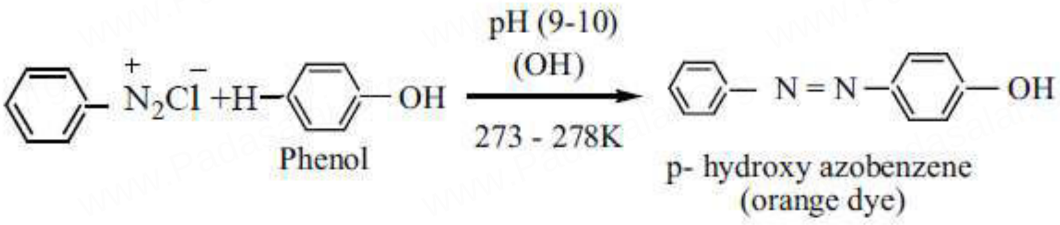
i) When primary amines are treated with carbon disulphide (CS_2), N - alkyldithio carbonic acid is formed which on subsequent treatment with $HgCl_2$,give an alkyl isothiocyanate.



$$\underset{Methylamine}{CH_3-\underset{\underset{H}{|}}{N}-H} + \overset{\overset{S}{\|}}{C}=S \longrightarrow \underset{N\text{ - methyl dithiocarbamic acid}}{CH_3-NH-\overset{\overset{S}{\|}}{C}-SH} \xrightarrow{HgCl_2} \underset{\substack{Methyl\ isothiocyanate \\ (Mustard\ oil\ smell)}}{CH_3-N=C=S} + HgS + 2HCl$$

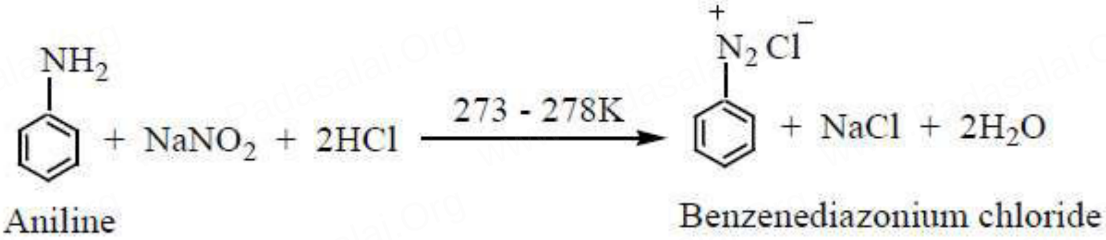
vii. Coupling reaction

Benzene diazonium chloride reacts with electron rich aromatic compounds like phenol, aniline to form brightly coloured azo compounds.



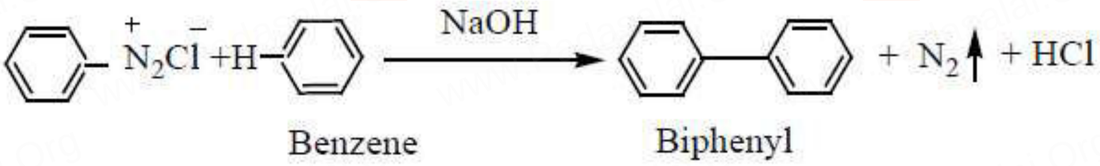
viii. Diazotisation

Aniline reacts with nitrous acid at low temperature (273 - 278 K) to give benzene diazonium chloride which is stable for a short time and slowly decomposes seven at low temperatures.This reaction is known as **diazotization**.



ix. Gomberg reaction

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction in known as the Gomberg reaction.



7. How will you distinguish between primary secondary and tertiary alphatic amines.

Reagents	Primary amine	Secondary amine	Tertiary amine
With HNO_2	forms forms alcohol	N-nitroso amine	forms salt.
With $CHCl_3$/KOH	forms carbylamine	No reaction.	No reaction
With CS_2 and $HgCl_2$	alkyl isothiocyanate is formed	No reaction	No reaction
With Diethyl oxalate	dialkyl oxamide, a solid at room temperature is formed.	Forms N,N-dialkyl oxamic ester, a liquid.	No reaction
With acetyl chloride	forms N-alkyl acetamide.	form N,N-dialkyl acetamide	No reaction

8. Account for the following

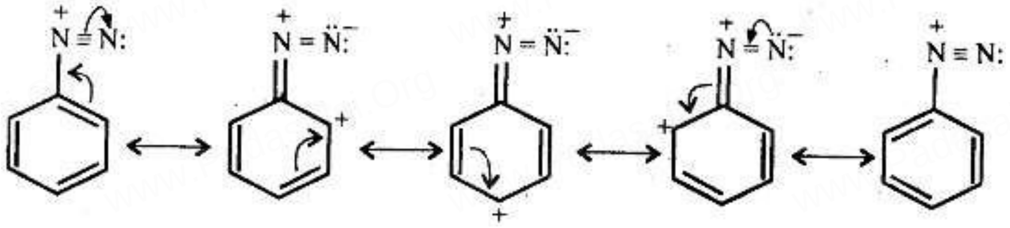
i. Aniline does not undergo Friedel . Crafts reaction

A Friedel Crafts reaction is carried out in the presence of AlCl$_3$. But AlCl$_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with AlCl$_3$ to form a salt.

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

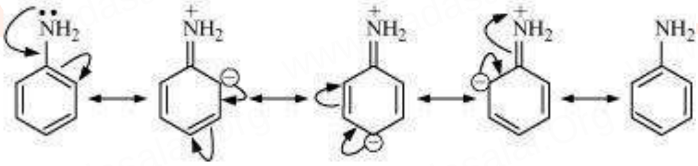
ii. Diazonium salts of aromatic amines are more stable than those of aliphatic amines

In diazonium salt, the structure goes under resonance due to which the dispersal of positive charge is more and we know that higher is the resonance higher is the stability. Therefore diazonium salt of aromatic amines is more stable than those of aliphatic amines.



iii. pKb of aniline is more than that of methylamine

Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK$_b$ of aniline is more than that of methylamine.

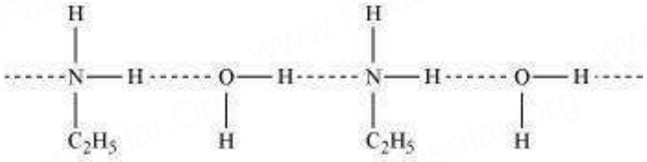


iv. Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

v. Ethylamine is soluble in water whereas aniline is not

Ethylamine when added to water forms intermolecular H-bonds with water. And therefore it is soluble in water. But aniline does not form H-bond with water to a very large extent due to the presence of a large hydrophobic -C6H5group. Hence, aniline is insoluble in water.



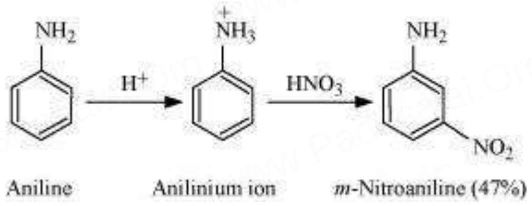
Ethylamine

vi. Amines are more basic than amides

The lone pair of electrons on the amine are more available to accept a proton and act as a base. This is because in amides, the carbonyl (C=O) group is highly electronegative, so has a greater power to draw electrons towards it, making the lone pair of the amide nitrogen less availble to accept a proton.

vii. Although amino group is o - and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m- nitroaniline

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

9. Arrange the following

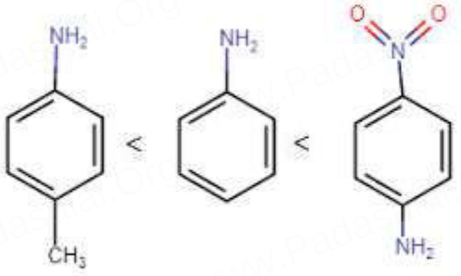
i. In increasing order of solubility in water, $C_6H_5NH_2$,$(C_2H_5)_2NH$,$C_2H_5NH_2$

The more extensive the H-bonding, the higher is the solubility.Thus, $C_2H_5NH_2$ undergoes more extensive H-bonding than $(C_2H_5)_2NH$. Hence, the solubility in water of $C_2H_5NH_2$ is more than that of $(C_2H_5)_2NH$.

$$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$$

ii. In increasing order of basic strength

a) aniline, p-toludine and p-nitroaniline



p-nitroaniline < aniline < p-toludine

In p-toluidine, the presence of electron-donating -CH_3 group increases the electron density on the N-atom. Thus, p-toluidine is more basic than aniline. -NO_2 group decreases the electron density over the N-atom in p-nitroaniline. Thus, p-nitroaniline is less basic than aniline.

b) In increasing order of basic strength $C_6H_5NH_2$,$C_6H_5NHCH_3$,p-Cl-$C_6H_4NH_2$,

i) Chlorine atom has both - I effect and + R effect so para chloro aniline is less basic than aniline

CH_3- group is electron donating group in so increases electron density in N - atom so, N - Methyl aniline is more basic than aniline

$$p\text{-}Cl\text{-}C_6H_4NH_2 < C_6H_5NH_2 < C_6H_5NHCH_3$$

iii. In decreasing order of basic strength in gas phase

$C_2H_5NH_2$, $(C_2H_5)_2NH$,$(C_2H_5)_3N$ and NH_3

In gas phase there is no hydrogen bonding , therefore stabalisation due to hydrogen bonding is not there. Therfore the only effect to determine the strength is the inductive effect.The +I effect increases with increase in the alkyl group.Therefore the basic strength will be the highest in $(C_2H_5)_3N$ and least in NH_3. Therefore the decreasing order of basic strength in gas phase will be

$$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$$

iv. In increasing order of boiling point C_6H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

The elcetronegativity of O is more than N. Therefore C_6H_5OH forms hydrogen bonding and because of the hydrogen bonding the alcohols will have higher boiling point than the amines with comparable molecular mass.Now between $(CH_3)_2NH$ and $C_2H_5NH_2$, $C_2H_5NH_2$ has more hydrogen atom attached the Nitrogen.Therfore the extent of hydrogen bonding will be more in primary amines i.e $C_2H_5NH_2$ as compared to sec or ter amines.Therfore $C_2H_5NH_2$ will have higher boiling point as compared to $(CH_3)_2NH$ .Therefore the increasing order of boiling point will be as given below.

Ans: $(CH_3)_2NH < C_2H_5NH_2 < C_6H_5OH$

v. In decreasing order of the pKb values $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and CH_3NH_2

Larger the value of Kb or smaller the value of pKb , stronger is the base.

(i) In $C_2H_5NH_2$, only one $-C_2H_5$ group is present while in $(C_2H_5)_2NH$, two $-C_2H_5$ groups are present. Thus, the +I effect is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Therefore, the electron density over the N-atom is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Hence, $(C_2H_5)_2NH$ is more basic than$C_2H_5NH_2$.

ii) In $C_6H_5NHCH_3$ is less basic than $((C_2H_5)_2NH$ and $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_6H_5NHCH_3$ the former will be more basic due to the +I effect of $-CH_3$ group. Hence, the order of increasing basicity of the given compounds is as follows:

$C_6H_5NHCH_3 < CH_3NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

We know that the higher the basic strength, the lower is the pKb values.

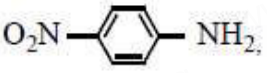
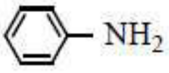
$C_6H_5NHCH_3 > CH_3NH_2 > C_2H_5NH_2 > (C_2H_5)_2NH$

vi. Increasing order of basic strength $C_6H_5NH_2$,$C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

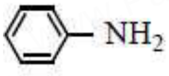
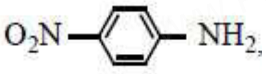
$C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the + I effect of two - CH_3 group in $C_6H_5N(CH_3)_2$ Further CH_3NH_2 contains one - CH_3 group while $(C_2H_5)_2NH$ contains two - C_2H_5 group. Thus, $(C_2H_5)_2NH$ is more basic than CH_3NH_2
Now $C_6H_5N(CH_3)_2$ is less basic than CH_3NH_2 because of the - R effect of - C_6H_5 group.
Hence, the increasing order of the basic strength of the given compounds is as follows

$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

vii. In decreasing order of basic strength

$CH_3CH_2NH_2$   , $CH_3 - NH_2$.

Aliphatic amines are more basic than aromatic amines.so $CH_3CH_2NH_2$and$CH_3 - NH_2$ are more basic .
$CH_3CH_2NH_2$ is more +I effect than $CH_3 - NH_2$, so $CH_3CH_2NH_2$ more basic than $CH_3 - NH_2$
In case of substituted aniline, electron withdrawing group like - NO_2, they have both - R effect as well as - I effect . as result all nitro amines are weaker bases than aniline .

$CH_3CH_2NH_2 > CH_3 - NH_2 >$  > 

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10. **How will you prepare propan -1- amine from butane nitrile**
i) butane nitrile **ii) propanamide** **ii) 1- nitropropane**

i) Butane nitrile converted into propan -1- amine

$$CH_3-CH_2-CH_2CN \xrightarrow{H^+/Hydrolysis} CH_3-CH_2-CH_2CONH_2 \xrightarrow[\text{Hoffmann's degradation}]{Br_2/KOH} CH_3-CH_2-CH_2NH_2$$

ii) propanamide converted into propan -1- amine

$$CH_3-CH_2-CONH_2 \xrightarrow{LiAlH_4/H_2O} CH_3-CH_2-CH_2NH_2$$

iii) 1- nitropropane converted into propan -1- amine

$$CH_3-CH_2-CH_2NO_2 \xrightarrow{Sn/HCl} CH_3-CH_2-CH_2NH_2 + 2H_2O$$

11. **Identify A,B,C and D**

$$CH_3-NO_2 \xrightarrow[6[H]]{LiAlH_4} CH_3NH_2 \rightarrow \text{———} \xrightarrow{HNO_2} + CH_3-CH_2-NH-CH_3 \xrightarrow{CH_3-CH_2Br_2}$$

$$(CH_3-CH_2)_2N-CH_3 \xrightarrow{H_2SO_4} [(CH_3-CH_2)_2NH^+-CH_3]HSO_4^-$$

A - Methyl amine **B - N -Metyl ethan-1- amine**
C - N,N-diethylmethylamine **D - Quarternary ammonium hydrogen sulphate**

12. **How will you convert diethylamine into**
i) N,N-diethylacetamide **ii) N- nitrosodiethylamine**

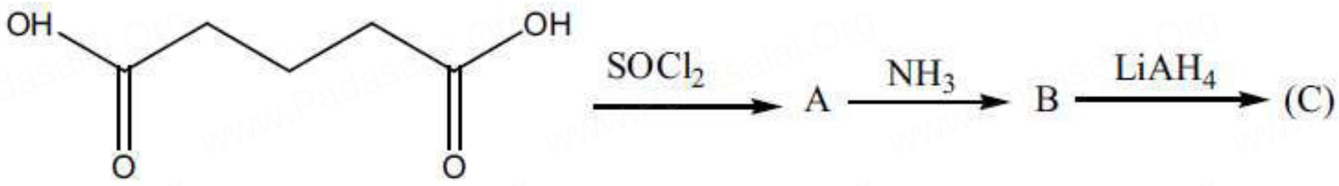
i) Conversion of diethylamine into N,N-diethylacetamide

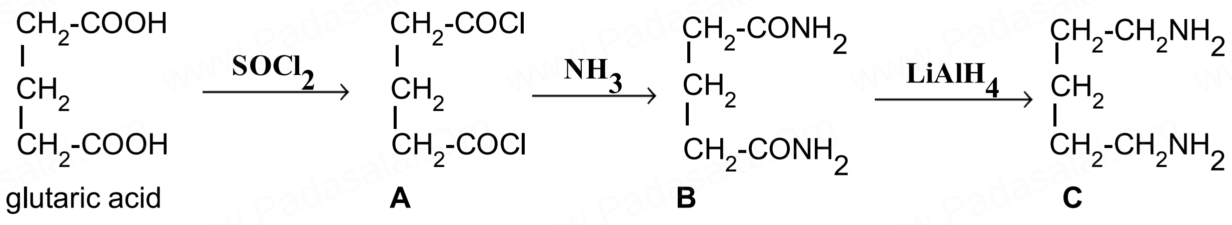
$$(CH_3-CH_2)_2N-H + CH_3COCl \xrightarrow{pyridine} (CH_3-CH_2)_2N-CO-CH_3 + HCl$$

ii) Conversion of diethylamine into N- nitrosodiethylamine

$$(CH_3-CH_2)_2N-H \xrightarrow{HNO_2} (CH_3-CH_2)_2N-N=O \text{ (N-nitrosodiethylamine)}$$

13. **Indentify A,B and C**





$$\begin{array}{c} CH_2-COOH \\ | \\ CH_2 \\ | \\ CH_2-COOH \\ \text{glutaric acid} \end{array} \xrightarrow{SOCl_2} \begin{array}{c} CH_2-COCl \\ | \\ CH_2 \\ | \\ CH_2-COCl \\ A \end{array} \xrightarrow{NH_3} \begin{array}{c} CH_2-CONH_2 \\ | \\ CH_2 \\ | \\ CH_2-CONH_2 \\ B \end{array} \xrightarrow{LiAlH_4} \begin{array}{c} CH_2-CH_2NH_2 \\ | \\ CH_2 \\ | \\ CH_2-CH_2NH_2 \\ C \end{array}$$

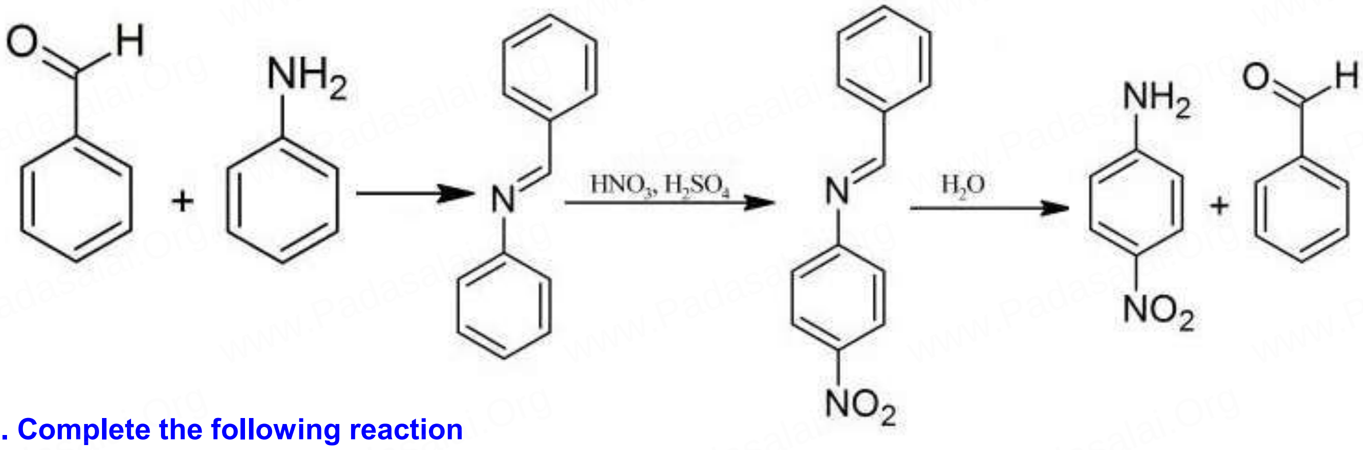
A- Glutaryl chloride

B -Pentanediamide (Glutaramide)

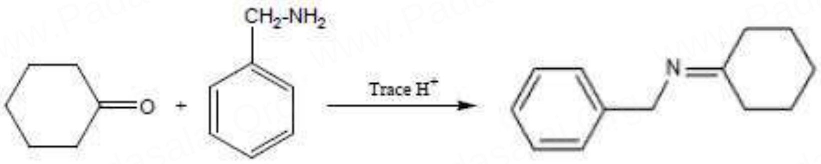
C-1,5 - diaminopentane

14. Indentify A,B,C and D

aniline + benzaldehyde $\rightarrow$ A $\xrightarrow{\text{Conc } HNO_3 / B}$ C and D

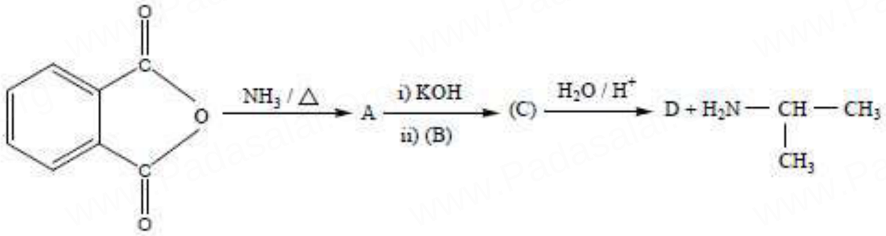


15. Complete the following reaction

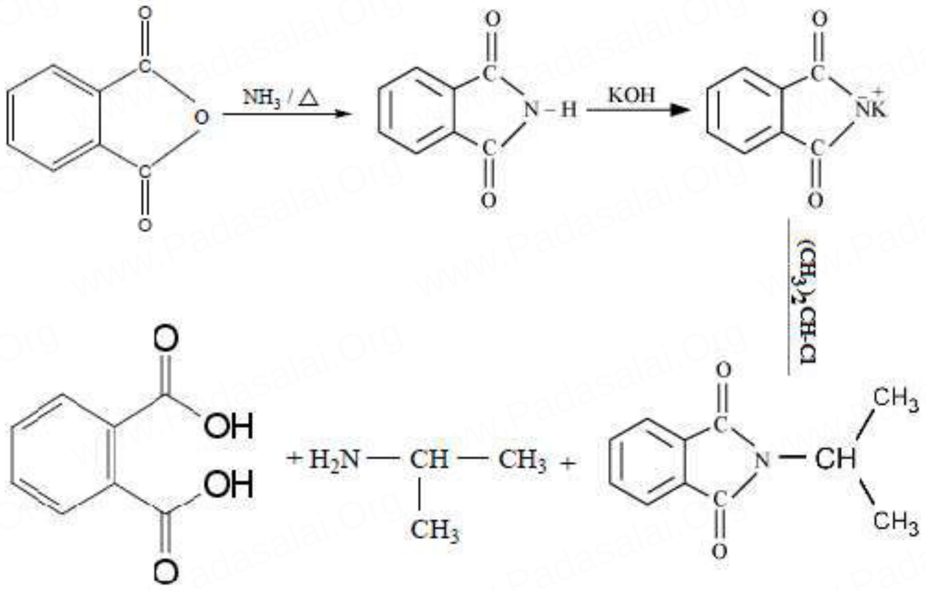


N-benzyl cyclo hexane imine

16. Predict A,B,C and D for the following reaction



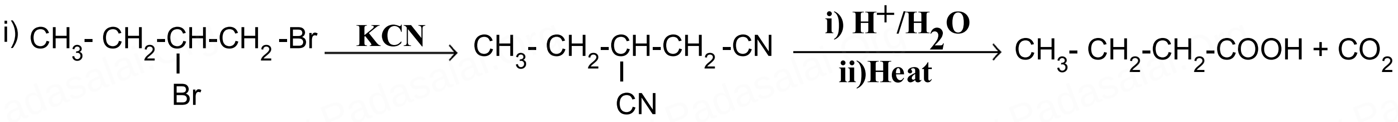
Ans:



A- phthalimide **B - 2 -Chloropropane**

C- N- isopropyl phthalimide **D- phthalic acid**

17. **A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO_2. (B) on heating with liquid ammoniafollowed by treating with Br_2 /KOH gives (c) which on treating with $NaNO_2$ and HCl at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74.Identify A to D.**



i) $CH_3-CH_2-\underset{Br}{CH}-CH_2-Br \xrightarrow{KCN} CH_3-CH_2-\underset{CN}{CH}-CH_2-CN \xrightarrow[ii)Heat]{i)\ H^+/H_2O} CH_3-CH_2-CH_2-COOH + CO_2$

ii) $CH_3-CH_2-CH_2-COOH + NH_{3\,(lig)} \xrightarrow{Heat} CH_3-CH_2-CH_2-CONH_2 \xrightarrow{Br_2/KOH} CH_3-CH_2-CH_2-CONH_2$

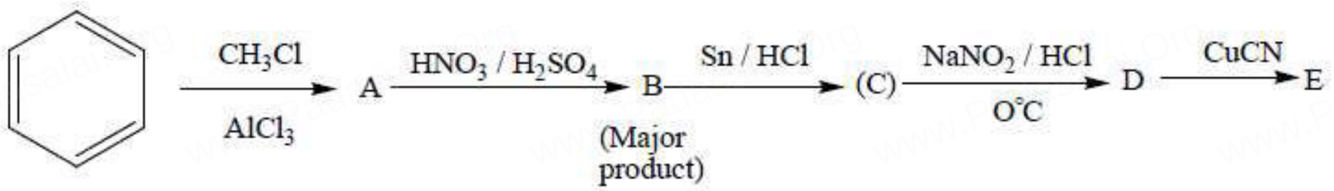
iii) $CH_3-CH_2-CH_2-CONH_2 \xrightarrow[Low\ T]{NaNO_2/HCl} CH_3-CH_2-CH_2-OH \xrightarrow[2(O)]{K_2Cr_2O_7/H^+} CH_3-CH_2-COOH$

A - 1,2 - diamino butane **B- 1,2 dicyano butane**

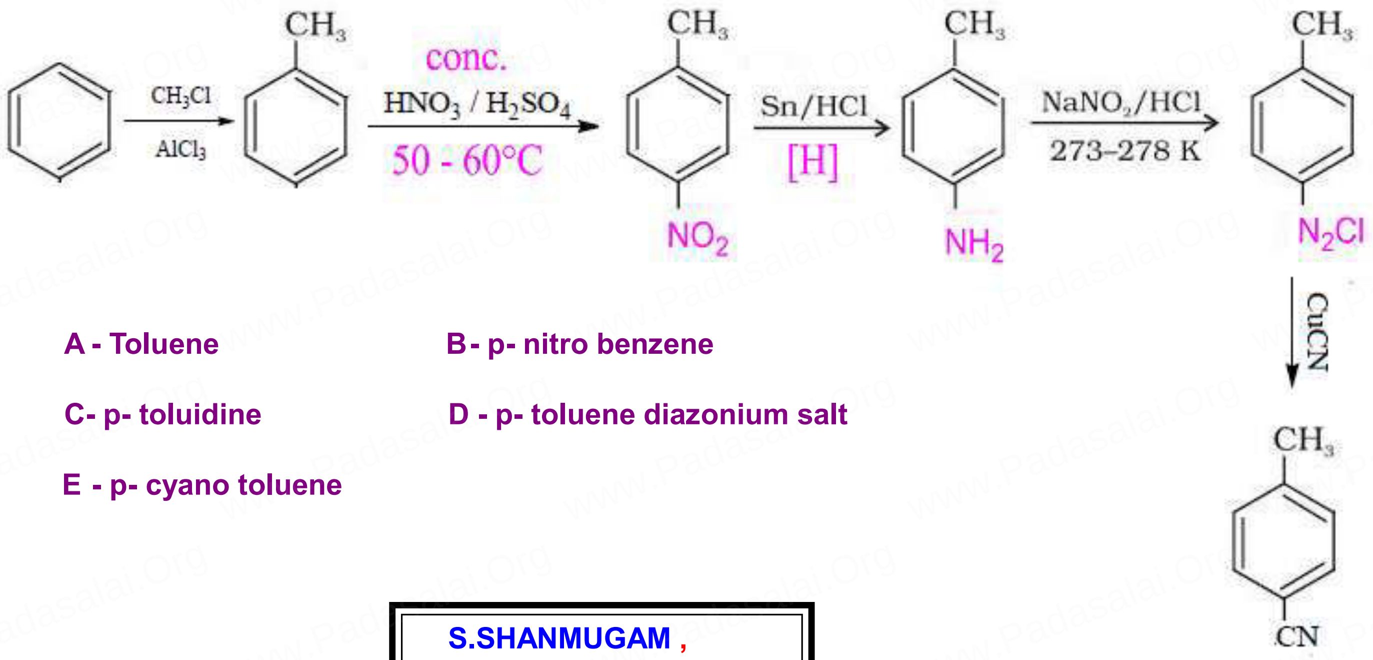
C- 1 - amino prpane **D - Propanoic acid**

Molecular mass of propanoic acid - 74

18. **Indentify A to E in the following frequency of reactions.**



Ans:



A - Toluene **B - p- nitro benzene**

C- p- toluidine **D - p- toluene diazonium salt**

E - p- cyano toluene

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