चौधरी PHOTOSTAT

"I don't love studying. I hate studying. I like learning. Learning is beautiful."

"An investment in knowledge pays the best interest."

Hi, My Name is

Chemical Science for CSIR NET *Career Endeavour*

Coordination Chemistry

6 July

- Coordination compound → Metal cation + Ligands
- Metal cation/atom → Lewis acid
  → Electophile
- Ligand → Any species (molecule or ion) having at least one electron pair and that can be donated to a metal cation.

Example:

An atom can donate electron only when its octet is complete otherwise not. So, molecule/Ion can donate, act as ligand.

More e⁻ → large attraction → less energy → ↑ stable → ↑ donation

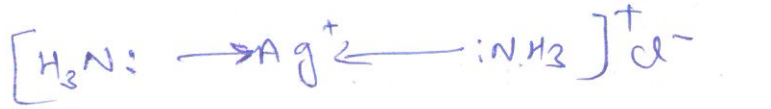
After completion or making of covalent bond, we don think about donation of e⁻.

Coordination compound:

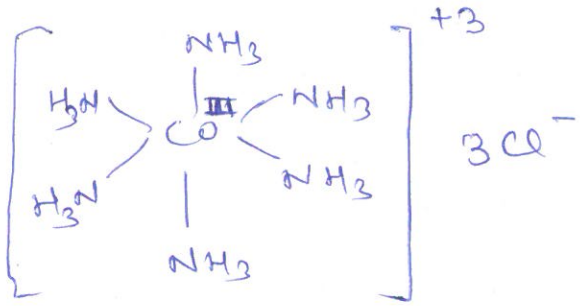
The compound in which a group of ligands is attached to a metal cation/atom through coordinate covalent bonds is called a coordination comp.

Ex:-

$[Ag(NH_3)_2]Cl$



$[Co(NH_3)_6]Cl_3$



Classification of complexes:-

1) Complexes having no complex ion.

Ex: i) $[Pt^{II}(NH_3)_2Cl_2]$ → Neutral, having no charge

↓

• It does not give any ion in aq. Sol.

ii) $[Co^{III}(NH_3)_3Cl_3]$

2) Complexes containing complex cation.

$[Co^{III}(NH_3)_6]^{+3}Cl_3$ — $[Co(NH_3)_6]^{+3}$ complex cation

$[Ag(NH_3)_2]^{+}Cl^{-}$ — $[Ag(NH_3)_2]^{+}$ complex cation

3) Complexes containing complex anion.

i) $Fe^{II} \cdot 6CN^{-} \rightarrow 4K^{+}[Fe(CN)_6]^{4-} \rightarrow K_4[Fe(CN)_6]^{4-}$

$[Fe(CN)_6]^{4-}$ complex anion

ii) $Co^{2+}\ 4Cl^{-} \rightarrow (NH_4)_2[CoCl_4]^{2-}$

4) complexes containing both complex cation and complex anion:-

Ex:- $[Pt^{+2}(NH_3)_4][Pt^{+2}Cl_4]$

$[Pt^{+2}(NH_3)_4]$ complex cation; $[Pt^{+2}Cl_4]$ complex anion.

$[Pt(NH_3)_4Cl_2][PtCl_4]$

★ To learn for both cation & anion complexes ★

Pt^{2+} → C.N 4 & Sq. Planar

Pt^{+4} → C.N 6 Octahedral

4) Complexes containing bridging ligands:
(Bridged complexes)

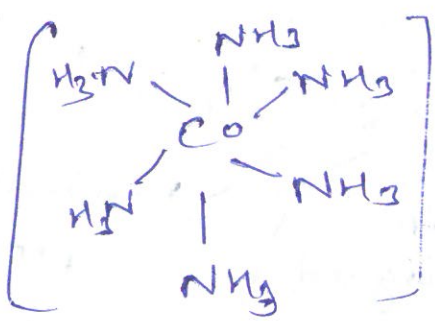
Ex- $\left[(H_3N)_4 Co(OH)(NH_2)Co(NH_3)_4\right]Cl_4$

$2x - 2 + 0 - 4 = 0$
$x = +3$

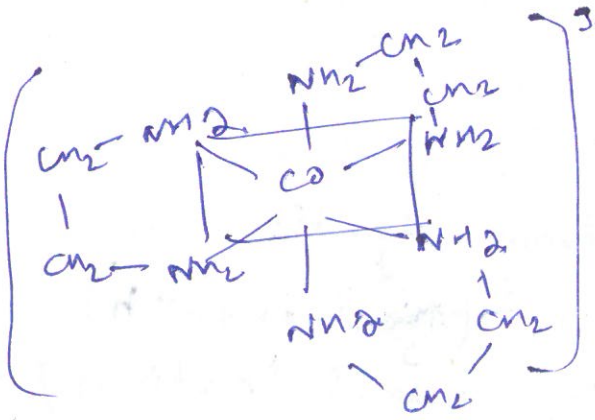
Coordination Number:

Number of donar atoms attached to a metal cation. (No. of coordinate bonds)

1) $[Co(NH_3)_6]^{3+}$



2) $[Co(en)_3]^{3+}$



→ No. of donar atoms → 6
No. of ligands → 3

3) en → $NH_2-CH_2-CH_2-NH_2$
(C, N)

Coordination sphere:

The square bracket [ ] in which a complex ion is enclosed.

$[Co(NH_3)_6]^{3+}$ → coordination sphere

Counter ion OR Ionization Sphere:

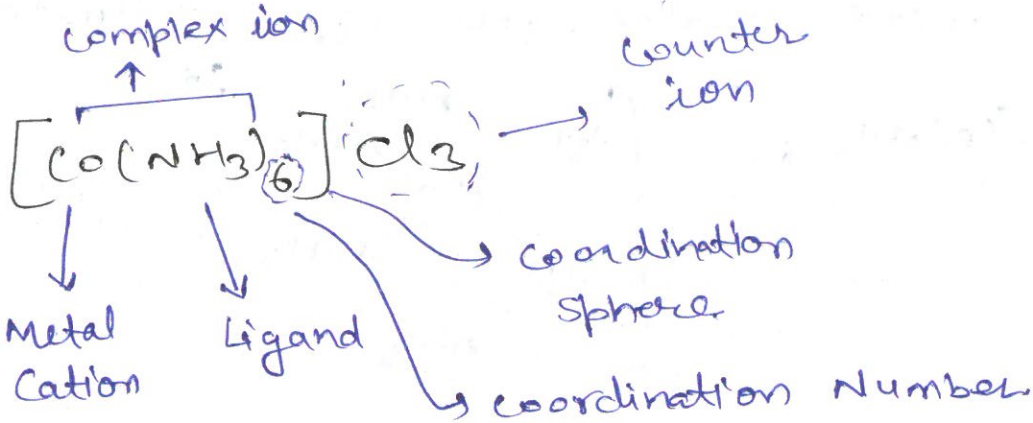
The ion (cation or anion) outside the coordination sphere.

$[Co(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$

↘ ↙

counter ion

⇒



Classification of Ligands:-

i) Monodentate Ligands:-

Mono → single

dentate → comes from dentis (teeth or tooth)

A ligand can bite a metal cation/atom by one donar atom is called monodentate ligand.

OR

A ligand that can donate one e⁻ pair from its donar atom to a metal cation/atom is called monodentate ligand.

ORGANOMETALLIC CHEMISTRY

19/9/19

Edward Frankland: Father of oreganometallic chemis

Difference btw organometallic & coordition compound

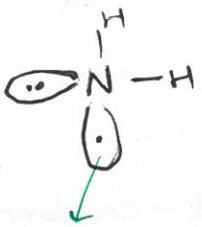
1) In coordination, wecner complexes

$[Fe(H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{2+}$ ⇒ only simple ligands like H_2O, NH_3, Cl (inorganic comp.)

But in organometallic, most of cases oreganic ligands are used (ligands formed by H & C)

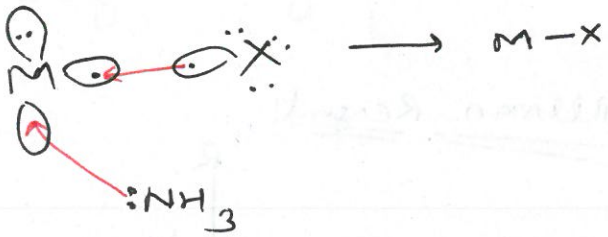
2) Coordination: Fe^{2+}, F^{3+}, F^{+4} → High O.S

organometallic: Fe(-2), 0 → Low O.S



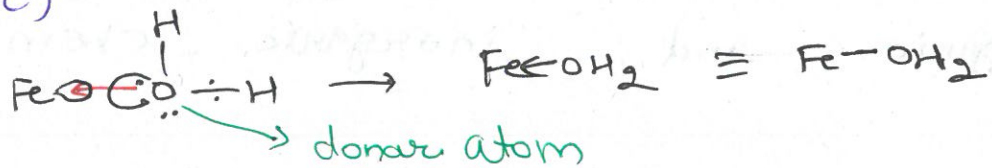
→ Jb tk odd e⁻ h, even e⁻ donate nhi krega.

This will donate



Metal don't used any e⁻ to make bond with NH_3.

Ligand: all properties are similar as donar (σ OC)

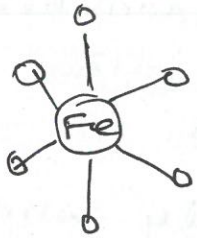


- Central atom is head of family.
- Transistion metal have filled & empty orbitals both.

even Zn also have vacant orbital.

$3d^{10}4s^2$ → filled, 4p, 4d ↦ empty

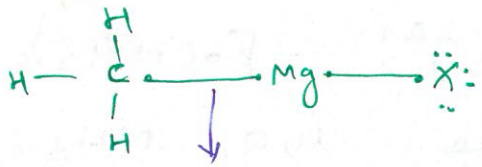
3)



Grignard reagent ($RMgX$)

I

Mg:- 2.8.2 — 1

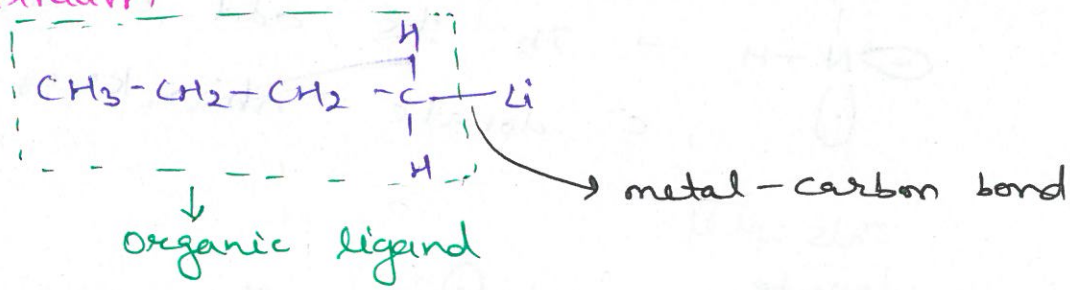


one metal-carbon bond

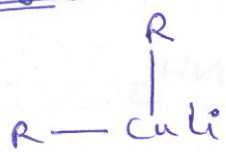
* For a compound said to be organometallic, there must be atleast one metal-carbon bond. For eg: Grignard reagents

Li - $1s^2 2s^1$

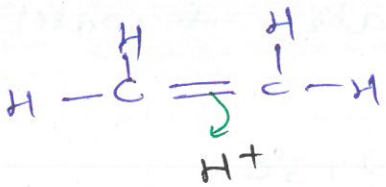
methyl lithium

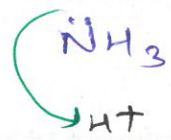


Gilliman Reagent:



Organometallic chemistry is a bridge btw Oreganic and inorganic chemistry.





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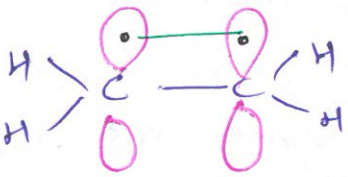
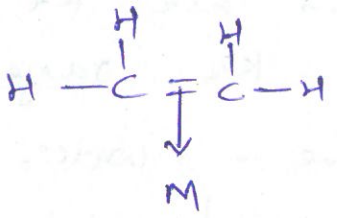
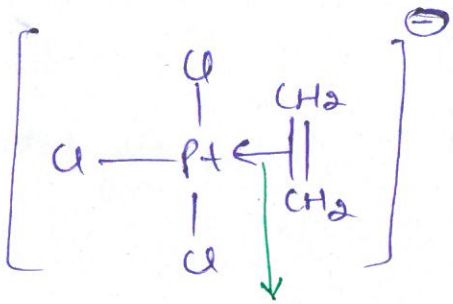




→ Organometallic compound

Zeise's Salt:

It uses only 3e⁻ to make this complex.



Pt – d^{10} system
10 valence e⁻

Organometallic comp.
(M – C bond)

→ In coordination: Low & High spin complexes depends on metal & ligand both.

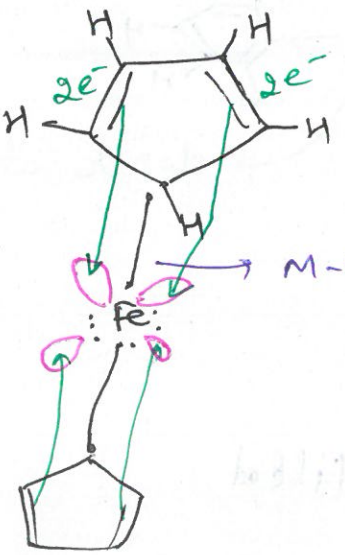
3d – $[Fe(H_2O)_6]^{2+}$ – H.S 4d – $[Ru(H_2O)_6]^{2+}$ L.S

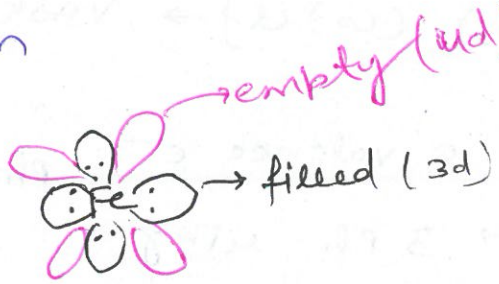
→ In organometallic, ligand is always strong & forms LS complexes.

Co – $3d^7 4s^2$

Co – $3d^9$ system

*





Cp_2Fe

Ferrocene

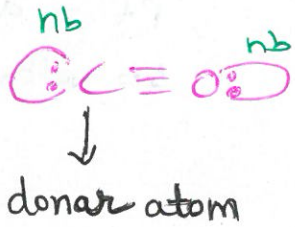
Organometallic compl

- Organometallic compounds are air & water sensitive.

Ferrocene: M.P greater than 273°C

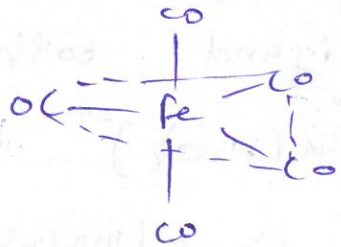
Air sensitive → air ki presence me oxidation ho jayega.

water sensitive – water ke presence me breakdown ho jayenge.



Lewis dot: St

OMC → $[Fe(CO)_5]$ ⇒ TBP geometry

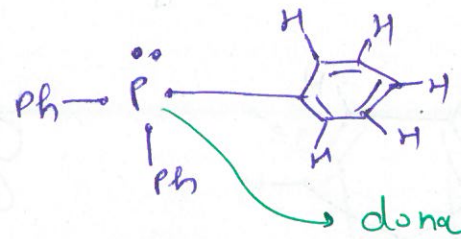


CO is not organic ligand (not H present)
But then also $[Fe(CO)_5]$ is omc.

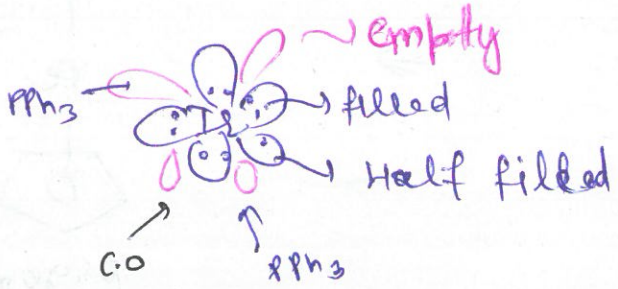
$[Fe(CO)_4]^{2-}$ → collman's reagent

$[Ir(PPh_3)_2(CO)Cl]$ → Vaska's complex

P → 5 valence e⁻
→ 3 Ph ring



Ir → $d^7 s^2$

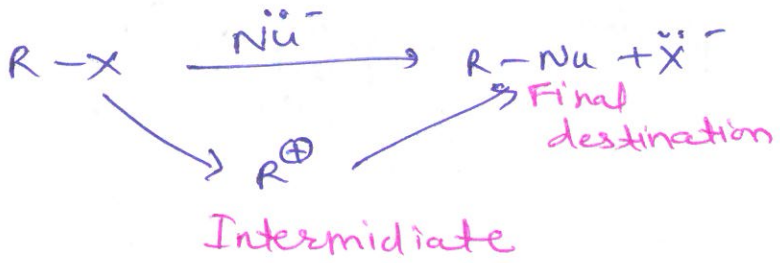


Reactive Intermidiate

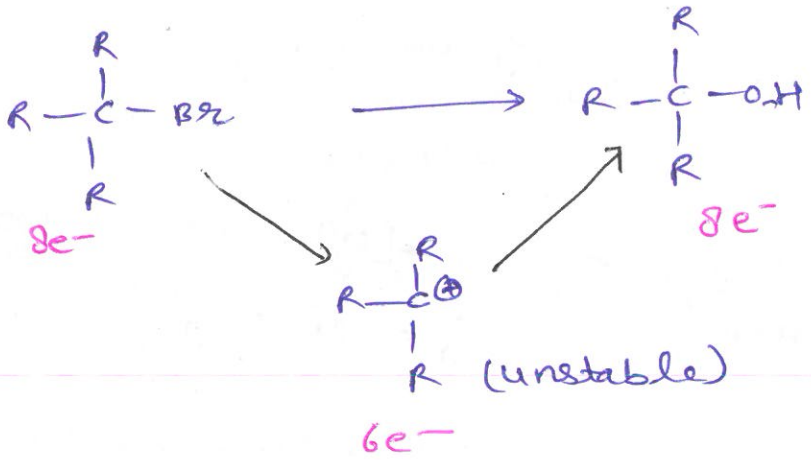
10/8/19

→ They are highly unstable

→ They are very short lived species.



→ Intermidiates is not final destination. It is the ~~state~~ b/w reactant & product.

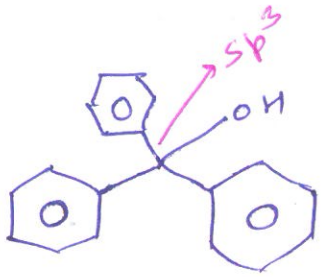


→ Intermediates are high unstable because their octet is not complete & these are not charged species.

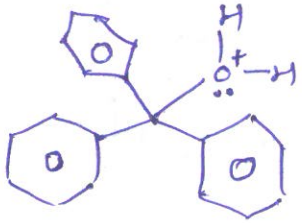
→ All are unstable & we find stability in unstability.

→ Intermediates are transient they formed during rxn & dissappears.

Carbocation :— [1902] (accidental Invention)

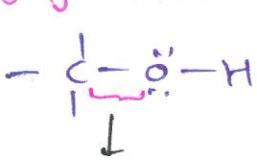


$H_2SO_4 \rightarrow H^+$
(fall on floor)

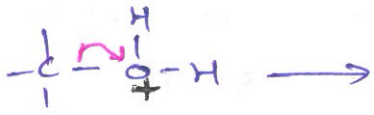


Colourless
(No conjugation)

Coloured



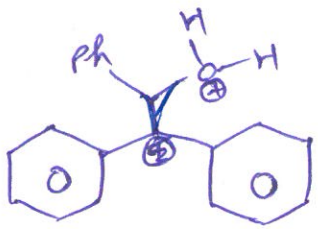
H^+



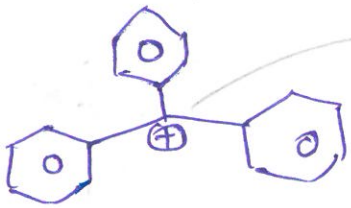
$\longrightarrow$ $+H_2O$

Polar bond
due to E.N diff.
(unhappy)

Very unstable
due to +ve charge on O.
(break)



$-H_2O$



1st charge in organic chemistry

conjugation, extent of delocalisation → coloured

(carbonium ion)

(+vely charged species)

→ Onium word is used when an central atom makes bonds more than its valency.

⇒ Wrp 14 tk jo valene e^- honge utni hi valency hogi IUPAC suggest these names.

($2e^- \rightarrow 1$ bond)

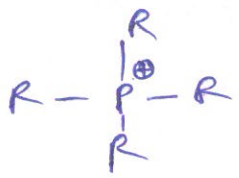
(ammonia)

(ammonium ion)

→ normal valency se ek bond extra bnaya h.

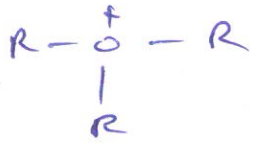
* Valance → outmost shell me e^-

Valency → Normal form me kitne bond bnayenge

*  → Phosphonium ion

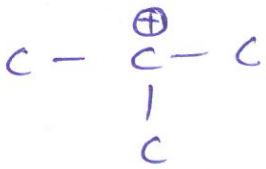
Valence e^- → 3
makes bond → 4
(valency)
So, onium word is used

* $R-\ddot{O}-R$ → Normal valency (valency = 2)

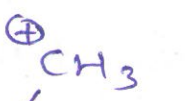
 - oxonium ion

*  sulphonium ion

S forms 2 bonds in normal valency

1) Carbonium Ion!- 

Here, carbon is not making bonds more than its valency (normal). So, onium word cann't used here.
So, the name is changed to Carbenium ion.



carbenium ion

ohla scientist gives this name.
Bonds less than their normal valency.

carbonium ion
↳ bonds more than their normal valency

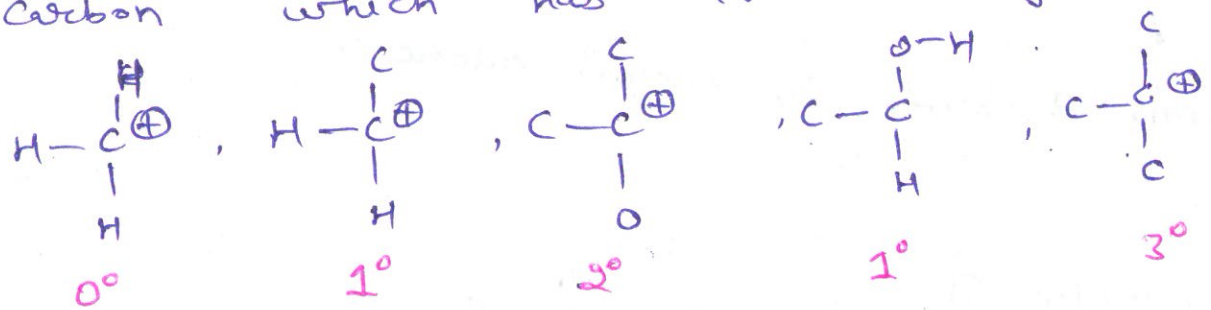
Then also, there is lot of confusion. then the generic name comes known as Carbocation.

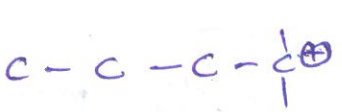
→ carbocation is a generic name which means the species in which carbon containing positive charge.

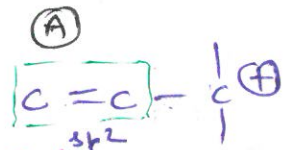
→ Carbocation contains both carbonium + carbenium ions both.

Degree of carbocation! –

The no. of carbon attached to the carbon which has +ve charge.



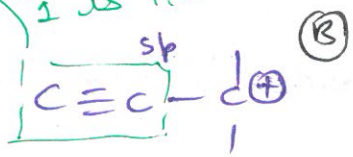
*  1°

*  Ⓐ

sp²

1°/allylic carbocation

1π is far & 1 is all

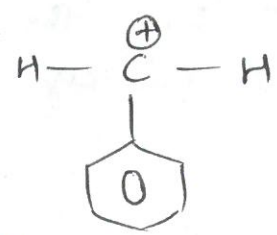
*  Ⓑ

sp

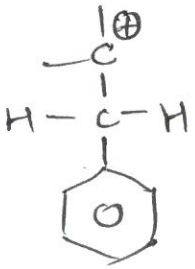
1°/Propargylic carbocation

So, conjugation takes place ($\pi \rightarrow p^E$)

More conjugation in Ⓐ bcoz less s- character due to sp^2.

* 

1°/Benzylic carbocation

* 

Homobenzylic carbocation.

Reagents in organic Synthesis :-

8/9/19

(A) oxidation

(B) Reduction

(C) Organometallic reagents

(D) Misscellenous Functions.

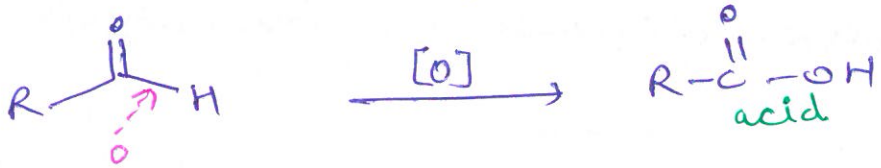
(A) Oxidation :-

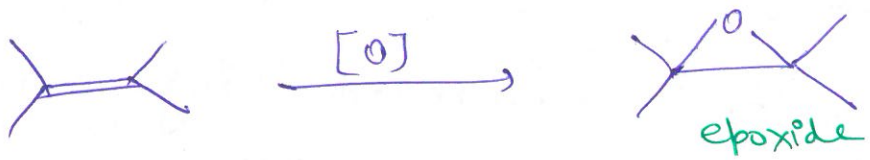
→ Removal of hydrogen.

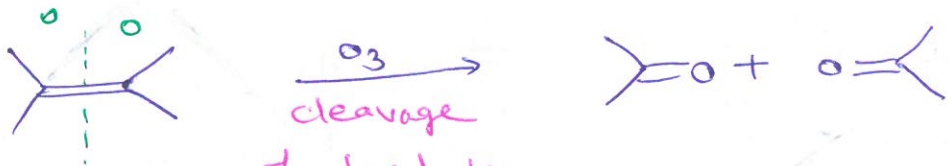
$R-CH_2-OH \xrightarrow{-H_2} R-\overset{H}{\underset{|}{C}}=O$

Primary alcohol → aldehyde

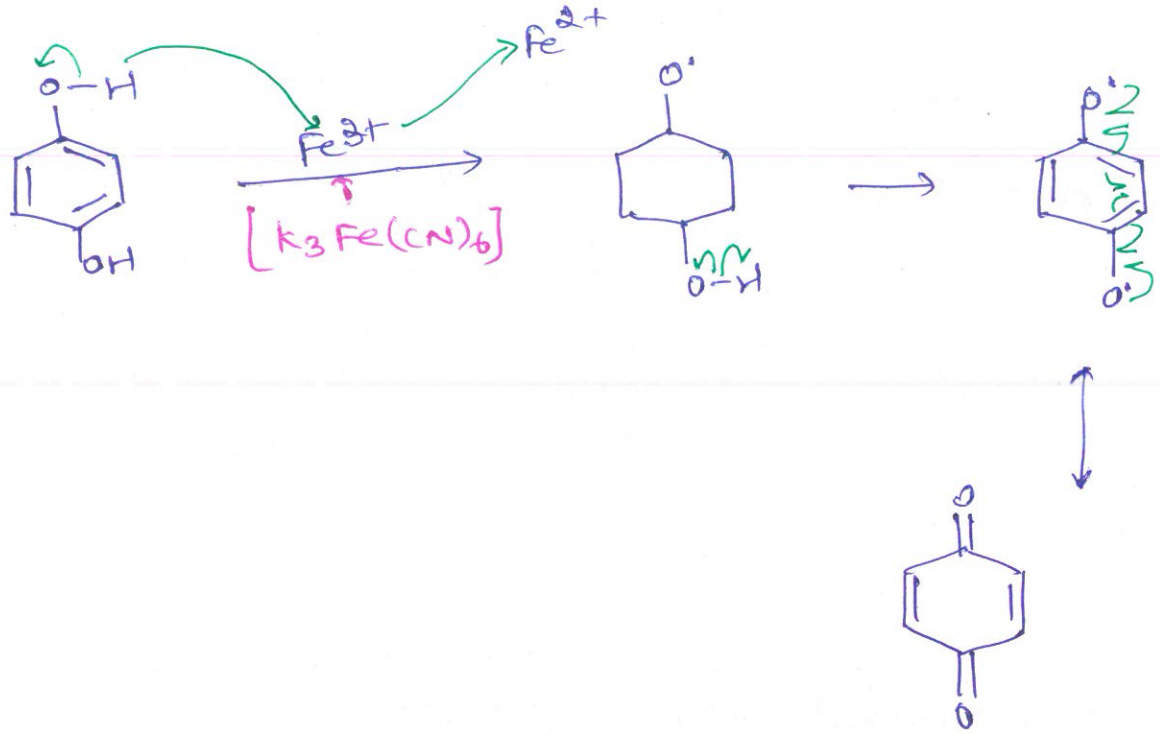
→ Addition of oxygen.







→ Removal of electrons

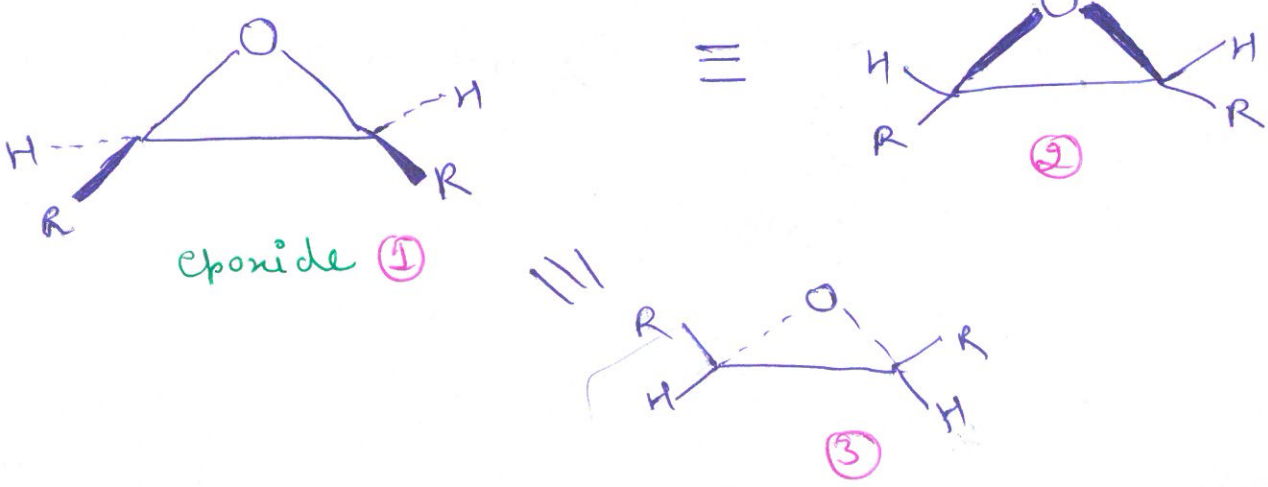


1) Oxidation of alkene :-

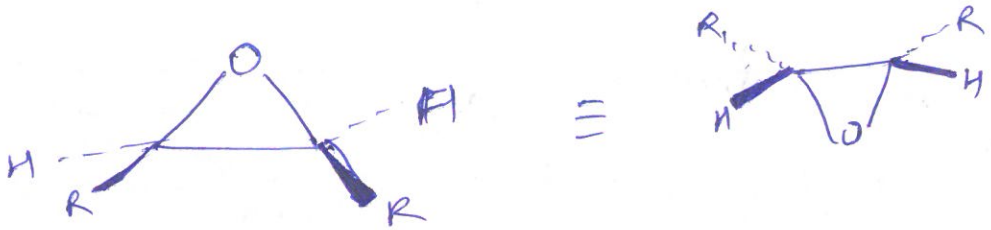
* Epoxidation
* Dihydroxylation
* Oxidative cleavage → ozonolysis

1) Epoxidation :-

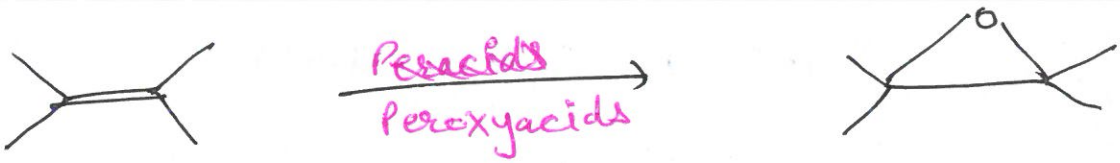
Epoxide : Three membered ring containing hetro atom as oxygen.



① , ② & ③ are identical st.

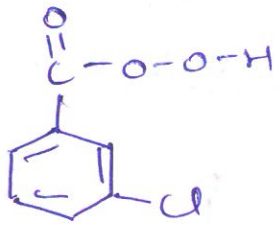


⇒



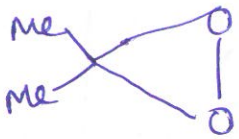
Peroxyacids are used for epoxidation of alkenes.

Peroxyacids →
- CH_3CO_3H
- $PhCO_3H$
- m-CPBA
- H_2O_2-AcOH
- CF_3CO_3H



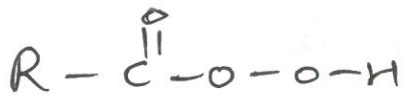
m-chloroperbenzoic acid

AcOH → acetic acid

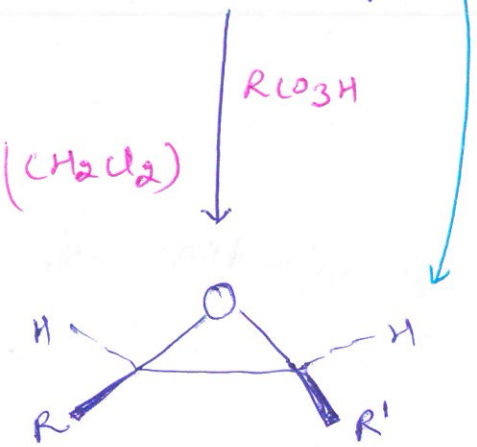
-  DMDO (Dimethyle dioxirane)
- Transition metal catalyst / t_{BuOOH}

(Name Rxn) → Sharpless Asymmetric epoxidation

Ti, V, Mo, Re



Representation of alkene :

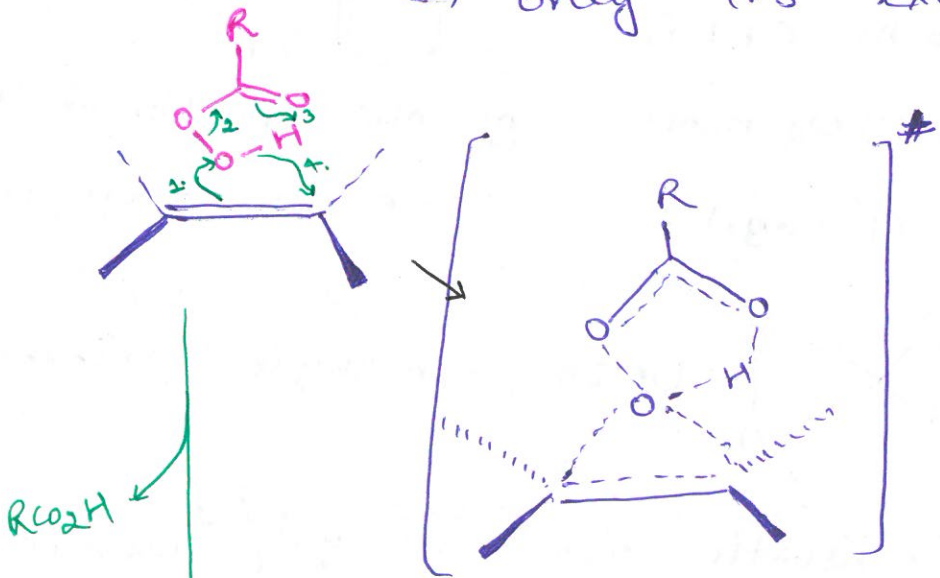


Mechanism:

→ concerted process

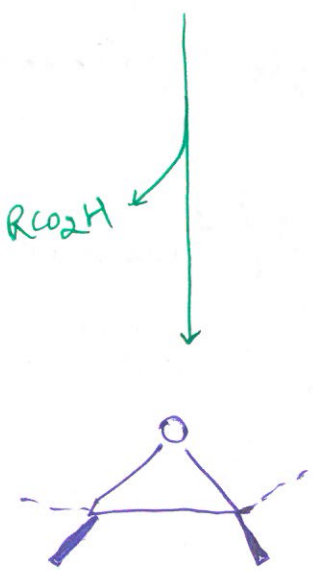
→ only T.S exist

1. Initiation



T.S (spiro comp.)

(Highly strained)



2. O—O (Peroxide) bond
↓
weak due to lp-lp repulsion
So, bond breakes

New bond bn the h or old bond break ho the h → Sbhi ko partial bond se represent krna h. — T.S

Thermodynamics

V. Imp

1) Basic Mathematics
- Unit conversion
- Differentiation
- Partial differentiation
- Total differentiation
- cyclic rule
- Definitions

2) Ist law of thermodynamics
- ΔU, ΔH
- Heat capacity
- Thermodynamic coefficient
- Isothermal Process
- Adiabatic Process ← Tricky Ques.
- Equipatition Theorem.

3) 2nd law of T.D
- carnot cycle
- Introduc
- ★ calcul of ΔS
- Refrigerato
- criteria of Spontanit

4) Miscellenous Topics:
- Kirchoff eqn
- ★ clausius clapeyron eqn
- Gibbs-Helmholtz eqn

5) Partial Molar Quantities
- chemical quantities Potential
- Gibb's Duhem eqn
- ★ ΔG_{mix} & ΔS_{mix}
- ★ Fugacity

$\log x = y$

$x = 10^y$

$\ln x = y$

$x = e^y$

Δz → large value change of z

dz → small value change of z

∂z → very small value change of z

UNIT CONVERSION :

1) Volume : $\boxed{1\,L = 1\,dm^3 = 10^{-3}\,m^3 = 10^{3}\,cm^3}$

$1\,mm = 10^{-1}\,cm$

$(1\,mm)^3 = (10^{-1}\,cm)^3 \Rightarrow 1\,mm^3 = 10^{-3}\,cm^3$

$1\,m^3 = 10^{6}\,mL$

$1000\,mL = 10^{-3}\,m^3$

10^{6}

2) Pressure :

S.I unit = Pascal (Pa)

$\boxed{\begin{aligned} 1\,atm &= 1.01325 \times 10^{5}\,Pa \\ 1\,bar &= 10^{5}\,Pa \end{aligned}}$

$1\,atm = 760\,mm\,Hg$

$1\,torr = 1\,mm\,Hg$

$1\,atm = 101325\,Pa$

$1\,atm = 101325\,N\,m^{-2}$

$1\,atm = 1.01325 \times 10^{5}\,N\,m^{-2}$

$= 1.01325 \times 10^{5}\,Pa$ (N m^{-2} = Pa)

$= 1.01325 \times \frac{10^{5}\,J}{Pa}\,Pa$

$= 1.01325\,bar$

3) Energy / Work :

S.I Unit = Joule

$\boxed{1\,cal = 4.18\,Joule}$

$w = -P_{ext}\,\Delta V$

$\boxed{\begin{aligned} 1\,Pa\,m^3 &= 1\,J \\ 1\,atm\,L &= 101.3\,J \\ 1\,bar\,L &= 100\,J \end{aligned}}$ → Most common.

$1\,atm\,L = 24.23\,cal$

Assignment - 1

1) $W = 3\ atm\ L$

$W = 101.3 \times 3\ J = 303.9\ J$

$W = \frac{101.3 \times 3}{4.18} \times 10^{-3} = 7.27 \times 10^{-2}\ kcal$

8) $1\ L\ Pa = \_\_\_\_\ atm\ m^3$

$1\ L\ Pa = \_\_\_\_\ 10^{-3} \times 101.3\ J$ (× $10^{+3}\ atm\ L$)

$\Rightarrow 1\ L\ Pa = \_\_\_\_\ atm\ m^3$

$V \times P \quad P \times V$

$\Rightarrow 1\ (1\ L)\ (1\ Pa)$

$\Rightarrow (10^{-3}\ m^3)\left(\frac{1}{1.01325 \times 10^5}\ atm\right)$

$\Rightarrow \frac{1}{1.01325} \times 10^{-8}\ m^3\ atm$

~~$1\ cm = 10\ dm$~~

~~$1\ cm^3 = 10^3\ dm^3$~~

11) $32\ Pa\ dm^3 = \_\_\_\_\ atm\ cm^3$

$1\ dm = 10\ cm$

$32 \times \frac{1}{1.01322 \times 10^5}\ atm\left(\frac{10^3}{10^2}\ cm^3\right)$

$\Rightarrow \frac{32}{1.01322} \times 10^{-2}\ atm\ cm^3$

$\simeq 31.9 \times 10^{-2}\ atm\ cm^3$

10) $1\ atm\ ml = \_\_\_\_\ Joule$

4) 14 7 torr L = _____ J = _____ Pam³

$7\left(\frac{1}{760}\ atm\right)(1\ L)$

$\Rightarrow 7 \times \frac{1}{760} \times 101.3\ J \Rightarrow \frac{7 \times 101.3}{760}\ J$

$= \frac{7 \times 101.3}{760}\ Pam^3$

$= 0.93\ Pam^3$

2) 1 mol CO_2 – 38 kJ

$44g\ CO_2 \rightarrow 38\ kJ$

$4g\ CO_2 \rightarrow \frac{38}{44} \times 4\ kJ = \frac{38}{11}\ kJ$

$= 3.4\ kJ$

32
12
44

3)

$0.1\ L = \_\ m^3$

$= 0.1 \times 10^{-3}\ m^3$

$0.1L = 10^{-4}\ m^3$

$0.1\ L = 10^{-4} \times 10^{3}\ dm^3$

$0.1\ L = 10^{-1}\ dm^3$

$0.1\ L = \frac{10^{-3}}{10^{3}}\ cm^3$

$0.1L = \div\ m^3$

$0.1 \times 10^{3}\ m^3 \Rightarrow 10^{2}\ m^3 = 0.1\ L$

6) $20K = \_\ ^\circ C$

$20 - 273\ K = +1^\circ C$

$0^\circ C = 273K$

$1K + 1^\circ C = 273.15$

$1^\circ C = \frac{5}{9}(F - 32)$

18) $n = 2$ moles

$T = 300K$

$P = 5$ atm

$PV = nRT \Rightarrow \frac{2 \times 300 \times 0.082}{5} \Rightarrow$