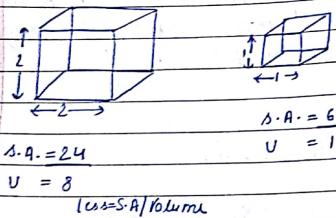


23rd february, 2017

Nanochemistry



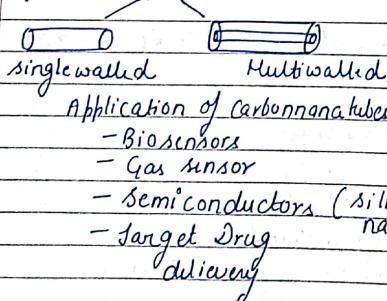
Types of Nano material-

① Nano material in 1-D-

These nano materials are obtained by decreasing the size of a macro particle in one dimension. It is used as a nanocatalyst due to high surface area per unit volume.

② Nano-material in 2-D-

eg: Carbon nanotubes



- 5 natural allotropes of carbon
- Carbon nano tube is an allotrope of Carbon.

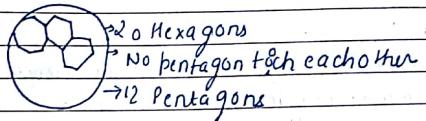
③ Nano-material in 3-D-

(we obtain a nano granule; in case of semiconductors it is called Quantum dot)

eg: Quantum dot

Buckminster fuller

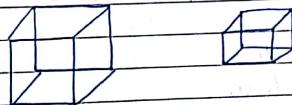
(discovered by Smalley & Sardley)



Properties of Nano Materials-

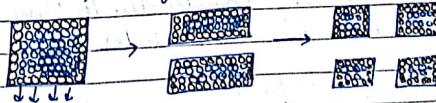
① Surface area per unit volume-

On decreasing the size of nano particles the surface area per unit volume increases.



② Surface energy -

On decreasing the size the number of surface molecules increases which are of high energy due to unsatisfied valencies or dangled valencies.



③ Catalytic activity -
Increases

④ Reactivity -
Increases

⑤ Optical Property -
The optical property changes drastically as we move from macro to nano level. This can be attributed to quantum confinement in nano materials. In macro particles we assume the conduction and valence bands to be continuous but at nano level they become discrete.

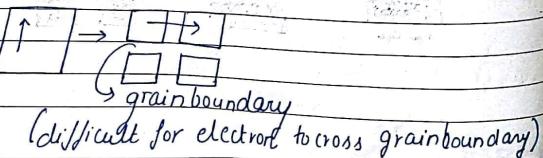


Gold : Yellow
nano-particle : Red

(Surface Catalyst) TiO_2 - White
nanoparticle - transparent

⑥ Electrical property -

The electrical conductivity changes due to generation of grain boundaries in nano particles.



(difficult for electron to cross grainboundary)

① Melting point -

It generally decreases due to decrease in number of core atoms or molecules which decreases the interaction b/w them.

② Synthesis of Nano-particles -

Atom / Molecules → Unit cell → Crystal → Lattice

(to synthesize we use dilute solution)

① Top Down strategy

(we will move from large to small particles)

Macroparticle → Nano particle

e.g.: $Ti-Al_2O_3 \rightarrow$ nano Alumina
Ball-Milling method

② Bottom-up strategy

(we synthesize nano-particle)

$TiCl_4 + O_2 \rightarrow TiO_2$
TIP → Nanoparticle

→ Precursor

(from which we synthesize)

In this strategy we synthesize nano particle from nano precursors like oxides under rxn. to form a mixture of desired nano size and thin agglomeration which undergoes sintering and then agglomeration

(we usually synthesize solid nanoparticle)

Molecule → Nucleus → Agglomeration
Nucleation → Agglomeration

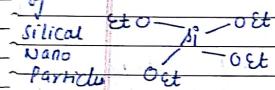
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solid phase
liquid phase
Gas phase.

liquid phase synthesis → Precipitation-Coprecipitation
 → Microemulsion
 → sol-Gel

Precipitation-Coprecipitation-

synthesis TEOS (Tetraethylorthosilicate)



In this technique we dissolve the precursor in water and start adding other reagent (NaOH) to get the precipitate silica nano-particles.

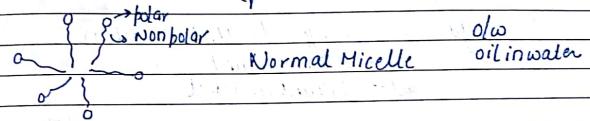
To get nanoparticles we have to optimize the following conditions -

- 1) The solution should be dilute
- 2) Temperature
- 3) Pressure
- 4) pH
- 5) Time of reaction

Coprecipitation is when we are precipitating more than one nanoparticle at the same time it is known as coprecipitation.

Micro Emulsion / Reverse Micelle -

The disadvantage of previous technique was we cannot optimise the size of nanoparticles in case of Micro emulsion technique we can optimise the size of nanoparticles.



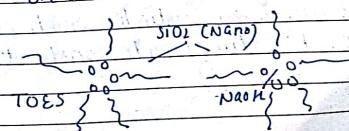
long non polar hydrocarbon (chain)
 and one polar head.

To increase miscibility of polar and non-polar compounds we add emulsifiers (salt of long chain fatty acids). The emulsifiers are sparingly less soluble in water and after a particular concentration (critical Micelle Concentration) they start forming Micelles.

w/o Reverse Micelle



In this technique we dissolve the precursor and the catalyst separately in water we add the aqueous solution in oil bath which contains emulsifier.



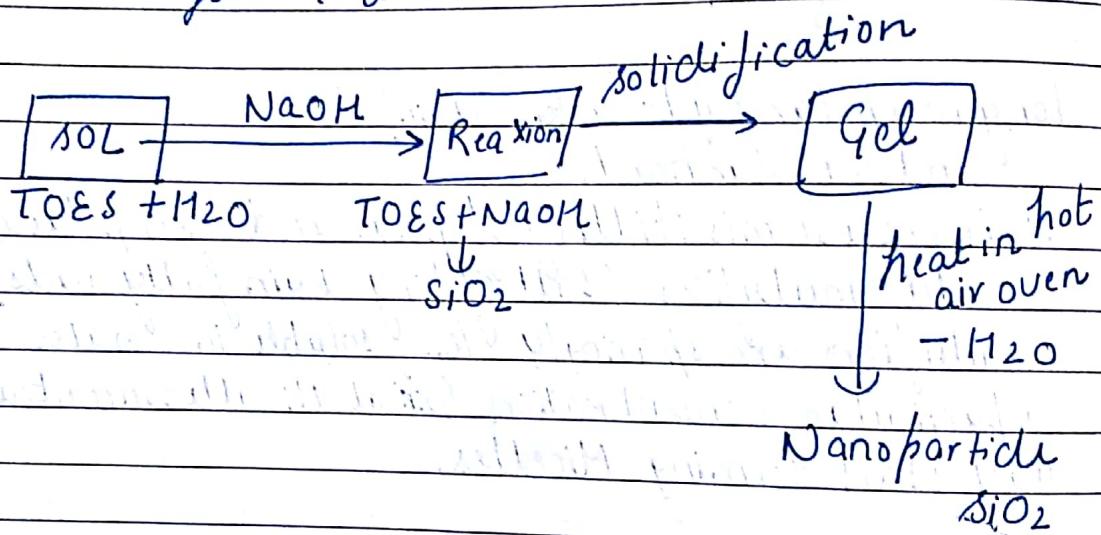
The aqueous part of emulsion will get placed in the centre of reverse micelle. The rxn. occurs at the centre of each micelle and we get nano particles of silica.

→ Sol-gel technique

gel sol - a type of colloidal solution

Sol - Solid in liquid

gel - liquid in solid



Chemical Kinetics

Methods of determination of order

- ① Integrated rate law method - Unimolecular
order
In this method we determine the rate constant by putting the values in different integrated rate law expression and assign the order for which we are getting a constant value of rate constant.

17th March, 2017

Electrochemistry

conductance - type

Effect of dilution

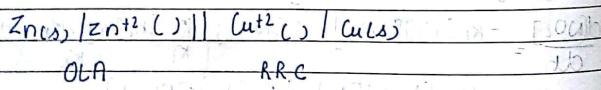
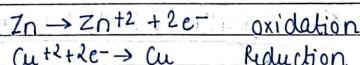
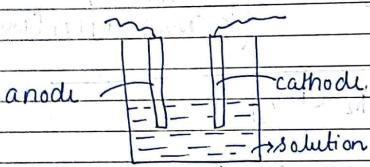
Kohlrausch's law

Transport no.

do you know { Electrochemical cell
Nernst equation }

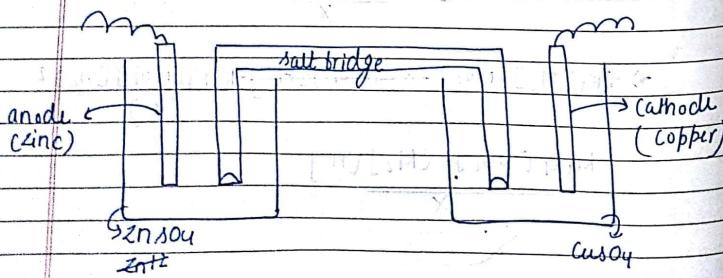
Cells →

Electrolytic cell and Electrochemical cell. Explain difference and give example



O.R.A

R.R.C



Agar-Agar is porous in nature.

KCl does the job

K⁺ Combines with SO₄²⁻ and maintain electro-neutrality.

Ques) What is salt bridge? what is its significance?

Salt bridge is an U-tube which consists of agar, agar gel and potassium chloride.

The significance of salt bridge -

- i) It gives passage for movement of ions.
- ii) It maintains electro-neutrality.

Electrochemical Series

Electrode potential - the tendency to lose or gain electron by a metal dip in its ionic solution.

Electrochemical series is constructed taking hydrogen electrode as reference for which S.H.E potential is considered to be zero.

The metals are arranged in increasing order of their reduction potential.

The metal above S.H.E will act as reducing agent as compared to S.H.E. It will easily undergo oxidation so they will be more reactive. So they will easily undergo corrosion.

Li $E^{\circ}_{\text{red}} = (-)$

Zn $E^{\circ}_{\text{red}} = (-)$

H $E^{\circ}_{\text{red}} = (0)$

Cu $E^{\circ}_{\text{red}} = (+)$

Nernst Equation-

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log(Q)$$

$n \rightarrow$ no. of e- transfer in a balanced redox reaction
The Nernst equation signifies dependency of emf of the cell to its concentration.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= E_{\text{reduction}} - E_{\text{oxidation}}$$

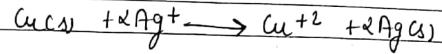
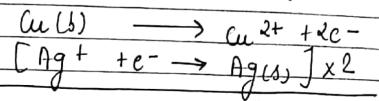
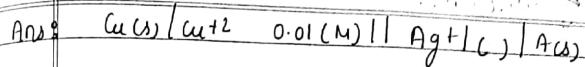
(Q) Can we use a copper vessel to store silver nitrate
 $E^{\circ}_{\text{red}} = +0.34$, $E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$

Ans: No, because silver nitrate will oxidize to silver.
 We can store

Q) The standard red

$$E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.799\text{ V}; E^{\circ}_{\text{red Cu}} = 0.337\text{V}$$

Consider Galvanic cell using these electrodes so that E_{cell} is +ve. For what conc. of Ag^+ will the emf of cell be zero if copper ion is 0.01M?



$$Q = [\text{Cu}^{+2}]$$

$$[\text{Ag}^+]^2$$

$$n = 2$$

$$E^{\circ}_{\text{cell}} = 0.462\text{V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$0 = 0.462 - \frac{0.0592}{2} \log \left(\frac{[\text{Cu}^{+2}]}{[\text{Ag}^+]^2} \right)$$

$$0.462 = 0.0592 \log \left(\frac{[\text{Cu}^{+2}]}{[\text{Ag}^+]^2} \right)$$

$$\log \left(\frac{[\text{Cu}^{+2}]}{[\text{Ag}^+]^2} \right) = 2 \times 0.462 = 0.924$$

$$\log \left(\frac{0.01}{[\text{Ag}^+]^2} \right) = 18.14611155$$

$$\frac{0.01}{[\text{Ag}^+]^2} = 1.4 \times 10^{-18}$$

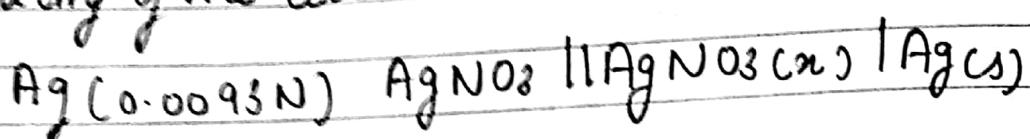
$$[\text{Ag}^+]^2 = \frac{0.01 \times 10^{-18}}{1.4}$$

$$[\text{Ag}^+]^2 = 7.14 \times 10^{-3} \times 10^{-18}$$

$$= 71.4 \times 10^{-22}$$

=

Qm flux of the cell



is 0.086V
calculate?

$$\epsilon^\circ_{\text{cell}} = 0$$

$$0.086 = 0 - 0.0592 \log(Q)$$

$$\frac{-0.086}{0.0592} = \log Q$$

$$Q = 0.035261216$$

$$\frac{0.0093}{[\text{Ag}^+]} = 0.035261216$$

$$[\text{Ag}^+] = 0.26$$

=

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Electrochemistry

Metallic C/ice electrons are responsible

\rightarrow Conductance \rightarrow Holar conductance

\rightarrow Electrolytic C/ice ions are responsible

\rightarrow Equivalent (specific conductance)

All constant $= \frac{l}{a}$ \rightarrow distance b/w electrodes

\rightarrow cross section area

* Resistance (R) $\rightarrow \Omega$

$C_{org} \rightarrow$ Conductance \rightarrow Siemens / (mho)

$\Omega \text{ m} \leftarrow \delta \rightarrow$ resistivity or specific resistance

$\text{sm}^{-1} \leftarrow K \rightarrow$ Conductivity / Specific Conductance

$$\# R = \delta l/a$$

$$\# C = K / \text{cell constant}$$

Equivalent conductance -

The electrolytic conductance of 1gm equivalent of an electrolyte in 'V' volume of solution.

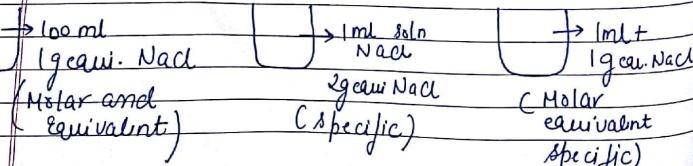
Molar Conductance -

The electrolytic conductance of 1 mole of an electrolyte in 'V' volume of solution.

Specific Conductance -

The Conductance of 1 unit volume of electrolytic solution is known as its specific conductance.

Eg:



$$\text{Equivalent (Aeq.)} = K \times \text{volume} = K \text{ Smol}^{-1} \text{ m}^2$$

conductance \rightarrow Conc.

$$1L = 1 \text{ dm}^3$$

$$1L = 1000 \text{ cm}^3$$

$$1L = \text{m}^3$$

$$K = 1 \text{ cm}^{-1}$$

$$C = N_A \cdot g \text{ cau/L}$$

$$\Lambda_{ca} = \frac{K \times 1000}{\text{Conc.}} \text{ Smol}^{-1} \text{ cm}^2$$

Ques) The resistance of 0.01 M solution of an electrolyte is 210Ω . Calculate Molar conductance if cell constant is 0.88 cm^{-1} .

$$R = 210 \Omega$$

$$\text{Cond.} = \frac{1}{R} = \frac{1}{210}$$

$$K = (C \cdot C) \times \text{Cond.}$$

$$= \frac{0.88 \times 1}{210}$$

$$= 0.8$$

$$\text{Conc.} = 0.01$$

$$\text{Molar cond.} = K \times 1000$$

Conc.

$$= \frac{0.88 \times 1000}{210 \quad 0.01}$$

$$= 419.04 \text{ Smol}^{-1} \text{ cm}^2$$

Cell constant is independent of the electrolytic solution taken. Specific to a cell.

Ques) A conductivity cell is filled with 0.05M KCl solution. Its specific conductance is $6.67 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ and its resistance is 243Ω and when the cell is filled with 0.01M NaOH observed resistance was ~~681~~ 681Ω find the Molar Conductance of NaOH solution.

$$0.05 \text{M KCl}$$

$$K = 6.67 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$$

$$R_{\text{KCl}} = 243 \Omega$$

$$0.01 \text{M NaOH}$$

$$R_{\text{NaOH}} = 681 \Omega$$

$$\Lambda_{\text{M NaOH}} = ?$$

$$K = \text{cell constant}$$

$$R$$

$$\text{Cell Constant} = K \times R$$

$$= 6.67 \times 10^{-3} \times 243$$

$$K_{\text{NaOH}} = \frac{\text{cell constant}}{K}$$

$$K = \frac{C \cdot \Lambda}{A}$$

$$6.67 \times 10^{-3} = \frac{1}{243} \text{ cell cons.}$$

$$C \cdot C = 6.67 \times 243 \times 10^{-3}$$

$$= 1620.81 \times 10^{-3}$$

$$K = \frac{1}{681} \times 1620.81 \times 10^{-3}$$

$$= 2.38 \times 10^{-3}$$

Effect of dilution :- 22nd March, 2017

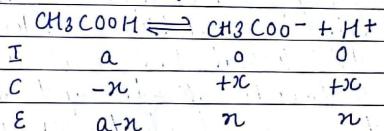
① On specific conductance-

$$\frac{n \text{ moles}}{1 \text{ ml}} \xrightarrow{100} \frac{n \text{ moles}}{100 \text{ ml}} \approx \frac{n}{100}$$

On increasing dilution the no. of moles per unit volume decreases and hence the specific conductance decreases on increasing dilution.

② on Equivalent and Molar conductance-

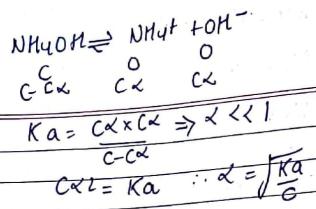
(a) for weak electrolytes-



$$K_a = \frac{x^2}{a-x} ; n \ll 1$$

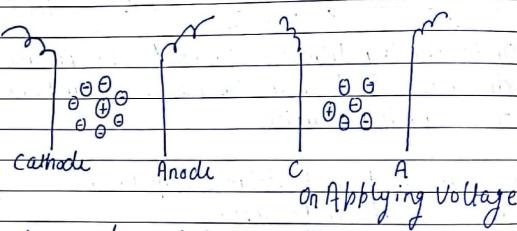
$$K_a = \frac{x^2}{a} ; n = \sqrt{K_a C}$$

On increasing dilution the degree of dissociation increases and hence equivalent and Molar conductance for weak electrolytes increases.



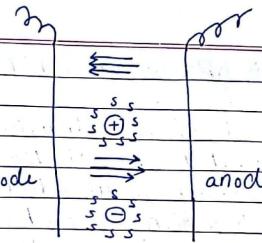
(b) for strong electrolytes -
For strong electrolytes the equivalent and Molar conductivity increase on increasing dilution which can be explained by two effects

(i) Asymmetric effect :-



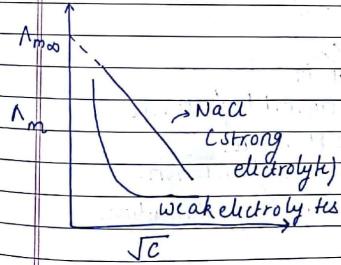
In absence of any potential applied each ion is symmetrically surrounded by its counterion. On application of potential the two kinds of ions will move towards cathode and anode. Due to this each ion will feel a back force due to counterions which will restrict its free movement. On dilution the asymmetric effect diminishes and hence Conductance increases.

(ii) Electrophoretic effect :-



In an electrolytic solution cations and anions are solvated (surrounded by solvated molecules) when potential is applied the solvated cations move towards cathode and solvated anions towards anode. Due to this counter movement they feel hindrance in mobility. On increasing dilution the ions get separated from each other and electro phoretic effect decreases which increases equivalent and Molar conductivity of strong electrolytes.

Graphical Representation



as shown in the graph we can determine the equivalent and Molar conductivity of strong electrolytes by extrapolating the graph.

while for weak-electrolytes we use Kohl Rauch's law.

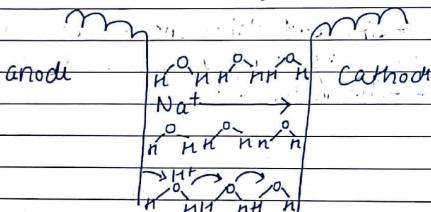
Kohl Rauch's law - at infinite dilution the electrolyte is completely dissociated into respective ions. The movement of ions are independent of each other (No intrionic interaction), so each ion contributes its own fraction in the overall equivalent or molar conductance.

$$\lambda^{\infty}_{\text{NaCl}} = \lambda^{\infty}_{\text{Na}^+} + \lambda^{\infty}_{\text{Cl}^-}$$

$$\lambda^{\infty}_{\text{CH}_3\text{COOH}} = \lambda^{\infty}_{\text{CH}_3\text{COO}^-} + \lambda^{\infty}_{\text{H}^+}$$

Qn) Why H^+ ion and OH^- are highly conducting as compared to other ions?

Because the movement of H^+ and OH^- ions are supported by water molecules by Grotius theorem.



Hop-Hop movement of H^+ ion due to H_2O Molecules.

Same in the case of OH^- ion.

Na^+, Cl^- have to go themselves.

22nd March, 2017

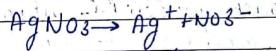
Application of Molar equivalent conductance at infinite dilution

1) Determination of degree of dissociation

$$\alpha = \frac{\Lambda_m}{\Lambda^\infty_m}$$

2) Determination of solubility and solubility products.

$$\Lambda_m = \frac{K}{S}$$



$$K_{\text{sp}} = (S)(S)$$

Qn) Calculate specific and Molar conductance of 0.0075M KCl solution given conductance $1.49 \times 10^{-3} \text{ S}$ and cell constant = 5 cm^{-1}

$$R = \frac{c \cdot l}{A} \quad \text{C.C.} \rightarrow \text{m}^{-1}$$

specific resistivity
conductance and conductivity
(Cor G) (K)

$K = \text{Specific conductance}$

$$G = K$$

$$(G) \quad \text{conductance} = \frac{l}{R}$$

$$\Lambda_m = \frac{K \times 1000}{\text{concentration (mol/l)}}$$

$$G = \frac{K}{C \cdot C}$$

$$1.49 \times 10^{-3} = \frac{K}{5}$$

$$5 \times 1.49 \times 10^{-3} = K$$

$$\Lambda_m = 5 \times 1.49 \times 10^{-3} \times 1000 \\ 0.0075$$

Ques) The specific conductance of water is $7.6 \times 10^{-2} \text{ S m}^{-1}$ and specific conductivity of 0.1 M KCl solution is 1.1639 Sm^{-1} . A cell has resistance of 33.2Ω when filled with 0.1 M KCl solution and 300Ω when filled with $0.1 \text{ M acetic acid}$. Calculate molar conductance of acetic acid.

$$K_{H_2O} = 7.6 \times 10^{-2} \text{ S m}^{-1}$$

$$K(0.1 \text{ M}) = 1.1639 \text{ Sm}^{-1}$$

$$R_{KCl} = 33.2 \Omega$$

$$R_{CH_3COONa} (0.1 \text{ M}) = 300 \Omega$$

$$\Lambda_m (CH_3COOH) = ?$$

$$\Lambda_m CH_3COOH = \frac{K_{CH_3COONa}}{\text{Concentration}}$$

$$\Lambda_m CH_3COONa = K_{CH_3COONa} \\ (0.1)$$

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$$K_{CH_3COONa} = ?$$

$$K_{KCl} = K_{KCl \text{ solution}} - K_{H_2O} \\ = 0.0076 - 1.1639 - 0.0076 \\ = 0.4039 \text{ Sm}^{-1}$$

$$G_{KCl} = \frac{1}{R_{KCl}}$$

$$K_{KCl} \approx \frac{1}{C \cdot C} \\ 0.4039 \approx \frac{1}{33.2}$$

$$1.0879 / 0.4039 \times 33.2 = C \cdot C$$

$$K_{CH_3COONa} = G_{CH_3COONa} \times C \cdot C$$

$$= \frac{1}{R_{CH_3COONa}} \times C \cdot C \\ = \frac{1}{300} \times 0.4039 \times 33.2 \\ = 0.0879$$

$$\Lambda_m CH_3COONa = \frac{1}{300} \times 0.4039 \times 33.2 \\ = 0.4469$$

$$= 1.20394 \text{ Sm}^2 \text{ mol}^{-1} \\ = 120.39 \times 10^{-3}$$

Ques) The equivalent conductances of ammonium chloride = 149.7, NaOH = 247.8, NaCl = 126.45 at infinite dilution are given. Calculate $\Lambda^{\infty}_{\text{NH}_4\text{OH}}$.

$$\Lambda^{\infty}_{\text{NH}_4\text{Cl}} = 149.7$$

$$\Lambda^{\infty}_{\text{NH}_4^+} + \Lambda^{\infty}_{\text{Cl}^-} = 149.7 \quad \text{--- (1)}$$

$$\Lambda^{\infty}_{\text{NaCl}} = 126.45$$

$$\Lambda^{\infty}_{\text{Na}^+} + \Lambda^{\infty}_{\text{Cl}^-} = 126.45 \quad \text{--- (2)}$$

$$\Lambda^{\infty}_{\text{NaOH}} = 247.8$$

$$\Lambda^{\infty}_{\text{Na}^+} + \Lambda^{\infty}_{\text{OH}^-} = 247.8 \quad \text{--- (3)}$$

$$\Lambda^{\infty}_{\text{NH}_4\text{OH}} = \Lambda^{\infty}_{\text{NH}_4^+}$$

$$\Rightarrow (1) + (2) + (3)$$

$$= 149.7 - 126.45 + 247.8 \\ = 271.05$$

Ques) $\Lambda^{\infty}_{\text{NaOH}} = 48.1 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$

$$\Lambda^{\infty}_{\text{NaCl}} = 126.5 \times 10^{-4}$$

$$\Lambda^{\infty}_{\text{BaCl}_2} = 280 \times 10^{-4}$$

$$\Lambda^{\infty}_{\text{Ba}(\text{OH})_2} = ?$$

$$\Lambda^{\infty}_{\text{NaOH}} = \Lambda^{\infty}_{\text{Na}^+} + \Lambda^{\infty}_{\text{OH}^-}$$

$$\Lambda^{\infty}_{\text{NaCl}} = \Lambda^{\infty}_{\text{Na}^+} + \Lambda^{\infty}_{\text{Cl}^-}$$

Ans) $\Lambda^{\infty}_{\text{BaCl}_2} = \Lambda^{\infty}_{\text{Ba}^+} + 2\Lambda^{\infty}_{\text{Cl}^-}$

$$\Lambda^{\infty}_{\text{Ba}(\text{OH})_2} = \Lambda^{\infty}_{\text{Ba}^+} + 2\Lambda^{\infty}_{\text{OH}^-}$$

$$\Rightarrow \Lambda^{\infty}_{\text{BaCl}_2} + 2\Lambda^{\infty}_{\text{NaOH}} \\ - 2\Lambda^{\infty}_{\text{NaCl}}$$

$$= 280 \times 10^{-4} + 2 \times 48.1 \times 10^{-4} \\ - 2 \times 126.5 \times 10^{-4}$$

$$\text{Osmality} = \text{m} = [280 + 48.1 \times 2 - 253] \times 10^{-4}$$

$$(2800.0) - (253.0) \times 10^{-4}$$

$$\Rightarrow 523.2 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

Final $\text{m} = 523.2 \times 10^{-4}$

saturated

Ques) The specific conductivity of CaF_2 was found to be $\lambda_{\text{CaF}_2} = 4.25 \times 10^{-3} \text{ Sm}^{-1}$ and specific conductivity of $(\text{K}_2\text{H}_5\text{O}) = 2 \times 10^{-4} \text{ Sm}^{-1}$ the molar ionic conductivities at infinite dilution of calcium ion is $104 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$ and of Fluoride ion is $48 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$. What is solubility of CaF_2 and $K_{\text{sp}} \text{ CaF}_2$?

$$K_{\text{CaF}_2} = 4.25 \times 10^{-3} \text{ Sm}^{-1}$$

$$K_{\text{H}_2\text{O}} = 2 \times 10^{-4} \text{ Sm}^{-1}$$

$$\lambda_{\text{Ca}^{2+}} = 104 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{F}^-} = 48 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

Solubility of $\text{CaF}_2 = ?$

$$K_{\text{sp}} \text{ CaF}_2 = ?$$

$$4.25 \times 10^{-3} \times 2 \times 10^{-4}$$

$$= 8.5 \times 10^{-7}$$

$$= 8.5 \times 10^{-7}$$

$$\delta = \frac{K_{CaF_2}}{N_m CaF_2}$$

$$= \frac{4.20 \times 10^{-3}}{N_m CaF_2}$$



$$K_{CaF_2} = (K_{CaF_2})_{\text{saturated}} - (K)_{H_2O}$$

$$= (0.00425) - (0.0002)$$

$$\Rightarrow 0.00405 \text{ Sm}^{-1}$$

$$N_m^{20}(CaF_2) = N_m^{20} Ca^{2+} + 2 N_m^{20} F^-$$

$$= (104 \times 10^{-4}) + 2(48 \times 10^{-4})$$

$$= 10^{-4} [104 + 96]$$

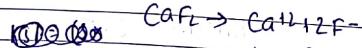
$$\Rightarrow [200 \times 10^{-4}] \text{ Sm}^{-1} \text{ mol}^{-1}$$

$$\delta = \frac{K_{CaF_2}}{N_m^{20} CaF_2} = \frac{(0.00405)}{(200 \times 10^{-4})} \text{ Sm}^{-1} \text{ mol}^{-1}$$

$$= 0.00405$$

$$0.0200$$

$$\Rightarrow 0.2025 \text{ m}^{-3} \text{ mol}$$



$\propto 2s$

$$K_{SP} = s \times 2s = 2 (SSL)$$

$$= 2 (0.2025)^2$$

$$\Rightarrow 0.0820 \text{ 12.5 }$$

23rd March, 2017

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Transport Number (transference Number)

transport no. is defined as fraction of current carried by cation or anion represented by 't'.

$$\frac{I_+}{I_+ + I_-} = \frac{\vartheta_+}{\vartheta_+ + \vartheta_-} = t_+$$

$$t_- = \frac{I_-}{I_+ + I_-}$$

Transport no. can never be greater than 1
Transport number can never be less than 0.1.

Determination of Transport No. :-

The transport no. can be determined by two methods

- 1) HITTORF'S METHOD
- 2) MOVING BOUNDARY

(i) Hittorf's Method - Theory

* The concentration in central chamber remains the same.

1) For Non attackable electrodes (Pt) -

	Anodic chamber	Cathodic chamber	
Case(i) (Cations)	+++	++ + + +	++ + + + + +
Case(ii) (Anions)	- - - - -	++ + + +	++ + + + + +
Case(iii) (Cation, Anion)	+++	++ + + +	++ + + + + +

decrease in conc. in Anodic chamber = $\frac{2}{2} = t^+$

overall decrease in conc. in all

decrease $t^+ = 0$; $t^- = 1 - 0 = 1$

Case ②

Total decrease = 3

Decrease in conc. of anodic chamber = 2

$$t^+ = \frac{2}{3}$$

$$t^- = \frac{1}{3} = \frac{1}{3}$$

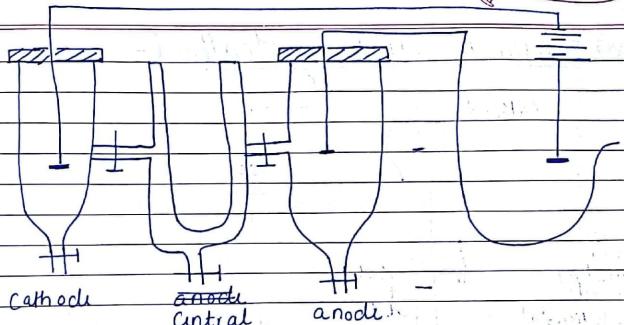
* More the Mobility of the ion,

More the transport No.

→ From Nernst's method, transport no. of cations is equal to the \rightarrow decrease in concentration in Anodic chamber

Total decrease in the conc. in the cell

Instrument-



Faraday's law-

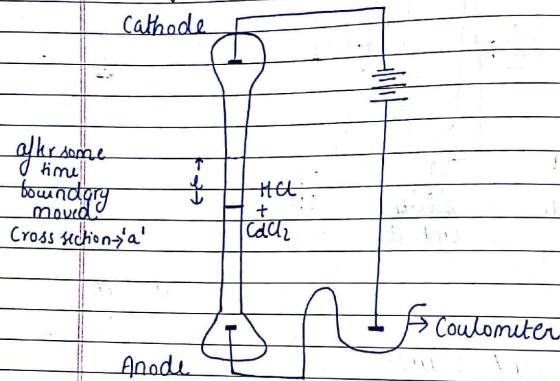
If 'n' no. of cells are connected in series then 1 gm-equiv of each electrolyte will be deposited or discharged in each cell on passing 1 Faraday charge.

$$1F = 96485 C$$

$$1 \text{ gm-equivalent} = \frac{\text{Moles}}{\text{n Factor}}$$

29 March, 2021

② Moving Boundary Method-



In this method we take two electrolytes principle electrolyte and indicator electrolyte. The three necessary conditions are

- (i) There should be a common anion in the two electrolytes.
- (ii) The speed of cation of principle electrolyte should be more than the speed of cation of indicator electrolyte.
- (iii) Indicator electrolyte should be denser than principle electrolyte.

For e.g. If we want to determine transport no. of H^+ and Cd^{2+} ions than principle electrolyte will be HCl . The indicator electrolyte will be $CdCl_2$.

Let conc. of $HCl = c$ (g equivalents/L)
Normal

Let boundary moved is = l

∴ Cross section area of tube = a

∴ Volume moved = axl

No. of g.eq. moved or discharged = $c \times axl$

Let the total charge passed = Q Faraday

Charge transferred by $H^+ = (c \times axl)$ Faraday

Transport No. of H^+ ion

$$\# t_+ = \frac{(c \times axl)}{Q \text{ (Faraday)}}$$

If 'n' g of Cd is deposited in coulometer
or $CdAg$)

$$\rightarrow t_+ = \frac{c \times axl}{\left(\frac{n}{\text{Eq. wt}}\right)}$$

Ques.) Calculate transport no. of H^+ and Cd^{2+} if conc. of $HCl = 0.1N$. Mass of Ag deposited = 0.1209 g
Movement of boundary = 7.50 cm and
cross section = 1.44 cm^2 .

$$\text{N} = \frac{\text{No. of Ions}}{\text{dm}^3}$$

$$\text{HCl} = 0.1\text{N}$$

Mass of Ag deposited = 0.1209 g

$$l = 7.50 \text{ cm}$$

$$a = 1.24 \text{ cm}^2$$

$$t_+ = C \times a \times l$$

$$\left(\frac{n}{\text{Faraday}} \right)$$

$$= (0.1) \times (1.24) \frac{10 \times 10}{10 \times 10} \times \frac{7.50}{10}$$

$$= \frac{(0.1209)}{108}$$

$$= (0.1) (1.24) (7.50) \times \frac{108}{10 \times 10 \times 10} \times \frac{1}{1.209}$$

$$= 0.08308$$

Ques) In a moving boundary experiment with 0.1N KCl using 0.005 N LiCl as indicator solution, a constant current of 0.005893 A was passed for 2180 sec and the boundary was observed to move 5.60 cm. Cross section area = 0.1142 cm²

Calculate transport no. of K⁺ and Cl⁻.

0.1N KCl

0.005 N LiCl

0.005893 amp

2180 sec

a = 0.1142 cm²

l = 5.60 cm

t_{K+} = ?

t = 5.60 cm t_a = ?

charge (Q) = current × time

$$= (0.005893 \times 2180) \text{ coulomb}$$

~~$$1 F = 96500 C$$~~

~~$$\text{charge (Q)} = (0.005893 \times 2180 \times 96500) F$$~~

~~$$t_+ = \frac{C \times a \times l}{Q}$$~~

~~$$= (0.1) \times 0.1142 \times 5.60$$~~
~~$$\frac{10 \times 10}{10 \times 10} \text{ cm}^2 \text{ sec}$$~~
~~$$= 0.005893 \times 2180 \times 96500$$~~

=

Corrosion - (10-15 marks) (from ppt.)

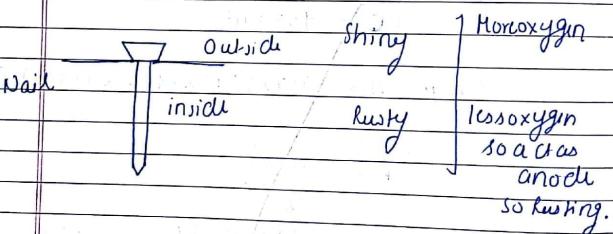
Surface phenomenon

Chemical attack

→ silver forms AgCl on corrosion which is insoluble so avoid further corrosion.

→ Soluble or liquid corrosion product.
 SnCl_4 is a type of volatile corrosion product.

Metal \rightarrow oxidation
Oxygen \rightarrow Reduction



→ Aluminium forms stable Al_2O_3 layer.

→ Volatile film - (MgO_2)
→ Porous film

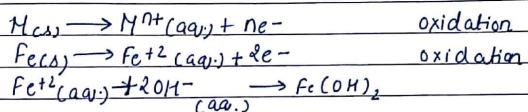
Impo. \rightarrow Pilling Bedworth rule.

30th March, 2017

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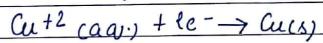
Mechanism of Electrochemical Corrosion

i) Anodic reaction

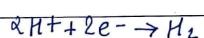


ii) Cathodic reaction

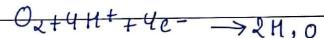
a) Electroplating



b) In acidic solution in the absence of O_2

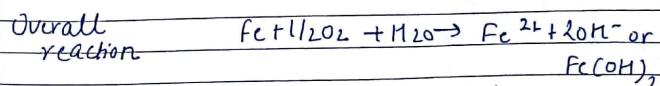
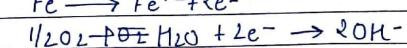
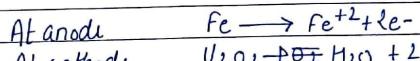


c) In acidic solution in the presence of O_2



d) In ~~neutral~~ or alkaline

Important # Rusting of iron occurs by O_2 in presence of aqueous solution



→ Factors affecting galvanic corrosion
higher the potential difference of two metals higher the corrosion

→ smaller anode larger cathode increases wt. of corrosion.

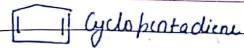
very important

Pitting Corrosion -

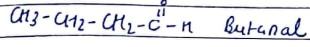
Most dangerous form of corrosion.

31st March, 2017

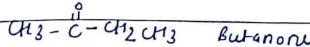
"ORGANIC CHEMISTRY"



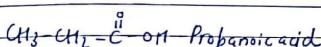
Syllabus



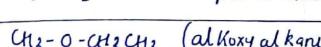
1) Prerequisite



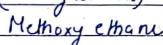
2) Substitution $\xrightarrow{\text{Nu}}$



3) Addition $\xrightarrow{\text{Nu}}$

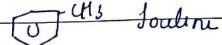
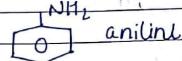
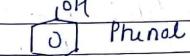
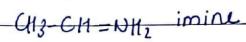
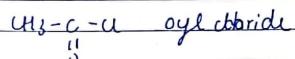
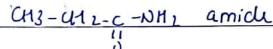
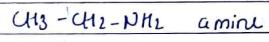
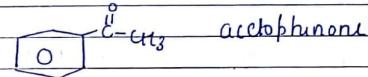
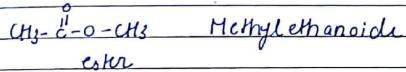


4) Elimination $\xrightarrow{\text{E}}$

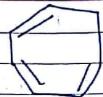


5) Dehydration/Reduction

Wolf Kishner Reduction



→ Mixing and reshuffling of atomic
to form new and equal no. of hybrid orbitals
which are of same energy and it is called hybridization



1,3,5-Cyclohepta triene

\oplus CH ₃ Carbocation	• CH ₃ Radical	\ominus CH ₃ Carbanion
sp^2 trigonal planar	sp^2 (1 lone e ⁻) trigonal ^{in P}	sp^3 trigonal Pyramidal

CH ₄	G.s. [TL]	[TL]	[TL]
	E.s. [TL]	[]	[TL]
	H.s. [TL]	[1]	[1][1]
			$sp^3 sp^3 sp^3 sp^3$

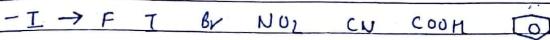
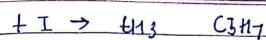
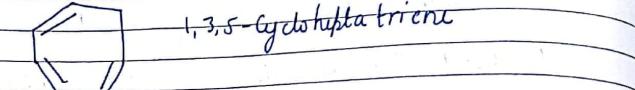
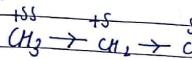
CH₄ → sp^3
tetrahedral

tendency to pull
shared pair of
electrons is called
electronegativity.

Reasons for Polarity-

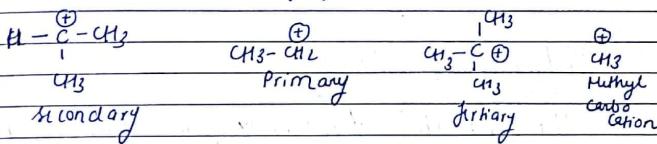
(i) Inductive effect-

The generation of polarity in an organic compound due to difference in electronegativity is known as inductive effect. In this effect more electronegative element pulls the shared pair of electrons (e^{-}) and generate a negative charge on it. It is a permanent effect. It is effective upto 3 carbons.



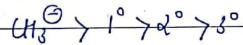
Application of Inductive effect-

i) Determination of stability of carbocations.

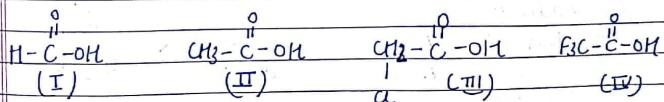
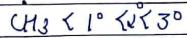


Stability (due to +I)
Tertiary > Secondary > Primary > Methyl carbocation

ii) Stability of carbanions.



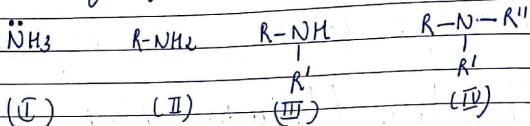
iii) Carbon free radical



(IV) > (III) > (II) > (I)
(Reactivity) (Acidic Strength)

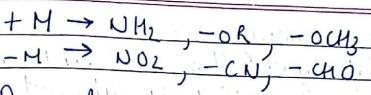
Basic strength of amines

aqueous
chloro



up to conjugation
generates delocalized charge.

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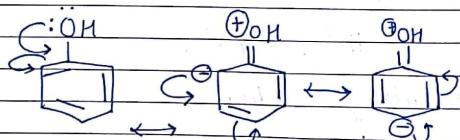


Draw resonance structure of Nitrobenzene?
Explain why it is meta directed?

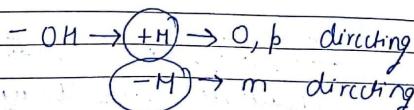
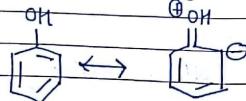
Mesomeric effect

The generation of polarity in an organic compound due to complete transfer of π electrons and/or lone pair of electrons is known as Mesomeric effect.

Conjugated system $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$



Benzene/Phenol undergo
Electron Substitution
Reaction



31st March, 2017

Tutorial (AgNO_3)

Ques) AgNO_3 solution containing $0.00739 \text{ g AgNO}_3/\text{g of}$
 solution is electrolyzed by silver electrodes.
 During the experiment 0.078 g Ag deposited at
 Cathode. At the end of experiment anode contains
 $0.314 \text{ g of solution containing } 0.2369 \text{ g of AgNO}_3$.
 Calculate transport No. of Ag^+ and NO_3^- ions.

$$a = 0.314$$

$$b = 0.236 \text{ g AgNO}_3$$

$$c = 0.078 \text{ g}$$

$$d = 1 \text{ g}$$

$$d = 0.00739 \text{ g AgNO}_3/\text{g of soln}$$

$$n = b = \frac{0.236}{170}$$

$$y = \frac{d(a-b)}{(c-d) \times 170} = \frac{(0.00739)(0.314 - 0.236)}{(1 - 0.00739) \times 170}$$

$$z = \frac{(c)}{\text{car. wt. of metal in Coulombe}} = \frac{0.078}{108}$$

$$\cancel{t_f = \frac{g-n}{z}}$$

$$t_f = \frac{(z)(n-y)}{(c)}$$

$$n = 1.3882 \times 10^{-3}$$

$$z = 7.2222 \times 10^{-4}$$

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$$y = 1 - 0.16 = 0.84$$

$$1.00306 \times 10^{-3}$$

$$0.99261$$

$$t_f^+ = -1.00306 \times 10^{-3} + 1.3882 \times 10^{-3}$$

$$7.2222 \times 10^{-4}$$

$$= (-0.38514) \times 10^{-3}$$

$$\Rightarrow +0.5332 \times 10^{-3}$$

$$\cancel{+0.5332}$$

$$(t_f^-) = (7.2222 \times 10^{-4}) - (1.3882 \times 10^{-3} - 1.00306 \times 10^{-3})$$

$$(7.2222 \times 10^{-4})$$

$$= \frac{(7.2222 \times 10^{-4})}{(7.2222 - 0.38514) \times 10^{-3}}$$

$$= 0.46669989 \times 10^{-3}$$

$$\Rightarrow 4.66699$$

Ques) The molar conductances at infinite dilution for sodium acetate and HCl are

$$\lambda^{\infty}_{HCl} = 426.16 \times 10^{-4} \text{ Sm}^2\text{mol}$$

$$\lambda^{\infty}_{CH_3COONa} = 91 \times 10^{-4}$$

Transport No. of H^+ ion in HCl is 0.821 and transport No. of acetate ion in sodium acetate is 0.556. Assume transport no. equal to the transport No. at infinite dilution. calculate Molar Conductance of acetic acid.

$$\lambda^{\infty}_{HCl} = 426.16 \times 10^{-4} \text{ Sm}^2\text{mol}$$

$$\lambda^{\infty}_{CH_3COONa} = 91 \times 10^{-4} \text{ Sm}^2\text{mol}$$

$$t^{H^+}(HCl) = 0.821$$

$$t^{CH_3COO^-}(CH_3COONa) = 0.556$$

$$t^{H^+} = \frac{I^+}{I^+ + I^-} = \frac{V^+}{V^+ + V^-} = \frac{\lambda^{\infty}_{H^+}}{\lambda^{\infty}_{H^+} + \lambda^{\infty}_{Cl^-}}$$

$$0.821 = \frac{\lambda_{H^+}}{426.16 \times 10^{-4}}$$

$$\lambda_{H^+} = (426.16 \times 10^{-4}) \times 0.821$$

$$= 349.87736 \times 10^{-4}$$

$$t^{CH_3COO^-} = \frac{\lambda^{\infty}_{CH_3COO^-}}{\lambda^{\infty}_{CH_3COO^-} + t^{H^+} \lambda^{\infty}_{Na^+}}$$

$$\lambda^{\infty}_{CH_3COO^-} = 0.556 \times 426.16 \times 10^{-4} = 91 \times 10^{-4}$$

$$= 50.596 \times 10^{-4}$$

$$\lambda^{\infty}_{CH_3COOH} = \lambda^{\infty}_{CH_3COO^-} + \lambda^{\infty}_{H^+}$$

$$= (349.87736 + 50.596) \times 10^{-4}$$

$$= 400.47336 \times 10^{-4} \text{ Sm}^2\text{mol}$$

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24th March, 2017

Molecular weight of $\text{AgNO}_3 = 170$

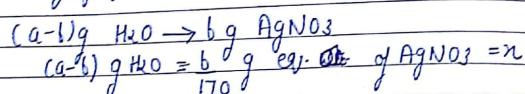
*decrease
in eqwt*

Mathematical Expression

In anodic compartment

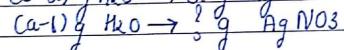
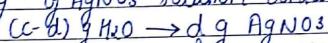
① After electrolysis

Let 'a' g of AgNO_3 solution contains = b g AgNO_3



Before electrolysis,

Let 'c' g of AgNO_3 solution contains = d g AgNO_3



$$= \frac{d(a-b)}{c(c-d)} \text{ g}$$

$$= \frac{d(a-b)}{(c-d) \times 170} \text{ g eq. wt of AgNO}_3$$

= y

AgNO_3 will be less before electrolysis Let e gm of Cu is deposited in Cu Coulometer .

$$\therefore \text{No. of g eq. wt of Cu deposited} = e = z$$

$$\left(\frac{63.4}{2} \right) \times \left(\frac{\text{eq. wt of Cu}}{170} \right)$$

$$t_+ = \frac{(y-n)}{z} = \text{Decrease in concentration in anodic chamber}$$

No. of g equi. deposited in Coulrometer

Imp. (Coulomber)

*decrease
in eqwt
24*

Ques] A dilute normal solution of silver nitrate was electrolysed b/w platinum electrode after passing a current for 2 hours a fall of concentration of 0.000524 g eqwt in anodic solution occurred. The mass of Ag deposited in Cu Coulometer placed in series was found to be 0.03879 g calculate transport no. of Ag^+ and NO_3^-

$$T_{\text{Ag}^+} = \frac{0.000524}{\left(\frac{0.03879}{2} \right) / (63.4)}$$

$$T_{\text{Ag}^+} = 0.418$$

$$T_{\text{NO}_3^-} = 0.58$$

(Photo in Phone)

Attackable electrode

$t_+ = \text{Decr. in expected rim}$

expected rim no. of g Cu deposited in Coulrometer

Mathematical Expression

After electrolysis-

Let 'a' g anodic solution contain 'b' g of AgNO_3 solution $(a-b)$ g of H_2O contains 'b' g of AgNO_3 $(a-b)$ g of H_2O gives $\frac{b}{170}$ g of AgNO_3 eq. wt of $\text{AgNO}_3 = n$.

Before electrolysis

Let 'c' g of AgNO_3 solution contains 'd' g of AgNO_3

$(c-d)$ g H_2O gives 'd' g AgNO_3

$(a-b)$ g H_2O gives 'y' g AgNO_3

$$= \frac{d(a-b)}{(c-d)} g$$

$$= \frac{d(a-b)}{(c-d) \times 170} g \text{ equiv. AgNO}_3$$

$$= y$$

1d g of Cu is deposited in Cu coulometer

$$\text{No. of g equiv. of Cu deposited} = \frac{e}{(63.4)} = z$$

expected rise in conc. of anodic solution = ~~0.000211~~ 0.0002

Increase in conc. of anodic chamber = $(n-y)$

Decrease in expected rise $\geq z - (n-y)$

$$T_{\text{Ag}^+} = \frac{z - (n-y)}{z}$$

(Ques) A solution of AgNO_3 was electrolyzed b/w silver electrodes before electrolysis 10g of solution contained 0.017889 g AgNO_3 . After experiments 20.099 g of AgNO_3 solution contained 0.062279 g of AgNO_3 . At the same time 0.009479 g of Cu was deposited in coulometer. Calculate T_{Ag^+} and $T_{\text{NO}_3^-}$.

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$$n = \frac{20.099 - 0}{170}$$

$$c-d = 9.82$$

$$a-b = 20.02$$

$$n = \frac{0.06227}{170}$$

$$y = 0.01788 \times 20.277$$

$$(10 - 0.01788) \times 170$$

$$= 0.000211$$

$$= 2.11 \times 10^{-4} \text{ gm}$$

$$z = \frac{0.009479}{31.4}$$

$$= 2.99 \times 10^{-4} \text{ g}$$

$$T_{\text{Ag}^+} = \frac{2.99 - (3.66 - 2.11)}{2.94}$$

$$= 0.48$$

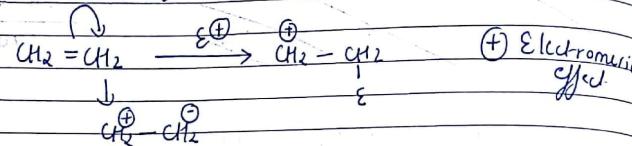
$$T_{\text{NO}_3^-} = 0.52$$

=

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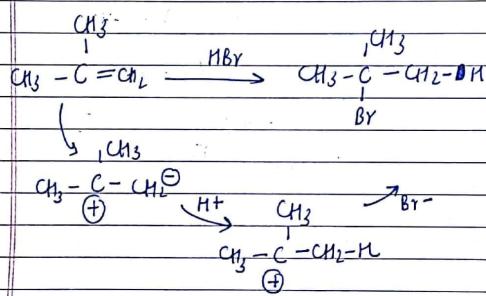
③ Electromeric effect -

It is a temporary effect.



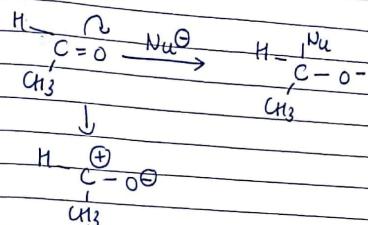
Generation of polarity in an organic compound due to complete transfer of π electrons in presence of an external agent.

(+) Electromeric effect \rightarrow if the agent attacks on the atom O's are transferred than it is known as + Electromeric effect.

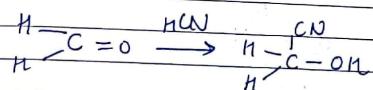


(-) E

Electro mERIC effect -



If agent attacks on atom where electrons are not transferred than it is known as - E effect.

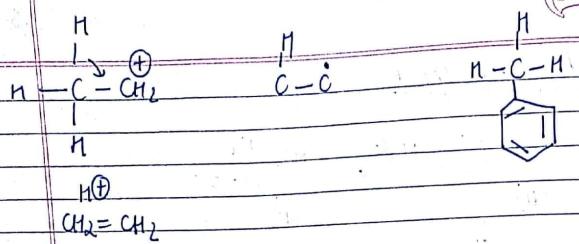


(4)

Hyperconjugation - (Bakut-Nathan effect or No-bond Resonance)

Generation of Polarity in an organic compound with atleast 1 α -Hydrogen

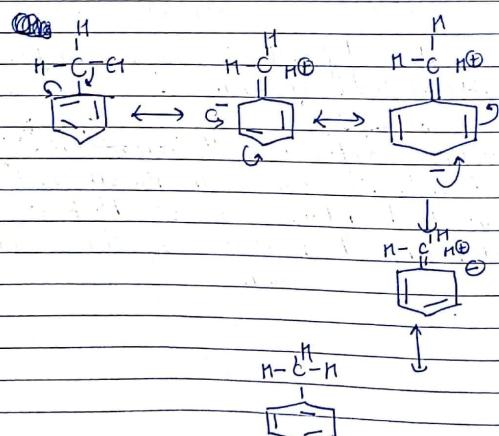
Organic compound with atleast 1 α -Hydrogen in which α' -Carbon is directly attached to an sp^2 hybridized carbon shows an effect similar to electromeric effect known as hyperconjugation which



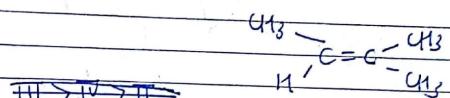
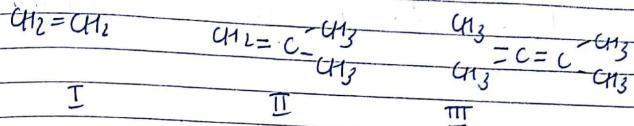
1- α carbon
 3- α Hydrogen
 3 hyperconjugative structure



Reactivity (Hyperconjugation)



Ques) Arrange the following in increasing order of stability?



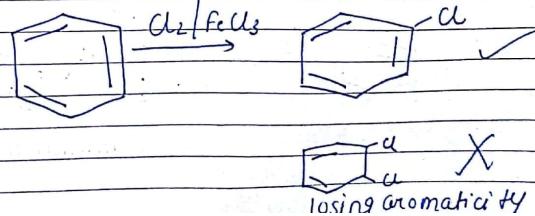
I < II < IV < III

More α Hydrogen
More Hyperconjugative structure.

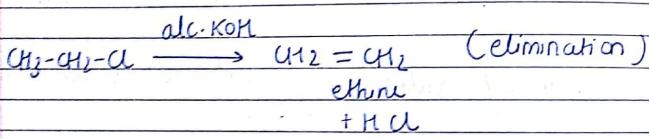
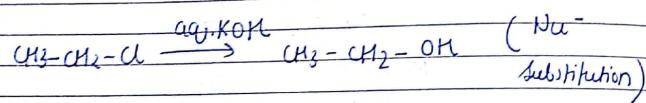
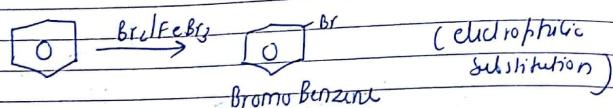
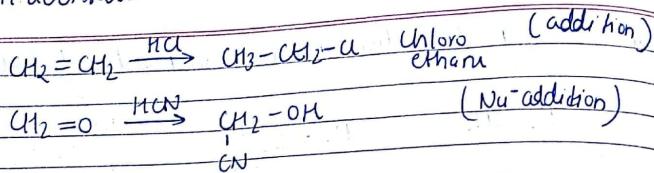
Saytzy's Rule: More substituted alkene is more stable.

Electrophilic Substitution Reaction

→ benzene and other aromatic compound show ESR.

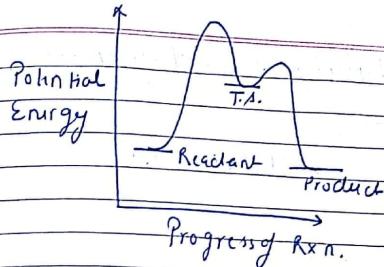


Benzene does not undergo addition reaction.
It does substitution reaction.

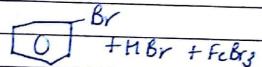
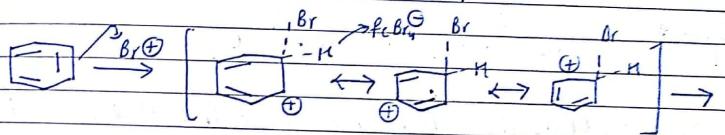


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(i) Halogenation-

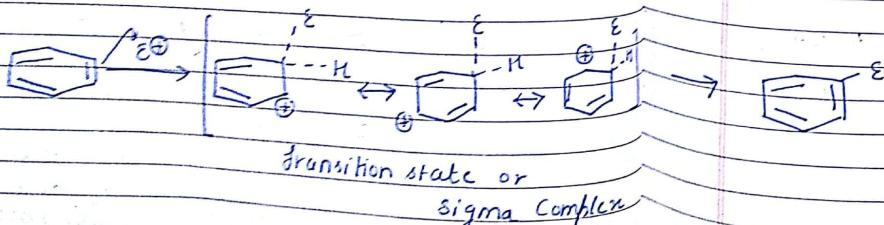


General Mechanism of Electrophilic Substitution Reaction

Reaction-

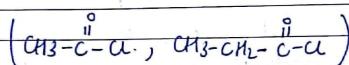
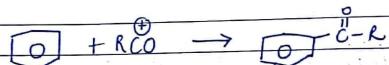
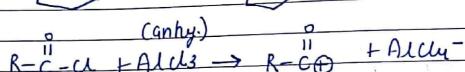
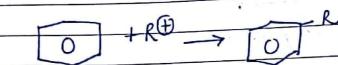
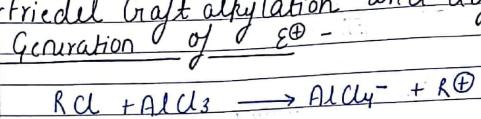
(i) Generation of E^{\oplus}

Mechanism:

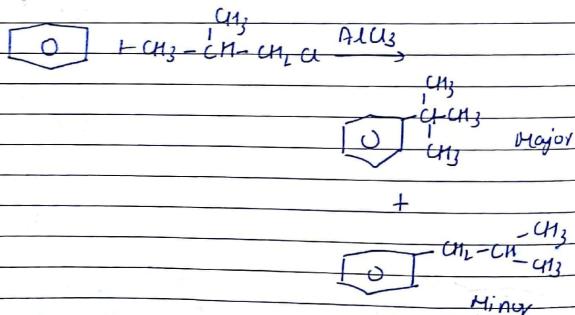


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(ii) Friedel-Crafts alkylation and acylation

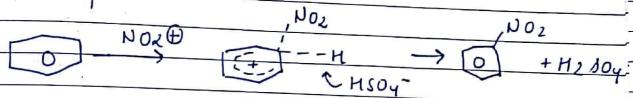
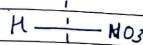
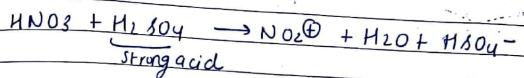


Qn) Complete the following rxn. predict Major and Minor product?

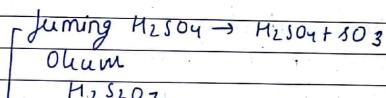
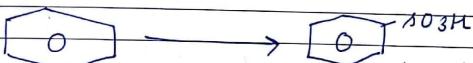


Reagents

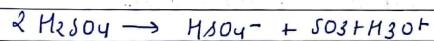
(iii) Nitration -



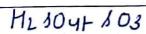
(iv) Sulphonation -



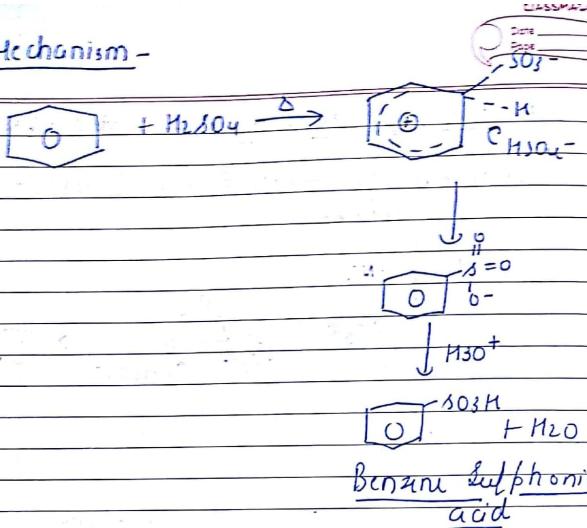
(i) Conc. $\text{H}_2\text{SO}_4 / 70-80^\circ\text{C}$



(ii) fuming sulphuric acid (H_2SO_7 Oulum)



Mechanism -

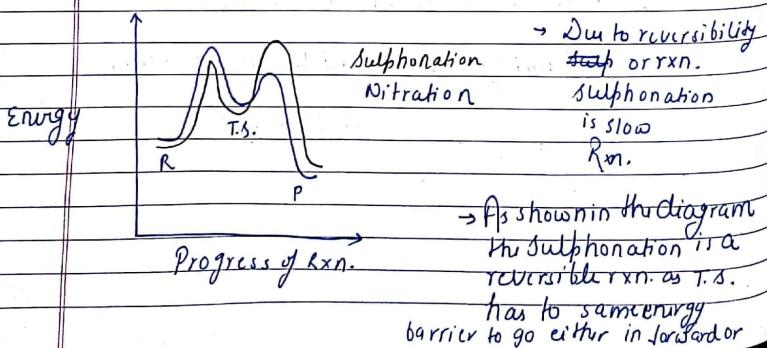


(Qn) Why SO_3^+ act as an electrophile?

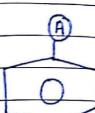
- due to +1 formal charge.
- due to vacant d' orbitals.

(Qn) It is observed that ~~sulphonation~~ sulphonation is a slow rxn. as compared to nitration explain why?

Sulphonation is a reversible rxn.



Reactivity and Orientation in Substituted Benzene -



O-p and activating

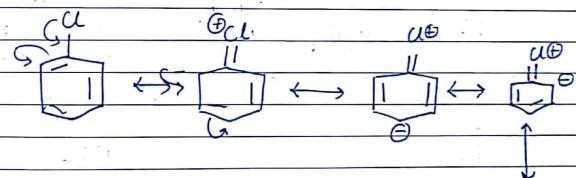
- Strong: $\text{CH}_3, \text{CH}_2\text{L}$
- Moderate: OH
- Weak: $-\text{CH}_3, -\text{CH}_2\text{L}, \text{L}$

mata and deactivating

- $-\text{NO}_2, \text{CH}_3, -\text{COOP}$

O-p / deactivating

- $-X$ (Halogen)



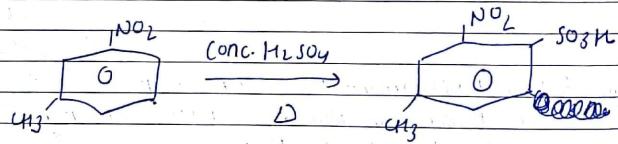
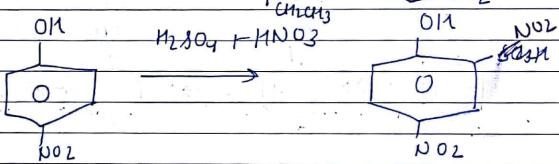
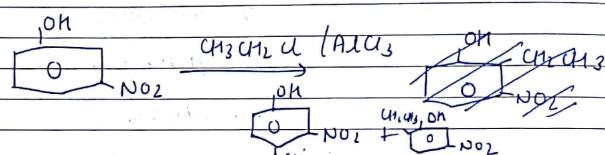
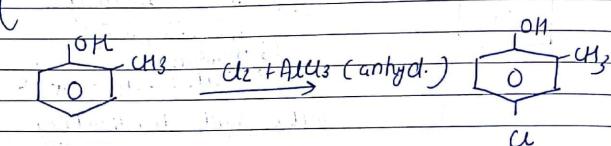
(Qn) O, N and Nitrogen are More electronegative than chlorine than why are they activating and Cl is deactivating?

In case oxygen and N' the overlapping is in b/w $2p-2p$ orbital of 'O' and 'C'. This is more effective overlapping as compared to $1s-2p$ of 'Cl' and 'C', so mesomeric effect is dominant over inductive effect.

backward direction.

Qn) Complete the following Rxn!

Substitution in Disubstituted Benzene.

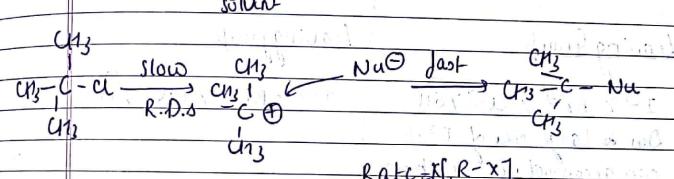
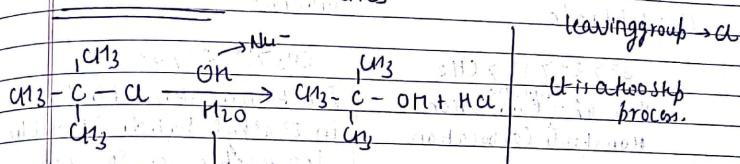


→ whenever there is an activating group than it will dominate over deactivating group.

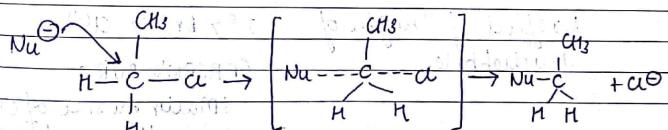
Aliphatic Nucleophilic Substitution (S_N)

S_N^1 (Unimolecular, Nucleophilic Substitution)

Mechanism and Kinetics



S_N^2 [Bimolecular Nucleophilic Substitution]



$\text{Rate} = k[R-X][\text{Nu}]$

Factors affecting SN^1 and SN^2

SN^1

① Substrate

$$3^\circ > 2^\circ > 1^\circ > CH_3$$

Non polar is C⁺ boration.
Hetero atom C⁺ boration.

SN^2

Substrate

$$CH_3 > 1^\circ > 2^\circ > 3^\circ$$

Due to more steric hindrance in 3° alkyl halide it will be less reactive for SN^2 rxn.

② Leaving Group

$$I^- > Br^- > Cl^- > OH^-$$

Due to large size of I⁻ it can accommodate -ve charge easily.

Leaving group

$$I^- > Br^- > Cl^- > OH^-$$

③ Effect of Nucleophile

No effect of strength of Nucleophile.

Effect of Nucleophile

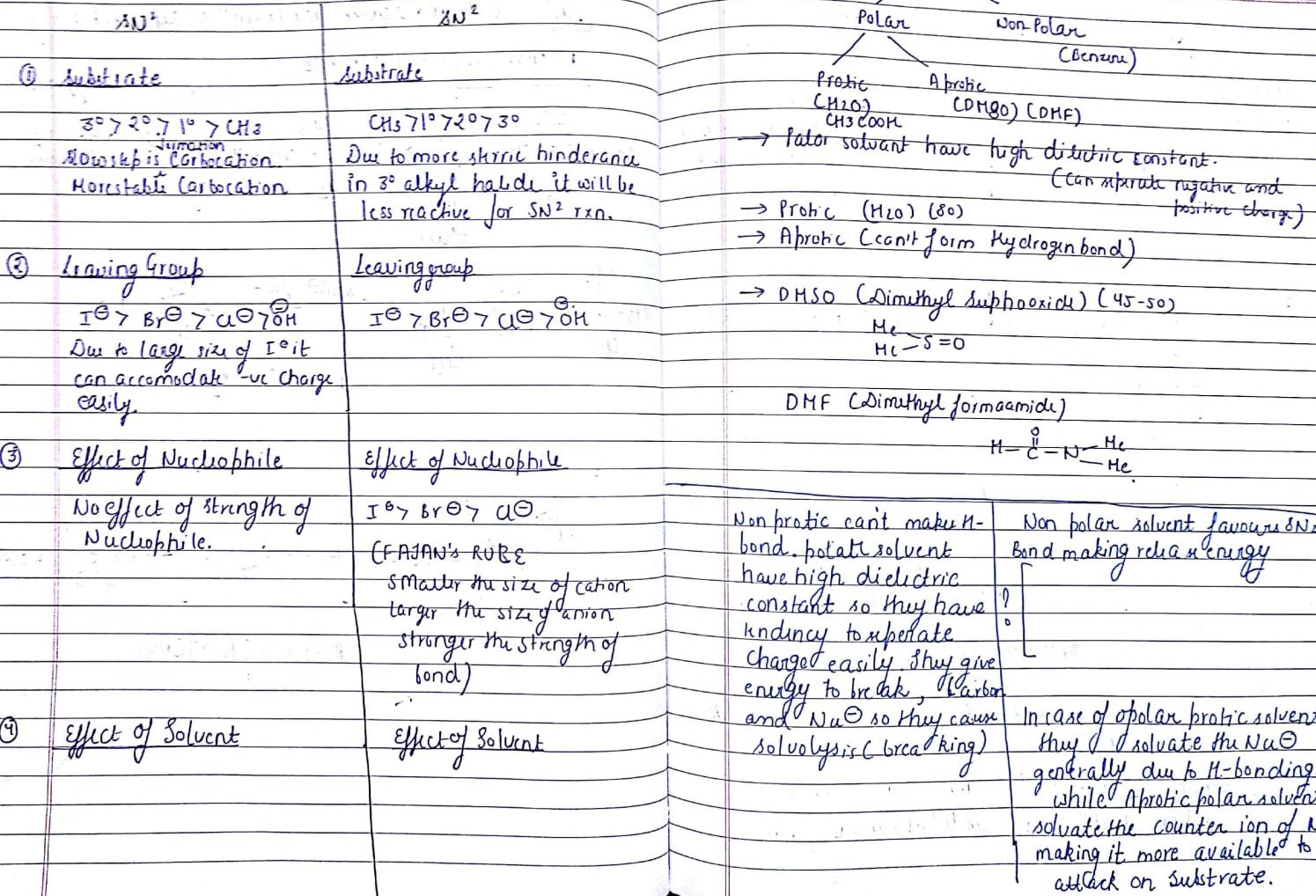
$$I^- > Br^- > Cl^-$$

(FARADAY'S RULE)

Smaller the size of cation larger the size of anion stronger the strength of bond)

④ Effect of Solvent

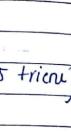
Effect of Solvent



7/04/17

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Aromatic	Non Aromatic	Anti Aromatic
1) $(4n+2)\pi c^{-3}$		$1\pi(4n)\pi c^{-3}$
2) Planar		3) Planar
3) Cyclic delocalized electron cloud		4) Cyclic delocalized electron cloud.

eg: g: 

Non aromatic (Cyclohepta-1,3,5-triene)

Antiaromatic (π hybrid but in ring it becomes planar)

Non aromatic

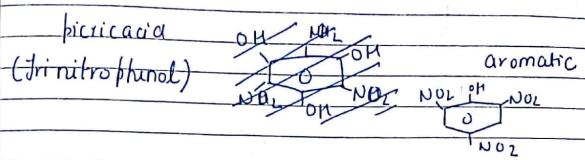


Aromatic (most stable aromatic cyclic carbocation)

(drobytium ion)

Qn) Classify the following compound as aromatic, Non aromatic and Antiaromatic.

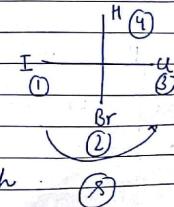
acetone, picric acid, acethanone, aniline, toluene, Naphthalene, Cyclobutadiene, furan

aceton $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{||}}}-\text{CH}_3$ Non aromaticacetophenone $\text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\text{C}}{\text{||}}}-\text{CH}_3$ aromaticaniline $\text{C}_6\text{H}_5-\overset{\text{NH}_2}{\underset{\text{C}}{\text{||}}}$ aromatictoluene $\text{C}_6\text{H}_5-\overset{\text{CH}_3}{\underset{\text{C}}{\text{||}}}$ aromaticNaphthalene $\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$ aromaticCyclobutadiene C_4H_4 antiaromaticfuran $\text{C}_4\text{H}_4-\text{O}-\text{C}_2\text{H}_4$ aromatic

R/S

Sequence Rule

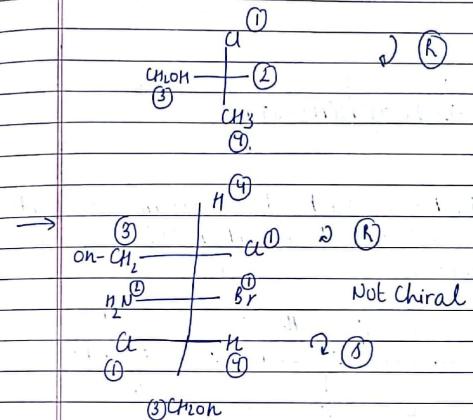
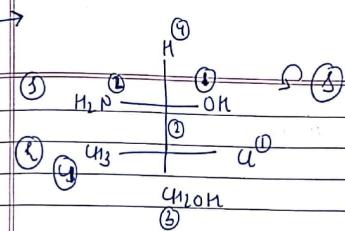
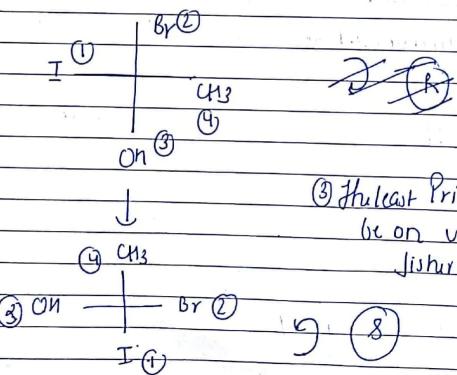
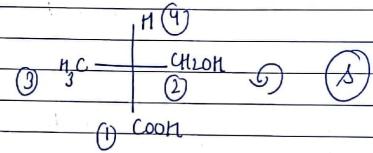
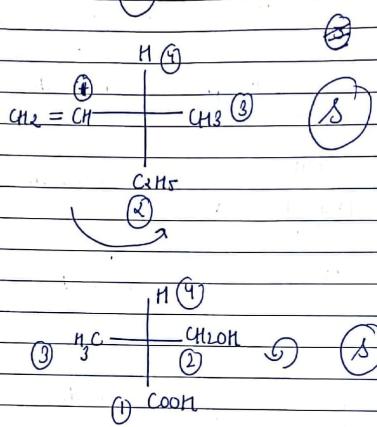
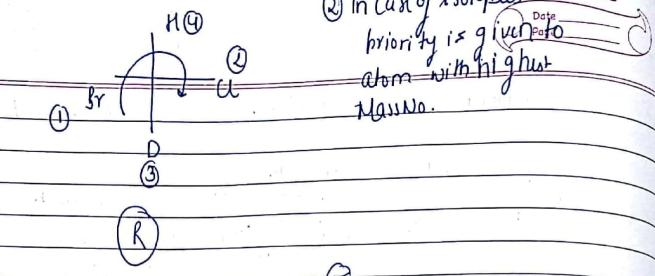
① The priority is given to group which has highest atomic no. atom directly attached to chiral carbon



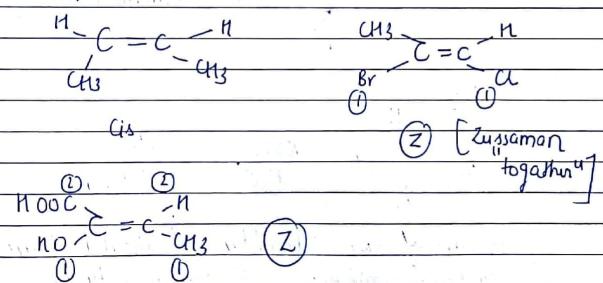
I → 2 → 3

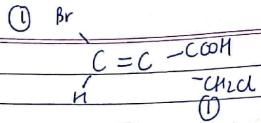
anti → s

clock → R



E/Z Nomenclature



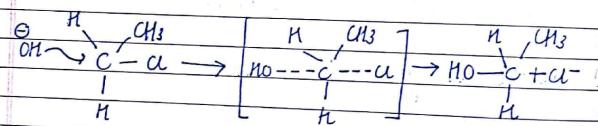


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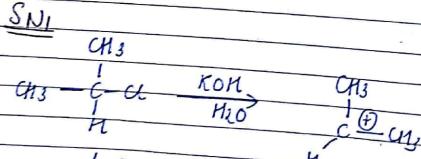
Stereochemistry

SNe

In this Nu^Θ attack from back side so obtain complete product with inverted geometry. This is known as wadler inversion.



No front side attack because free 'p' orbital doesn't have  and always have 

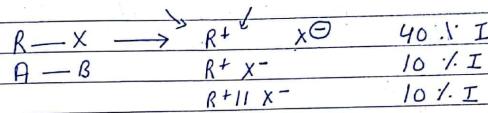


In case of SN₁, ideally we should obtain 100% racemic mixture but in actual More product with inverted geometry which can be

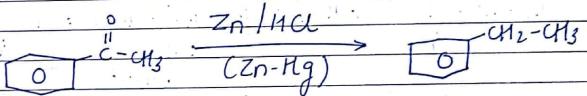
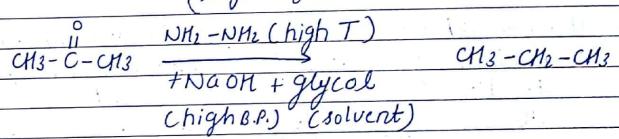
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35

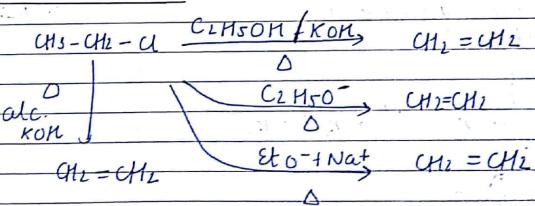
justified by formation of ion-ion pair and solvated ion pair.



- ## Wolff Kishner Reduction and Clemmison Reduction

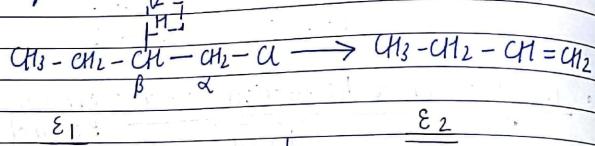


- ## • Elimination Reaction:

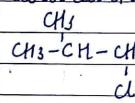


Note: All are same reagent.

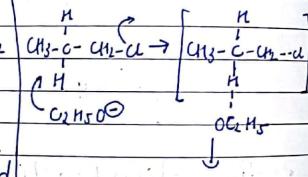
In elimination reaction we need strong base which is responsible for α - β elimination in alkyl halide also known as 1,2-elimination or dehydrohalogenation (removal of HX).



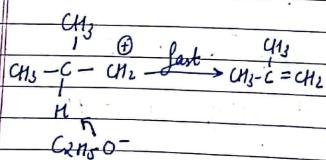
- 1) It is a two step process. slow step which is formation of carbocation.



- 1) In the same step, base is removed and also β -H is removed



Second step is fast in which β -Hydrogen will be removed by strong base to give alkene.



- 2) Substrate:

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

More stable carbocation
more reaction
(Generation of C^+)

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

[saytzyf]

In case of E_2 rxn. The order of reactivity will be same as of E_1 elimination. This case of dehydrohalogenation is similar to E_1 elimination due to stability.

Fisher drop (5 marks)

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- ③ Effect of leaving group

More the size, More the stability
 $\text{I}^- > \text{Br}^- > \text{Cl}^-$

$$\text{I}^- > \text{Br}^- > \text{Cl}^-$$

- ④ Effect of Base

Rate \propto [Substrate]

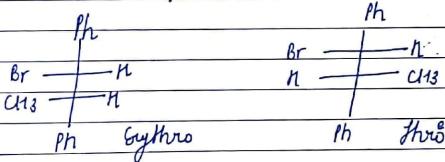
Strong base for E_2 elimination
[$\text{C}_2\text{H}_5\text{O}^-$ is a stronger base than $\text{CH}_3\text{O}^- > \text{OH}^-$]

- ⑤ Solvent

Polar solvent

Non polar solvent

Stereochemistry in E_2 elimination:
(Anti elimination)



Fisher projection formulae is a form of Newman projection.

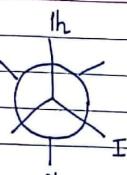
Newmann's projection:

classmate

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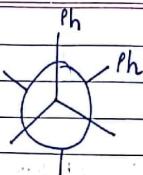
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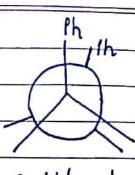
Staggered

I



Gauche

II

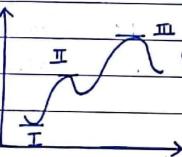


Eclipses

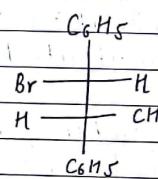
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Energy

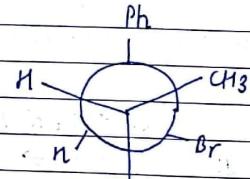
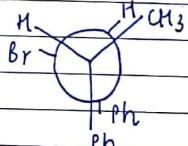
III > II > I



(a) Draw ecliptic of

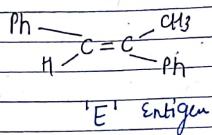


Shreya



Elimination happens

Qn) Explain stereochemistry of dihydrohalogenation of given erythro isomer



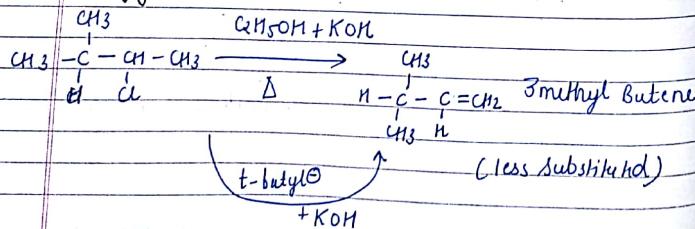
Qn) Compare E_2 and $\text{S}_{\text{N}}2$?

- Biomolecular elimination
- Both are single step rxn.
- Good Nu⁻ $\text{S}_{\text{N}}2$
- Solvent \rightarrow Both Non-polar solvent
- High temp \rightarrow elimination rxn.
- Substrate

\rightarrow the only point of difference is high temperature favours elimination otherwise we always obtain mixture of substituted and eliminated product.

* E_2 and $\text{S}_{\text{N}}2$ compete with each other we obtain mixture of both the products is obtained. High temperature favours elimination.

Hoffmann's elimination:



Hoffmann's elimination is

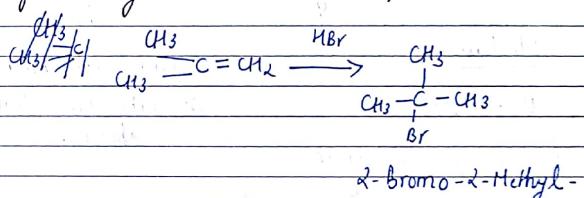
It is the formation of less substituted alkene if a bulky base is used. Presence of highly electro-negative leaving group always leads to formation of less substituted alkene.

Electrophilic addition:

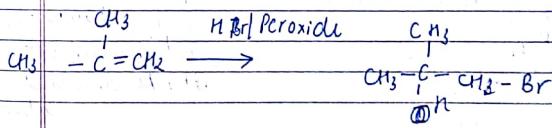
The compounds with unsaturated bonds b/w C-C show electrophilic addition.

Benzene won't show as it will lose its aromaticity

1) Hydrohalogenation - (Markanikov)



Peroxide effect / Kharasch's effect:



In presence of peroxide, HBr adds on an alkene against markanikov's addition as the reaction follows free radical mechanism.

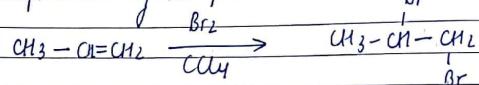
* HI or HCl do not show peroxide effect / Kharasch's effect.

HIO₃: It does not show effect because (I[•]) free radical readily diminishes to Iodine molecule.

HCl: Due to high electronegativity so homolytic cleavage of HF and HCl bond is difficult.

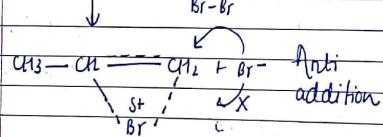
Halogenation:

In presence of non polar solvent.

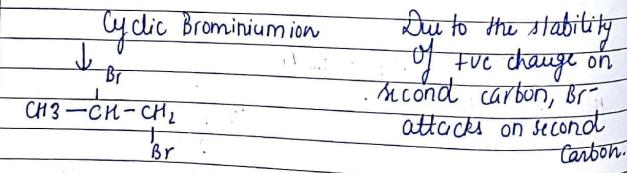


Mechanism:

$\text{CH}_3 - \text{CH} = \text{CH}_2$ Alkene is attacking on Br₂
So, hydrolytic cleavage happens.



Cyclic Brominium ion

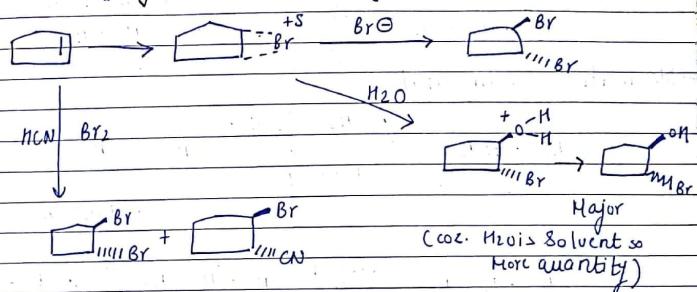


(Is alkene anti addition Racemic Mixture (CCl₄))

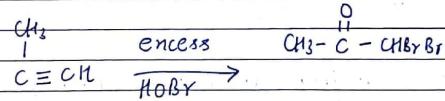
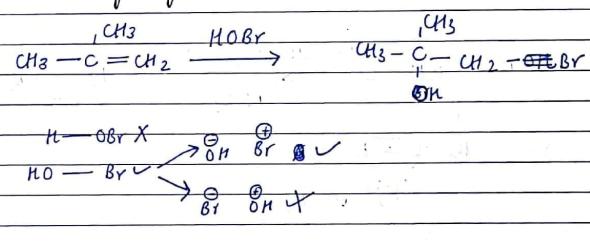
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Addition of Br₂ in presence of H₂O :

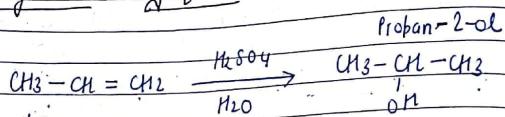


Addition of hypohalous acid :

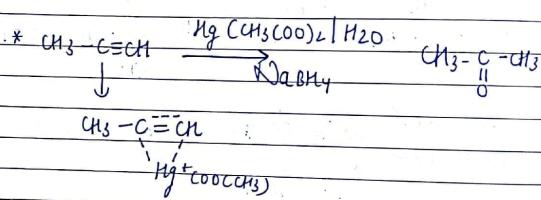
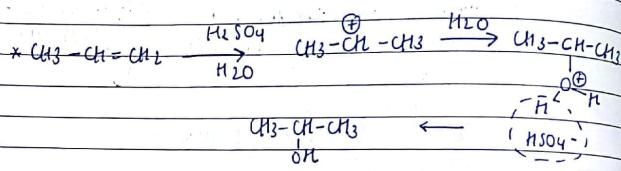
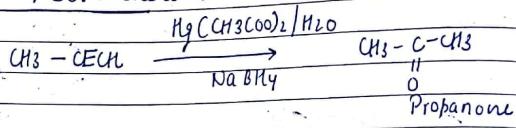


Notes : (NaNH₂ works similar to alcoholic KOH)

Hydration of Alkenes and Alkynes:

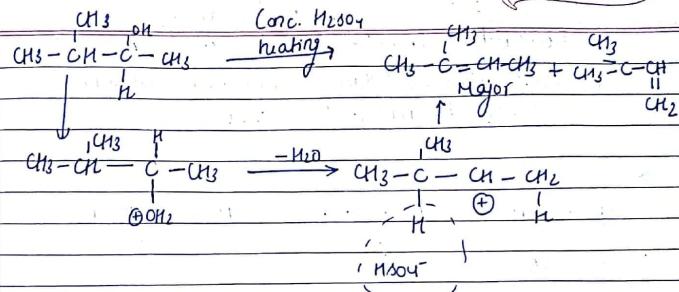
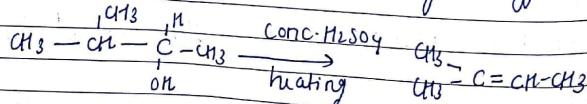


Mercuration / Denucleuration



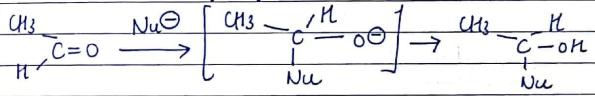
Dehydration in Alcohol:

Alcohols undergo elimination rxn. in presence of strong acid to give alkenes according to Zeff rule.



Nucleophilic Addition Reaction

Carbonyl compounds undergo nucleophilic addition rxn. by following general mechanism.



(Q) Which is more reactive towards nucleophilic addition?

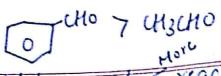
Alddehyde > Ketone

(Q) Due to?

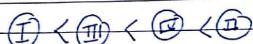
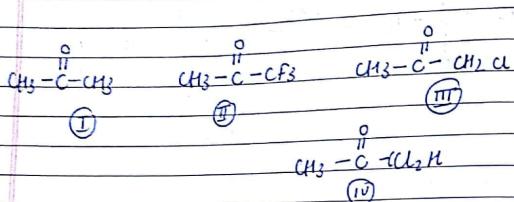
It can be explained by two factors

i) In case of Ketones the transition state is destabilized due to +I group and hence they are less reactive.

ii) Ketones are sterically hindered so nucleophiles cannot attack easily.

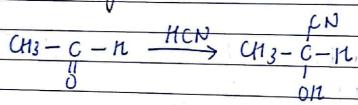


Benzaldehyde is less reactive as compared to aliphatic aldehydes because ^{here} Reactant is stabilized due to Resonance.

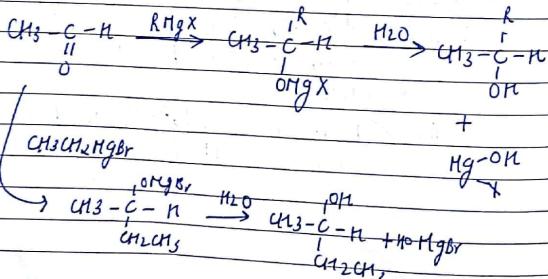


More $\text{C}=\text{O}$ group More Reactivity
less $\text{C}=\text{O}$ group stabilize transition state

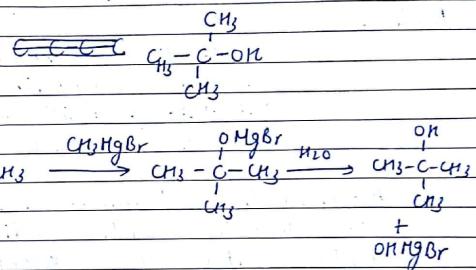
① Addition of HCN:



② Grignard Reagents: RMgX



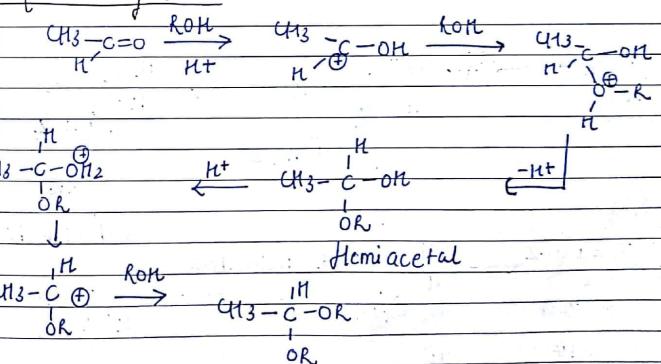
Ques) How will synthesize tertiary butyl alcohol from ketone?



→ Aldehydes always give 2° alcohol on reaction with Grignard reagent except formaldehyde which give primary alcohol

→ Ketones always give tertiary alcohol with Grignard reagents.

③ Addition of Alcohols:



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Addition of Ammonia and its derivatives

NH_3 , $\text{NH}_2\text{-Z}$, ($\text{Z} \equiv -\text{OH}, -\text{NH}_2, -\text{NH}-\text{O}-$, $-\text{R}$)

Ammonia

$\text{NH}_2\text{-OH}$ hydroxyl amine

$\text{NH}_2\text{-NH}_2$ hydrazine

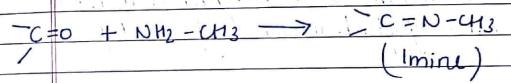
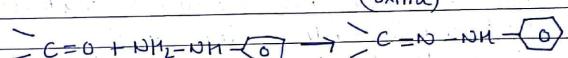
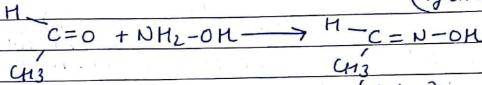
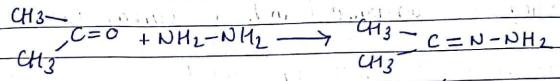
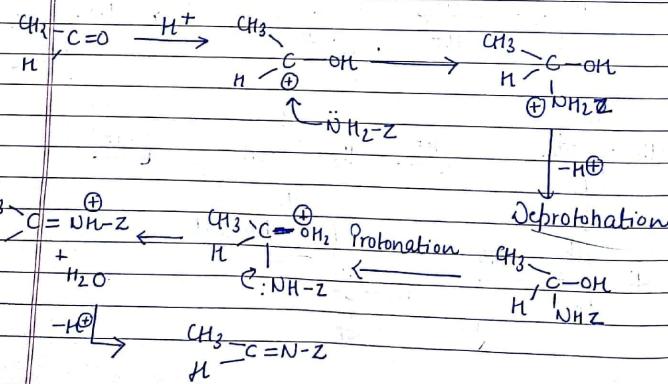
$\text{NH}_2\text{-NH}-\text{O}-$ Phényl hydrazine

$\text{NH}_2\text{-R}$ Amine

The addition of amines ammonia and its derivative is done in acidic medium. The proton from acid protonates oxygen to generate positive charge on carbon.

It makes carbonyl carbon more reactive to be attacked by a weak nucleophile (Ammonia and its derivatives).

The condition should not be highly acidic as it may cause protonation of ammonia or its derivative they loose their nucleophilicity therefore condition should be moderately acidic.



Ques) How will you synthesize meta-nitro $\text{C}_6\text{H}_4\text{NO}_2$ benzene from Benzene?

