Unit - III

Organic Reaction & their mechanism

① **Electron displacement effects:-** The behaviour of an organic Compd is influenced to a large extent by the e- displacement taking place in its Covalent bonds. These displacements may be of a permanent nature or may be temparary in nature taking place only on demand in the +nce of another molecule. (Reactant) The displacement of e's in Organic molecules are :-

① **Inductive effect** → This is a Permanent Effect operating in Polar Covalent bonds. It Comes into the existance when an e- withdrawing (e- donate or attracting) gp is attached to a chain of singly bonded C- atom. It results in the displacement of Sigma σ e-s of C-C bond leading to the development of partial (+) or -ve charges in the ↓sing order of magnitude on all the C- atoms of the chain. It is reffered to as I effect. It defined as

"The displacement of σ e's allong a a saturated C- due to the +nce of an e- withdrawing or e- repulling gp at one end of the chain (

8 resulting in the development of partial + or (−)ve charges in the rising order of the magnitude 9 is called indiective effect or I effect

It is of two types.

10 inductive effect

(1) −I effect :- When the substituent gp attached 11 to the chain of C- atom is an e^- withdrawing gp. effect is called −I effect.

12

1 $\underset{4}{C} - \underset{3}{C} - \underset{2}{C} - \underset{1}{C} - X$ where $X = Cl$

2 than C is $\delta(+)$ & $Cl^{\delta(-)}$

3 $$\underset{3}{\overset{\delta\delta\delta+}{C}} \text{---} \underset{2}{\overset{\delta\delta+}{C}} \rightarrow \underset{1}{\overset{\delta+}{C}} \rightarrow \overset{\delta-}{X}$$

4

5 So the trce of an e- withdrawing gp cause the displacement of σ e⁻ of all c−c bond 6 and induced partial +ve charge on all the C- atom of chain. The displacement 7 of e⁻ on account of inductive effect is shown by putting arrow heads on all C-C bond (→)

The inductive effect vises sharply as one moves away from e- ~~de~~ withdrawing gp. Some common gp which cause −I ~~de~~ effect in the order ~~de~~ of their ↓sing -I effect are

$-NO_2 > -CN > -Cooh > -F > -Cl > -Br > -I > -oh > C_6h_5-$

+I - effect → this effect comes into existance when an e- repelling gp is attached to one end of a saturated c- chain. Then e- repelling gp is less electronegative than C, due to its e- replilling nature. it acquires a paratial δ+ charge in Ist c (C_1) of the chain develops a δ ~~paratial~~ Partial (-)ve charge. The (-)ve charge on C_1 repells the σ e's of $C_1 - C_2$ bond & less -ve on (C_2). This effects continues and all the carbon atom of the chain develop partial -ve charges in the order of ↓sing megnitude.

$$\overset{\delta\delta\delta-}{C} - \overset{\delta\delta\delta+}{C} - \overset{\delta\delta-}{C} — \overset{\delta-}{C} — \overset{\delta+}{Y}$$

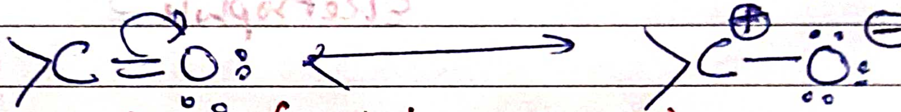
This effect also ↓ses sharply and become almost negligiable the IIIrd c- atom of the chain

Some common gps causing +I effect in the order of their ↓sing effect are

$(CH_3)_3C \rightarrow (CH_3)_2CH \rightarrow CH_3CH_2 \rightarrow CH_3$

In general +I effect of the alkyl gp is in the order 3° > 2° > 1° gps.

Electromeric effect :- It is a temporary effect due to inductive effect. It is operating in unsaturated compds only at the demand of a nearby reagent. It involves a complete transfer of π e⁻s



$$>C=\ddot{O}: \longleftrightarrow >\overset{\oplus}{C}-\ddot{O}:^{\ominus}$$

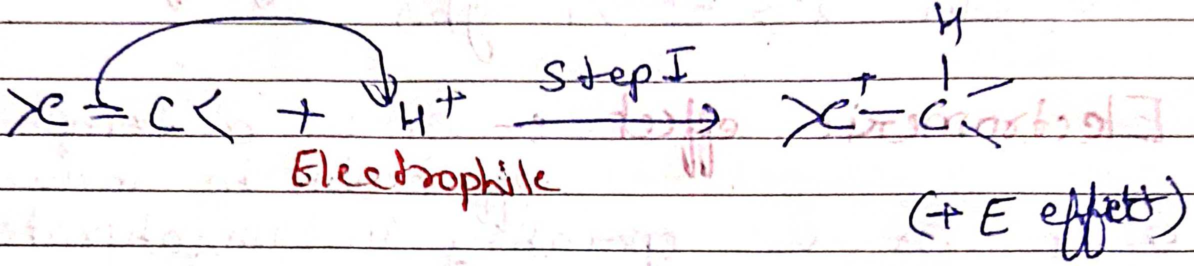
only (π e⁻) (Not in alkanes)

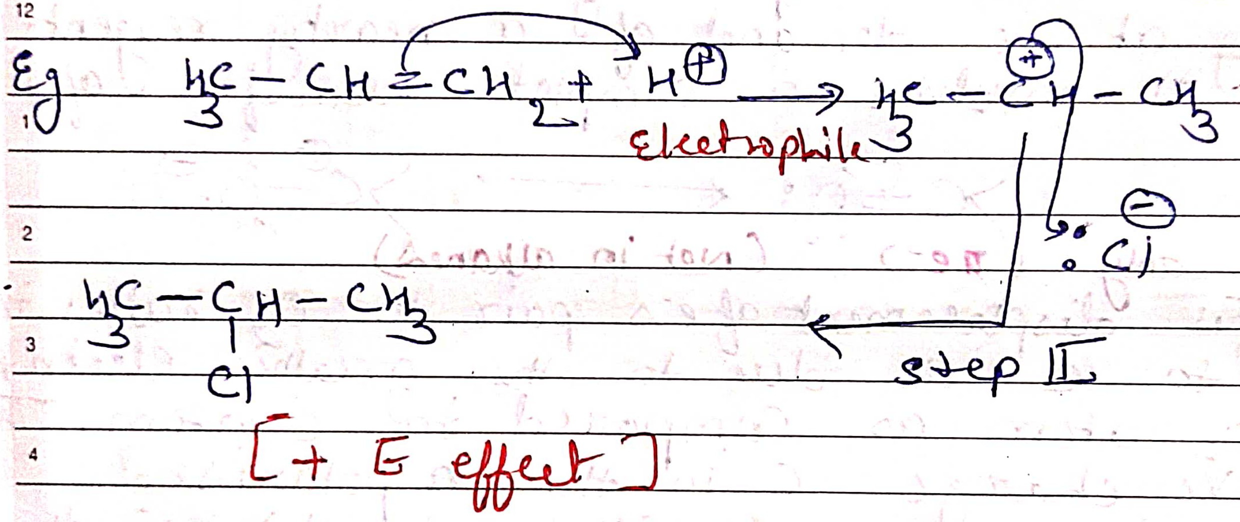
This displacement of e⁻s pair to O_2 rather than O to C is due to the greater electronegati of O_2 atom as compared to C-atom. The +ve charge C in the a polarised structure of CO (carbonyl gp) is the centre attack by neucleophile

The complete transfer of the shared paired of π e⁻s of a multiple bond to the more electronegative atom of the bonded atom due to the requirement of an attacking reagent is called electromeric effect.

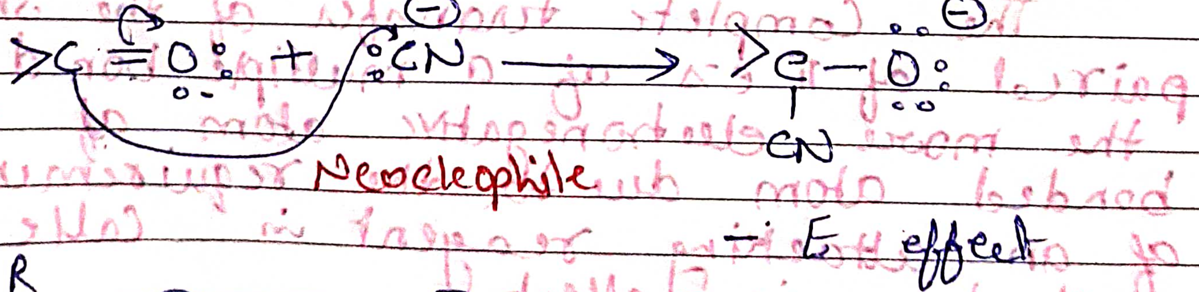
When the transfer of π e⁻s takes place towards the attacking reagent (electrophile) effect is called +E effect and when the transfer of π e⁻s

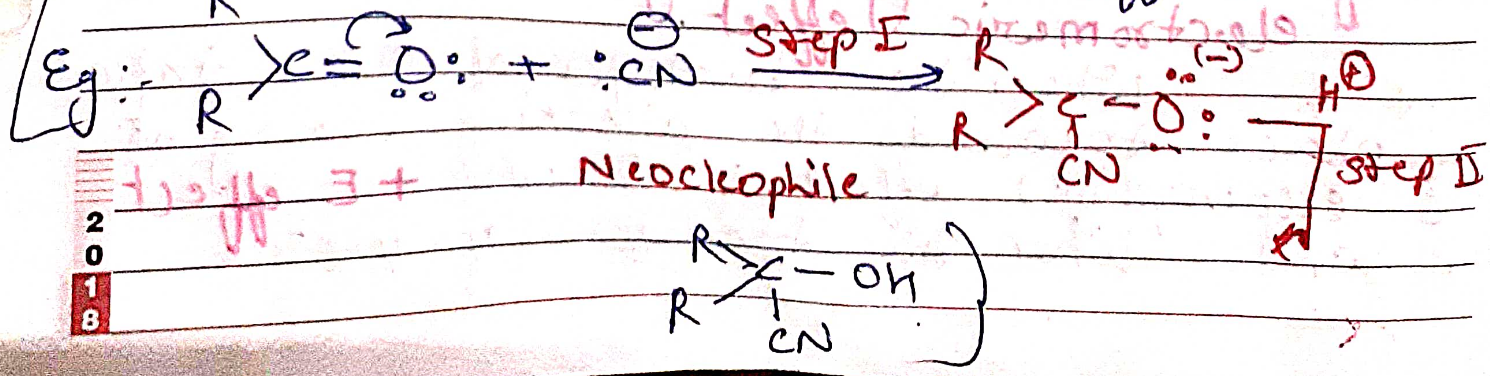
occurs away from the attacking reagent (nucleophile) effect is called
-E effect.





(II)





~~Field effect :- It is also called Symphoric effect. Involves & displacements, but It differ from other electronic effects~~

Bond Fission Or cleavage of bond :-

Organic Compounds are Covalent Compounds having − or = bonds or multible Covalent bonds b/w C atoms. most of the Organic reacⁿ involves the fission of Covalent bonds. once in the molecule of reactant. The fission of a Covalent bond may take place in either of the following two ways :-

1) Homolytic fission :- When a Covalent bond breaks up in such a way that each atom forming the Covalent bond takes away one e^- of the Shared pair, the cleavage of bond is Called homolytic fission or symmetrical fission.

$$A{\cdot}\,\Big|\,{\cdot}B \xrightarrow[\text{Homolytic fission}]{} \dot{A} + \dot{B}$$

free Radical

Heterolytic fission :- When a Covalent bond is break up in Such a way that both the e's belonging to the Shared pair are taken away only by one of the atom forming the Covalent bond The Cleavage of bond is Called Heterolytic fission or Unsymmetrical fussion. The atom taking away both the Shared e's is obviously more electronegative.

$$A \; {:}B \xrightarrow{\text{Heterolytic}} A^{+} + B^{-}$$

$$A{:} \quad B \xrightarrow{\text{Heterolytic-}} A{:} + B^{+}$$

heterolytic fission occurs most radily with the polar compounds in polar solvents.

Reac^n Intermediates :- Bond fission results in the formation of short lived fragments Called Reac^n Intermediates. Among The important reac^n intermediates are Carbonium ion ~~or~~ Carbanions, Carbon free radical and Carbenes.

1) Carbonium ion (Carbocations) ⇒ Organic ion

Which Contain possitively charged C-atom are called Carbonium ion Or Carbocations. They are formed by heterolytic bond fission

$$-\overset{|}{\underset{|}{C}}:Z \longrightarrow -\overset{|}{\underset{|}{C^+}} + Z^-$$

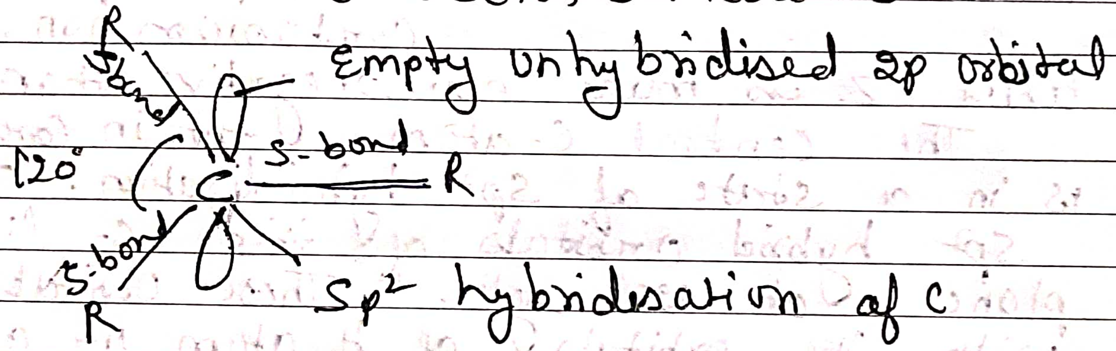
Carbonium ion.

Where Z is more electronegative than C

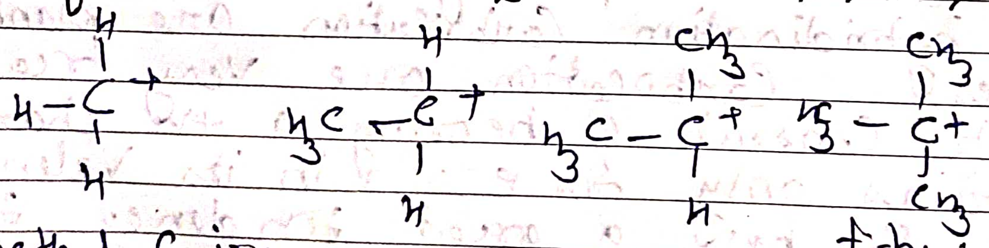
The central C-atom pnt in carbocation is in a state of sp^2 hybridization. The three sp^2 hybrid orbitals of this C- lie in one plane at 120° angle. These orbitals overlap with the orbitals of H atom or alkyl gp to to form σ bond. The two Unhybridised 2p orbital remain vacant in carbocation.

The +ve charge is pnt on the central C which is sp^2 hybridised. Due to sp^2 hybridisation carbocation are planner species. Carbocation are very reactive bc'z central C bearing a +ve charge contains only six e^-s in its valence shell & has a great tendency to complete the octate. Hence a carbocation combines readily with any substance that can donate a pair of e^-s to it.

The Stability of Carbocations is in the order is 3° > 2° > 1°. The relative Stability of Carbocations can be Explain On the basis of inductive effect. When an e^-s repelling gp (alkyl gp) is attached to the central C- bearing +ve charge. The magnitude of +ve charge on the central C rises due to pumping of e^-s by the e^- repelling gp & make the carbocation more stable.



The order of the reactivity is the reverse of stability. The reactivity of carbocations are 1° > 2° > 3°



$H-\overset{H}{\underset{H}{C^+}}$ $H_3C-\overset{H}{\underset{H}{C^+}}$ $H_3C-\overset{CH_3}{\underset{H}{C^+}}$ $H_3C-\overset{CH_3}{\underset{CH_3}{C^+}}$

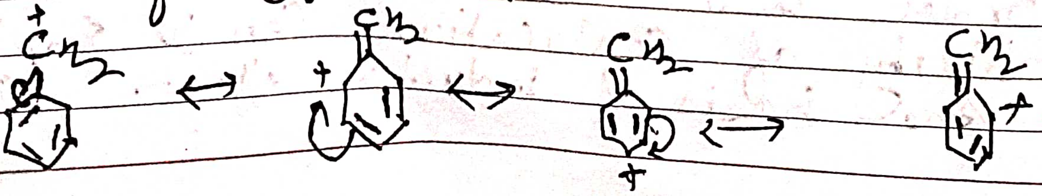
methyl C ion Ethyl c ion Isopropyl C ion ~~t-bu~~ t-butyl C ion

primary secondary tertiary

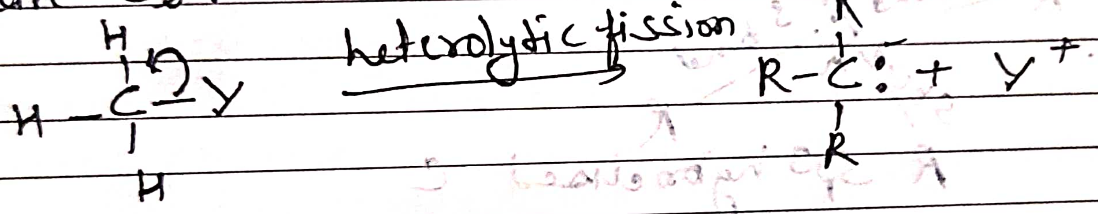
Resonance forms of allyl C^+ ion

$CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$

Resonance of Benzyl c ion

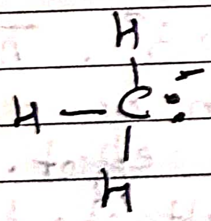


★ Carbanions :- A chemical species which posses a -vely charged C centre are called Carbanions. The central C bearing the negative charge contain a pair of available e^-s. It has a complete octate. It is formed by heterolytic fission of C-Y bond where Y is less electronegative than C.



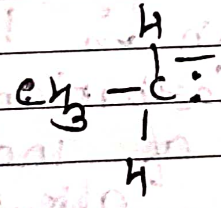
$$H-\overset{H}{\underset{H}{C}}-Y \xrightarrow{\text{heterolytic fission}} R-\overset{R}{\underset{R}{C}}\!:^- + Y^+$$

Carbaions.



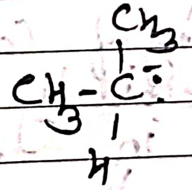
$$H-\overset{H}{\underset{H}{C}}\!:^-$$

methyl Carbanion (1°)



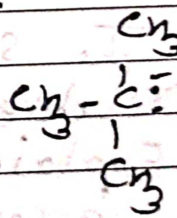
$$CH_3-\overset{H}{\underset{H}{C}}\!:^-$$

Ethyl C (1°)



$$CH_3-\overset{CH_3}{\underset{H}{C}}\!:^-$$

isopropyl C 2°

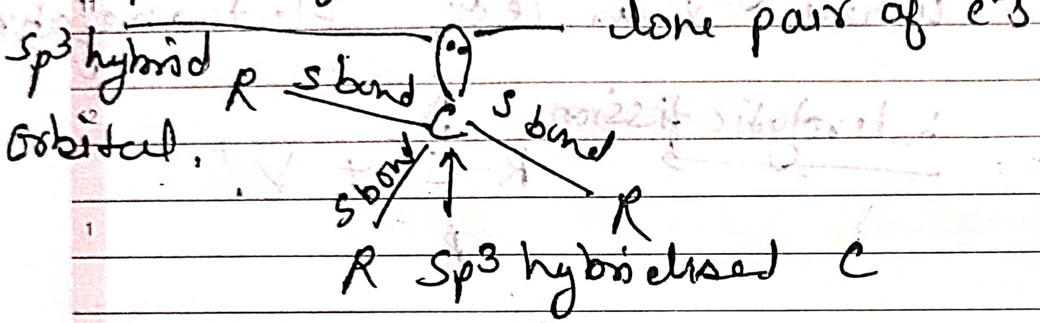


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}\!:^-$$

t butyl (3°)

The central C atom tnt in carbanion is ~~a~~ in a state of Sp3 hybridisation. Among the four sp3 hybrid orbitals; The three hybrid orbitals overlap with the orbitals of alkyl gp or H-atom & form σ bonds. The 4th sp3 hybrid orbital contain the lone pair of e^-s. Carbanion usually assums ~~pr~~ pyramidal structure.

8 Although the Central C atom in a Carbanion possess an octate, the carbanions are
9 very reactive intermediate due to +nce of -ve charge on central c-atom. The
10 central C atom posses a easily available pair of e⁻s. ~~The~~

11 

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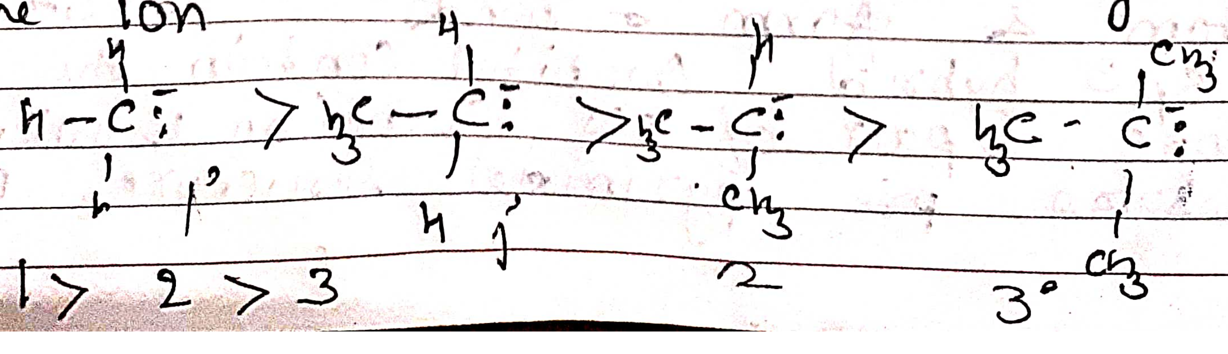
1

2

The Stability of Carbanion is 1° > 2° > 3°. The
3 relative Stability of Carbaniones Can be Explained in term of inductive effect.
4 greather the no. of alkyl gp attached to the central c atom, greater is the ↑se in
5 the magnitude of -ve charge on central C due to +I effect & lesser to
6 the stability to the Carbanion. In 3° Carbanian three alkyl gps are attached
7 to the central C-atom bearing -ve charge. The alkyl gps are e⁻ repelling gp & have a tendency to ↑se the -ve charge on central c. This ↑se the stability of the ion


$$H-\overset{H}{\underset{H}{C}}{:}^{-} > H_3C-\overset{H}{\underset{H}{C}}{:}^{-} > H_3C-\overset{H}{\underset{CH_3}{C}}{:}^{-} > H_3C-\overset{CH_3}{\underset{CH_3}{C}}{:}^{-}$$

1 > 2 > 3

Types of attacking Reagents:-

The Species which attack on a Substrate molecule and bring out about a chemical change are called attacking reagents.. The attacking reagents common in organic reactions may be classified into following two Catagaries.

I) Electrophilic reagent
II) Nucleophilic reagents.

I) Electrophilic Reagent Or Electrophiles:-

The Electrophilic (philic - loving = Electron loving) reagent are those species which posses an affinity of e^-s. These reagent posses the deficiency of e^-s. & therefore in chemical reacn they attack on those centres which are rich in e^-s. Electrophiles posses an e^-s deficient atom or centre. This is why they are have a thust for e^-s and attack at e^- rich centre.

A reagent which can accept an e-pair in a reacn is called electrophile. The term electrophile means "electron loving" and indicates that it attack ~~rea~~ regions of ~~low~~ high e- density (+ve Centre) in the Substrate molecule. Electrophile are e- deficient. They may be +ve ion or ~~H+~~ neutral molecules with e⁻ deficient centres. for Eg H^+, Cl^+ Br^+ I^+, NO_2^+ RC_3^+ $\overset{+}{S}O_3H$ $AlCl_3$

It is represented by E^+

Nucleophilic Reagent or Nucleophiles

A Reagent which can donate an e⁻ pair in a reacⁿ is called nucleophile. The name nucleophile means "nucleus loving" and indicates that is attack region of low e⁻ density (Positive centres) in the substrate molecule. Nucleophiles are e⁻ rich. They may be -ve ions or ~~nuet~~ neutral molecule with free e⁻ pair.

Eg

Cl^-, Br^- I^-, CN^-, OH^-, RCH_2^-

NH_3 RNH_2; H_2O ROR

It is represented by Nu^-

Types of Organic Reac^n

The organic reac^n can broadly classified into four Catagaries

(I) Substitution Reac^n
(II) Addition Reac^n
(III) Elemination Reac^n
(IV) Rearrangement reac^n

① **Substitution Reac^n** The reac^n which involved the direct replacement of an atom or a gp of atom by some other atom or a group of atom are reffered to as Substitution reac^n

① **Nucleophilic Substitution Reac^n** → The Substitution Reac^n which are brought about by the attack of neuclophile are termed as nucleophilic Substitution and represented as SN reac^n

$$\underset{\text{alkyl halide}}{R-X} + \underset{\text{strong Neucleophile}}{OH^-} \longrightarrow \underset{\substack{\text{alcohol}\\ \text{S. product}}}{R-OH} + \underset{\substack{\text{Halide ion}\\ \text{weaker}\\ \text{nucleophi}}}{X^-}$$

In this reac^n a weaker nucleophile is usualy replaced by a stronger nucleophile this reac^n are of two type.

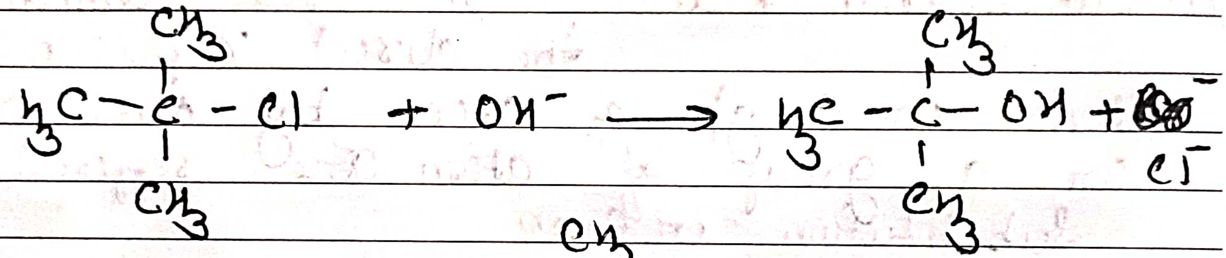
1) **S_{N^1} Reac^n** → It is unimolecular Substitution reac^n. The S_{N^1} Reac^n are those nucleophilic

Substitution reac^n in which the rate of reac^n depends ~~up~~ only upon the Concentra^n of substrate and not upon the concentra^n of the attacking nucleophile.

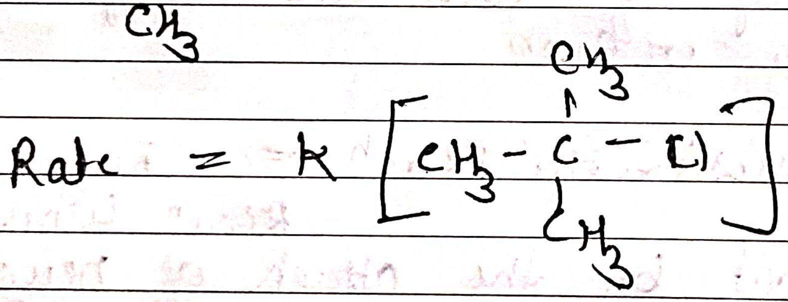
Rate ∝ Substrate

It is a Ist order reac^n and rate law involves only the Concentration of the Substrate

Eg.

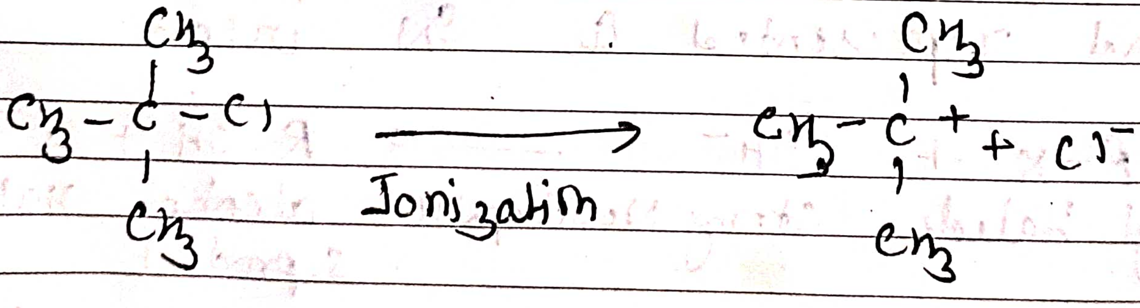


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Cl + OH^- \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + Cl^-$$



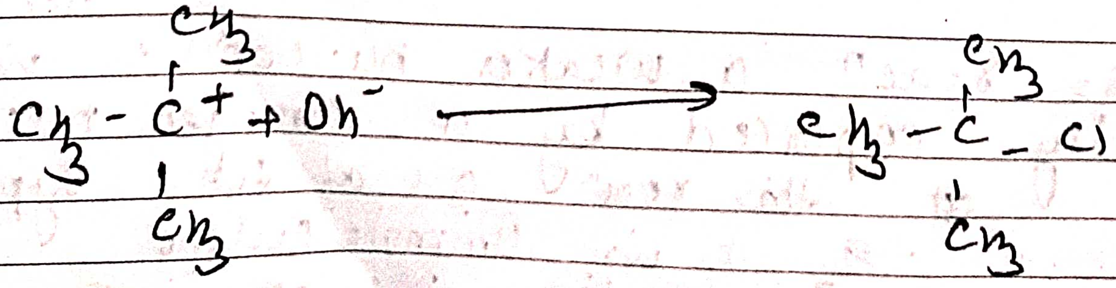
$$Rate = K\left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl\right]$$

Ist step



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow[\text{Ionization}]{} CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + Cl^-$$

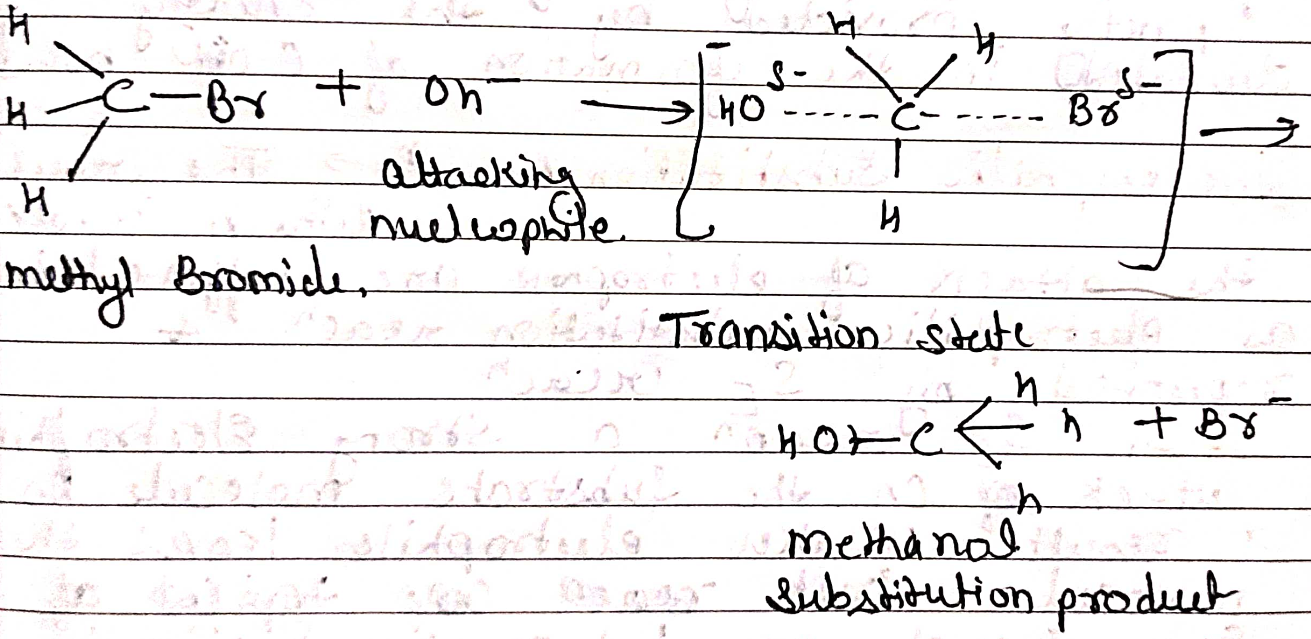
Step II



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + OH^- \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl$$

2) S_N2 reac^n → bimolecular Substitution nucleophilic reac^n. The S_N2 reac^n are those reac^n in which the rate of reac^n depends up on the concentra^n of the substrate as well as on the concentra^n of the attacking nucleophile. Thus a S_N2 reac^n is a second order reac^n and has the rate law

Rate = k [Substrate] nucleophile.

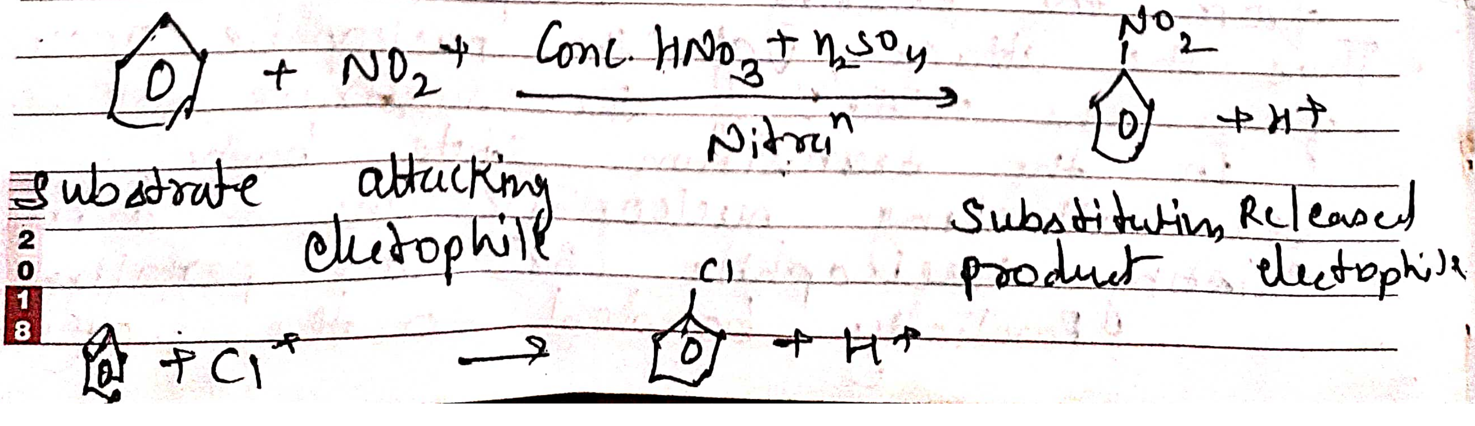


The attacking nucleophile attacks on the Substrate (CH_3Br) at the face most remote from the existing nucleophile. (Br^-) Thus the attack of the nucleophile occurs from the rear of the substrate molecule. In the transition state both the attacking nucleophile (OH) & already existing nucleophile (Br^-) are ~~probably~~ Partially bonded to the C-atom of the Substrate molecule (----C----) Showing as the attacking nucleophile (OH) is Stronger one). The e- density Shift ~~of~~ towards it and a permanent C-OH bond is formed. As the Same time C···Br are broken & Br^- leaves the transition state from the front side. The energy needed for the cleavage of C-Br bond is partly provided by the energy liberated in the formation of C-OH bond

2) Electrophilic Substitution Reac^n → The reac^n which involved the attack of electrophile are reffered to as electrophilic substitution reac^n & represented by S_E reac^n

In S_E reac^n a strong Electrophile attack ~~of~~ on the Substrate molecule. As a result weaker electrophile leaves the molecule. ~~Such reac^n are typical of~~ Some example are halogenation, nitration Sulphonation and fridal craft reac^n.

S_E Reac^n of Benzene are



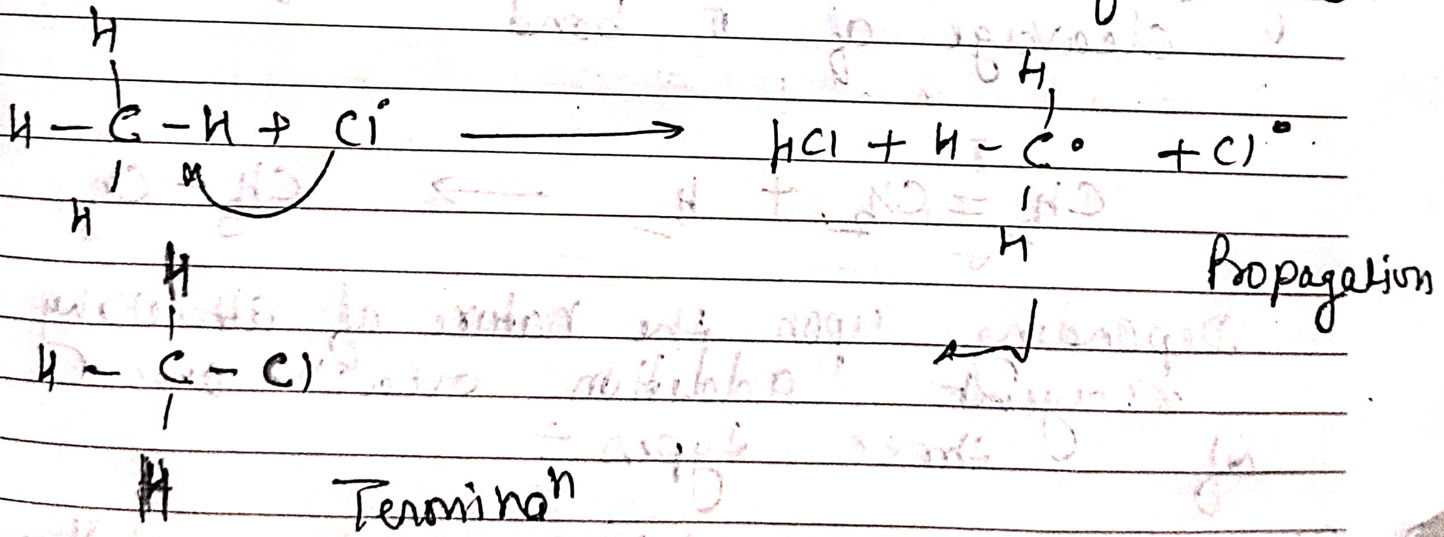
8 3) Free Radical Substitution Reac^{n} → The reac^{n} which are brought about by the attack of free radicals are called free radical substitution reac^{n}.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

(I) Initiation (II) Propagation (III) Termina^{n}

$$Cl_2 \xrightarrow{h\nu} Cl^{\circ} + Cl^{\circ}$$ Initiation

chlorine free radical



$$H-\overset{H}{\underset{H}{C}}-H + Cl^{\circ} \longrightarrow HCl + H-\overset{H}{\underset{H}{C}}^{\circ} + Cl^{\circ}$$

Propagation

$$H-\overset{H}{\underset{H}{C}}-Cl$$

Termina^{n}

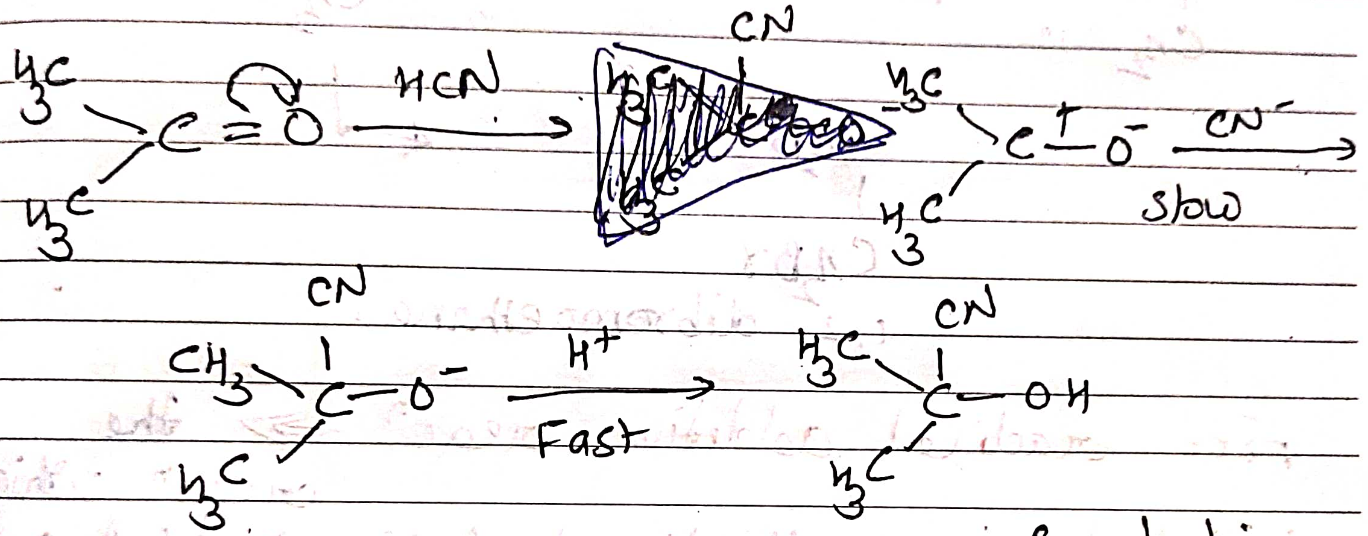
14.2 Addition Reac^n ⇒ When a reagent is added at the site of a = or ≡ +nce in the substrate molecule, the reac^n is reffered to as an addition reac^n, a = bond is composed of one σ & one π bond where as a ≡ is made up of one σ & 2 π bonds. A π bond is weaker than a σ bond & need less energy for its cleavage. When a attacking reagent attacks on a substrate containing = or ≡, the π bond get broken & reagent gets added at the side of the cleavage of π bond

$$CH_2 \overset{\pi}{\underset{\sigma}{=}} CH_2 + H_2 \longrightarrow CH_3 - CH_3$$

Depanding upon the nature of attacking reagent addition reac^n are of three types :-

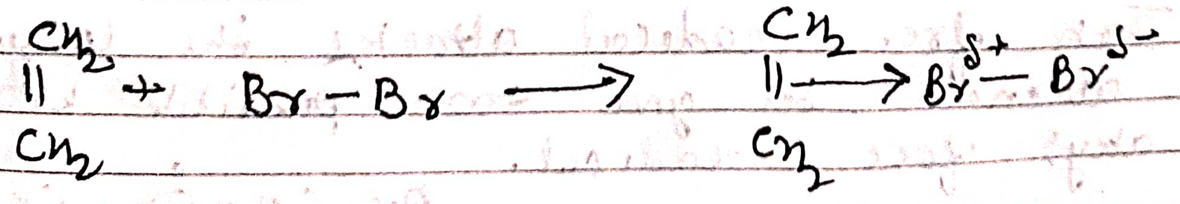
① Nucleophilic addition reac^n ⇒ When reac^n is initiated by the attack of nucleophiles are termed as neucleophilic addition reac^n.

This reac^n is very common in Carbonyl Compds. >C=O There exist a = bond b/w C & O, due to electromeric effect, the e⁻ forming C-O π bond get transferred to O_2 atom being O is more electronegative than C, so the C-atom of >C=O develops a +ve charge. for Eg addition of HCN to acetone takes place.



acetone Cynohydrin.

Electrophilic addition reacⁿ → The addition reacⁿ initiated by the attack of electrophiles are called electrophilic addition reacⁿ. These reacⁿ are usually shown by alkenes & alkynes. for Eg addition of Cl_2 in ethylene



When Br_2 attack on ethylene the π e⁻s of = bond induce polarisaⁿ in Br_2. Then $Br^{\delta+}-Br^{\delta-}$ formed gets loosely attached to to π cloud of $CH_2=CH_2$ to get formed π complex.

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \longrightarrow Br^{\delta+}-Br^{\delta-} \longrightarrow \begin{matrix} CH_2Br \\ | \\ {}^{+}CH_2 \end{matrix} + Br^{-}$$

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix}$$

1,2 dibromoethane.

Free radical addition reac^n ⇒ the reac^n which initiated by attack of free radical are called free radical addition reac^n

$$RO \mid OR \xrightarrow[\Delta \text{ or } h\nu]{\text{homolytic fission}} R\dot{O} + R\dot{O}$$

Organic Peroxide

$$RO + HBr \longrightarrow ROH + Br^{\circ}$$

Then free radical attacks the unsymmetrical alkene to give two possible bromo akyl free radical.

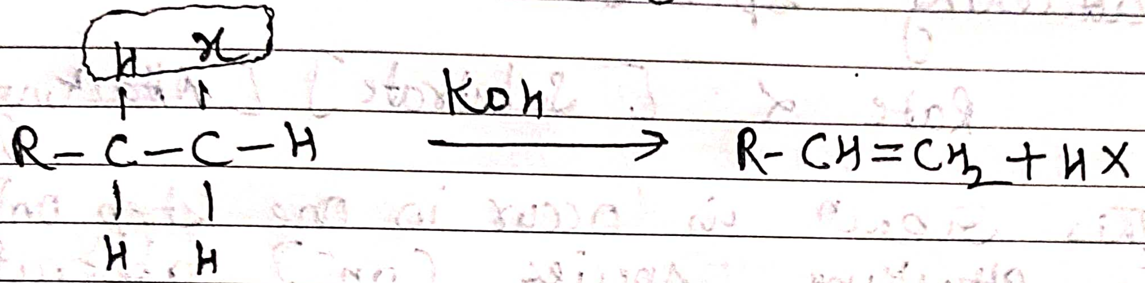
$$CH_2=CH-CH_3 + \dot{Br} \nearrow Br-CH_2-\dot{C}H-CH_3$$

2° free radical more stable

$$\searrow \dot{C}H_2-\underset{Br}{CH}-CH_3$$

1° free radical less stab

8) Elimination Reac^n ⇛ The reac^n involving the loss of 2 or 4 atoms or gps from the same or the adjacent C atom in a substrate molecule leading to the formation of a multiple bond are called elimination reac^n.



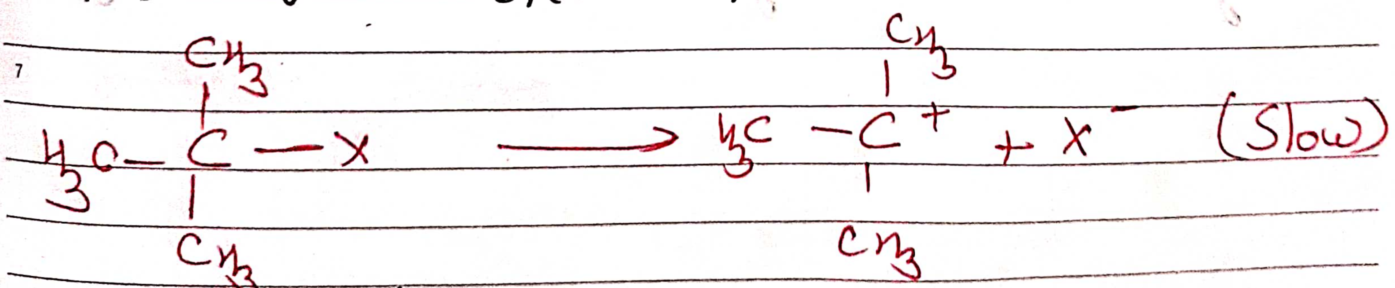
$$R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{X}{C}}-H \xrightarrow{KOH} R-CH=CH_2 + HX$$

Θ reac^n are of two types :-

① E$_1$ reac^n → It is also known as Unimolecular eliminan^n reac^n. The E$_1$ reacn are those reac^n in which the rate of reacn ~~in which are the rate of~~ depends only upon the concentran^n of the substrate.

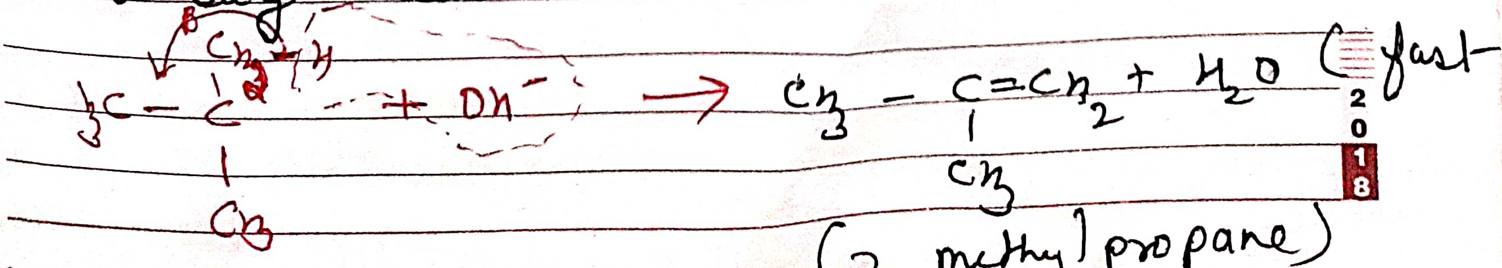
Rate ∝ [Substrate.]

Reac^n are like SN$_1$ reac^n.



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-X \longrightarrow H_3C-\underset{CH_3}{\overset{CH_3}{C^+}} + X^- \quad (\text{Slow})$$

t-butyl halide



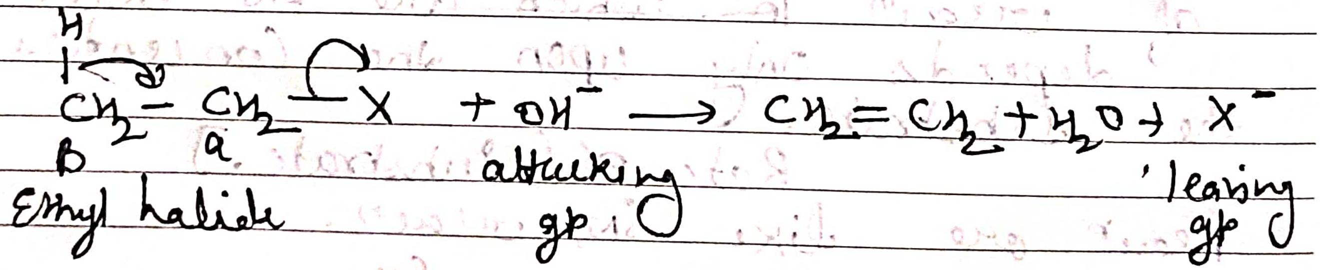
$$H_3C-\underset{CH_3}{\overset{CH_2-H}{C^+}} + OH^- \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + H_2O \quad (\text{fast})$$

(2 methyl propane)

⑪ E_2 Reactions (B) → also Bimolecular elimination reacⁿ called. The E_2 reacⁿ are those elimination reacⁿ in which the rate of reacⁿ depends upon the concentration of both the substrate & attacking species.

Rate ∝ [Substrate] [Attacking speices]

This reacⁿ is occur in one step only. The attacking species (OH^-) abstracts a proton from β-C- atom resulting in the simultaneous release of the leaving gp (X^-) ~~eg~~ for Eg The dehydrogenation of ethyl halide in the of KOH



$$\overset{H}{\underset{\beta}{CH_2}} - \underset{\alpha}{CH_2} - X + \underset{\text{attacking gp}}{OH^-} \longrightarrow CH_2=CH_2 + H_2O + \underset{\text{leaving gp}}{X^-}$$

Ethyl halide

Rearrangement Reac^n ⇒ The reac^n involving the rearragement of atoms or gp in the substrate molecule leading to the forma^n of structural isomer of the original substrate molecule are refferred to as elimination reac^n.

Intramolecular → These reac^n proceeds by an intramolecular change. The migration gp or atom is not fully detached from the system and always remain associated with the substrate molecule during the process of migration. for Eg Isomerisation of n-butane into isobutane. in pnce of $AlCl_3$

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[\Delta]{AlCl_3} CH_3-\overset{CH_3}{CH}-CH_3$$

n- ISO

1) Intermolecular → In this reac^n the migration gp leaves the substrate molecule during the process of migration and later on gets reattached at some other site of the rest of substrate molecule. This leads to the forma^n of structural isomer of the original substrate molecule.

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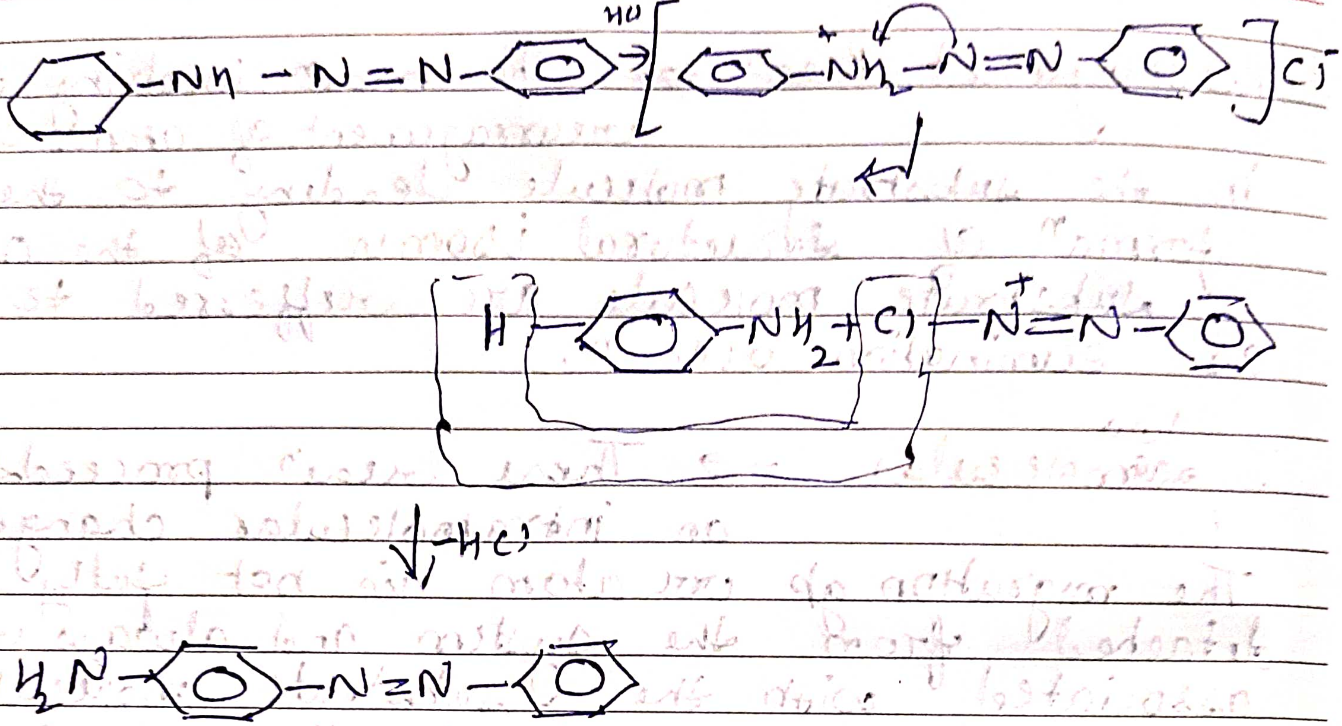

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