Toppersnotes
Unleash the topper in you

CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - I

ORGANIC CHEMISTRY

SIERRA INNOVATIONS

Index

ORGANIC

Reaction Mech :-

Reactant → Substrate, Reagent

$X-Y+Z \longrightarrow X+Y-Z$

$X-Y+Z$ → Reactant ; $X+Y-Z$ → Prod.

→ Substrate is a sp. at C reagent attack.

→ Reagent is the attacking species.

- Case (1)

Org sp + Inorg. sp. →
(Subs) (reagent)

- Case (2)

Org sp + Org sp.

Here the org. sp. C excess of charge density is the reagent & another one is substrate.

Reagents

Electrophile	Nucleophile.
electro + phile	Nucleo + phile
e⁻	Nucleus
phyllous (loving)	phyllous (loving)
① That means electrophiles are e⁻ loving sp.	① Nucleophiles are the Nucleus loving sp.
② These are electronically deficient sp; attacks at	⊕ve charge loving sp.

site that is electronically rich.

(3) These are lewis Acids, bcz these have the tendency to accept e⁻ pair from external source.

(2) These are electronically rich sp. Attacks at the site. i,e electronically deficient.

(3) These are lewis bases bcz they have tendency to donate it's e⁻ pair.

Classification of Electrophile :-

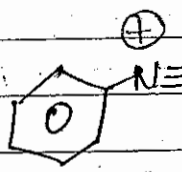
⊕ve charge sp.

eg: H^+, R^+, Cl^+, Br^+, I^+

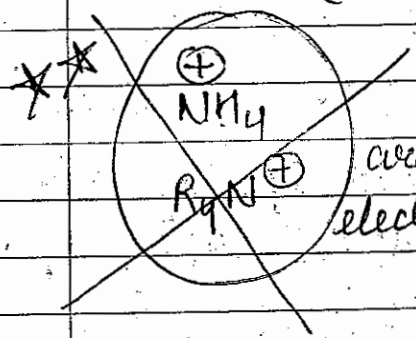
$CH_3-\overset{\oplus}{C}=O$ (acylium ion)

$\overset{\oplus}{N}O_2$ (Nitronium ion)

$\overset{\oplus}{N}O$ (Nitrosonium ion)



(Diazonium ion)



are not electrophiles

Neutral sp

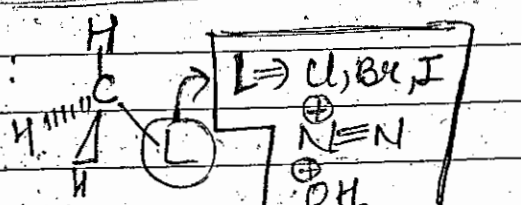
(1) Sp. having vacant p-orb

eg: BF_3, BCl_3, BBr_3, $:CCl_2$ (dichlorocarbene)..

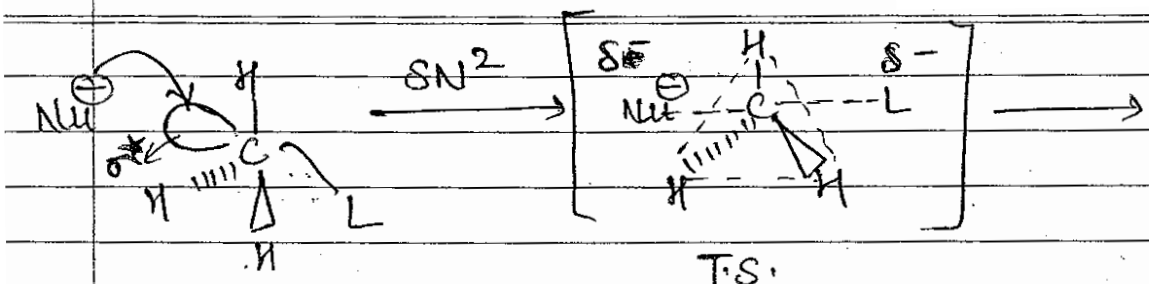
(2) Sp. having vacant d-orb.

eg: $FeCl_3$, $FeCl_2$, etc.....

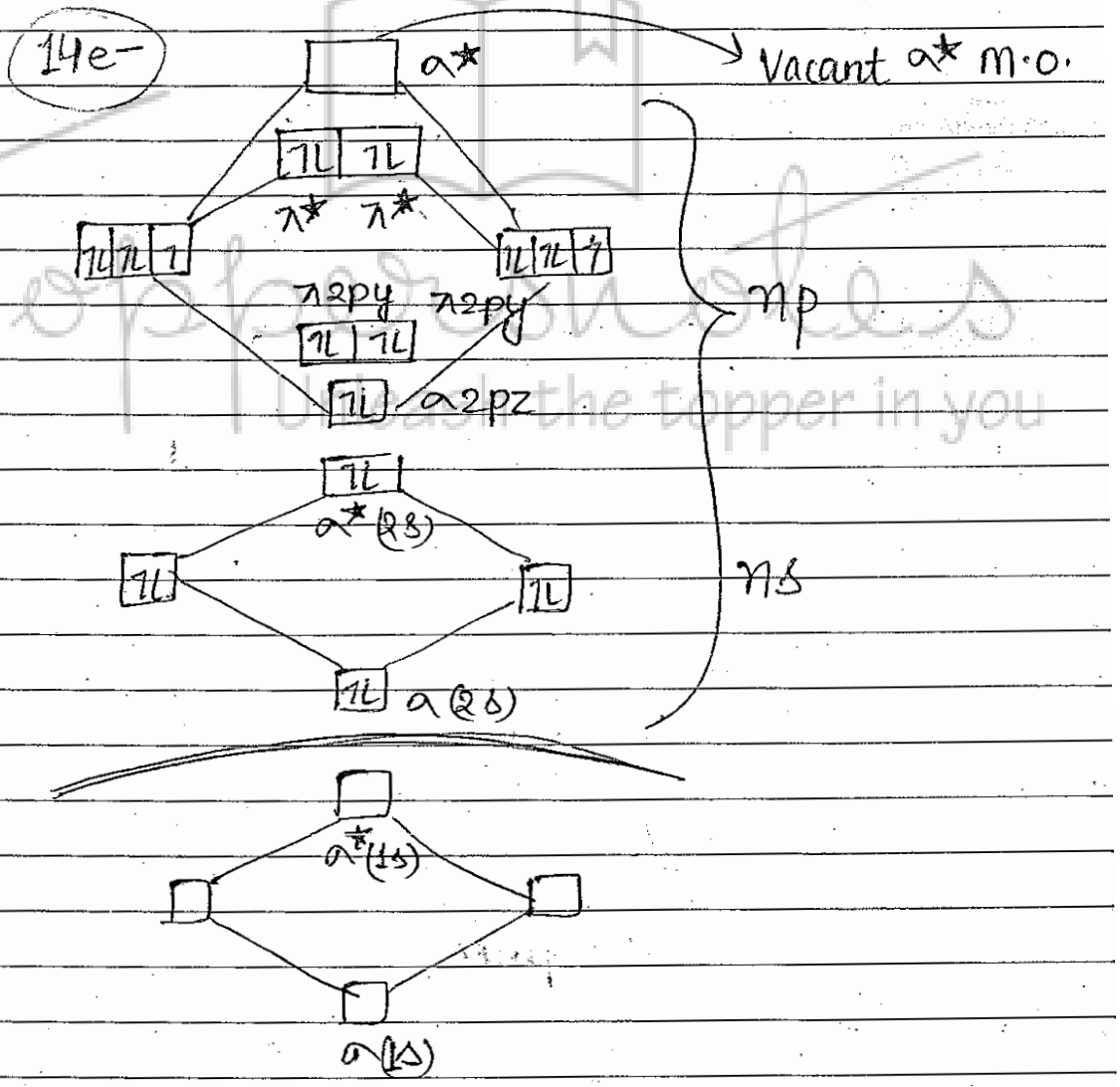
(3) Sp. having low lying π^* Molecular Orb.

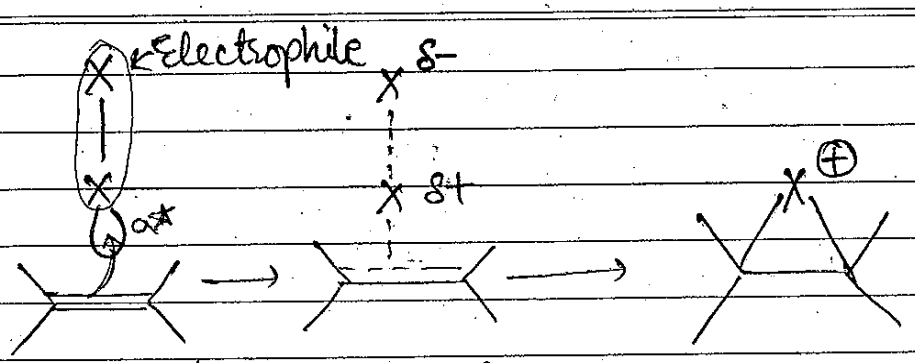


OTS, OBS, OMS etc



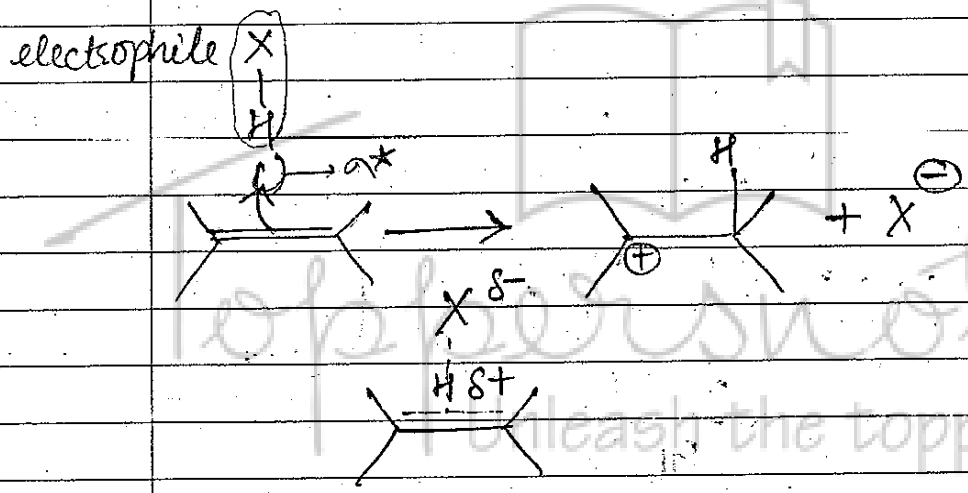
Br_2, Cl_2, I_2, ICl, BrCl, IBr etc all behaves as electrophile by (due to) low lying σ^* M.O.





Nucleophile π-complex

⟹ HCl, HBr, HI etc



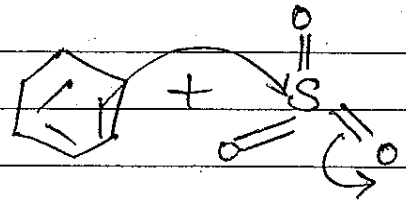
(π-complex)

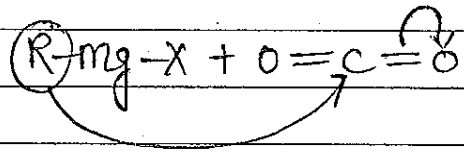
IV # π-Bonded molecule :-

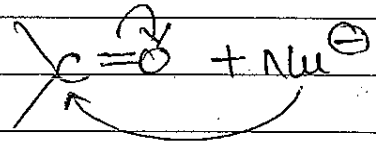
$Nu^{\ominus}$ + A=B

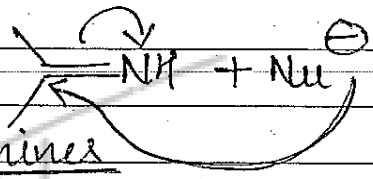
$Nu^{\ominus}$ + A≡B

(behaving as electrophiles)

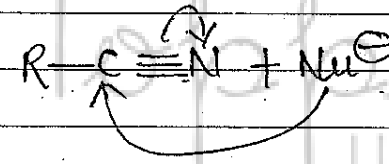
eg: 

eg: 

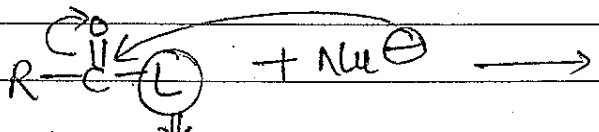
eg: 

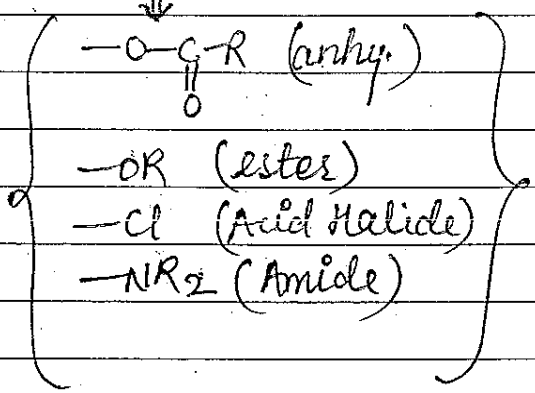
eg: 

Amines

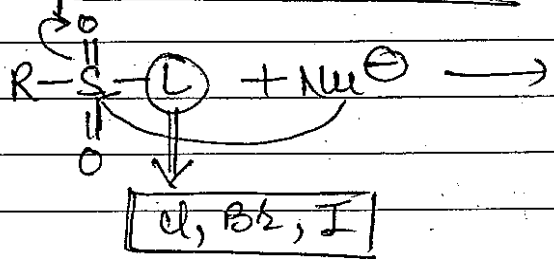
eg: 

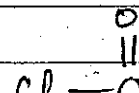
eg: Carboxylic Acid derivatives :

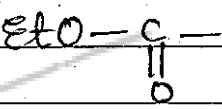


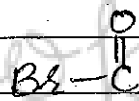


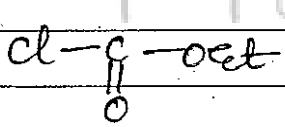
eg: Sulphonic Acid derivative:

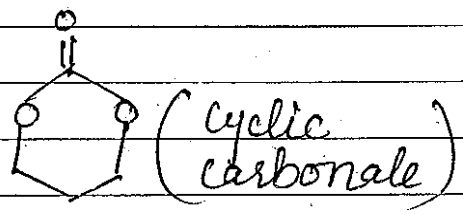


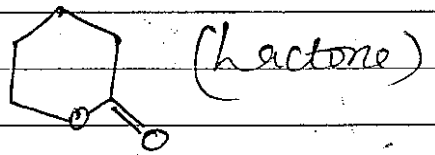
eg:  ≃ $COCl_2$ (Phosgene)
(Carbonyl Chloride)

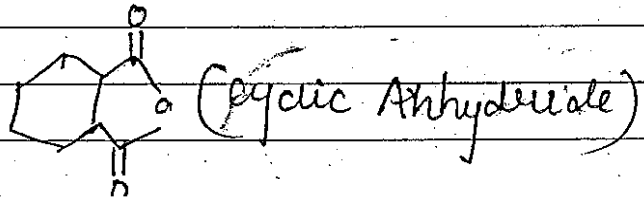
eg:  ≃ Et_2CO_3
(Ethyl Carbonate)

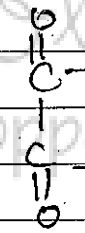
eg: 

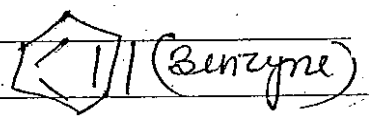
eg: 

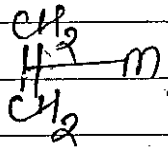
eg: 
(Cyclic Carbonate)

eg: 
(Lactone)

eg: 
(Cyclic Anhydride)

eg: 

eg: 
(Benzyne)

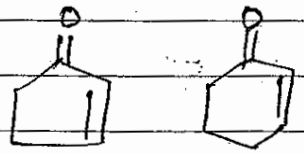
eg: 
Behaves as electrophile
attacked by Nu⊖
(DMG Rule)

eg: $CH_2=CH-$ (EWG)

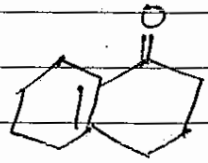
- $-CHO$
- $-COR$
- $-COOR$
- $-CN$
- $-NO_2$ etc.

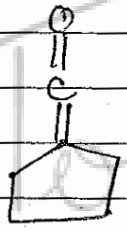
Behaves as electrophile; attacked by Nu⊖ & give Michael Adelt^n

eg:



eg: $CH_2=C=O$ (Ketene)



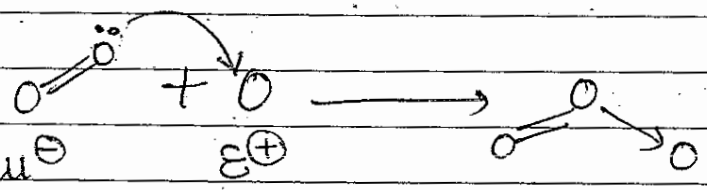


eg: $R-N=C=O$
(Isocyanate)

V

Element in their atomic State:-

O S



(जो e⁻ donate करे)

Classification of $Nu^{\ominus}$:—

⊖ve charge वाले

eg: $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$, $OH^{\ominus}$, $SH^{\ominus}$, $SR^{\ominus}$, $OAc^{\ominus}$, $OPh^{\ominus}$, $OR^{\ominus}$, $CN^{\ominus}$ etc.

Mcs having lp

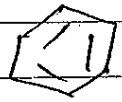
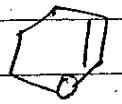
eg: H_2O, ROH, H_2S, RSH, NH_3, $R-NH_2$, R_2NH,

etc.

Organo Metallic Reagents

eg: R-mg-X
R-Li
R_2CuLi
R_2Zn
R_2Cd etc.

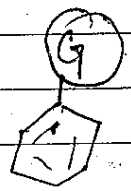
π-bonded Mcs.

$CH_2=CH_2$,  ,  ,  , 

, $CH\equiv CH$

$CH_2=CH-$(ERG) ,

—OH
$-NH_2$
$-NR_2$
—OR



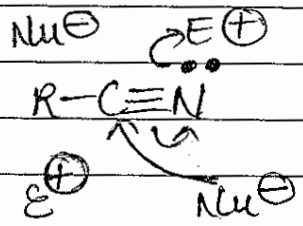
—OH
$-NH_2$
—OR

NOTE :

* There are some sp. C behaves as a electrophile as well as $Nu^{\ominus}$.

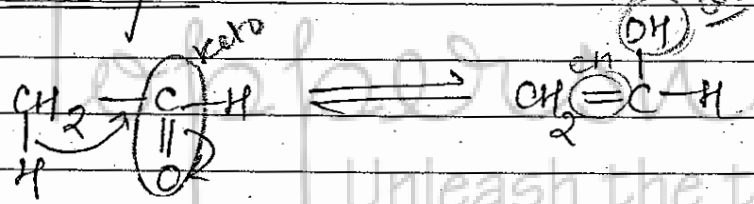
eg ① Br_2, I_2 $\rightarrow E^{\oplus}$ ⟹ when behave as $E^{\oplus}$ it uses its low lying σ^* M.O.

$\rightarrow Nu^{\ominus}$ ⟹ uses lp.

② 

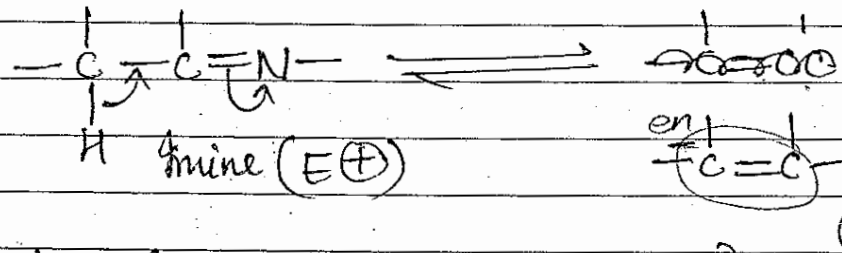
(C≡N can behave both as $E^{\oplus}$ & $Nu^{\ominus}$)

③ Carbonyls :



(keto form) behave as * (electrophile)

(enol form) behaves as * ($Nu^{\ominus}$)

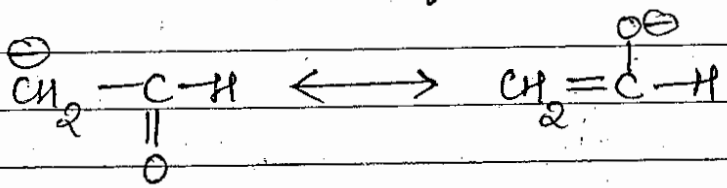
④ 

* (Imines & enamines are Tautomers)

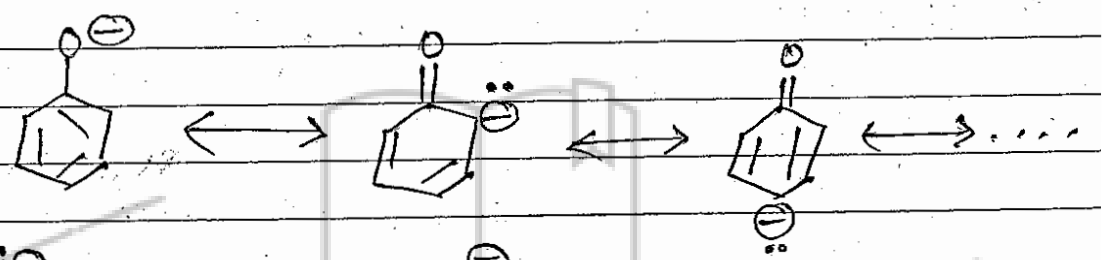
Ambidentate $Nu^{\ominus}$:

एक से ज्यादा sites होती है for attack but कोई एक ही site अति h for attack की so.

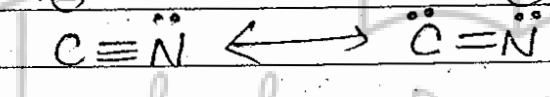
eg ①



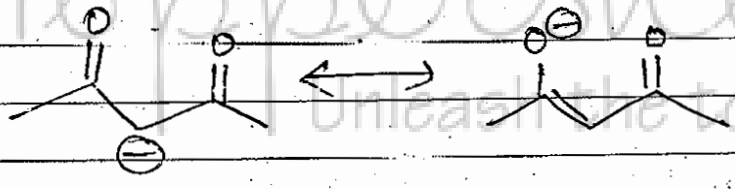
②



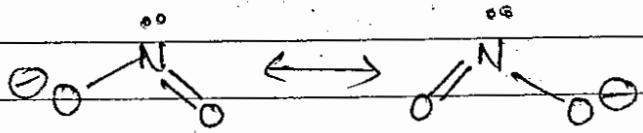
③



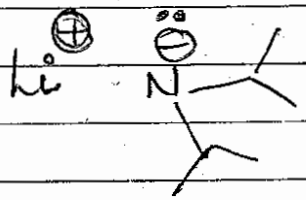
④



⑤



★★ LDA (Lithium diisopropyl amide)



↓

Non-nucleophilic Strong Base होता h.

LDA is Non-Nucleophilic strong base bcz of the steric factor it does not behaves as the $Nu^{\ominus}$

Rxn Mech :-

Reactant ⟶ T.S ⟶ Prod.
or
Intermed.

⟶ A detailed & step-wise descreiption of pathway by which reactants & converted to Prod. k/a Sxn Mech.

⟶ An acceptable mech. not only deals with the structural changes but also deals with the energy changes (thermody. parameters) that occures at every step of the rxn.

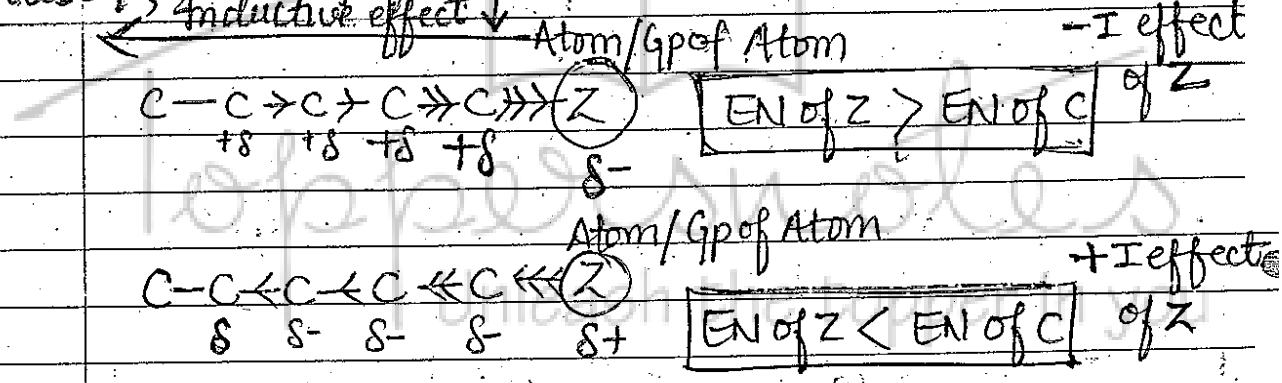
⟶ If we deals with a sxn mech. then following steps are observed:-

1. Electronic displacement.
2. Bond Cleavage.
3. Types of Intermed.
4. Type of Mech.

Electronic Displacement:

Permanent	Temporary
→ Also occurs in the ⊖nce of reagent.	→ Always occurs only in the ⊕nce of reagent.
eg: Reso, Inductive effect, Hyper conjugation.	eg: Electromeric effect

dist ↑, Intensity of Inductive effect ↓



→ Inductive effect arises bcz of difference in Electro⊖vity.

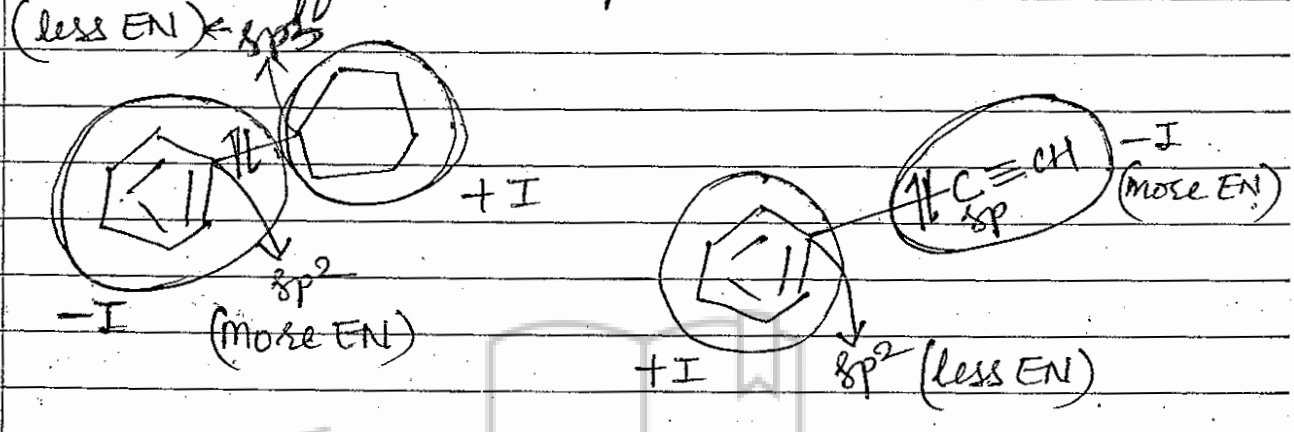
→ Inductive effect is the dist dependent electronic factor. i,e as well as the dist from the source ↑es, Intensity of Inductive effect ↓es.

→ There is no Inductive effect in b/w C & H bond

→ Permanent displacement of σ e⁻ along the C-chain when an atom

→ In Inductive effect there is partial displacement of $a\bar{e}$ occurs.

→ Inductive effect is respective in Nature.



→ Since Inductive effect arises bcz of diff. in EN.

⇒ Inductive effect
⇓
difference in electro⊖vity.
⇓
EN depends upon

Nature of Element
⇓
$\chi^{\oplus}, \chi, \chi^{\ominus}$

EN Order:
$\chi^{\oplus} > \chi > \chi^{\ominus}$

%.S-character.
⇓
(%.S ↑ ; EN ↑)

EN ∝ %.S-character

Hybridn

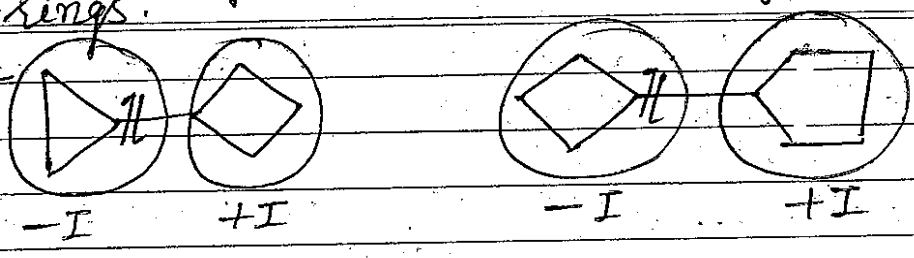
	sp	sp^2	sp^3
%.S	50%	33.33%	25%
EN	sp > sp^2 > sp^3		

B.A.
⇓
B.A ∝ %.S
B.A ↑, %.S ↑
EN ↑

Ring Size
⇓
Smaller rings are more electro⊖ve than larger rings.
EN △ > □ > ⬠

★ Smaller rings & more EN than larger rings.

eg:



Type of Inductive effect:-

Imp

+I effect

$\overset{\ominus}{C}H_2 > \overset{\ominus}{N}H > O^{\ominus} > -\underset{\underset{O}{\|}}{C}-O^{\ominus} > 3^\circ > 2^\circ$

$> CH_3-CH_2 > CT_3 > CD_3 > CH_3 >$

$T > D > H$

−I effect

$-\overset{\oplus}{O}F_2 > -\overset{\oplus}{O}R_2 > -\overset{\oplus}{N}F_3 >$

$-\overset{\oplus}{N}Cl_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 >$

$-NO_2 > -CN > -SO_2R >$

$-CHO > -\underset{\underset{O}{\|}}{C}- > -\underset{\underset{O}{\|}}{C}-OH >$

$F > Cl > Br > I > OR > OH$

$-C\equiv CH > \text{(C}_6\text{H}_5\text{)} > CH=CH_2$

$> H.$

Applicatn of Inductive effect:-

1. Stability of Intermed.
2. Reactivity of Alkyl Halides.
3. Reactivity of Carbonyl Cmpds.
4. Reactivity of Alcohol.
5. Acetic Nature of H-atom.
6. Acidic Nature of Cmpd
7. Basic Nature of Cmpd.

① Stability of Intermed :-

Carbocation ($R^{\oplus}$)	Carbanion ($R^{\ominus}$)
→ electronically deficient sp.	→ electron rich sp.
→ Less EN element has tendency to bear ⊕ve charge.	more EN element has tendency to bear ⊖charge
Stability of carbocation $\propto$ strength of ERG $\propto \frac{1}{EWG} \propto \frac{1}{EN}$	Stability of $R^{\ominus}$ $\propto$ Strength of EWG $\propto \frac{1}{\text{Strength of ERG}}$
Stability of $R^{\oplus}$ $\propto +I \propto +H \propto +R$ $\propto \frac{1}{-I} \propto \frac{1}{-H} \propto \frac{1}{-R}$	$\propto -I \propto -H \propto -R$ $\propto \frac{1}{+I} \propto \frac{1}{+H} \propto \frac{1}{+R}$

Stability of Carbocation :

eg $CH_3-CH_2^{\oplus}$ $CH_2=CH^{\oplus}$ $CH\equiv C^{\oplus}$

EN of Carbon having ⊕ charge ↑

Stability ↓