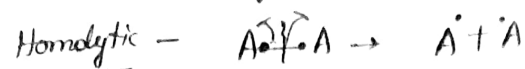


ELECTRONIC EFFECTS

Fission - cleavage of bond



observed in non polar solvents, conditions HCLP-R

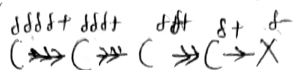


ions are formed.

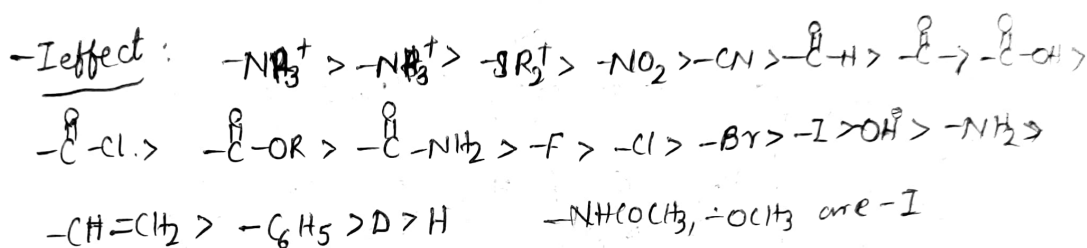
Observed in polar solvents.

Electron displacement:

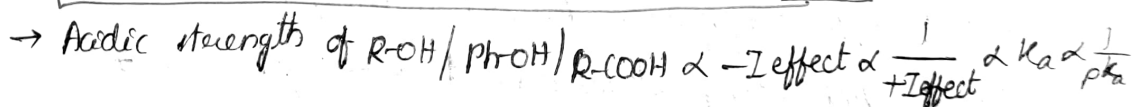
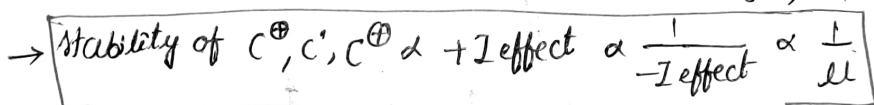
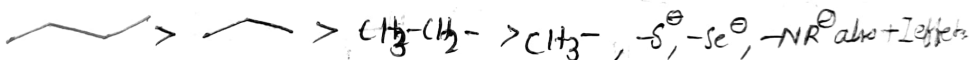
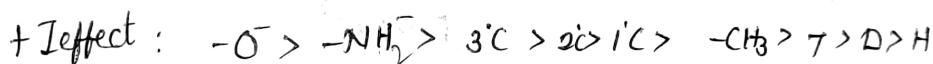
① Inductive effect - permanent effect, sigma bonded e's.



negligible after 3rd C.

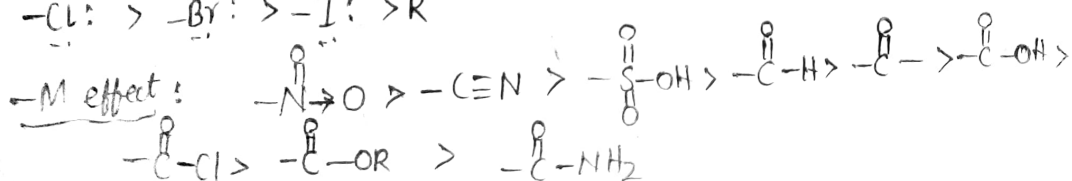
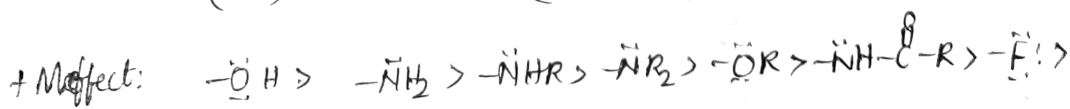
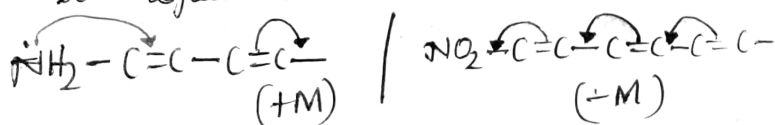


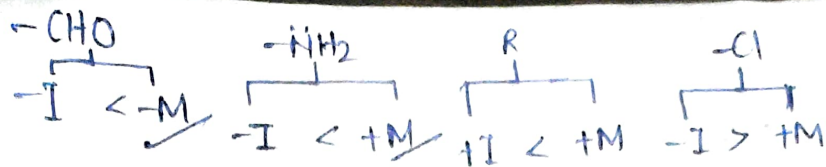
$-NHCOCH_3, -OCH_3$ are -I



② Mesomeric effect or resonance effect:

Complete transfer of π e's to adjacent bond (or) l.p of e's or π e's transfer to adjacent atom.

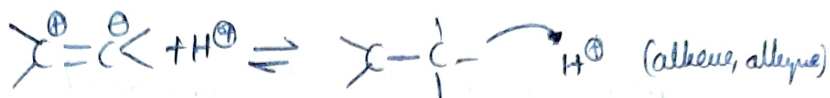




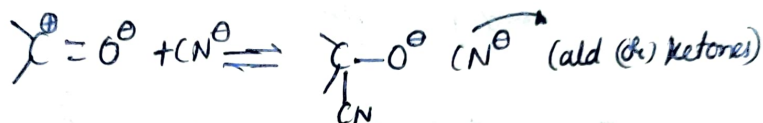
III Electromeric effect :

It is temporary effect it involves both conjugation & lone pairs of e's

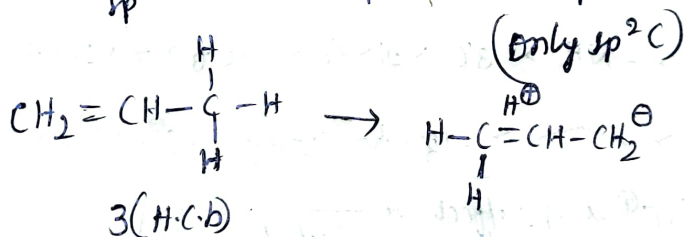
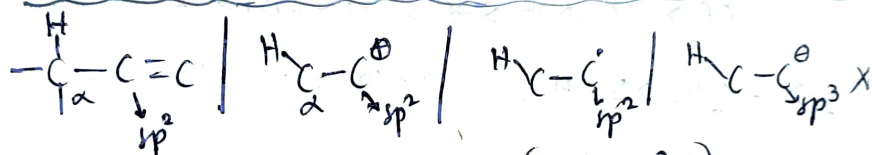
+E effect : complete transfer of π e's towards attacking reagent



-E effect : complete transfer of π e's away from attacking reagent.



IV Hyperconjugation / σ - π conjugation / No bond resonance :



→ No. of hyperconjugation bonds \uparrow stability \uparrow
 No. of resonating structures \uparrow stability \uparrow energy \downarrow

NOTE : Due to ortho effect basicity & acidity decreases.

Reaction intermediates : These are of 6 types

① C^+ ② C^- ③ C^\cdot ④ carbene : CH_2 ⑤ Nitrene $\text{R}-\ddot{\text{N}}:$

⑥ Benzene 

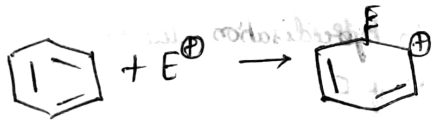
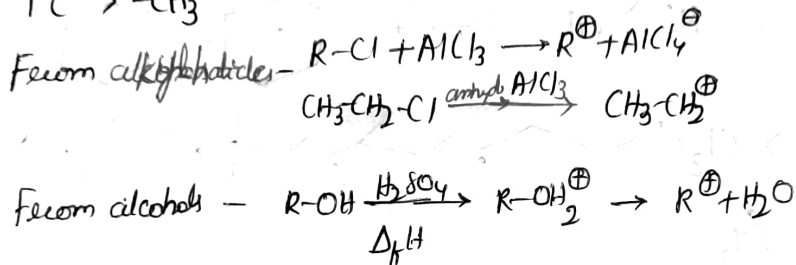
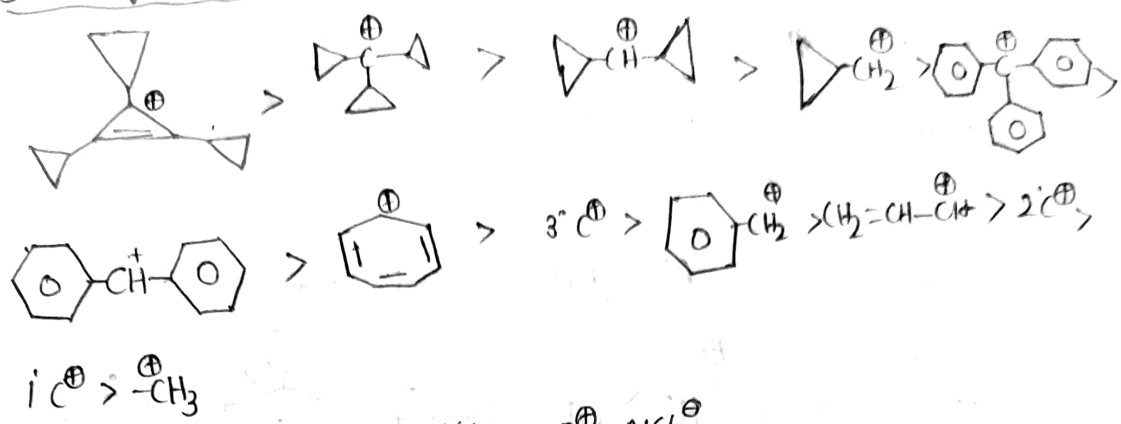
① Carbocation C^+ :

→ sp^2 , sextet config, diamagnetic, Lewis acid
 electrophile



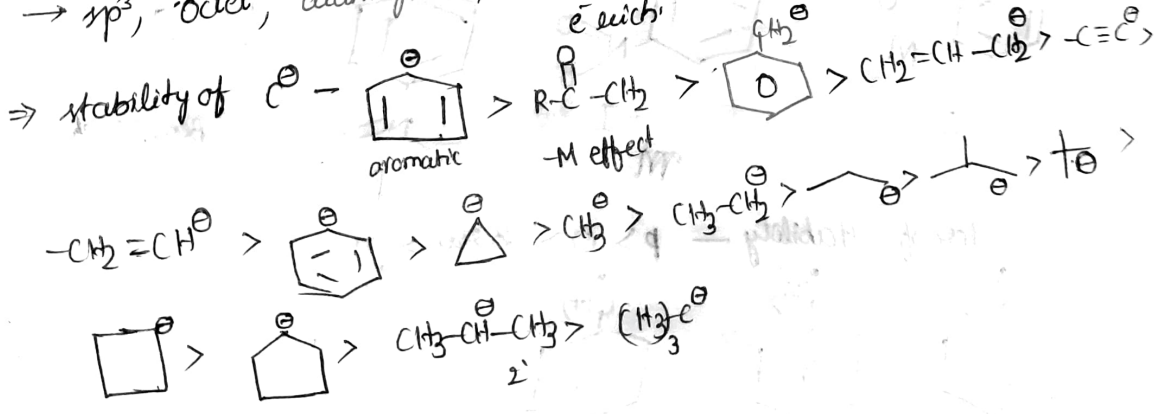
→ Stability of $C^\oplus \propto +M \propto +H \propto +I \propto \text{aromaticity} \propto \text{resonance} \propto \text{back bonding}$
 $\propto \frac{1}{-M, -H, -I} \quad \frac{1}{E, N} \propto \frac{1}{\% \text{ s character}}$

Stability order:

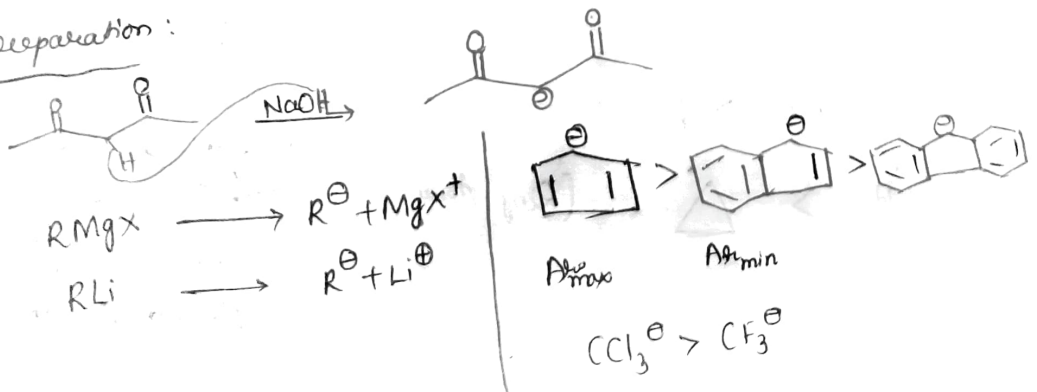


(ii) Carbanion C^\ominus

→ sp^3 , octet, diamagnetic, Lewis base, e^- rich



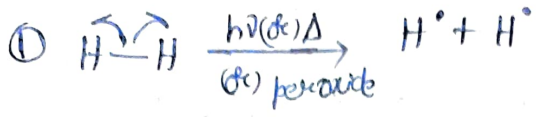
Preparation:



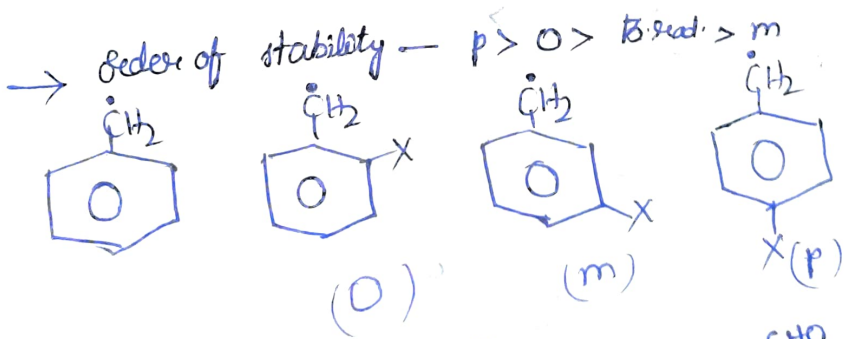
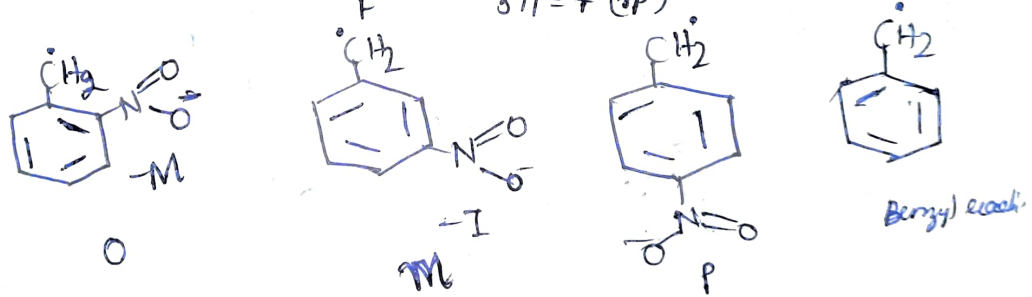
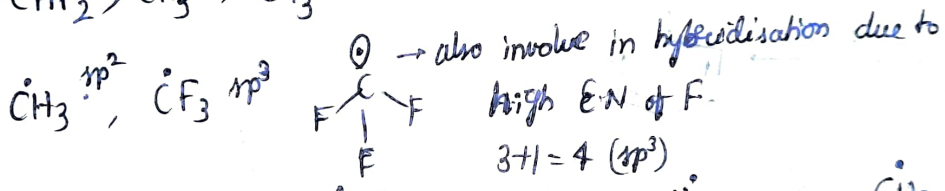
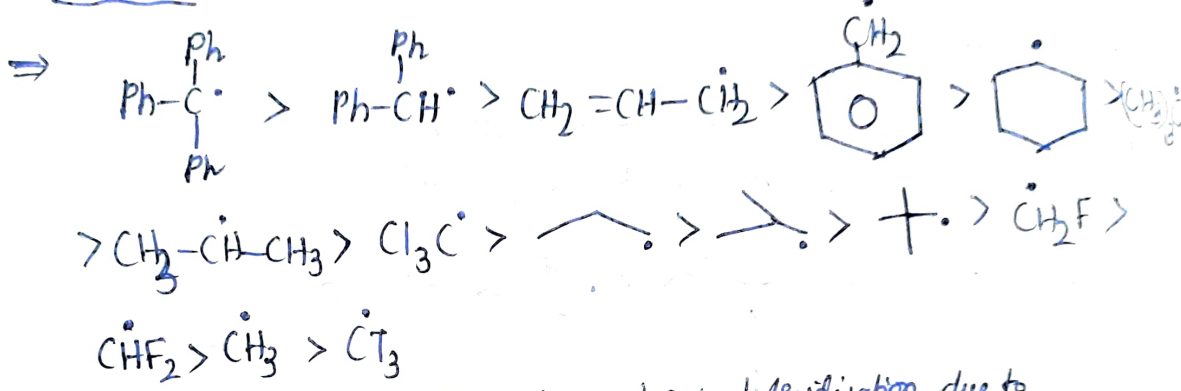
III) Free radicals: Compounds which contains odd number of e^- ($2n+1$) e^- is known as free radical

Free radicals are generated in presence of light, heat & peroxides.

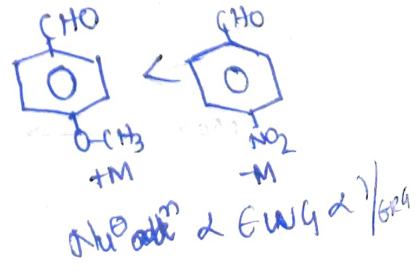
$\rightarrow sp^2$, paramagnetic, electrophile, $7e^-$.



Stability: $+M$ & $-M$ effects are stabilized.



$\rightarrow B.Rad. > p > m > o$



④ Carbene: $(:C:R_2) -$

→ diradical, sextet config, divalent
valency 6. (electrophilic in nature)

Carbene

Singlet



→ $2 + 1(1p) = 3 sp^2$
diamagnetic, unstable,
total spin = 0, trigonal planar
against Hund's rule

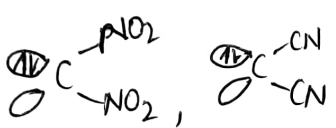
Triplet



$2 + 0(1p) = 2 sp$
paramagnetic, acc. to Hund's rule
more stable; linear.

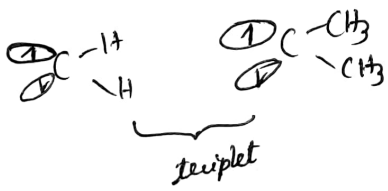
→ More electronegative atoms then the carbene is singlet carbene.

Ex:

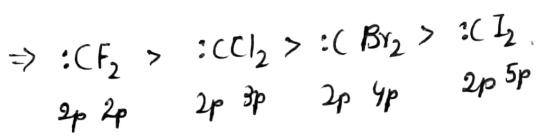
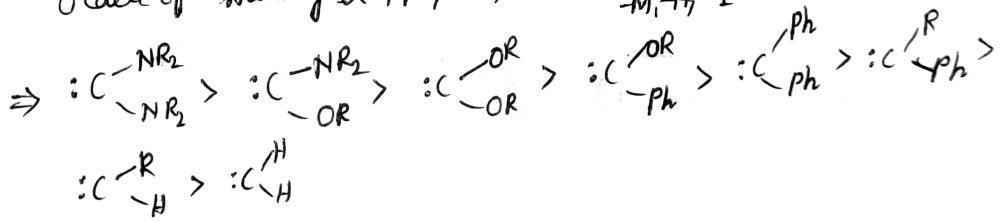


if R = less E.N atoms then the carbene is triplet.

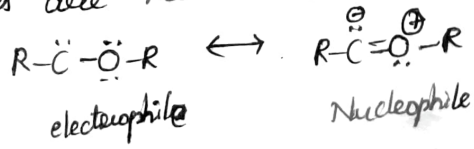
Ex:



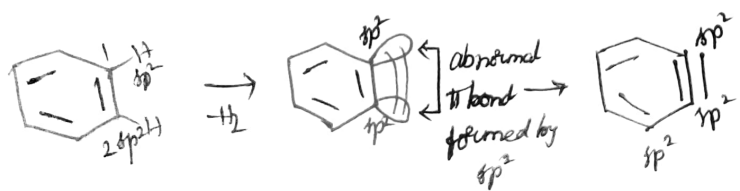
Order of stability $\propto +M, +H, +I \propto \frac{1}{-M, -H, -I}$



→ Carbenes are neutral electrophiles



⑤ Benzyne: 1,2 didehydrobenzene (C_6H_4) & derivatives are benzyne.



Benzynes formation is only exception of hybrid orbitals to form π bond.
Highly unstable, more reactive.

Nitrenes ($R-\ddot{N}:$)

singlet



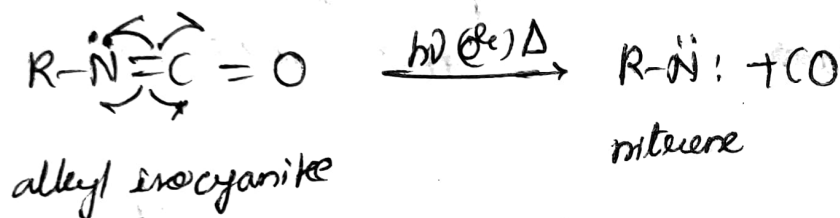
→ Less stable, diamagnetic

Triplet



→ More stable, paramagnetic

Preparation:



Planarity & linear compounds:

$sp^2 - sp^2 \rightarrow$ planar

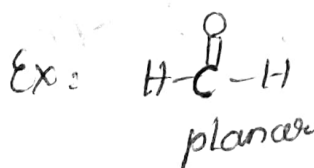
$sp^2 - sp \rightarrow$ planar

$sp - sp \rightarrow$ linear

$sp - sp^3 \rightarrow$ non planar

$sp^2 - sp^3 \rightarrow$ non planar

$sp^3 - sp^3 \rightarrow$ non planar



Non planar
due to ring
strain



no resonance



Non planar
due to H & H
repulsions