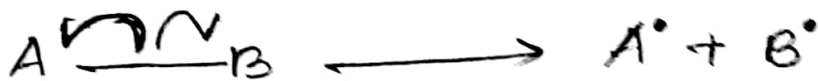
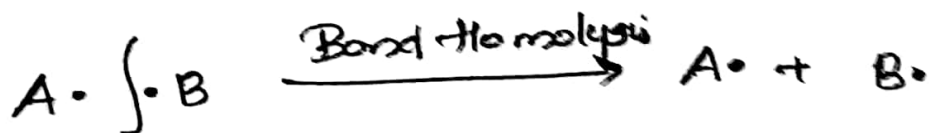


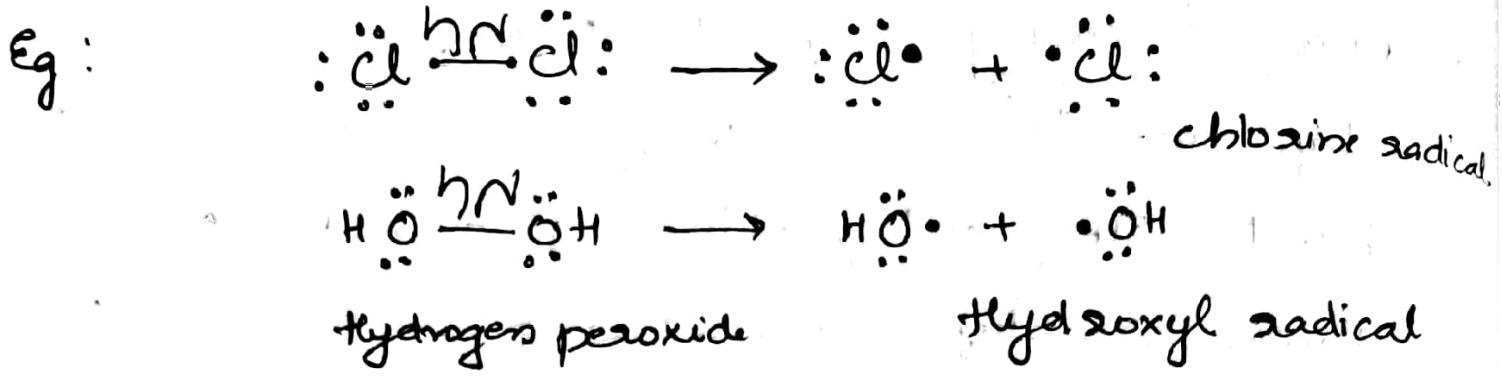
Fundamental Concepts of Organic Reactions Mechanisms

Types of Bond fission

(A) Homolytic bond fission / Homolysis

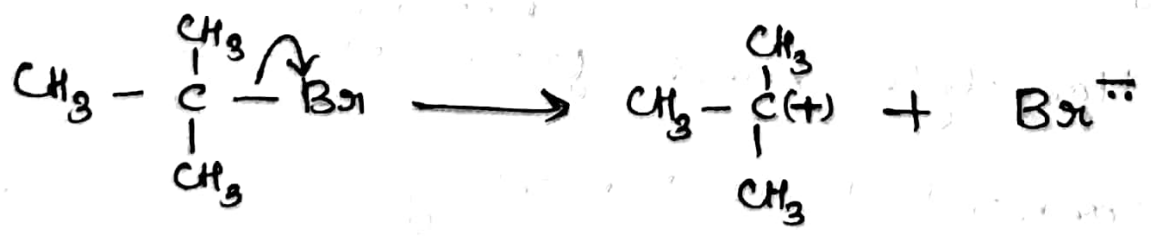
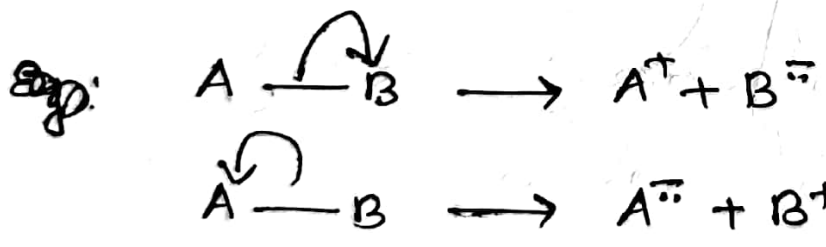
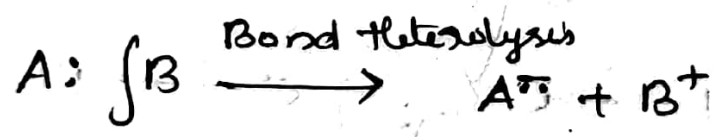
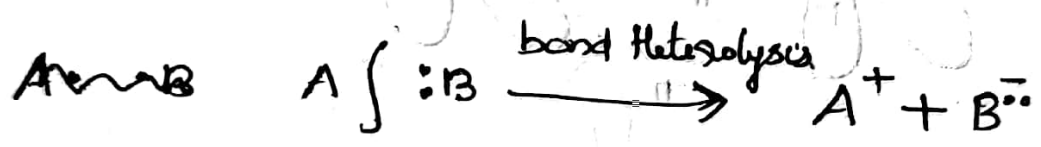
→ Covalent bond breaking in a symmetrical way such that each fragment retains one of bonding e.





2) Heterolytic bond fission / Heterolysis

→ Bond breaks in unsymmetrical way such that one product fragment retains both of the bonding e^s



Types of reagents

① Electrophiles ^{loving} e^- loving species, +ve charged,
→ electron deficient species & hence e^- seeking
is electron acceptor.

Eg: H^+ , Cl^+ , Br^+ , NO_2^+ , $C_6H_5N_2^+$, R^+ ,

BF_3 , $AlCl_3$ etc.

② Nucleophiles ^{loving} Nucleus loving, -ve charged.

→ Electron rich species & hence e^- donate
is Nucleus loving.

Eg: ~~OH^- , Cl^- , CH_3O^- , NH_2^- , R^- , HSO_4^- , H_2O , NH_3~~

Eg: OH^- , Cl^- , CH_3O^- , NH_2^- , R^- , HSO_4^- , H_2O , NH_3

ROH , $R-NH_2$, ROB .

③ Free Radicals

→ Species that has an unpaired e^-

→ Highly reactive.

→ Formed from homolytic cleavage of covalent bond.

→ Eg: Cl^\cdot , CH_3^\cdot , $(CH_3)_3C^\cdot$, $C_6H_5-CH_2^\cdot$, $C_6H_5^\cdot$

Electron displacement effects in Organic Molecules

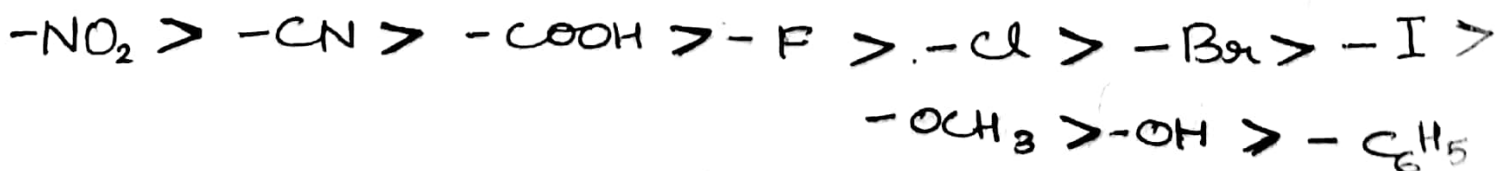
Inductive Effect

"The presence of an e^- withdrawing or donating atom or group attached to a carbon chain of a molecule by a covalent bond induces polarity in that bond. This in turn, may cause induction of polarity in an adjacent, otherwise non-polar, bond and this effect may further be transmitted through the adjacent C-C σ bonds in the chain". This phenomenon is called inductive effect or I effect.

Types:

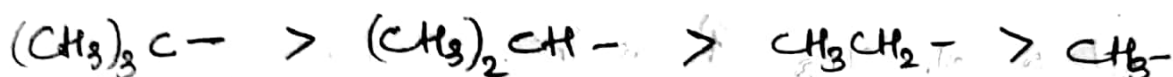
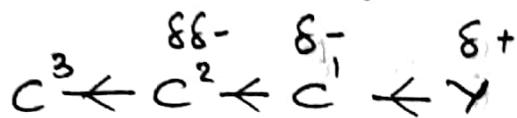
① e^- withdrawing inductive effect / $-I$ effect
If X is more electronegative than C. The e^- of C-X is shifted towards X, developing δ^+ on C and δ^- on X. δ^+ on C cause C²-C bond to attract towards C & continues

$\delta^+ \quad \delta^+ \quad \delta^-$
 $-C^3 \rightarrow C^2 \rightarrow C^1 \rightarrow X$ $-I$ effect



② e^- releasing inductive effect / +I effect

If a group Y is less electronegative than C, tends to repel the bond pair from it & it termed as +I effect



characteristic of I effect

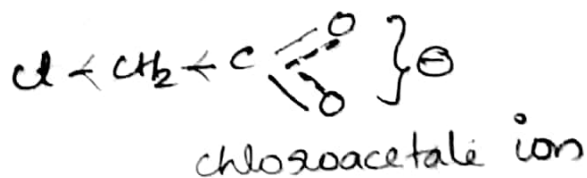
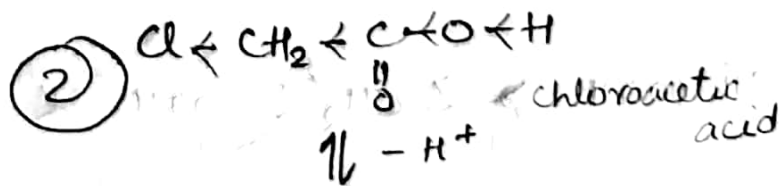
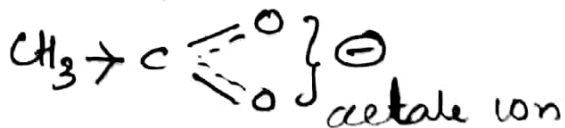
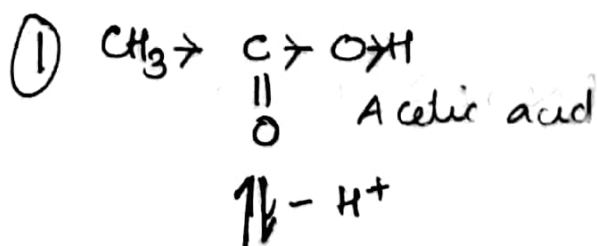
→ Permanent e^- displacement effect

→ Not transfer of e^- but mere displacement

→ I effect weakens with increasing distance from substituent

* Explanation for the effect of substituents on the acidity of aliphatic acids

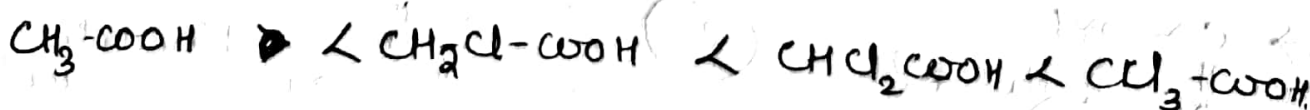
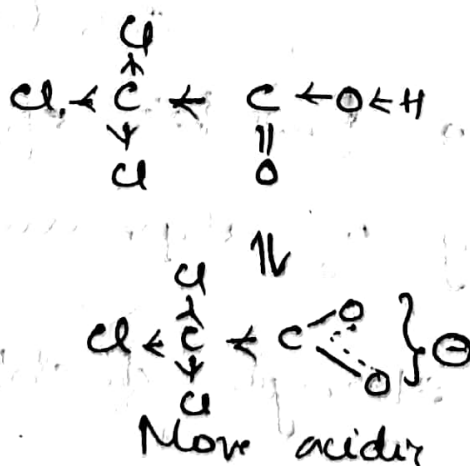
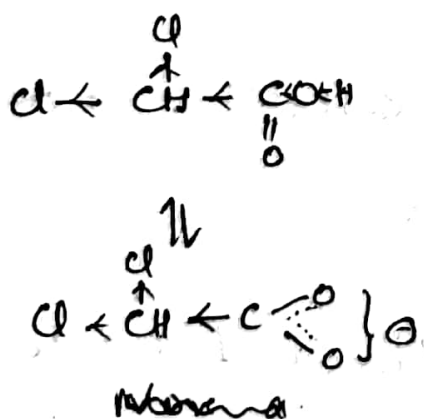
① Relative strengths of chloroacetic acid & acetic acid



In ② → -I effect on Cl ↓ uses e⁻ density around H — easily facilitate proton and in chloroacetate ion -ve charge is dispersed by same effect & stabilizes the ion. — ↑ uses the acidity of acid

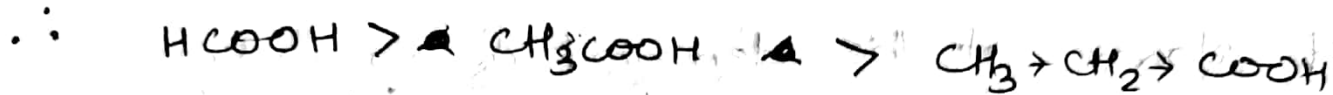
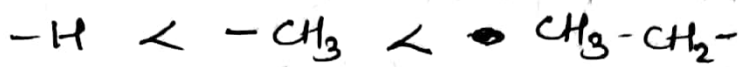
In ① → +I effect of CH₃ ↑ uses the e⁻ density around H — suppress the release of proton (H⁺) — In acetate ion, same effect intensify the -ve charge & thereby destabilize the ion — ↓ uses the acidity of acid

• In dichloroacetic acid & trichloroacetic acid



② Relative acidic strengths of formic acid, acetic acid, propionic acid

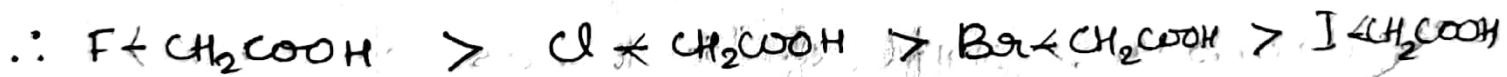
+I effect ↑ses in the order



pKa : 3.77 4.76 4.87

③ Relative acid strengths of Fluoroacetic acid, chloroacetic acid, bromoacetic acid & iodoacetic acid

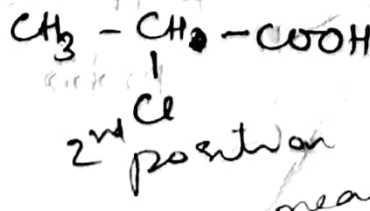
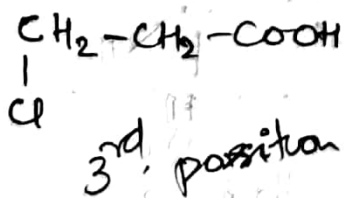
-I effect of halogens ↓ses in the order



④ Relative acid strengths of 2-chloropropionic acid and 3-chloropropionic acid

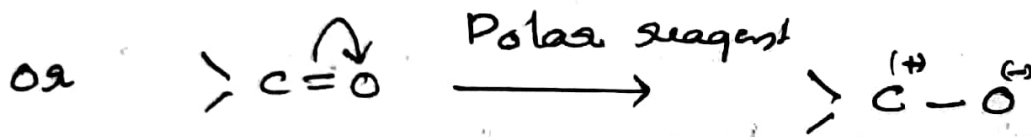
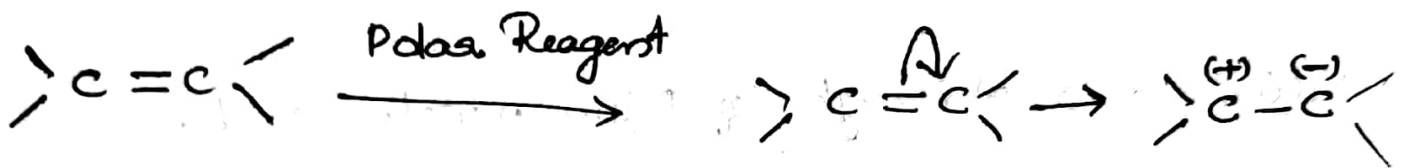
→ I effect ↓ses with ↑ing distance of substituent

3-chloropropionic acid is weaker than 2-chloropropionic acid



Electromeric Effect

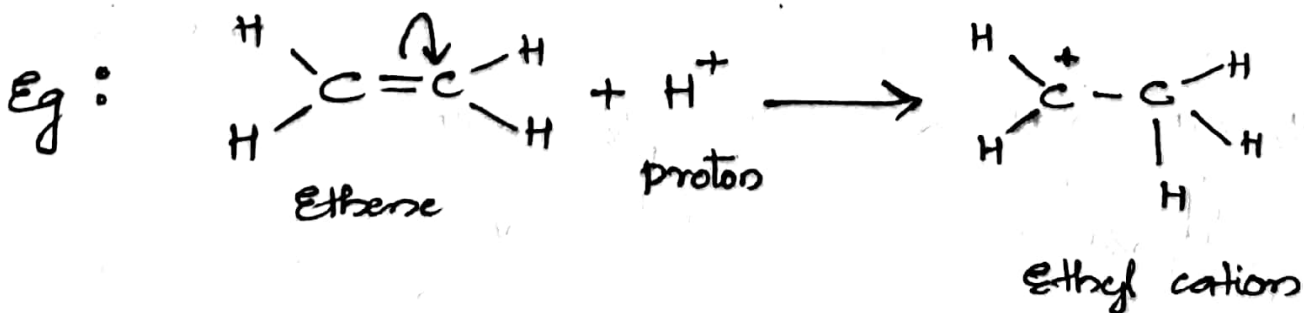
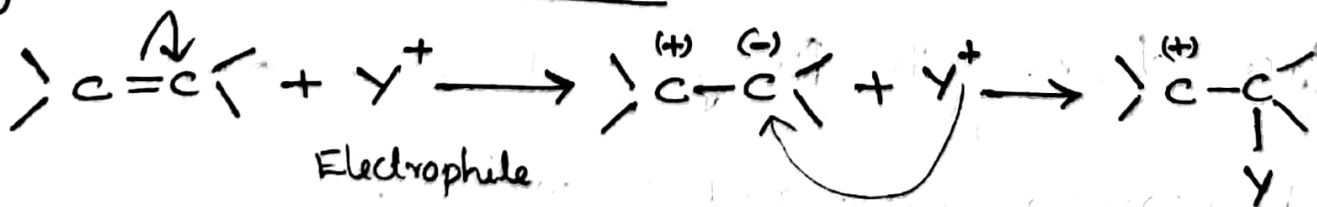
"Temporary effect involving the complete transfer of a shared pair of π -e's of a double bond / triple bond in a molecule to one of the bonded atoms at the demand of an attacking reagent"



Types:

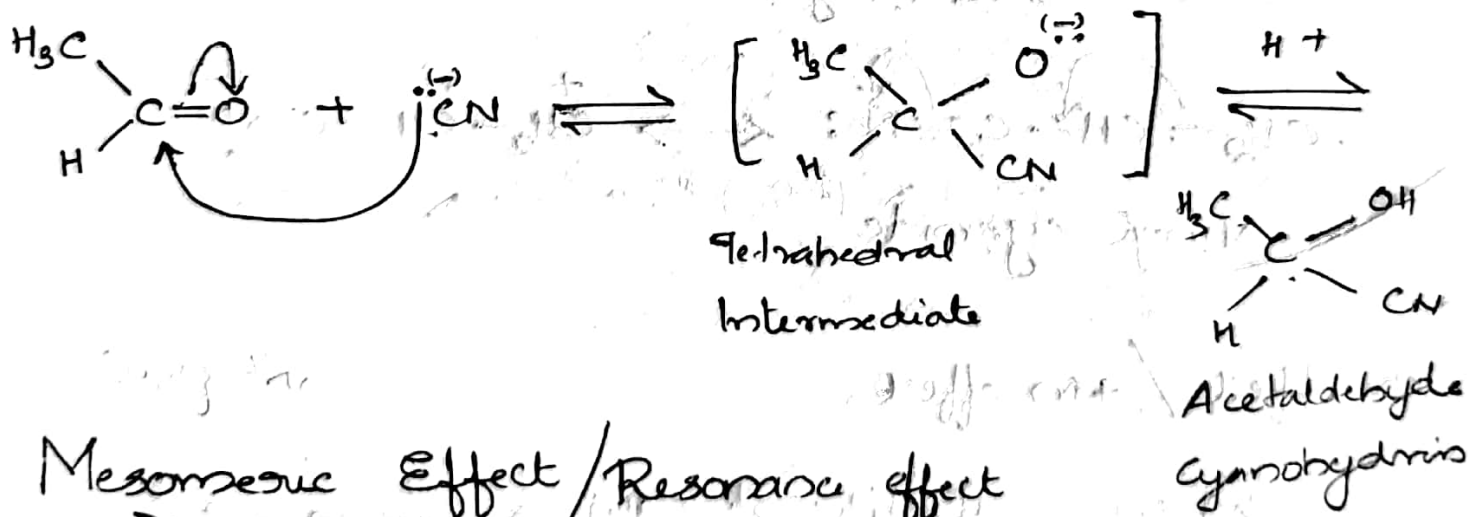
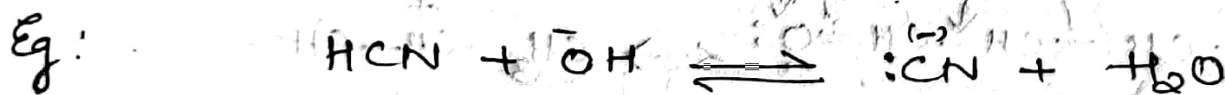
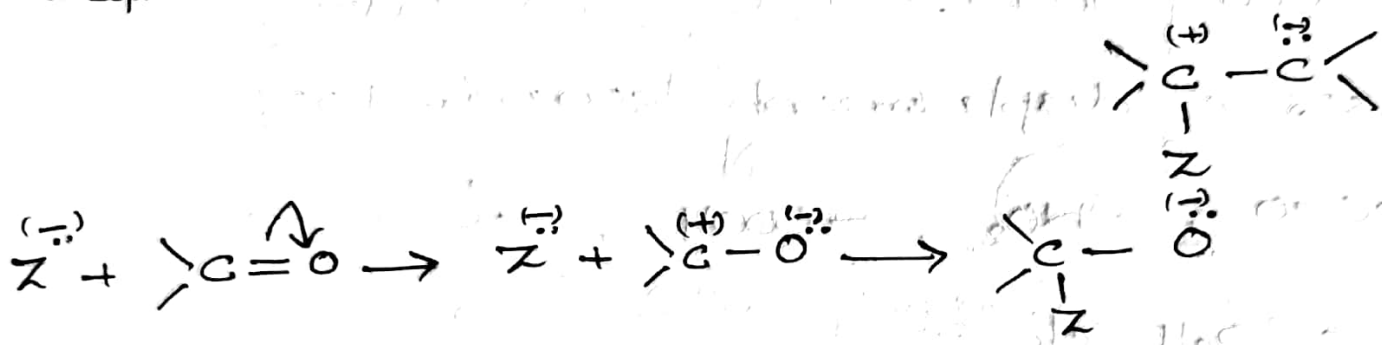
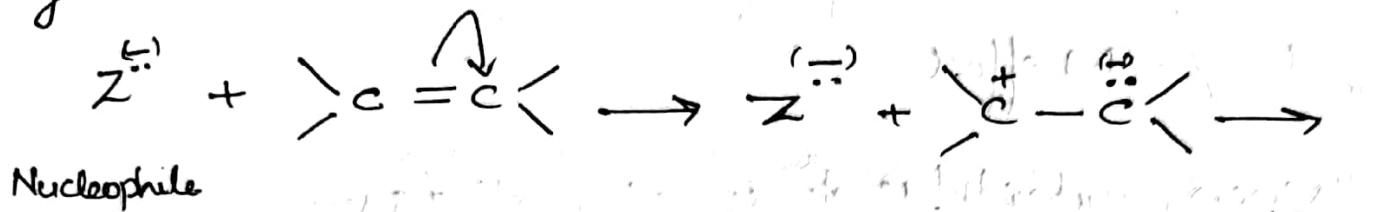
① +E effect

Electromeric shift of the π -e's of a multiple bond towards that atom to which the reagent gets attached — +E effect



② -E effect

Electromeric shift of π e's of a multiple bond is away from that atom to which the reagent gets attached is called -E effect



Mesomeric Effect / Resonance effect

It is defined as the polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of e's present on an adjacent atom

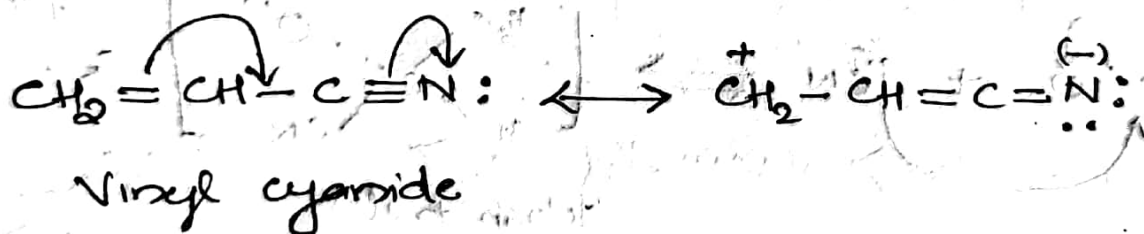
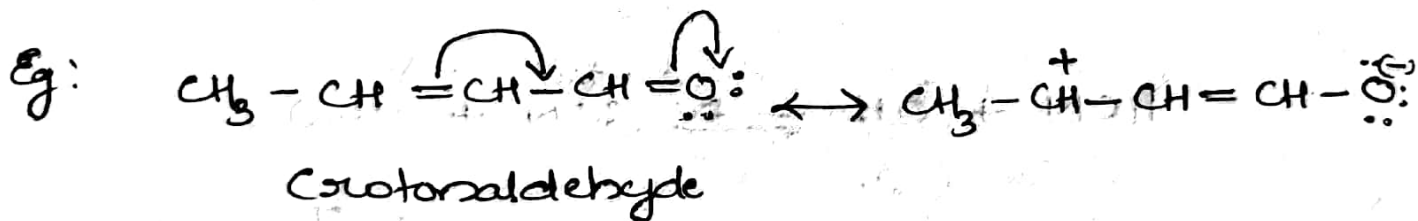
→ Permanent e^- displacement effect

→ Permanent polarisation

Types:

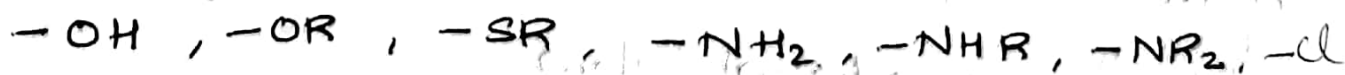
(-)R effect / (-)M effect

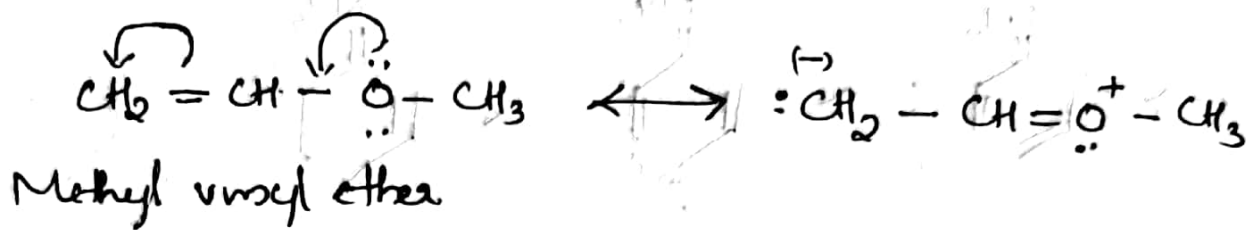
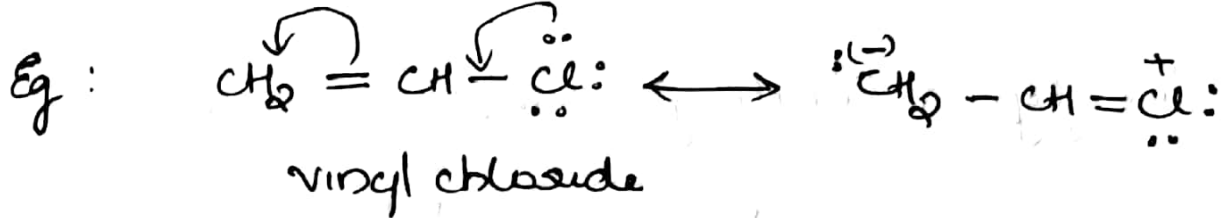
When substituent is e^- withdrawing, causes e^- displacement towards itself



(+)R effect / (+)M effect

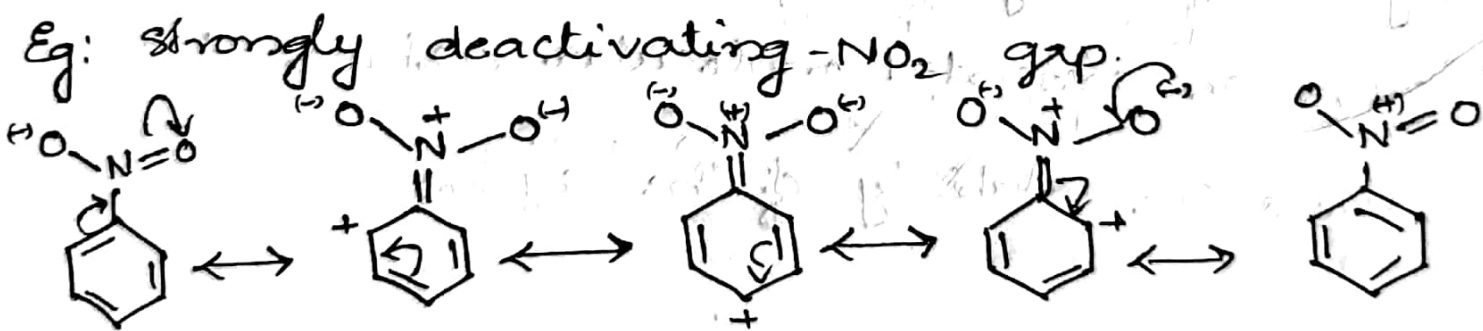
When substituent with one/more lone pair of e^- present adjacent to multiple bond - causes e^- displacement away from themselves





M effect and relative reactivity of substituted

benzene
Groups having $-M$ effect ($-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$ etc) are called deactivating groups, because they make benzene ring less reactive towards electrophilic aromatic substitution by withdrawing electrons from the ring by resonance.

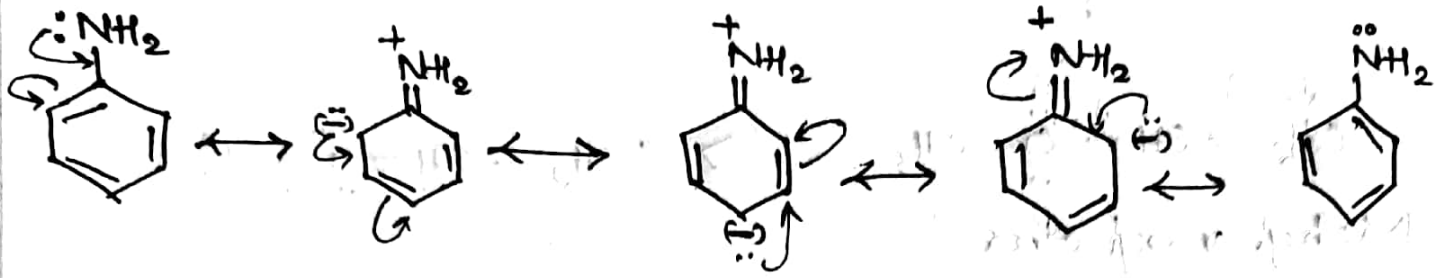


Groups with $+M$ effect ($-\text{OH}$, $-\text{OR}$,

$-\text{NH}_2$ etc) are called activating groups.

because they make benzene ring more reactive towards electrophilic aromatic substitution, to the ring by resonance.

Eg: Strongly activating substituent -NH₂



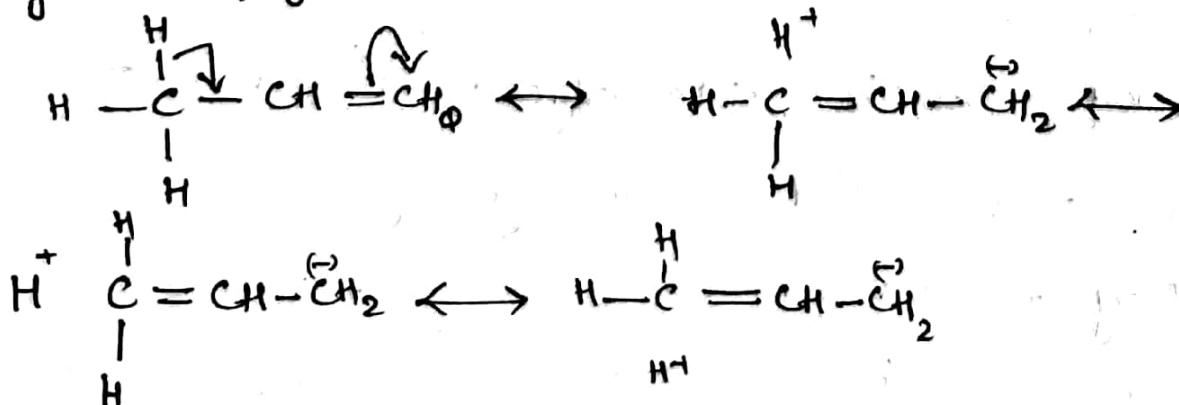
Hyperconjugation / Baker-Nathan effect

Criteria: α -carbon

No bond resonance

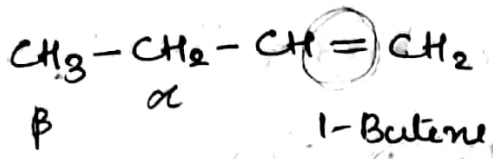
It is the stabilising interaction that result from the interaction of the electrons in a σ -bond (usually C-H or C-C) with an adjacent empty or partially filled p-orbital or a π -orbital to give an extended molecular orbital that increases the stability of the system

Eg: Propylene.



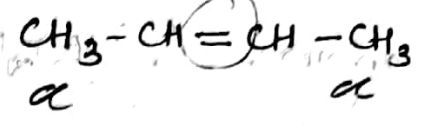
More stable than ethylene. bc α carbon

α -carbon \rightarrow functional group \rightarrow carbon \rightarrow carbon \rightarrow carbon



1 α carbon
 $2 \text{H} \Rightarrow 2$ hyperconjugative structures

Buto-2-ene



$2 \alpha \Rightarrow 6 \alpha \text{H}$
 $\Rightarrow 6$ hyperconjugative str

More stable



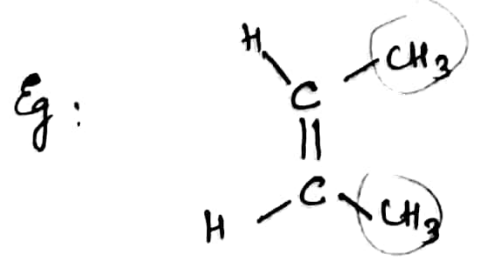
$(\text{CH}_3)_2\text{C} = \text{C}(\text{CH}_3)_2 > (\text{CH}_3)_2\text{C} = \text{CH} - \text{CH}_3 > \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 >$
 $2 \alpha \text{C} \Rightarrow 12 \alpha \text{H} > 9 \alpha \text{H} > 6 \alpha \text{H}$
 $12 \text{ str} > 9 \text{ str} > 6 \text{ str}$

$\text{CH}_3 - \text{CH}_2 - \text{C}(\text{CH}_3) = \text{CH}_2 > \text{CH}_3 - \text{CH} = \text{CH}_2 > \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2 >$
 ? ? ?

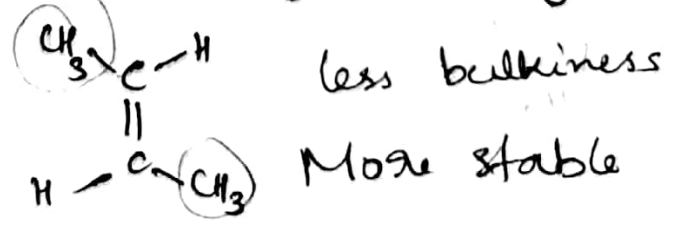
Steric effect

\rightarrow Influence of spatial arrangement/configuration of molecules upon their stability & properties as well as upon their rates.

\rightarrow Arise due to 'spatial crowding' of bulky groups.



Cis-2-butene

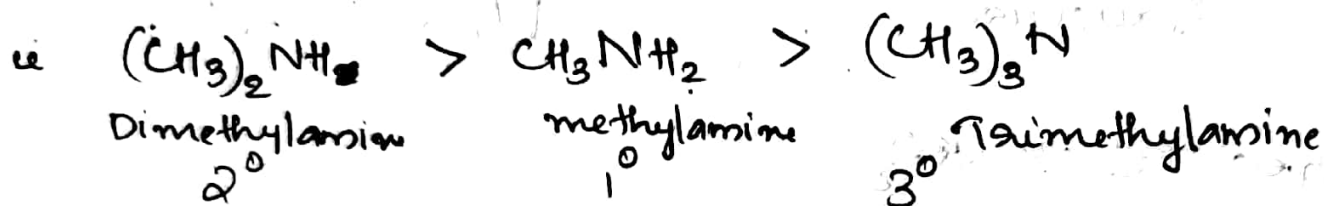


Trans-2-butene

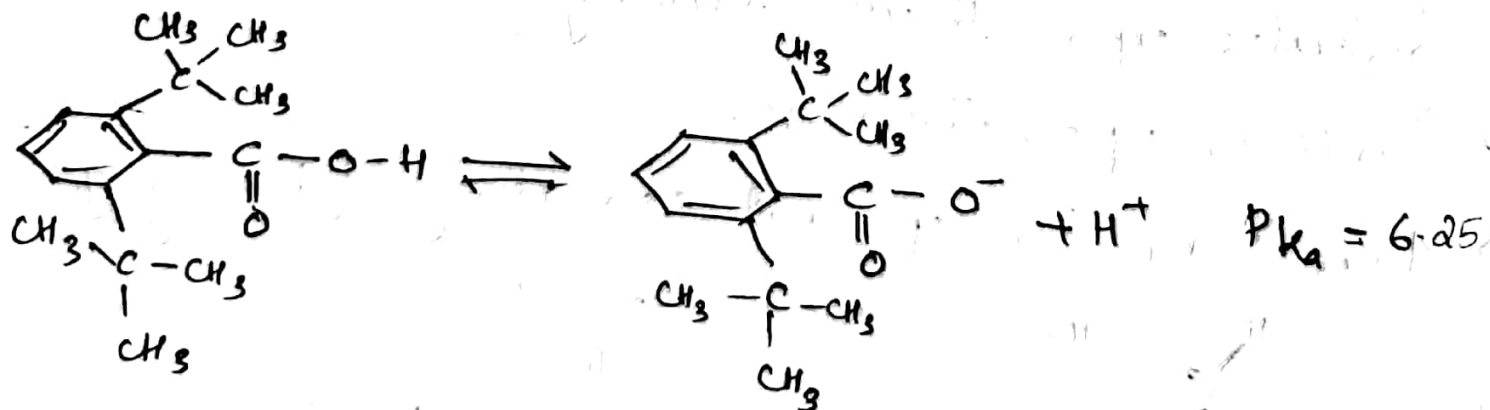
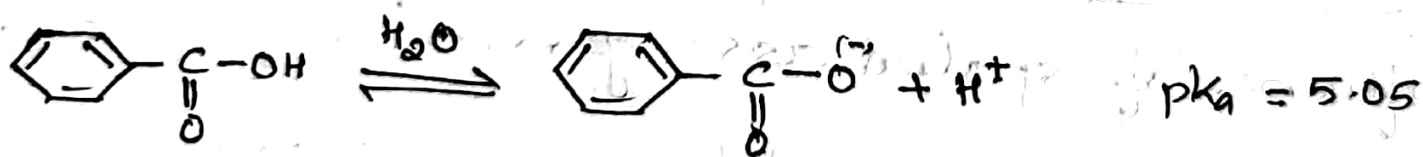
copy the next example here

① Basicity of amines

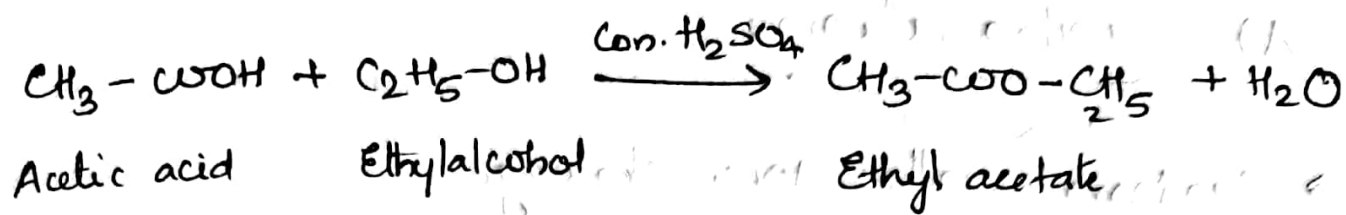
In terms of +I effect of CH_3 we expect 3° amine ($(\text{CH}_3)_3\text{N}$) to more basic than 1° amine but, it is not the case due to steric hindrance or bulkiness, it is the least basic



② Acidity of carboxylic acid is found to ↓ by the presence of bulky group in its molecule because they cause steric hindrance to the stabilization of the anion.

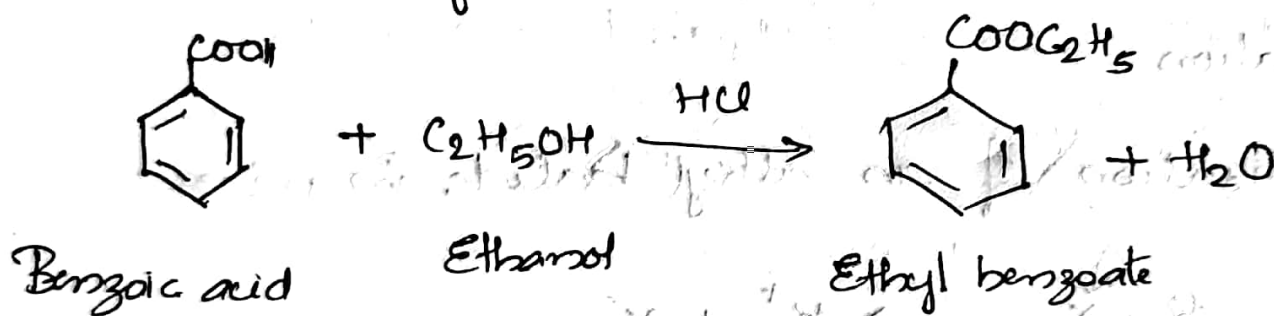


⊕ Acetic acid is esterified easily with an alcohol & $\text{Con. H}_2\text{SO}_4$

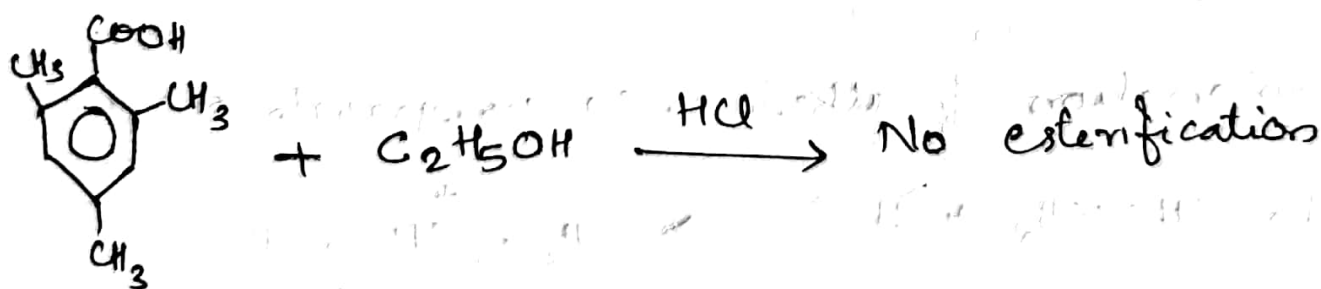


When ↑ no. of alkyl grp ↑ on α-carbon, rate of esterification ↓ due to steric hindrance

⊕ Benzoic acid esterified easily with ethanol in presence of HCl



2,4,6-trimethylbenzoic acid not easily esterified.



Reaction Intermediates

(A) Carbocations

- Carbon with +ve charge
- e⁻ deficient
- Tendency to accept e⁻
- short-lived & highly reacting species

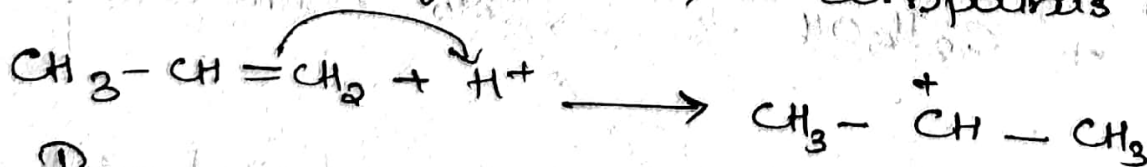
Eg: CH_3^+ , CH_3CH_2^+ , $\text{C}_6\text{H}_5\text{-CH}_2^+$ etc

Formation

① Ionization of an alkyl halide in polar solvent



② protonation of alkene, CO compounds, nitriles etc



Propene

Isopropyl cation

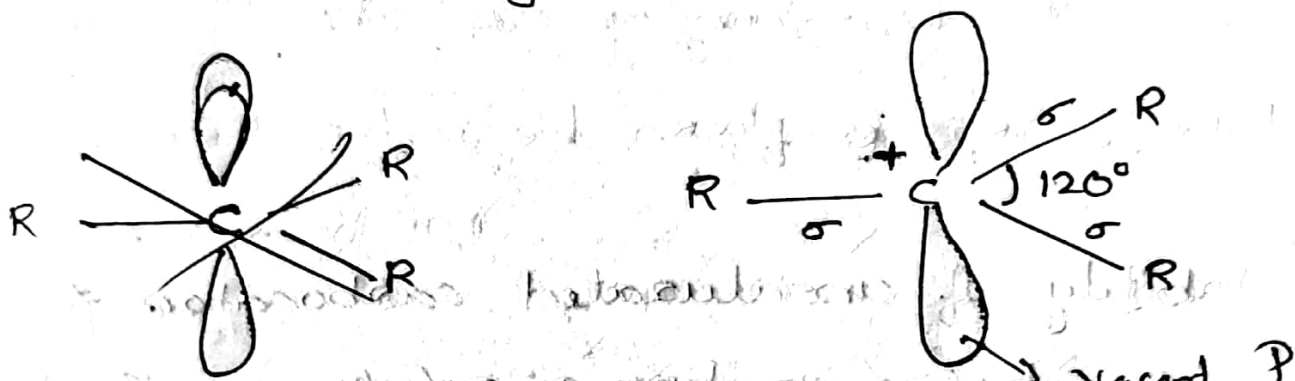
Hybridisation & structure:

→ sp^2 hybridised

→ Three sp^2 hybrid orbital contain an ~~ap~~ unpaired e^- each & arranged in trigonal planar fashion.

→ Bond angle $- 120^\circ$

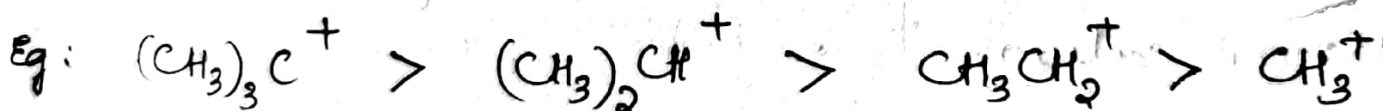
→ structure - Trigonal planar



Stability

(a) Stability of alkyl cations

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



Explanation:

① I effect - Alkyl grp has +I effect, thus disperse the +ve charge on C & stabilise the carbocation.

More stable (3°) - 3 CH_3 grps

2° - 2 CH_3 grps

1° - 1 CH_3 grp

CH_3^+ - No CH_3

• Hyperconjugation : $3^\circ \rightarrow 9 \alpha\text{-Hydrogen}$
 $\Rightarrow 9$ Hyperconjugative str
 \Rightarrow More stable

$2^\circ \rightarrow 6$ Hyperconjugative str

$1^\circ \rightarrow 3$ " " "

$\text{CH}_3^+ \rightarrow$ No $\alpha\text{-Hydrogen}$

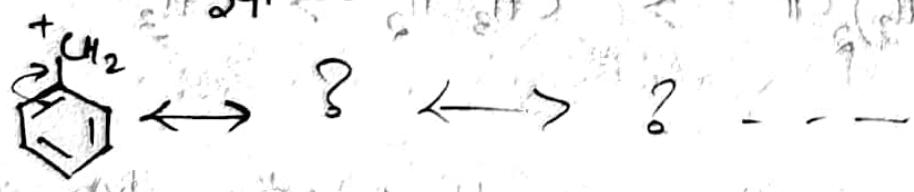
(b) stability of unsaturated carbocation & carbocations containing one/more phenyl ring

Ex: Allyl carbocation stabilise through resonance



H.W

Benzyl cation



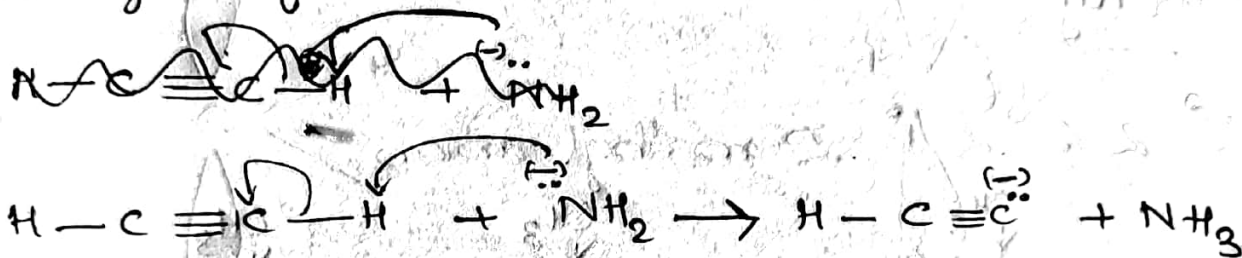
* Greater the no. of phenyl grp attached, greater no. of resonating str, More stability

(B) Carbanions

- Carbon with -ve charge
 - short lived & highly reactive
 - e⁻ rich & so react they are nucleophile & Lewis base
- Eg: CH_3^- , $\text{C}_6\text{H}_5\text{CH}_2^-$, CH_3CH_2^- , $(\text{CH}_3)_2\text{CH}^-$ etc

formation:

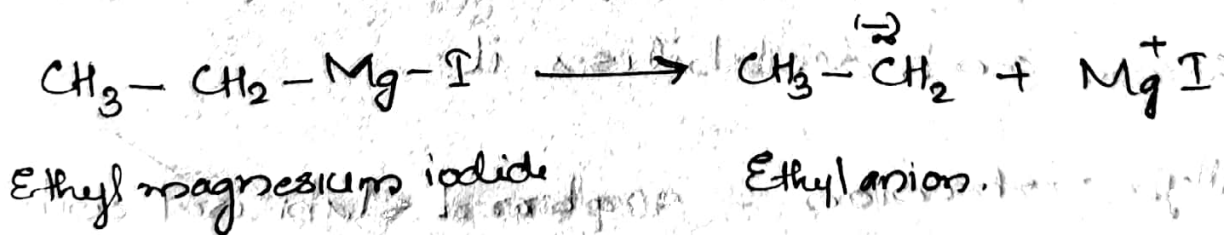
① Heterolytic fission



② Decomposition of certain anions



③ Decomposition of organometallic compounds.



Hybridisation & structure

- sp^3 hybridised
- 4 sp^3 hybrid orbital in tetrahedral fashion
- 3 sp^3 " " " forms σ bond with 3 atoms

and remaining sp^3 containing unshared e^- pair

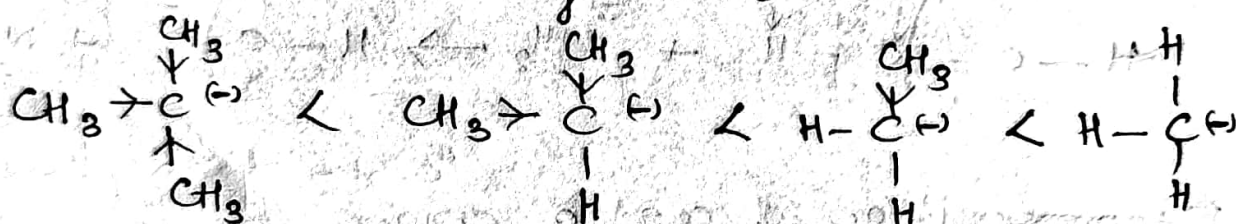
→ shape - pyramidal

→ Bond angle - 109.28°



◎ Stability

* $3^\circ < 2^\circ < 1^\circ < \text{methyl anion}$.



t-butyl anion

isopropyl anion

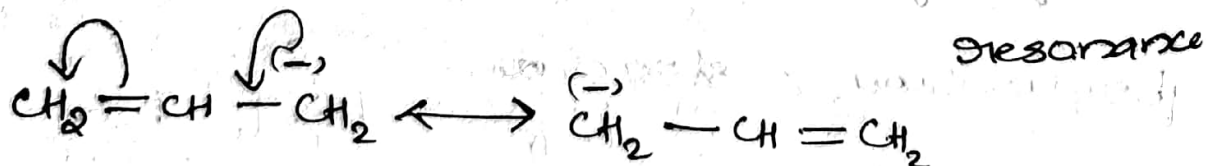
Ethyl anion

Methyl anion.

Can explained on the basis of CH_3 group's

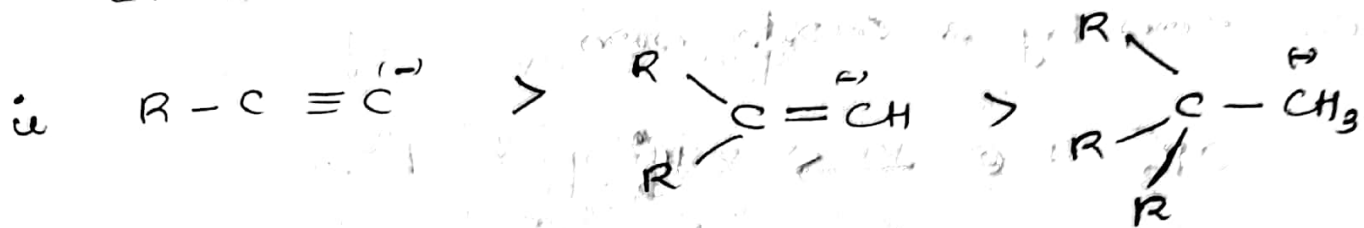
+I effect, it intensify the δ^- charge on the carbon and destabilises it.

* Allyl carbanion - explained stabilised with



H.W

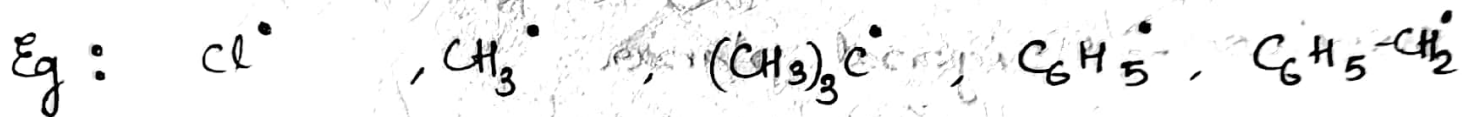
Benzyl anion



Free Radicals

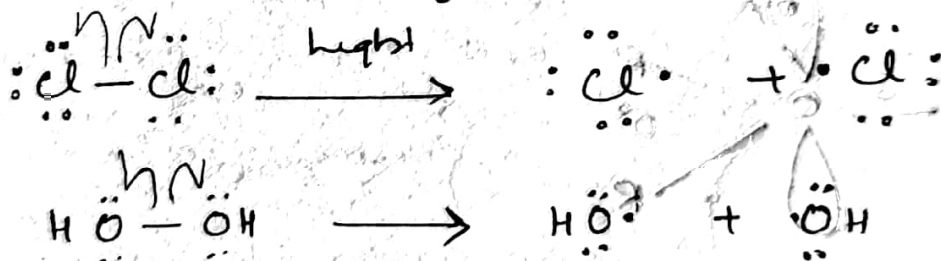
→ Atom/groups having unpaired e

→ Neutral & highly reactive intermediate

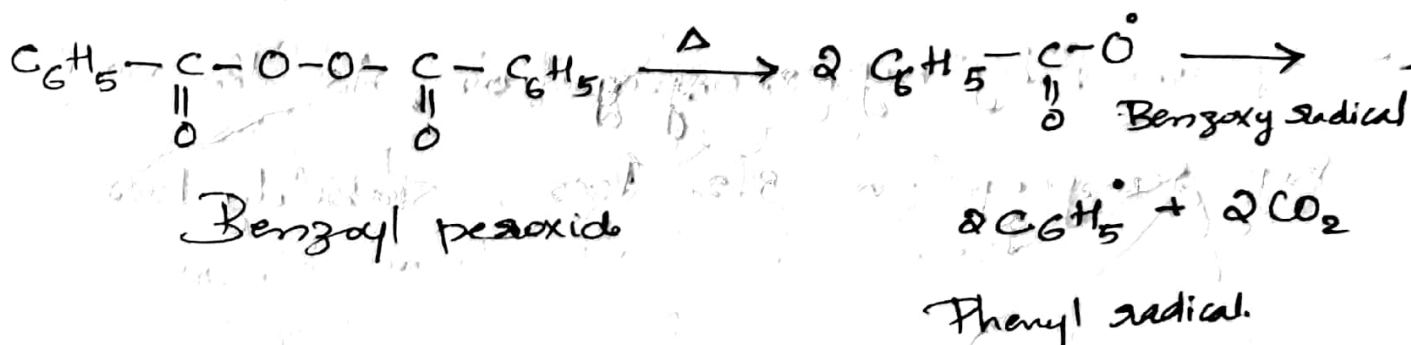
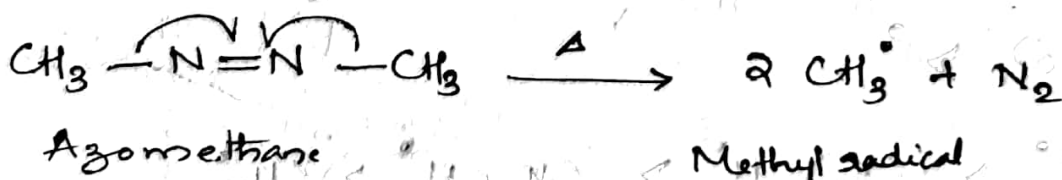


Formation

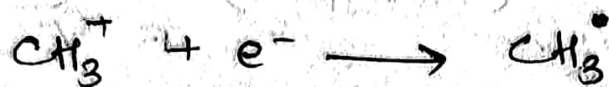
① photochemical homolysis



② Thermal homolysis



③ Gain of e^- by a carbocation / loss of an electron by a carbanion.



Hybridisation & structure

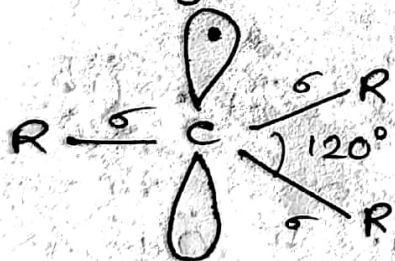
→ sp^2 hybridised

→ 3 sp^2 hybrid orbitals contains an unpaired e^-

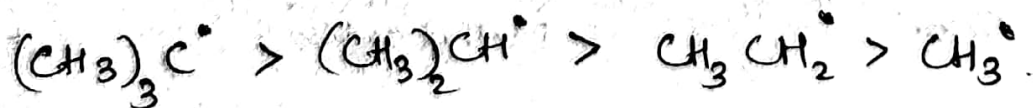
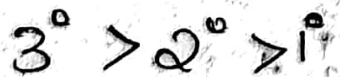
→ Structure - Trigonal planar

→ one p orbital is unhybridised.

→ Bond angle - 120°



Stability:



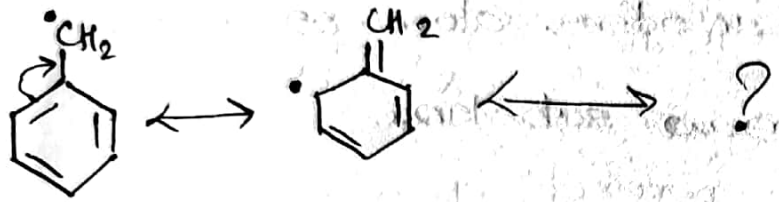
→ Explained by hyperconjugation, As the no. of hyperconjugative σ C-H bonds, stability \uparrow ses.

① Allyl radical stabilised by resonance



H.W

Benzyl radical



Larger the no. of phenyl rings with unpaired e, the greater will be resonance str. More the stability.

