

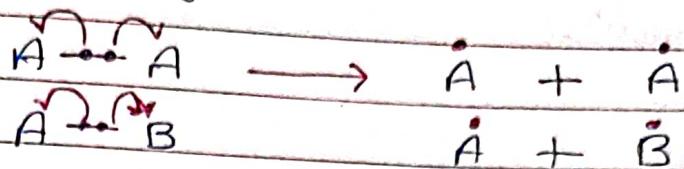


## B. Types of Bond cleavage:-

Two types -

- ① Homolysis / Homolytic bond cleavage
- ② Heterolysis / Heterolytic " "

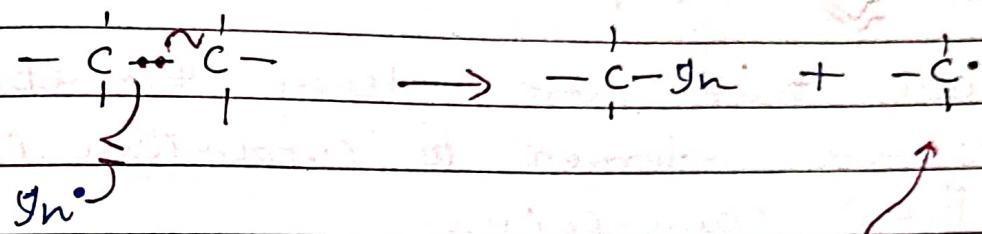
### Homolytic:



• It occurs generally in non-polar bonds.

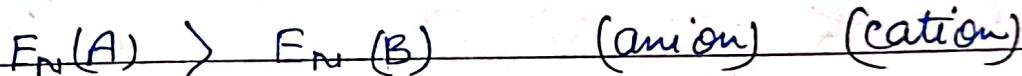
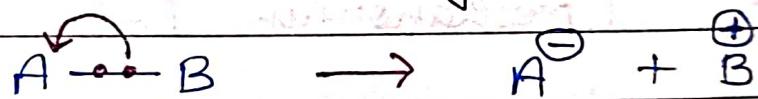
$\Delta/\text{hv}$

• Radical Initiators ( $\text{Un}^\bullet$ )



- odd e- species called as free radical.
- non polar solvents

## Heterolytic bond cleavage -



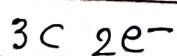
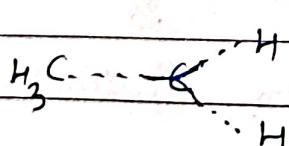
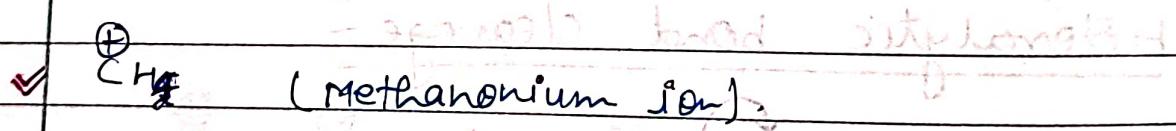
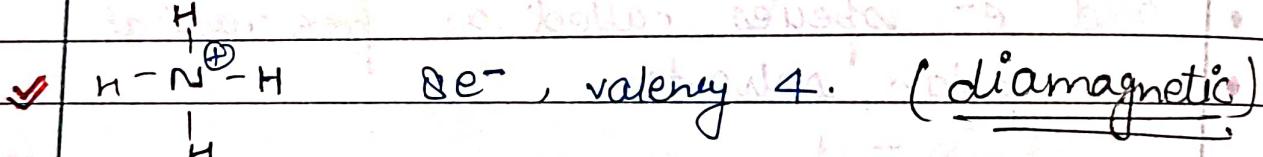
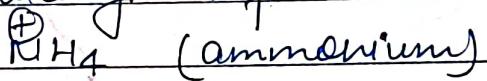
- Polar solvents.
- generally occurs in ~~non~~ polar bonds.
- If -ve charge are present on carbon called as carbanion.
- If +ve charge present  $\rightarrow$  carbocation

## Reactive intermediate :-

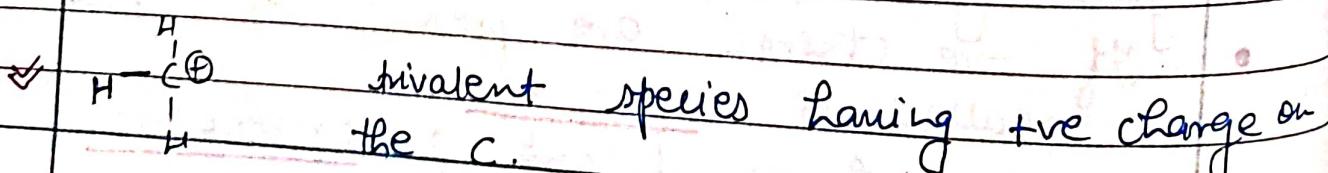
- Real species (exist.)
- specific life time.
- Isolated
- Determine its str./shape.
- Carbocation
- carbamion
- free radical
- carbene
- nitrene.
- Benzyne.

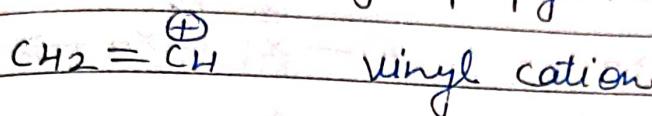
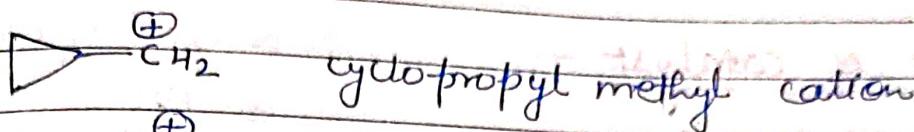
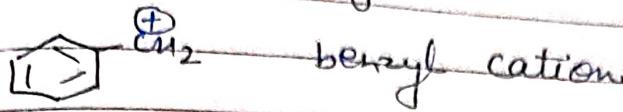
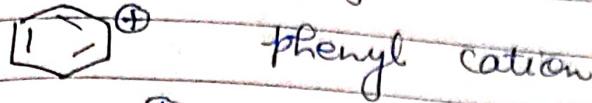
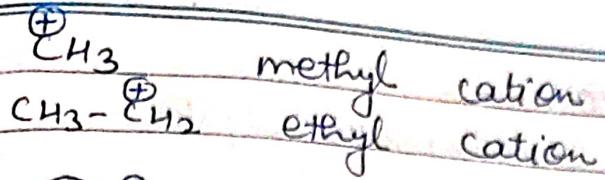
## Carbocation :- / carbonium ion (not used) :-

- species have more valency than its actual valency referred to carbonium ion



$$m/z = 17$$



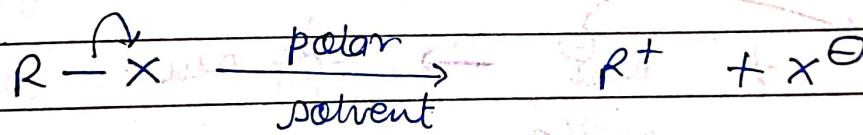


### characters-

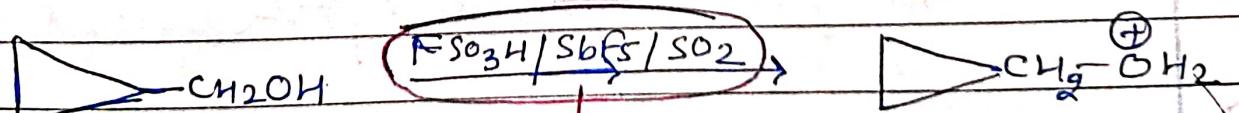
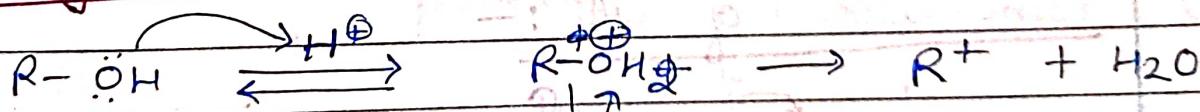
- $\text{R}^+ \rightarrow$  sentet of  $e^-$
- $\text{R}^+ \rightarrow e^-$  deficient cts, as electrophiles.
- $\text{R}^+ \rightarrow$  Acts as Lewis acids.  
( $e^-$  pair acceptor).

### Methods of generation :-

#### ① Direct ionization -

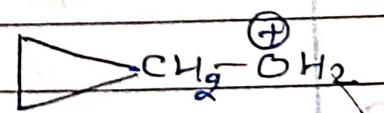


#### ② Dehydration -

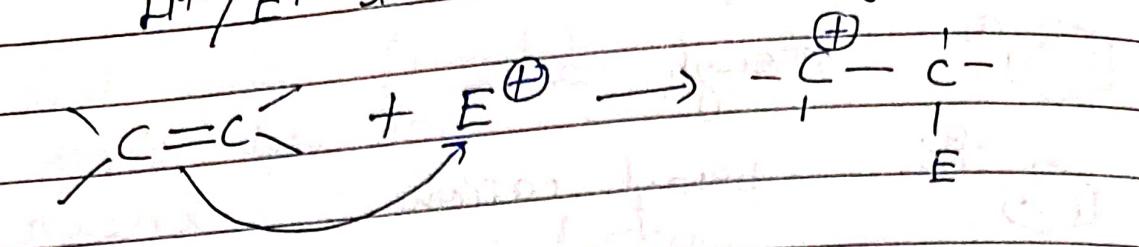


Super aniol

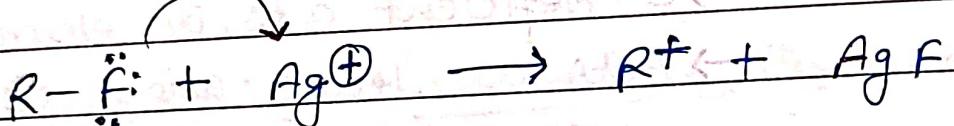
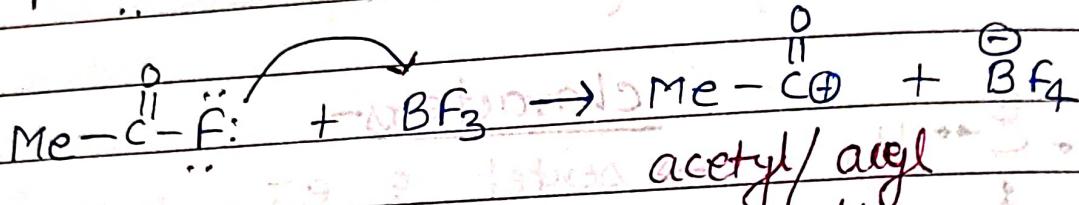
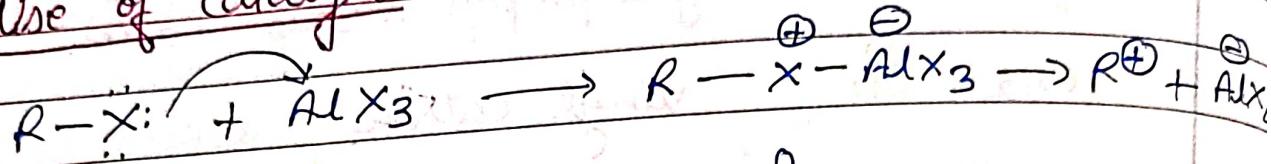
- 78°C



3- Addition of proton -  
 $H^+ / F^+$  to unsaturated system.

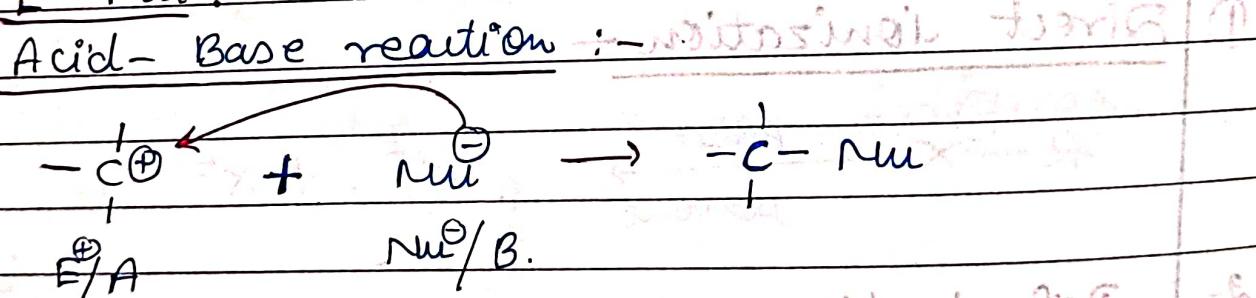


4) Use of catalyst -

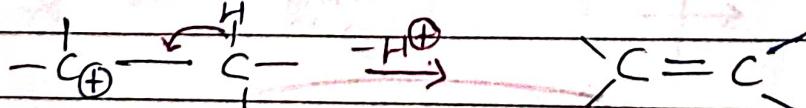


Reactions of carbocation ( $C^+$ ):-

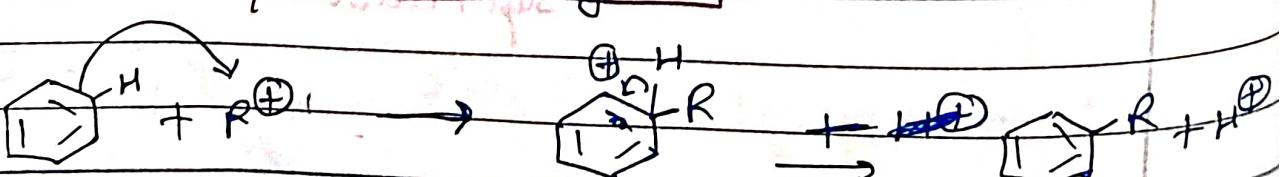
①  $E-nu$  :-



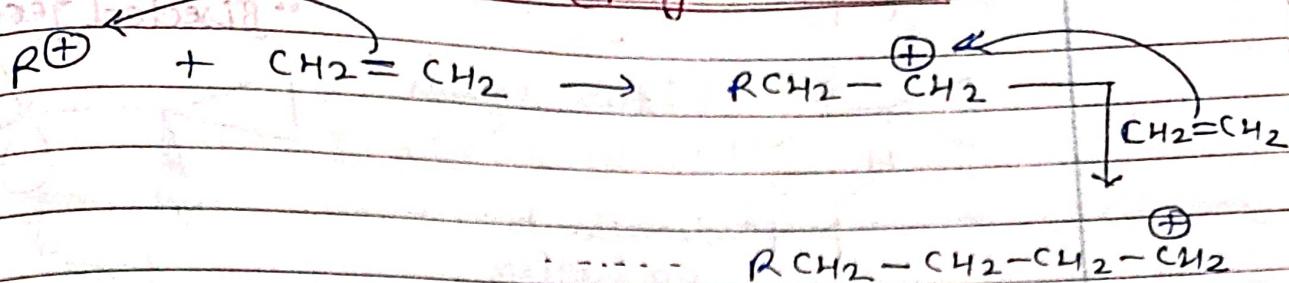
② Elimination of  $H^+$  :-



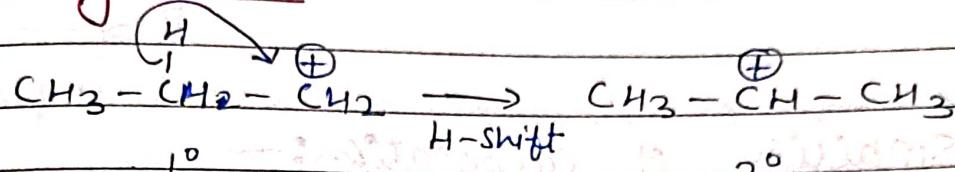
③ Substitution/ Aromatic system :-



④ Addition to  $C=C$ . (polymerization):

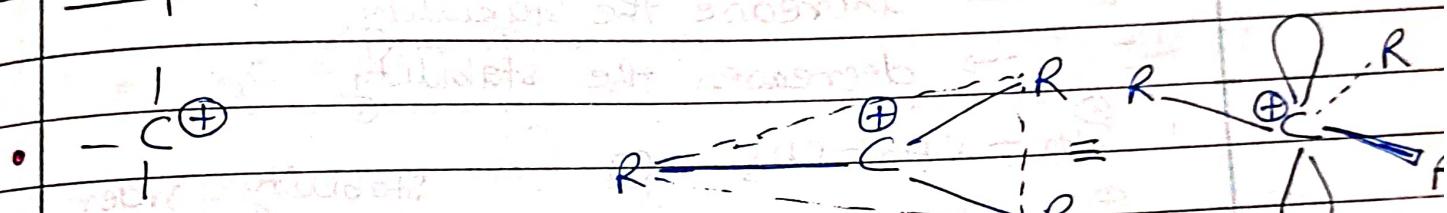


## Rearrangement :-



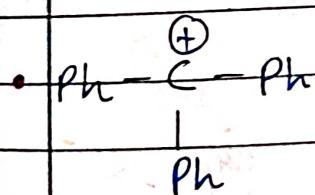
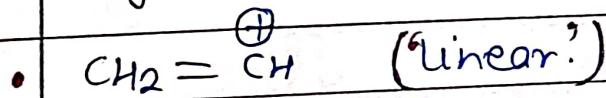
Alkyl shift, aryl shift.

## Shapes & structures :-

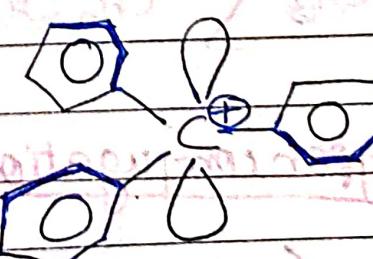


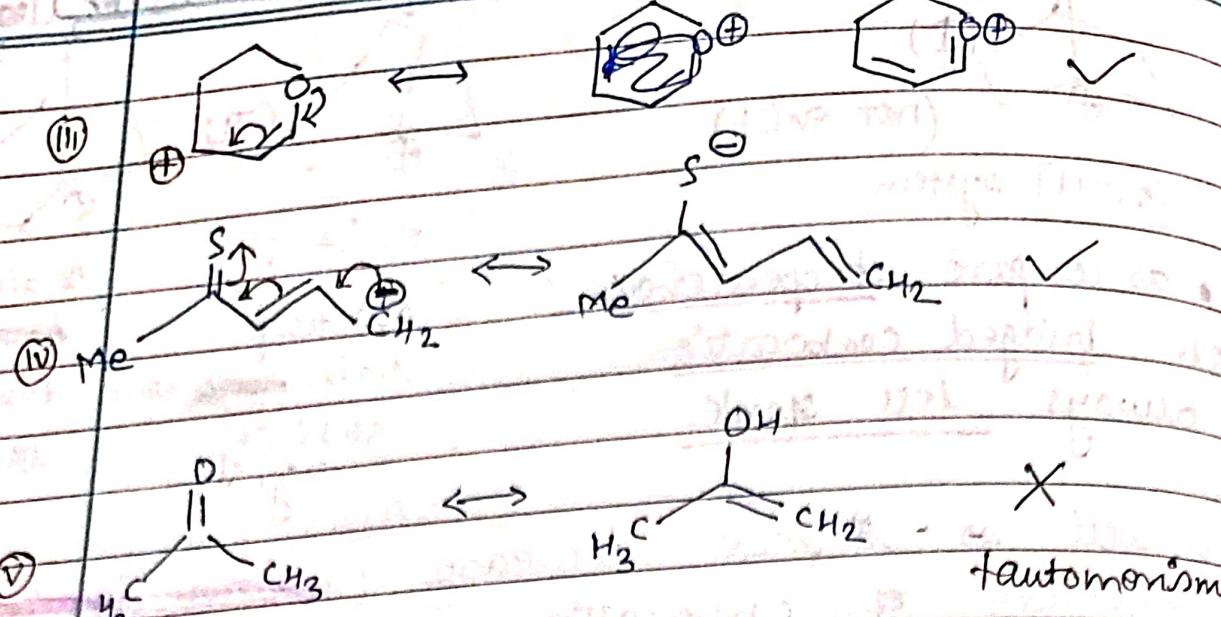
~~3σ bonds~~  $\Rightarrow \text{sp}^2$

"trigonal planar."



triphenyl methyl cation.





## CARBANION :-

- Trivalent species having complete octet & bearing -ve charge



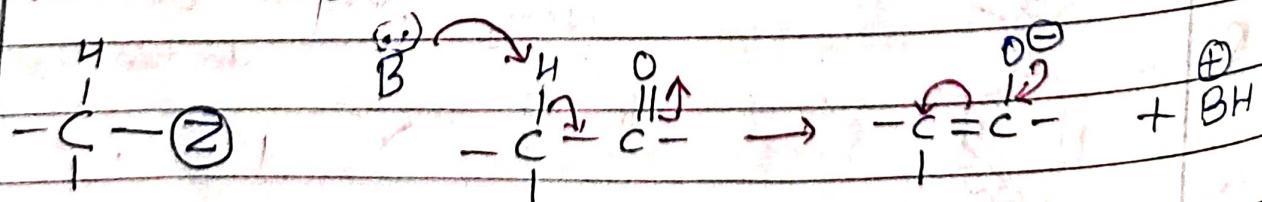
$\text{Be}^-$  (trivalent) (diamagnetic)

Acts as  $\text{nu}^-$

Lewis base

## Methods of generations :-

### ① Abstraction of acidic proton :-



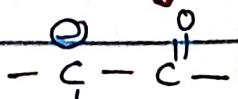
$$\text{Z} = -\text{CHO}$$

$$= -\text{CO}$$

$$= -\text{NO}_2$$

$$= -\text{CN}$$

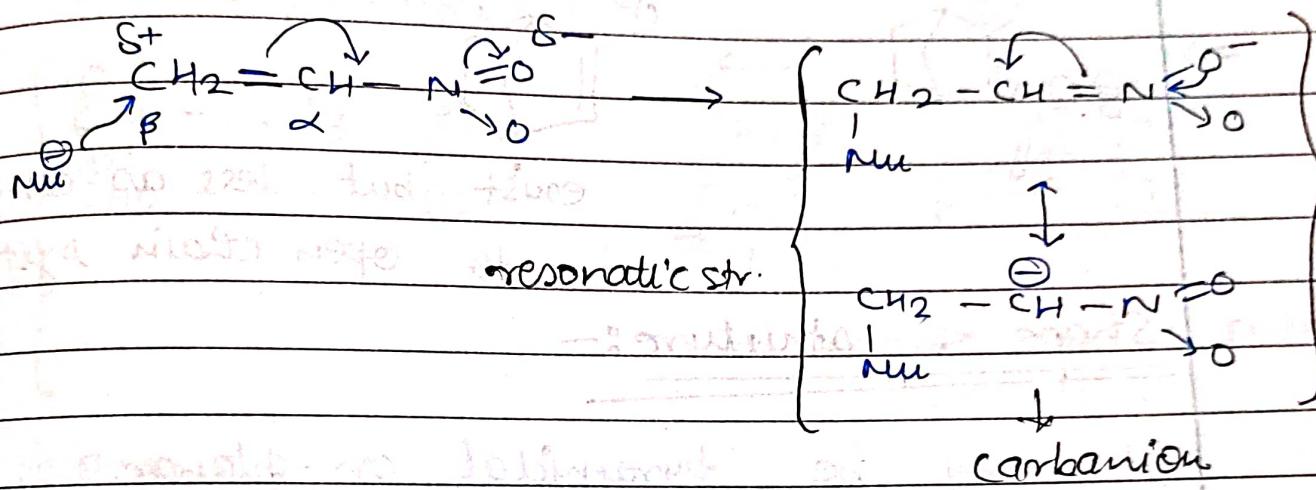
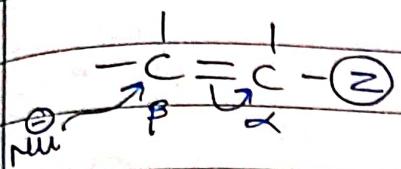
(enolate)



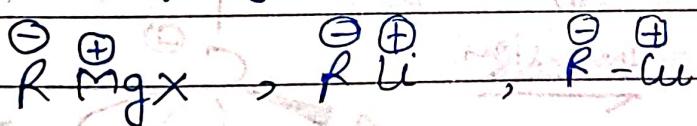
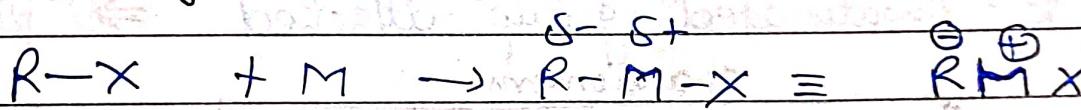
1 carbanion

- if e<sup>-</sup> rich species donates its e<sup>-</sup> to proton acts as base.
  - if it donates its e<sup>-</sup> to c then acts as nucleophile.

② Addition to  $\alpha, \beta$ -unsaturated compound:

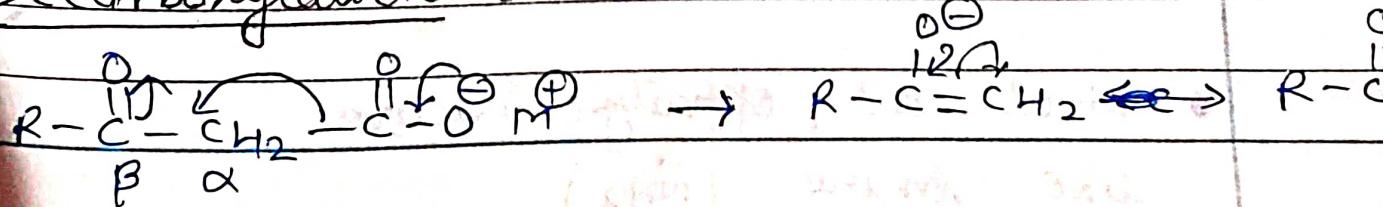


③ From alkyl halide :-

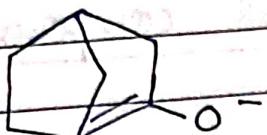
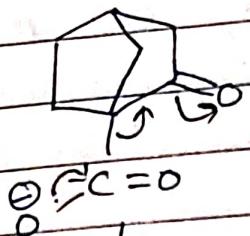


- All organometallic reagents have carb generate carbanion

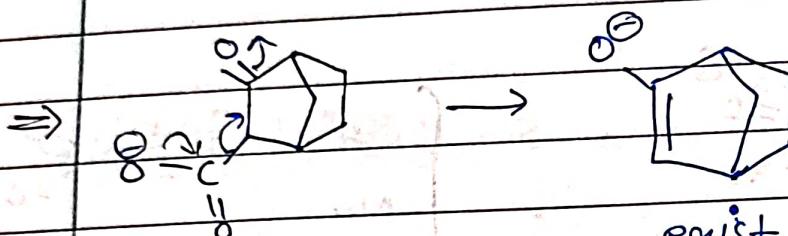
## ④ Decarbonylation :-



- decarbonylation not take place here  
carbanion not exist at bridged system



against Brexit rule



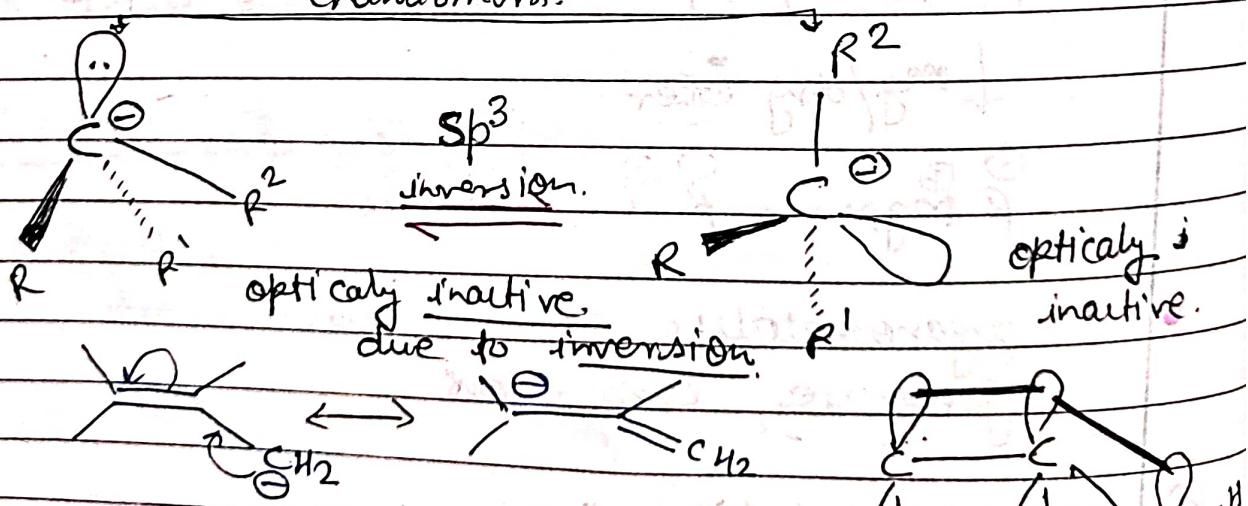
exist but less as compare  
to open chain system.

## Shape & structure:-

It may be pyramidal or planar.

If H & alkyl group attached  $\Rightarrow$  pyramidal

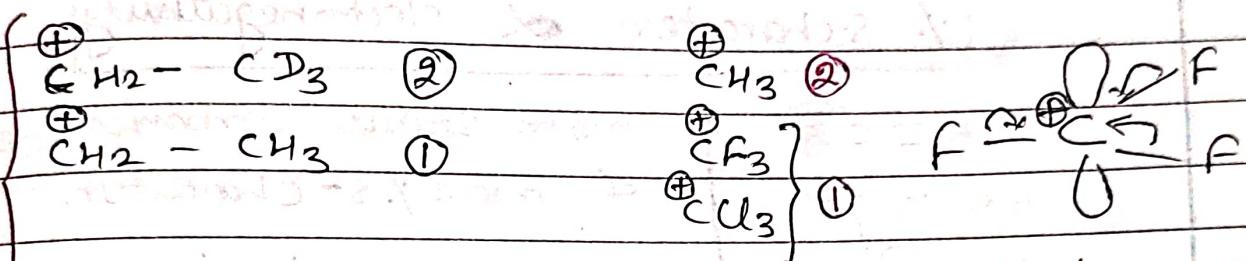
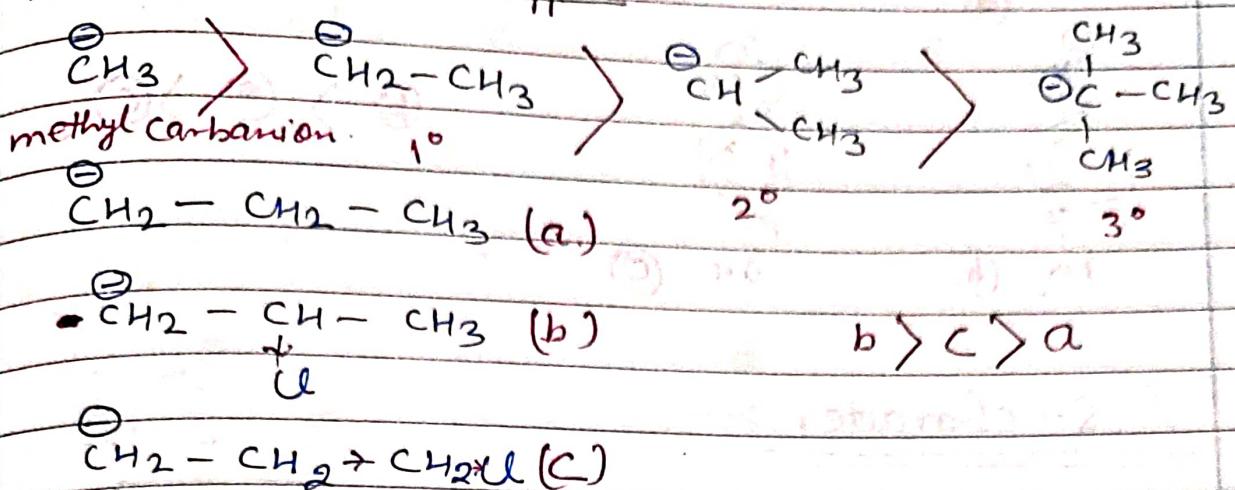
If unsaturated group attached  $\Rightarrow$  planar.  
e.g.  $\text{CH}_2=\text{CH}_2$



- chiral but optically inactive like Amine. ( $\text{NH}_3$ )

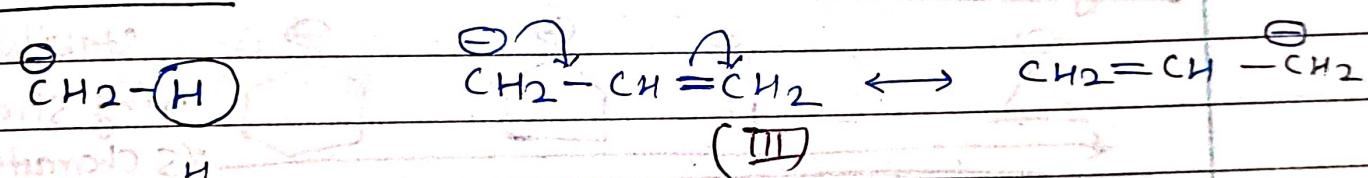
## Stability order :-

Field / inductive effect :-

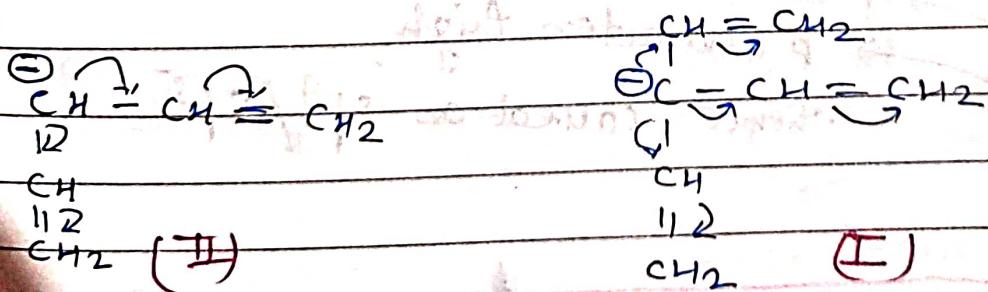


+ R more effect as compare to  
- I effect.

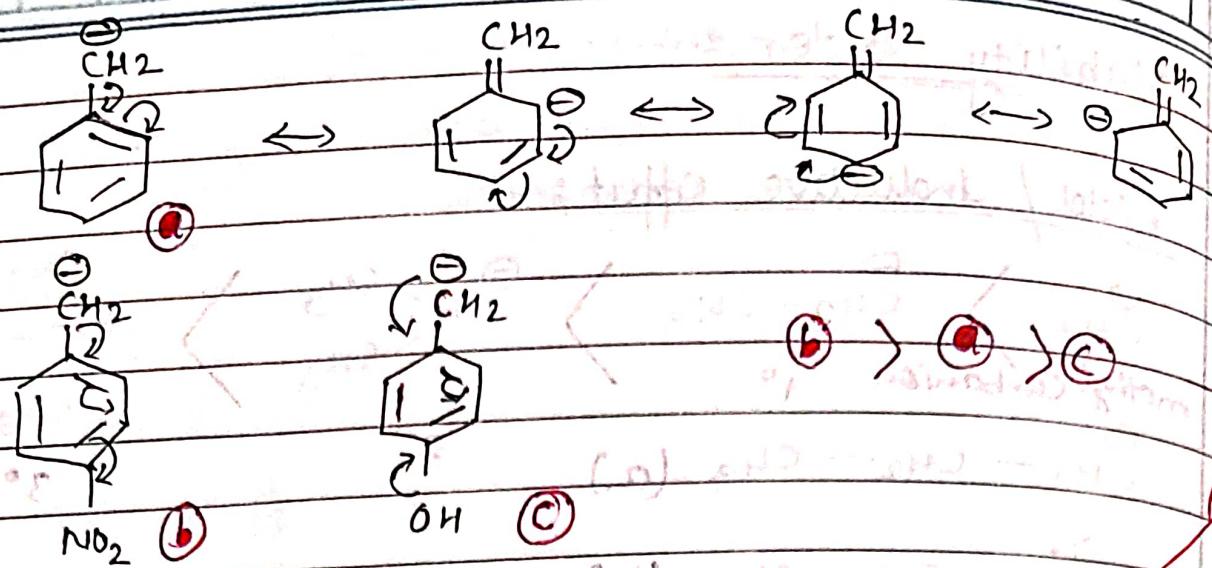
## Resonance :-



$\text{CH}_2-\overset{\oplus}{\underset{\ominus}{\text{C}}}-\text{H}$        $\alpha$  H present but hyperconjugation not  
occur b/c here no empty orbital  
for back bonding.

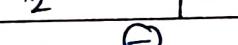
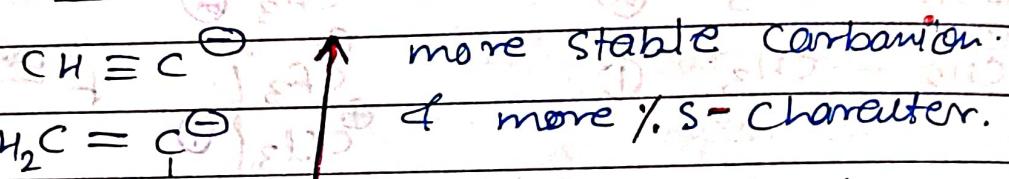


$(I) > (II) > (III)$



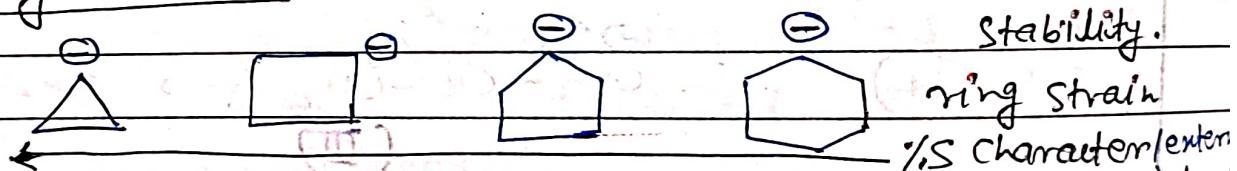
### ③ % s-character :-

$\% \text{ s-character} \propto \text{electronegativity}$

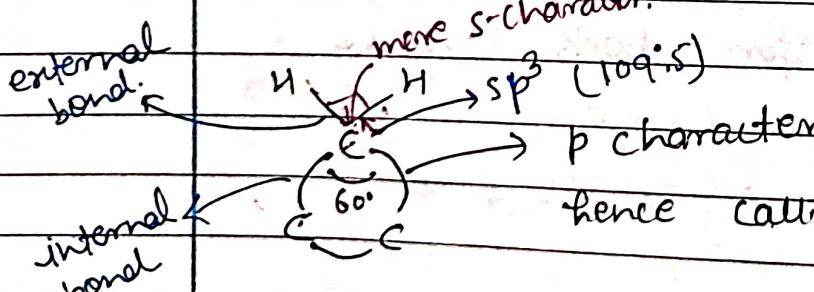


when size  $\downarrow$

### ④ Ring Strain :- internal bond s character $\downarrow$ p-character



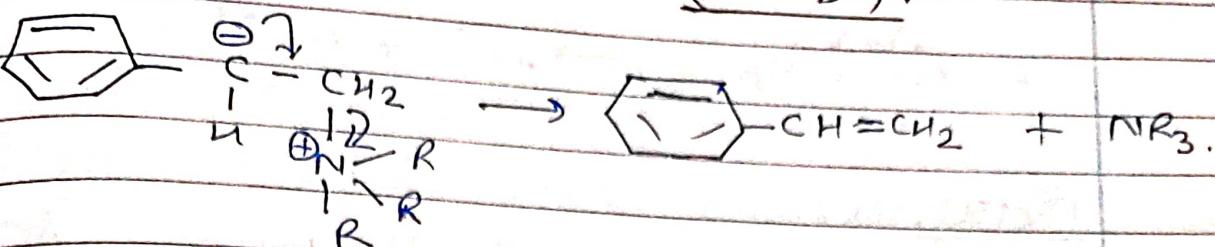
stability of carbonion  $\propto$  ring strain



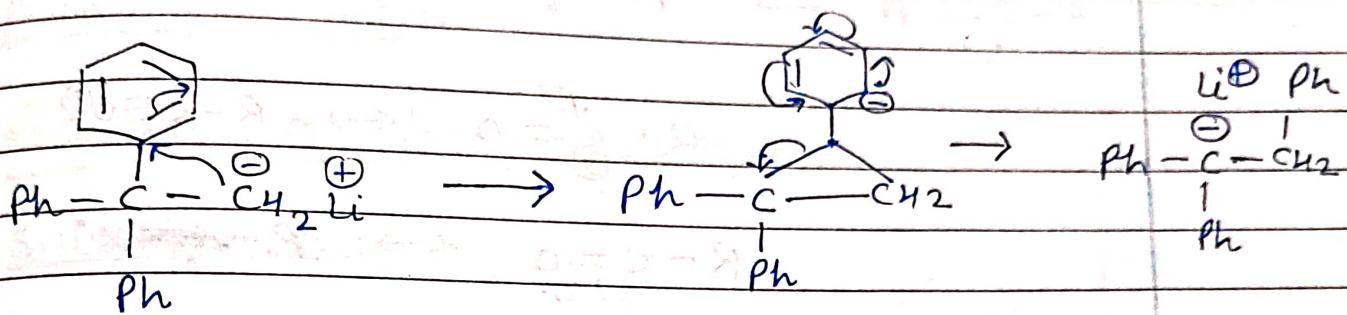
ring strain  $\propto$  s-character.

- In external bond ( $\text{C}-\text{H}$ ) % s character  $\uparrow$  & p character  $\downarrow$  when size of ring  $\downarrow$

## Elimination Reaction :- (E<sub>1</sub>C<sub>b</sub>)



## Rearrangement :-



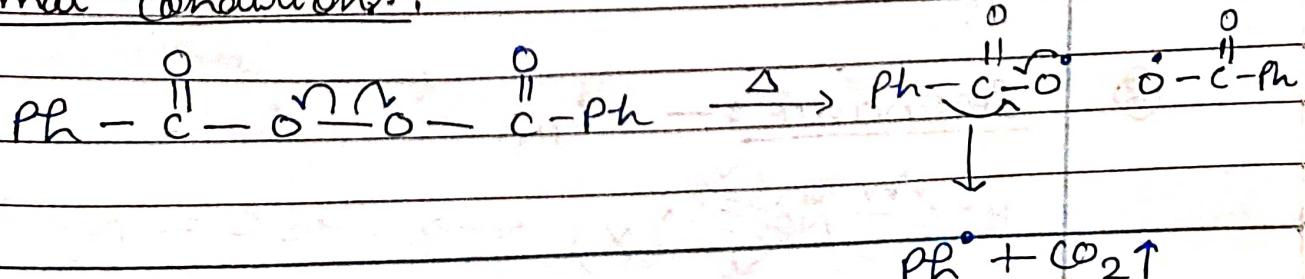
- Rearrangement in carbocations is not possible in alkyl systems. only aryl gp show rearr.

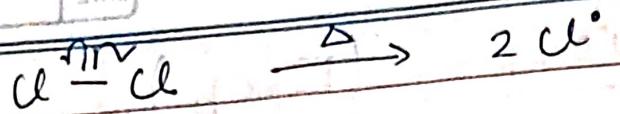
## FREE RADICAL :-

- Neutral species with one equivalent carbon, septet of e<sup>-</sup> (7e<sup>-</sup>), acts as E<sup>+</sup>.
- paramagnetic.
- 7e<sup>-</sup>, so acts as E<sup>+</sup> (e<sup>-</sup> deficient)

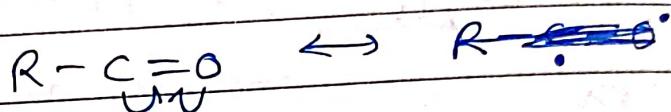
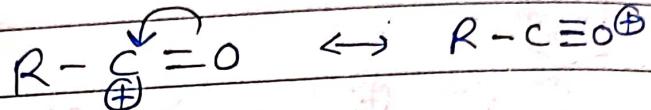
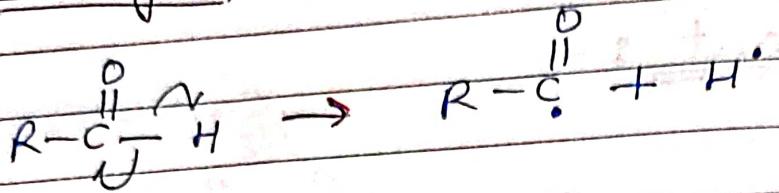
## Methods of generation of free radical :-

### Thermal conditions:-





Photolysis :-

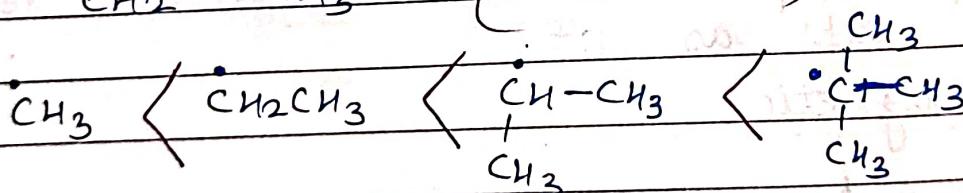


Stability order :-

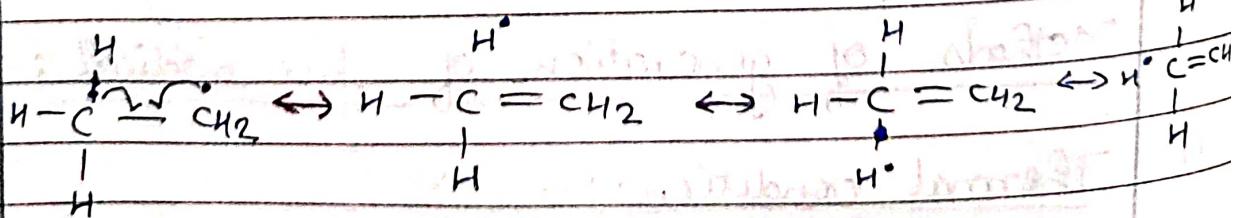
① Inductive effect :-

$\text{CH}_2-\text{CH}_2-\text{NO}_2$  (least stable due to  $-I$  effect)

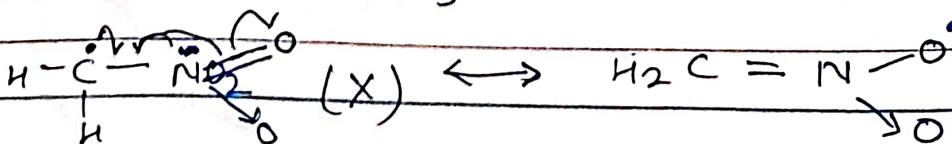
$\text{CH}_2-\text{CH}_3$  (more stable)

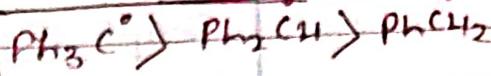
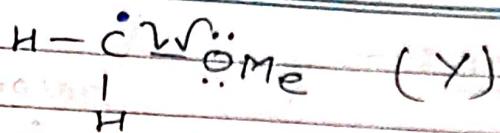
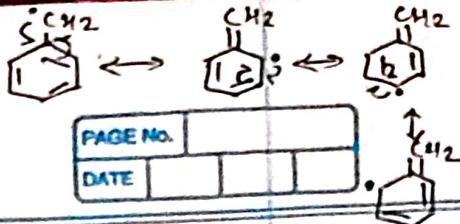
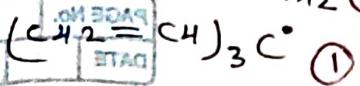
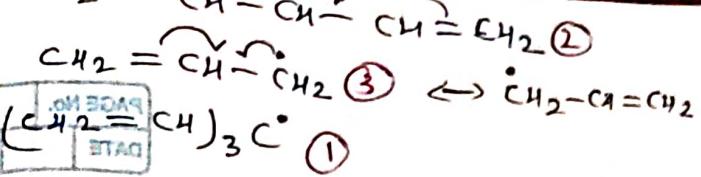


methyl radical



② Resonance :-  $\text{CH}_3$



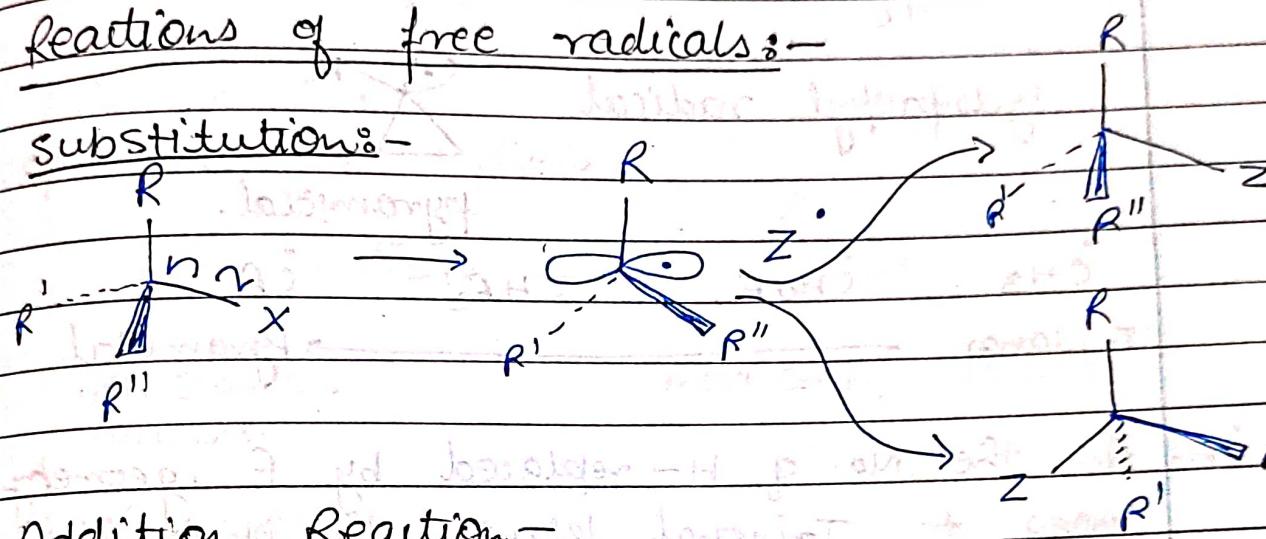


$X$  &  $Y$  both are more stable.

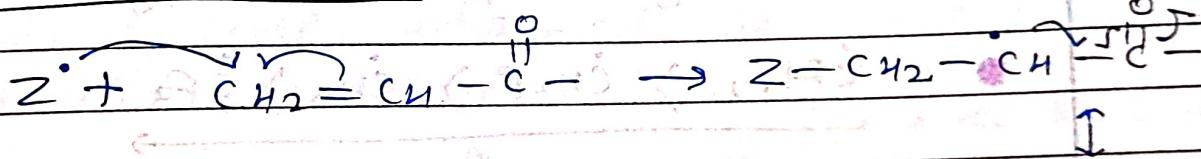
In free radical when EWG or ERG attached, both stabilized the free radical species. This effect is called as captodative effect or push-pull effect.

Reactions of free radicals:-

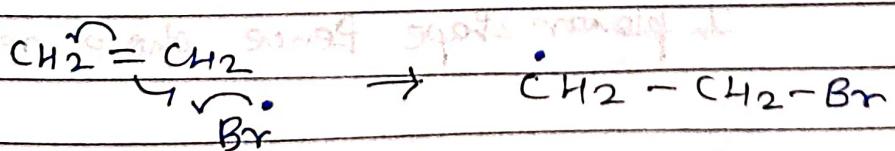
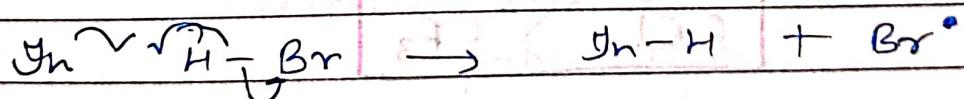
① Substitution -



② Addition Reaction -



③ Radical Initiator :-



# Shape & Structure :-

Planar

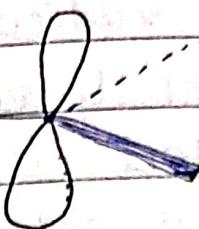
$\rightarrow$   $sp^2$  hybridization,  $\dot{C}H_3$ , Alkyl radical.

Pyramidal

$\rightarrow$   $sp^3$  "  $\dot{C}F_3$

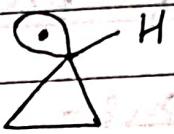


pyramidal.

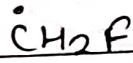
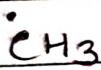


planar.

cyclo-propyl radical



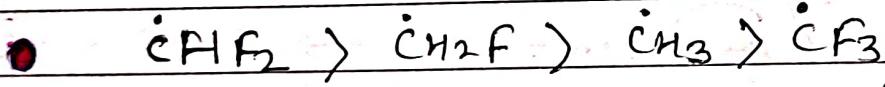
pyramidal.



T. Planar.

$\rightarrow$  Pyramidal.

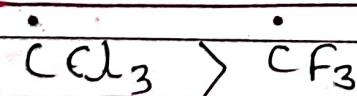
in  $\dot{C}F_3$  As the no. of H-replaced by F, geometry goes to Trigonal planar to pyramidal



Stability order.

$\Rightarrow$   $\dot{C}HF_2$  &  $\dot{C}H_2F$  show resonance

$\Rightarrow$  but  $\dot{C}F_3$  not b/c its str. is pyramidal.



In planar shape hence show resonance.

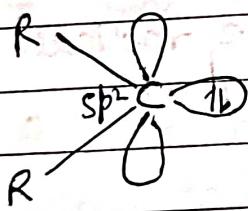
•  $Ph_3C \rightarrow$  Propeller shape.

## CARBENES :- [-C-]

- Outer most shell having 6 e<sup>-</sup>
- carbene are divalent neutral species. in which C - having 6 e<sup>-</sup> (sextet of e<sup>-</sup>).
- e<sup>-</sup> deficient hence electrophile.

### Types of carbene :-

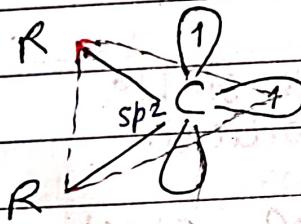
- singlet carbene.
- bent shape or V-shape.
- sp<sup>2</sup>



### triplet carbene

bent shape or  
V-shape.

sp<sup>2</sup>



more stable.

- less stable.

130° - 150°

- 100° - 110°

100° - 110°

130° - 150°

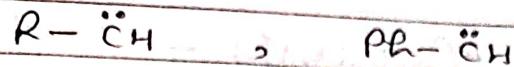
### Singlet :-



The carbene which is directly attached with lone pair.  $\Rightarrow$  singlet.

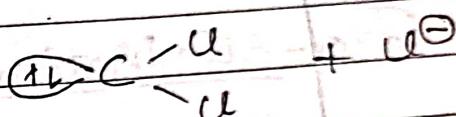
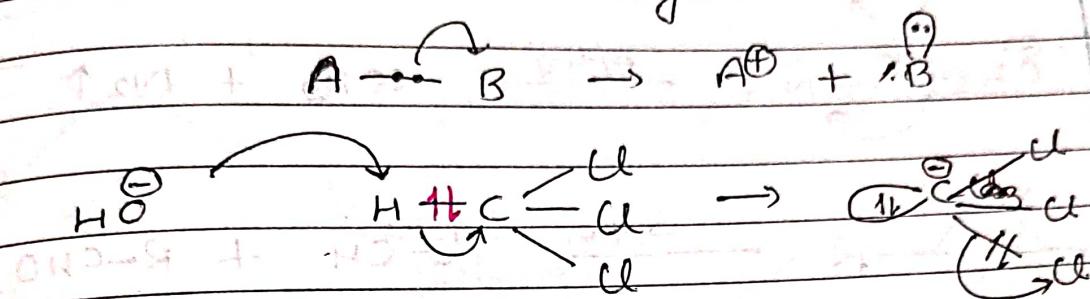
singlet carbene show resonance.

## Triplet carbene:-



$:CH_2$  (carbene or methylene)

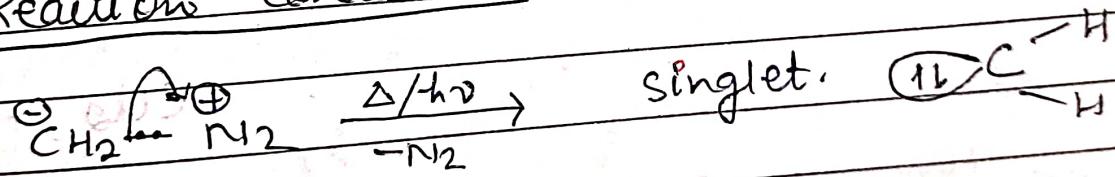
the carbene which generate by ionic mechanism then it exist in singlet.



singlet.

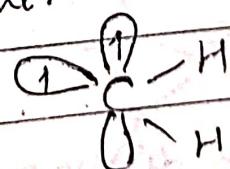
methylene can exists in singlet or triplet.

## Reaction conditions :-



$\downarrow \Delta/\text{hv}$  inert solvent.

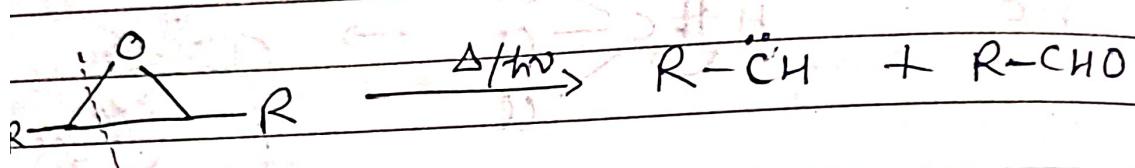
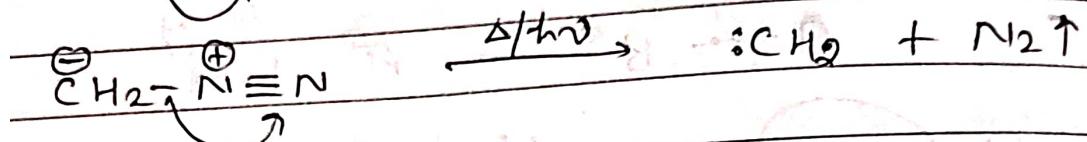
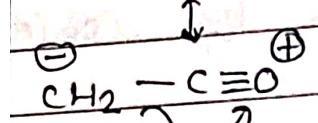
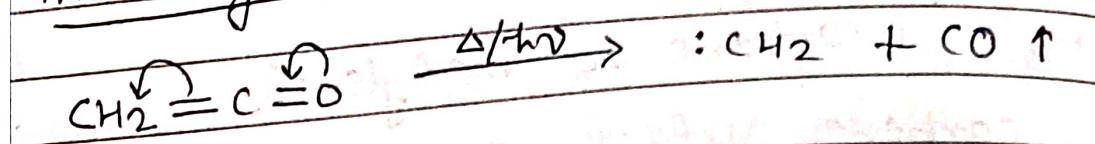
Triplet



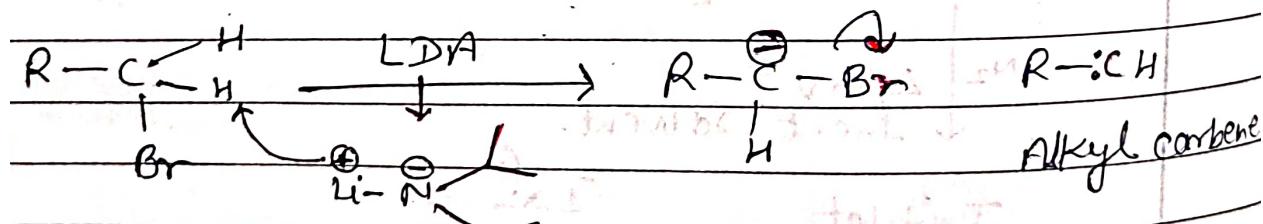
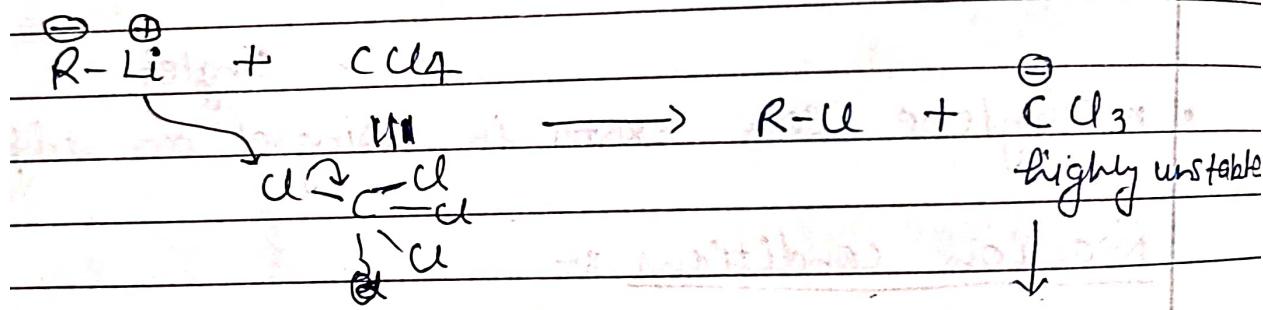
On starting formed singlet but go to stabilization it converts in triplet.

## Methods of generation :-

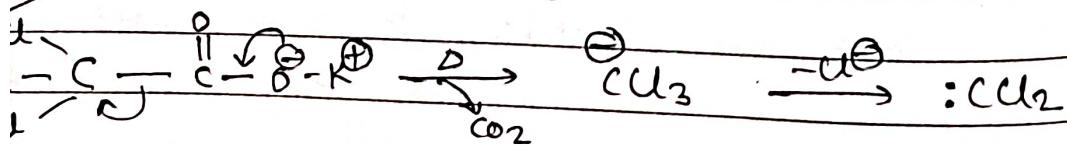
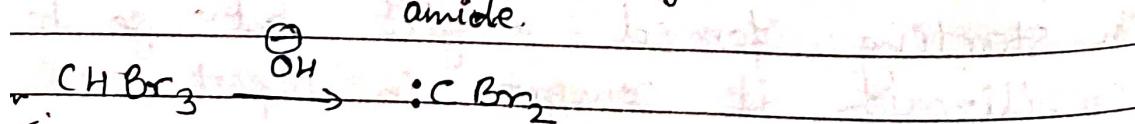
### Thermalysis & photolysis -

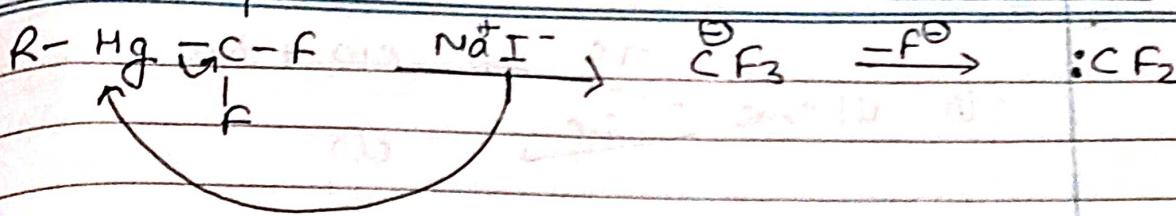


### Elimination Reaction :-



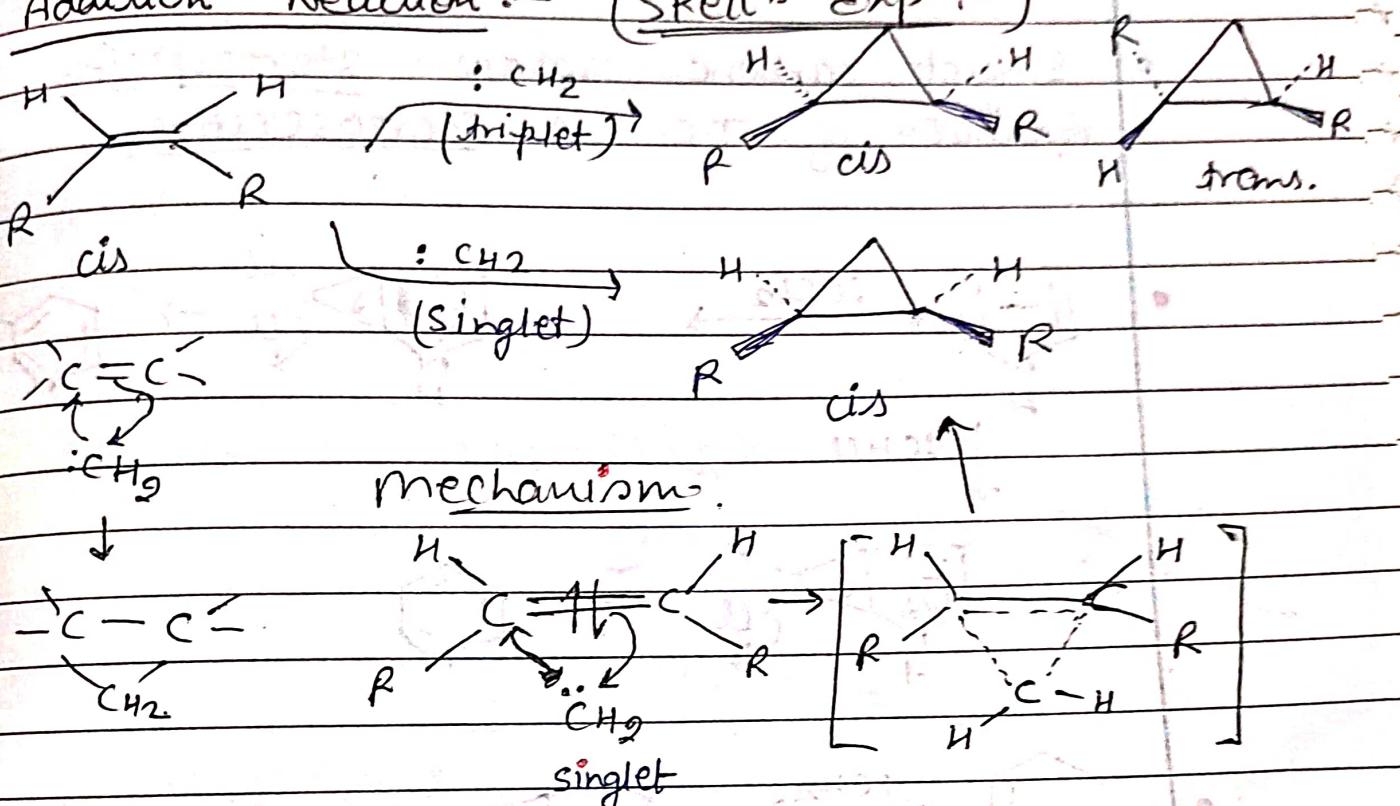
Lithium diisopropyl amide.



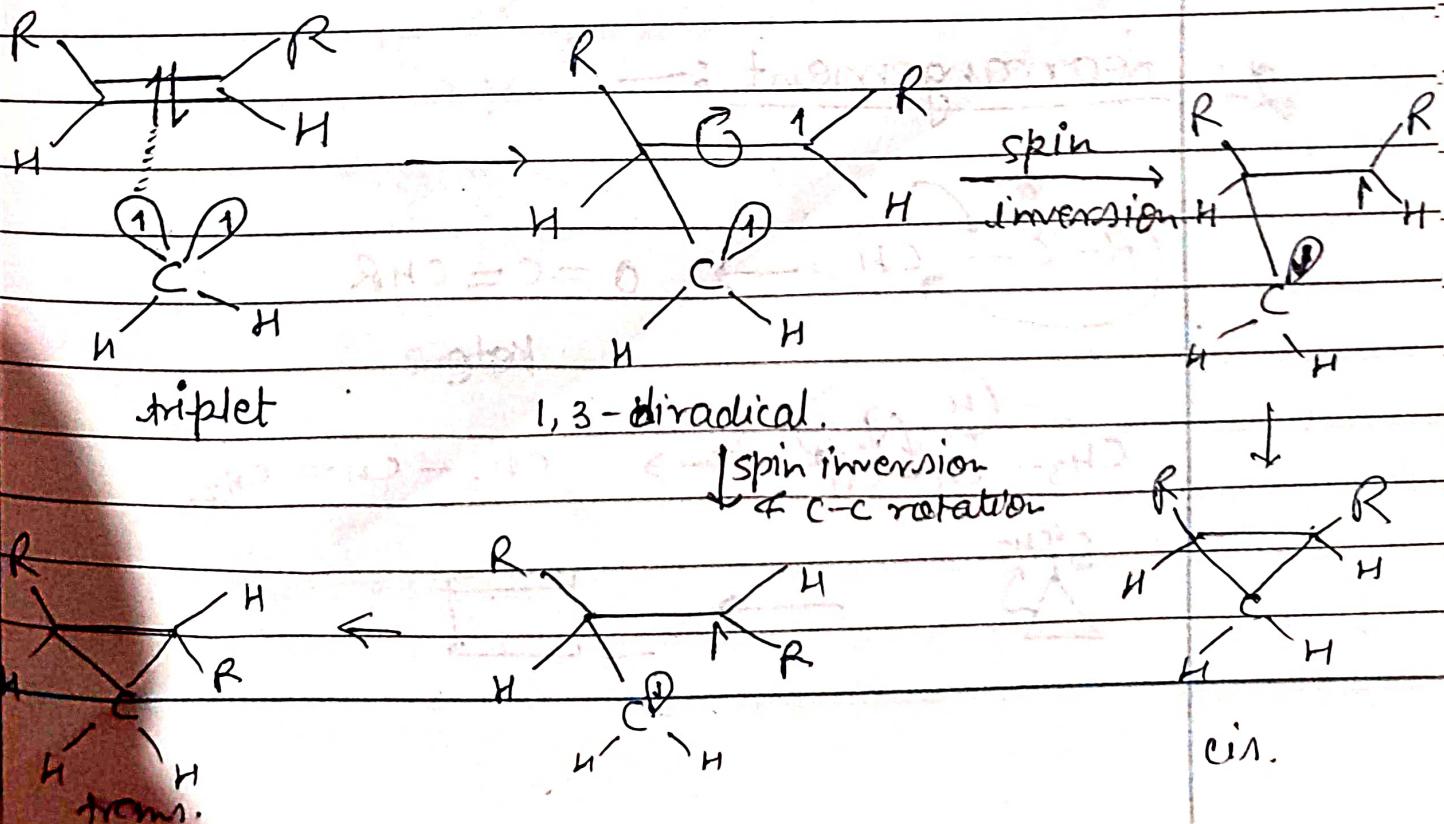


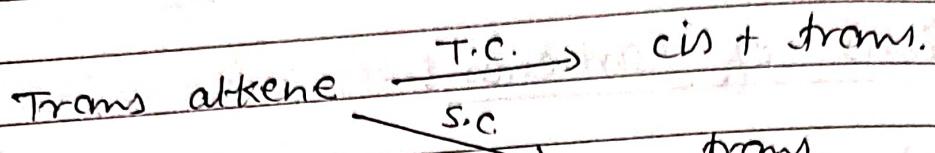
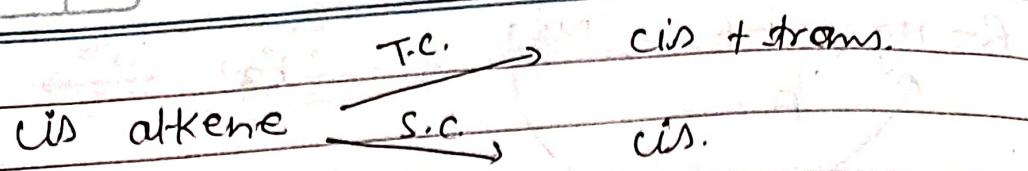
## Reactions of Carbenes :-

① Addition Reaction :- (Skell's exp. :-)

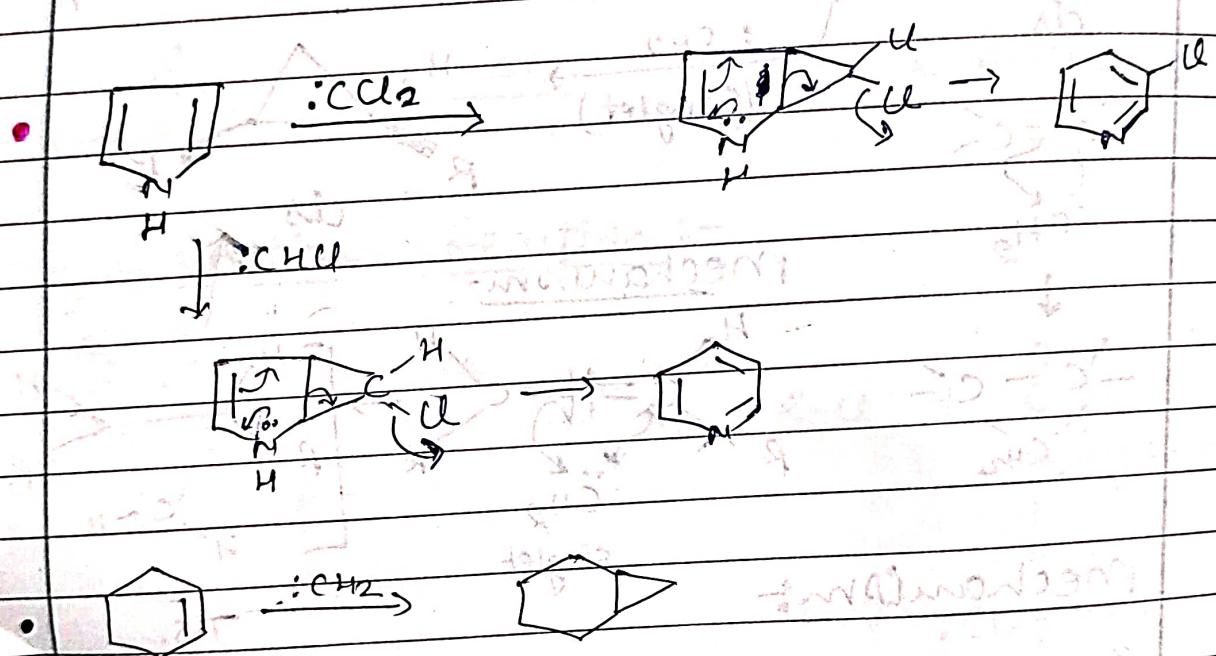


## Mechanism :-

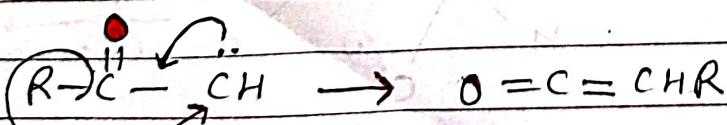




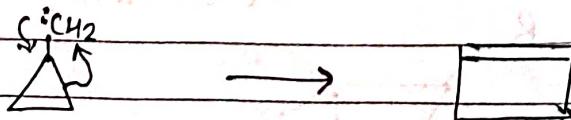
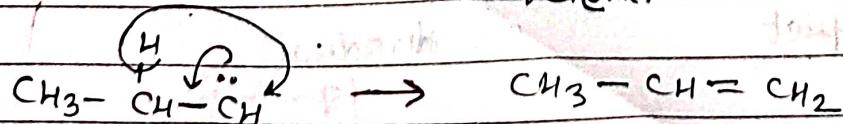
- Singlet carbene show stereospecific.
- Addition of T.C. is stereoselective.



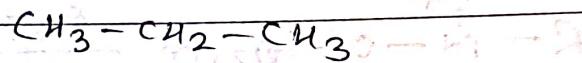
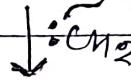
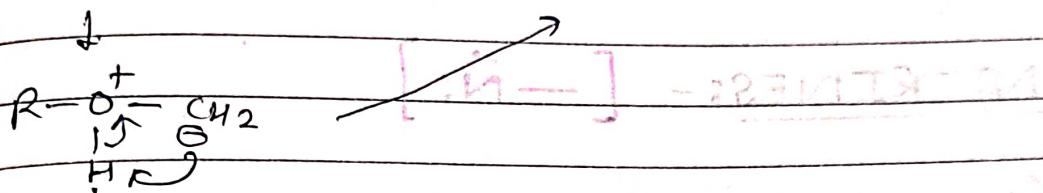
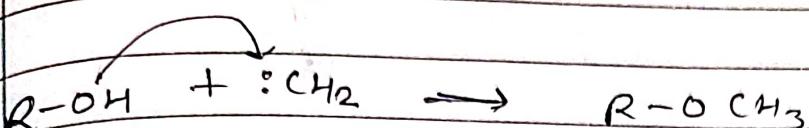
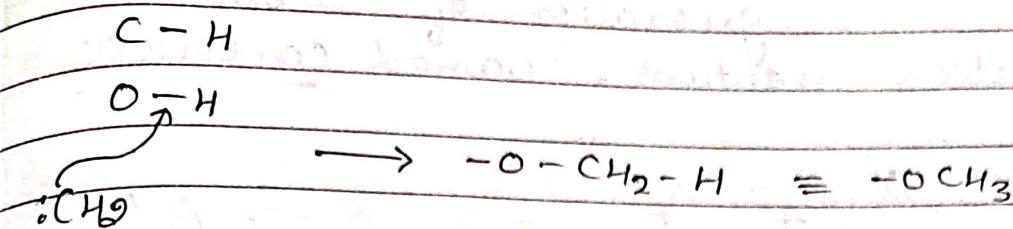
## 2- Rearrangement :-



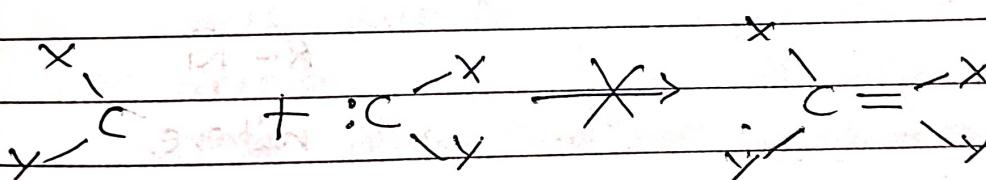
Ketene.



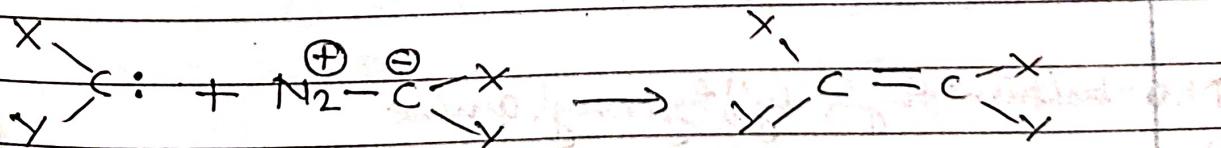
## Insertion Reaction :-



## Dimerization :-

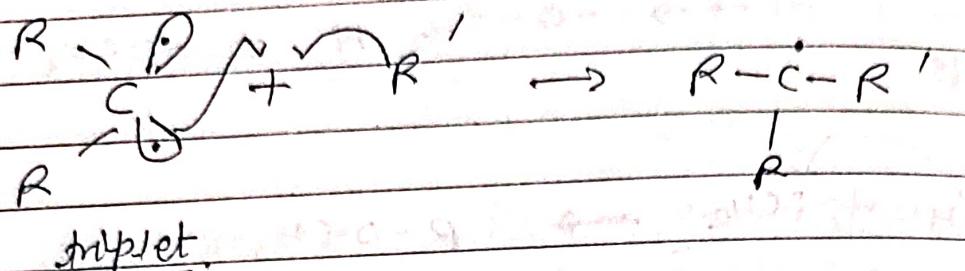


"highly reactive species"



Carbene  
precursor.

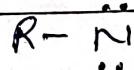
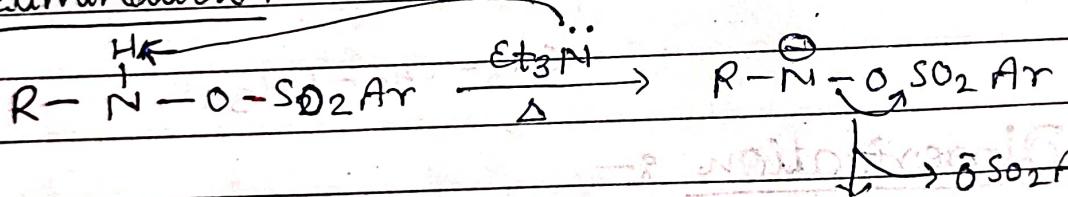
Carbenoid:- If there is any doubt about generation of carbene in the reaction mixture, named carbenoid.



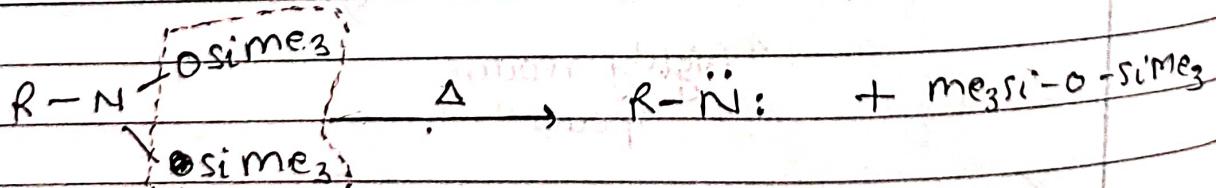
### NITRINES:- $[-\ddot{\text{N}}:]$

- ✓ It is analogues of carbene.
- ✓ Neutral monovalent, having sextet of e<sup>-</sup>.
- Methods of generation:-

#### ① Elimination:-

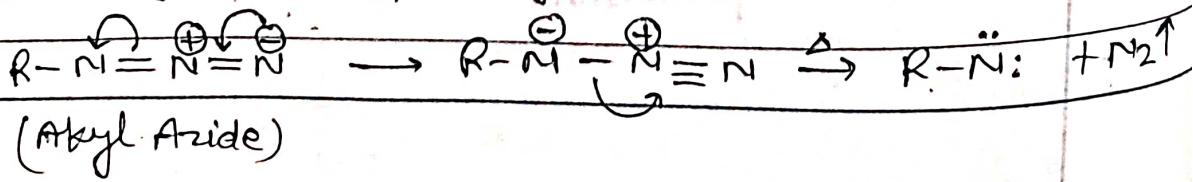


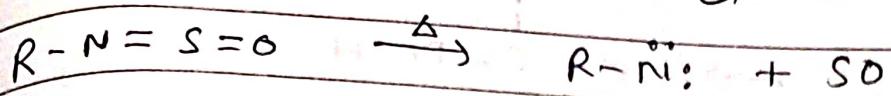
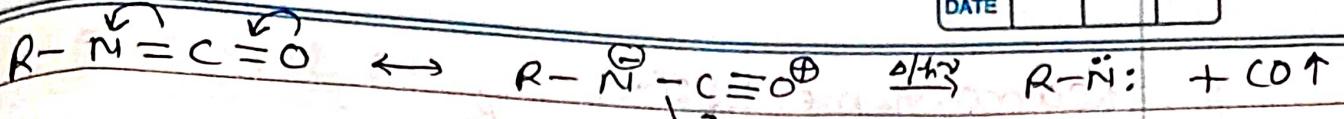
nitrone.



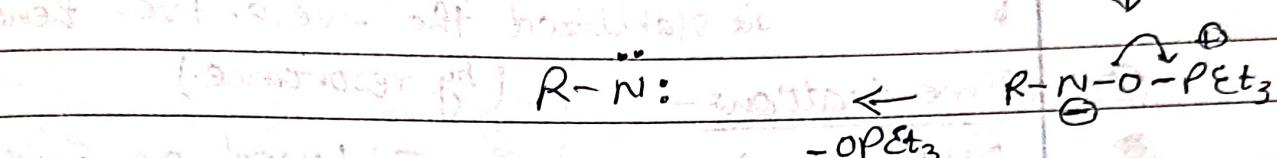
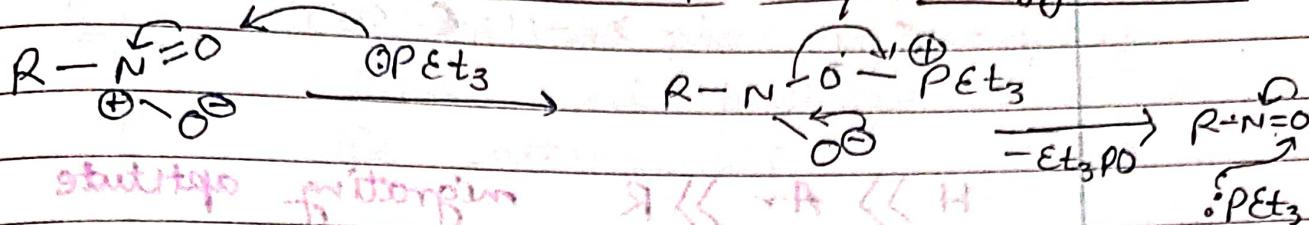
$\text{N},\text{O}$ -bis(trimethylsilyl)hydronium amine.

#### ② Heterolysis or photolysis:-

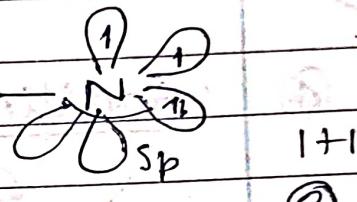
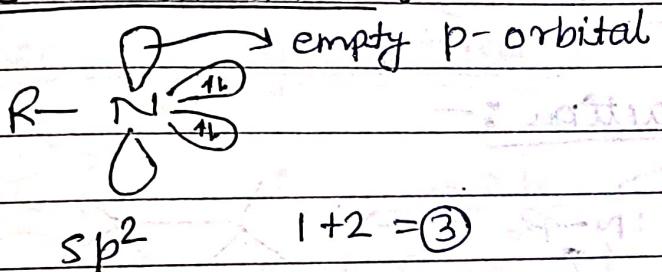




From nitroso & Nitro compound / Deoxygenation :-



Shape & Structure of Nitrene



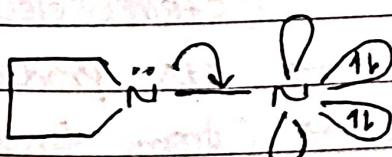
"singlet"

less stable due to

interelectro. if obeys Hund's rule of

repulsion (don't follow Hund's rule). maximum multiplicity.

more stable,

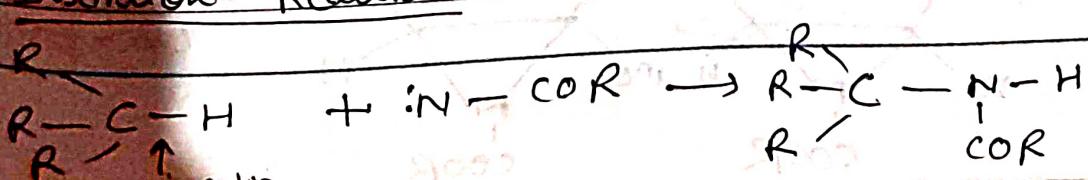


(singlet nitrene)



Reactions of Nitrene :-

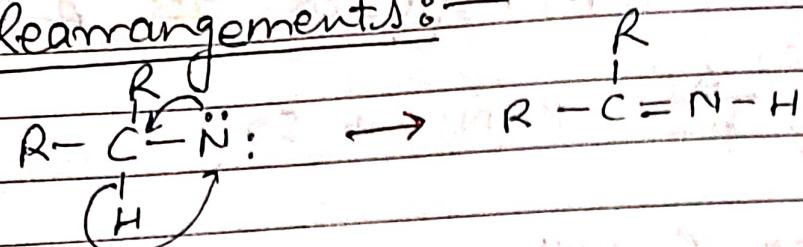
Inception Reaction - (C-H insertion) -



PAGE No. \_\_\_\_\_  
DATE \_\_\_\_\_

DCM =  $\text{CH}_2\text{Cl}_2$  (dichloro methane)  
DBM =  $\text{CH}_2\text{Br}_2$  (dibromo methane)

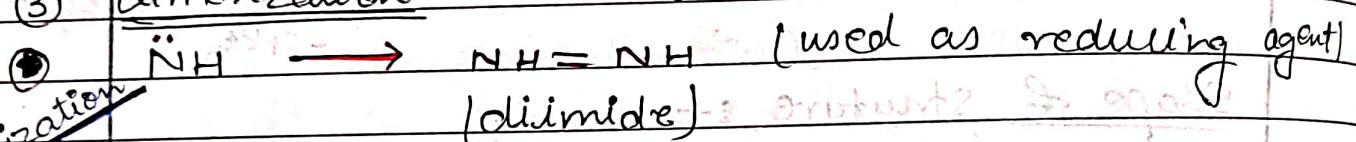
## 2- Rearrangements :-



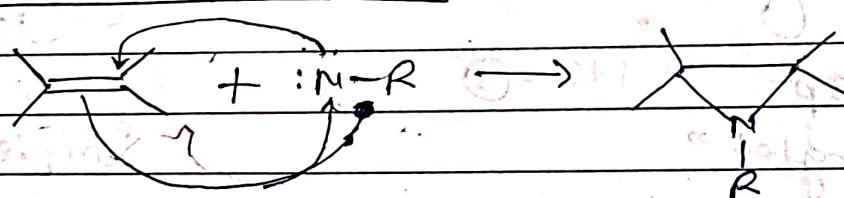
$\text{H} \gg \text{Ar} \gg \text{R}$  migrating aptitude

it stabilized the -ve or +ve hence  $\text{Ar} > \text{R}$ .

### ③ Dimerization :- (by resonance.)



### ④ Addition Reaction :-



cis-alkene + triplet nitrene  $\rightarrow$  cis + trans.

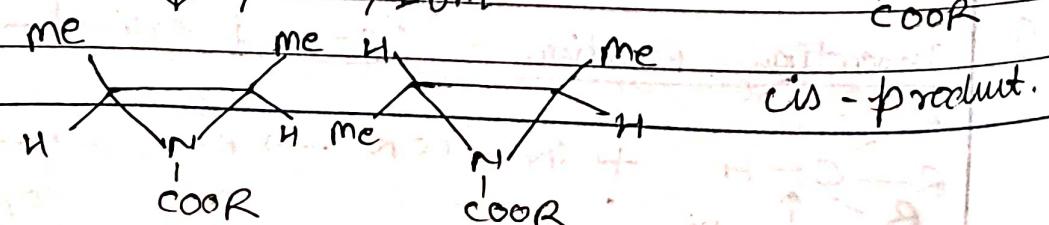
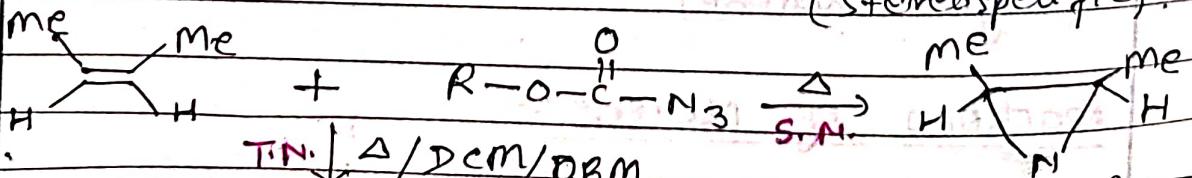
trans-alkene + triplet nitrene  $\rightarrow$  cis + trans.

(stereoselective).

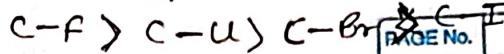
cis-alkene + singlet nitrene  $\rightarrow$  cis product

trans-alkene + singlet nitrene  $\rightarrow$  trans product.

(stereospecific).



C-Br bond weak.

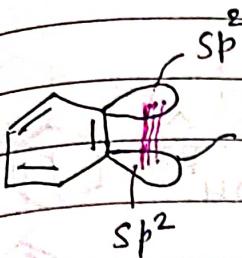


## BENZXNE :-



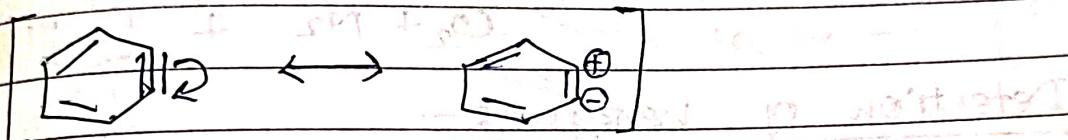
Dehydrobenzene (benzyne).

Aromatic

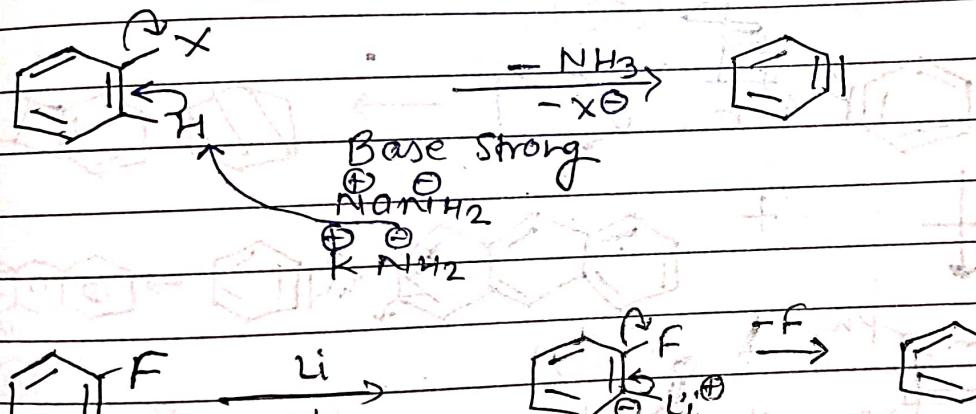


- lies in the plane of the ring.
- triple bond produced strain in the intermediate.

## Resonating structures :-



## Methods of generation :-



## From cyclic compound :-

