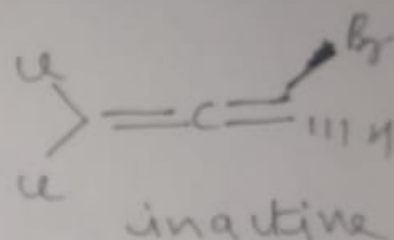
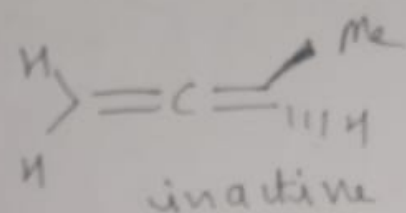
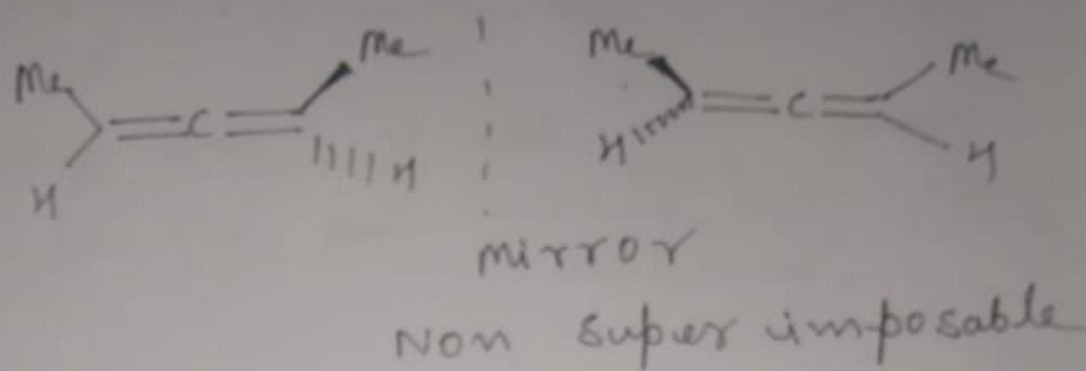
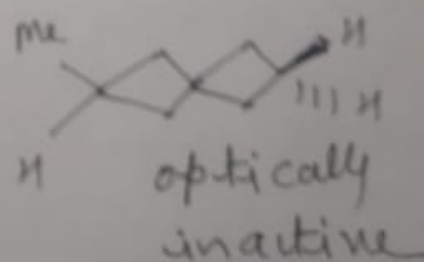
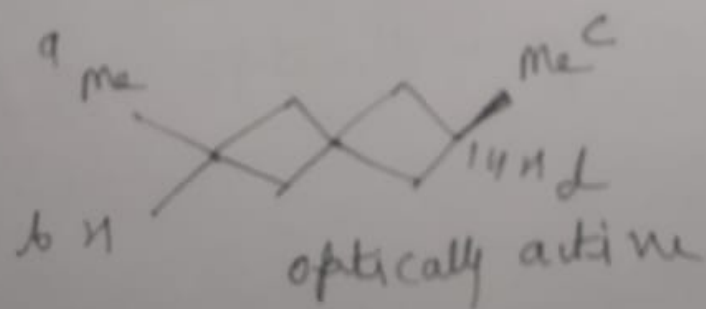


It is totally asymmetric molecule and it has  $C_1$  symmetry.



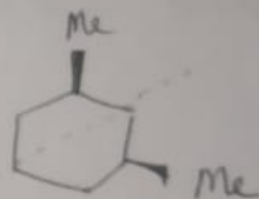
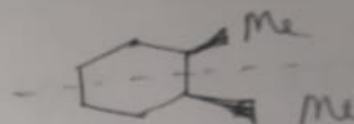
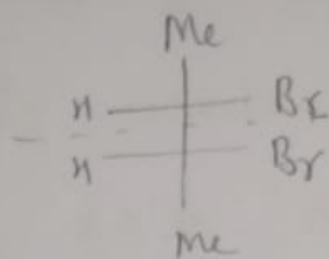
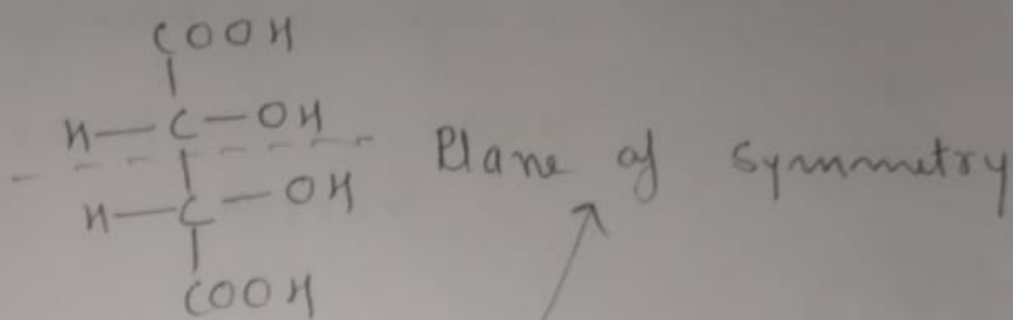
Optical isomerism in spiranes  $\rightarrow$

When two rings are fused with one carbon atom. They are called spiranes. Spiranes are optically active if they do not have  $a \neq b$  and  $c \neq d$ .

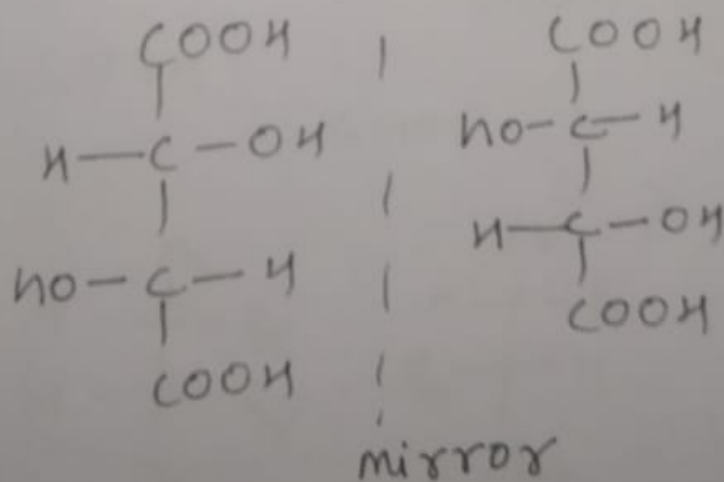




3) compound should not have a plane of symmetry.



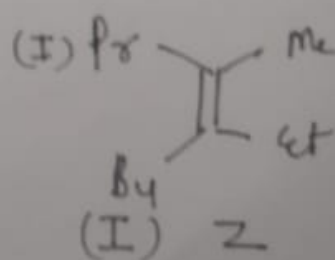
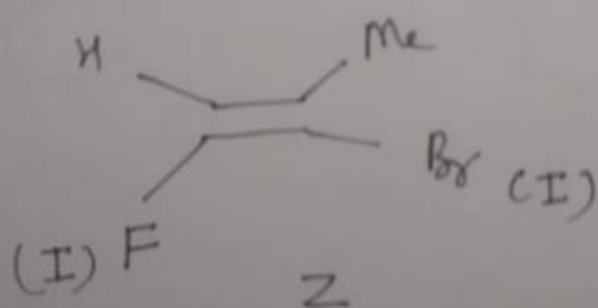
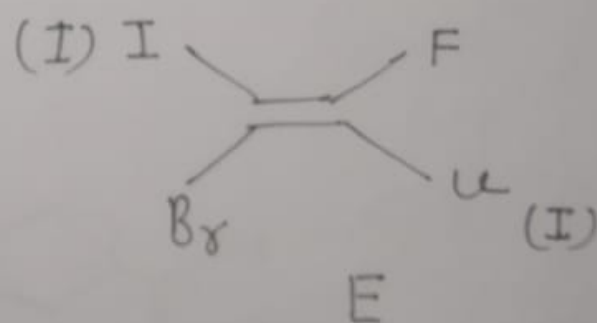
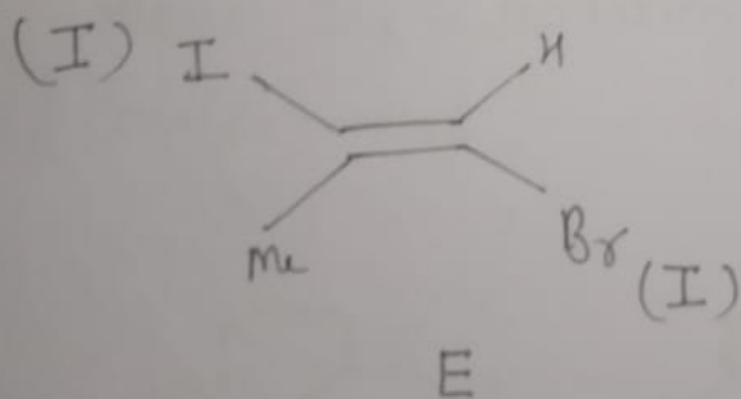
• Enantiomers  $\rightarrow$  Non super imposable mirror image ~~is~~ is called enantiomer.

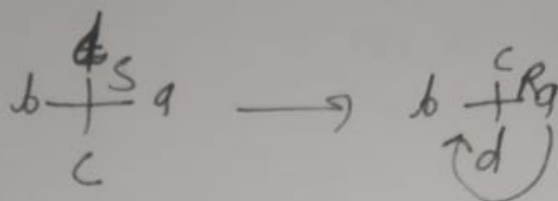
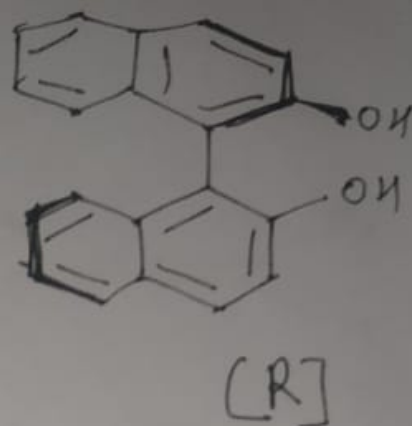
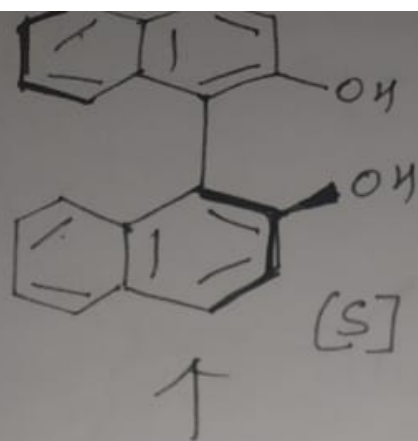


## E and Z configuration →

- when higher priority groups are on the same side. It is Z (Zusammen)
- when higher priority groups are on the opposite side. It is E (Entgegen)

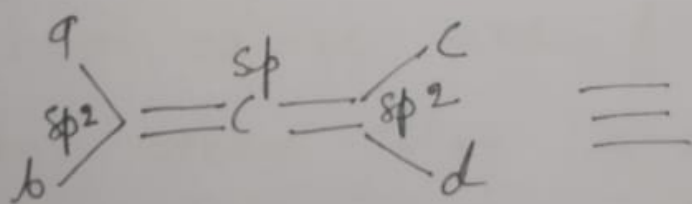
Note: Priority of the group should be according to R,S configuration



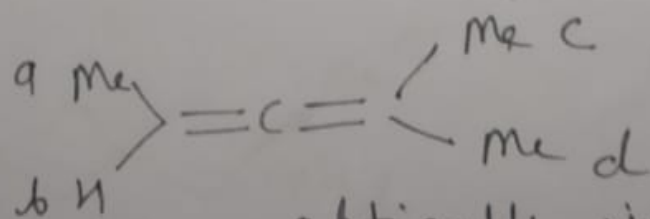


optical ~~anti~~ isomerism in Allenes  $\rightarrow$

Allenes show optical ~~anti~~ isomerism  
if  $a \neq b$  and  $c \neq d$

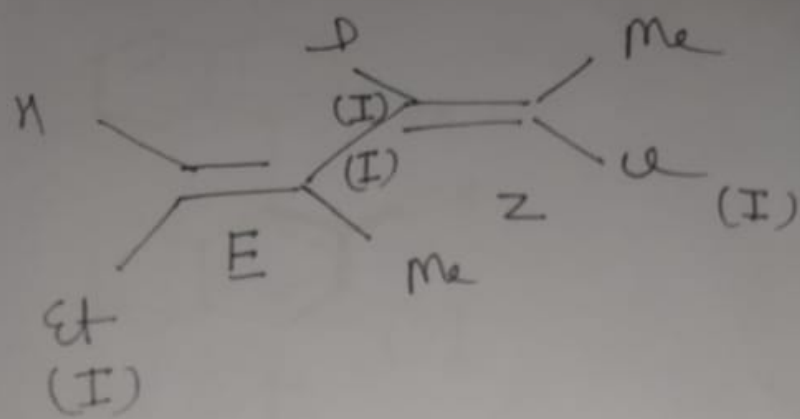


optical active

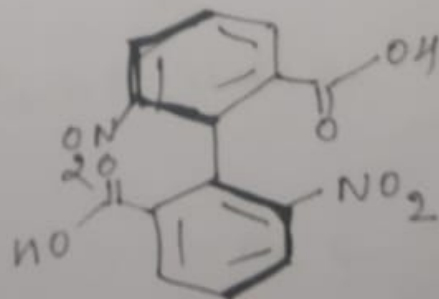
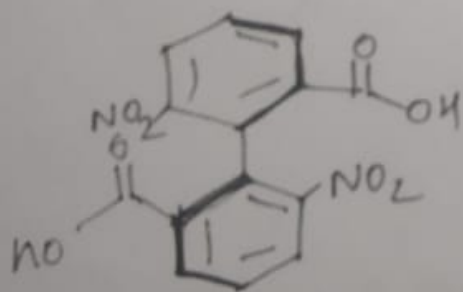


optically inactive

because  $c = d$



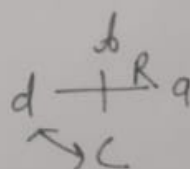
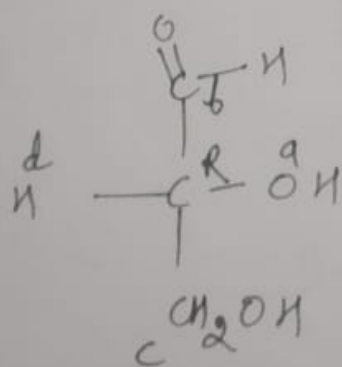
Atropisomerism  $\rightarrow$  Atropisomerism is arising from hindered rotation about a single bond, where energy differences due to steric strain or other contributors create a barrier to rotation that is high enough to allow for isolation of individual conformers.



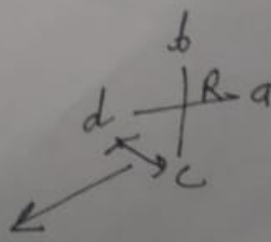
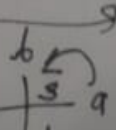
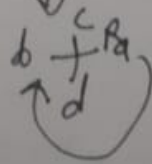
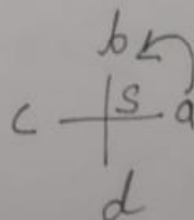
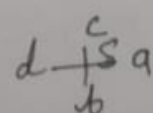
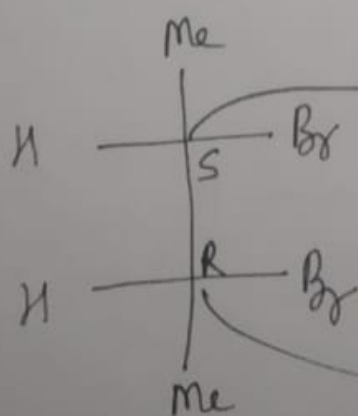


and S configuration or CIP rule  
(Cahn, Ingold and Prelog's rule) ÷

- 1) Select the priority of group according to atomic no or mass no.
- 2) The group of lowest priority should be away from observer.
- 3) observe the rotation from a to b
  - i) clock wise  $\rightarrow$  R (Rectus)
  - ii) Anticlock wise  $\rightarrow$  S (Sinister)

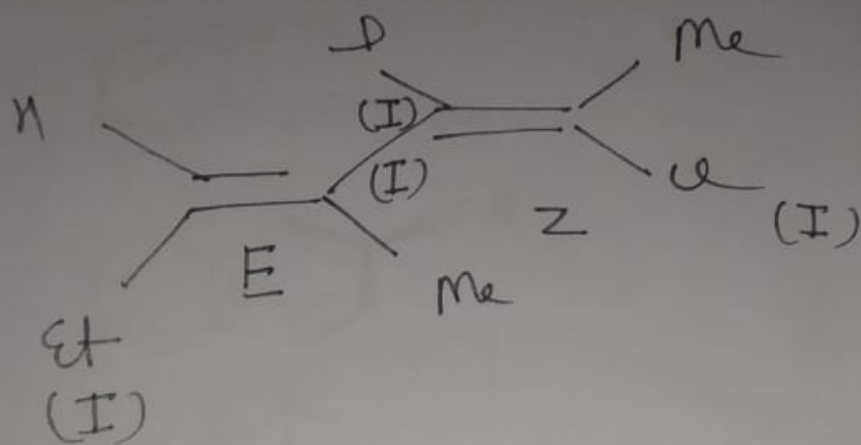


Inter change

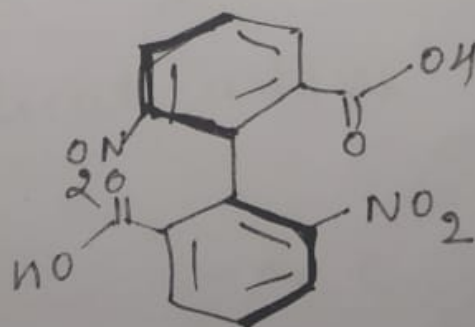
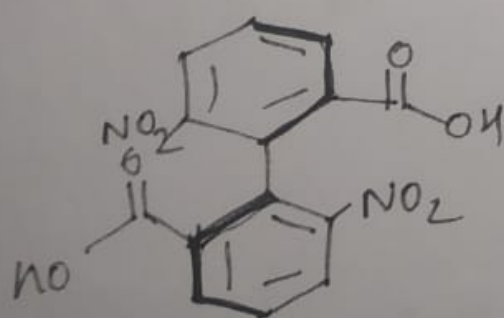


(23)

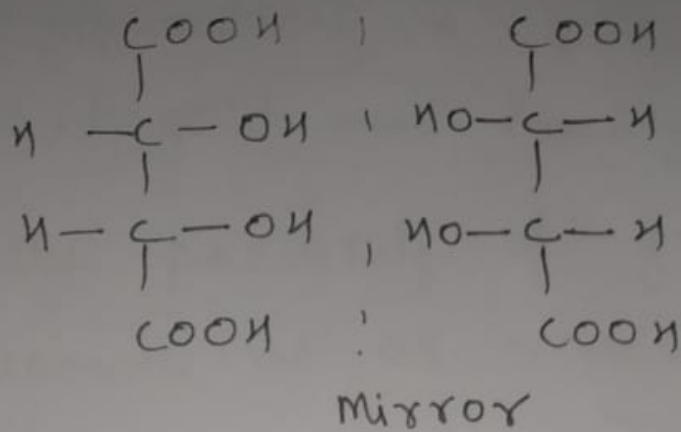
+



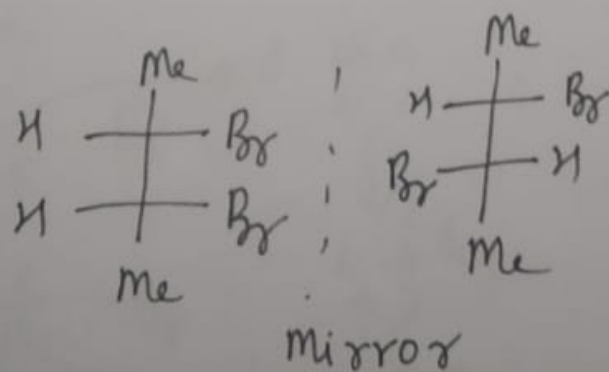
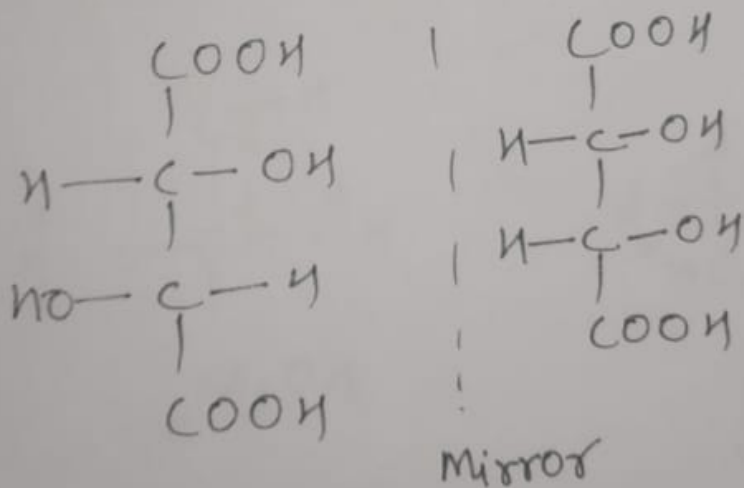
Atropisomerism  $\rightarrow$  Atropisomerism is arising from hindered rotation about a single bond, where energy difference due to steric strain or other contributors create a barrier to rotation that is high enough to allow for isolation of individual conformers

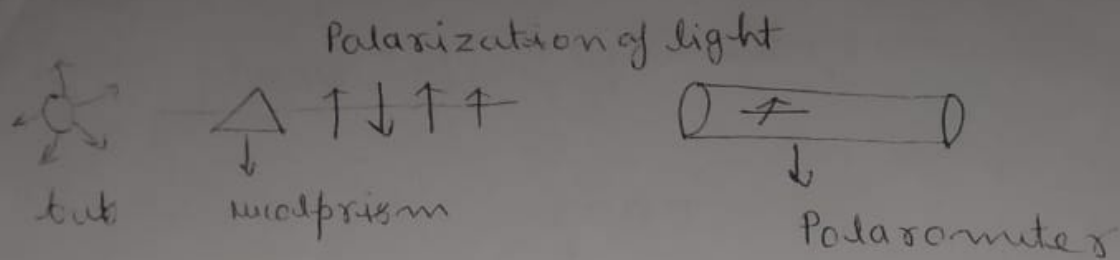






Diastereomers  $\rightarrow$  Non-superimposable compounds which are not mirror image of each other are called diastereomers.

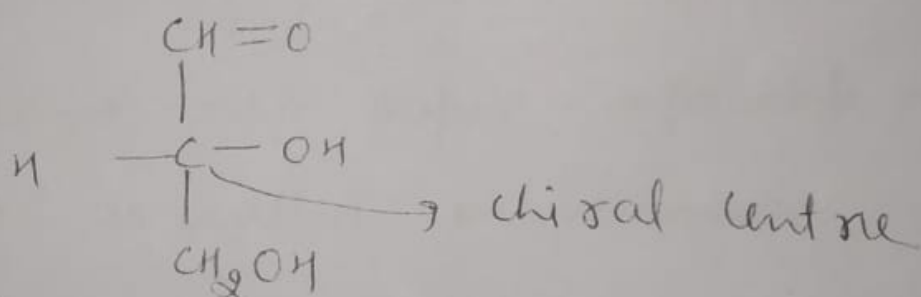




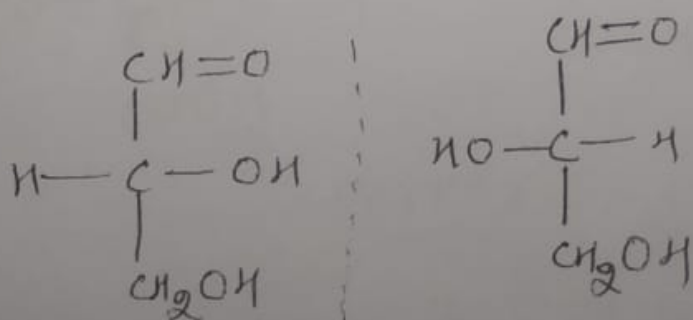
The compounds which rotates the plane of polarized light are called optical isomers and phenomenon is known as optical isomerism.

Criteria for optical activity  $\rightarrow$

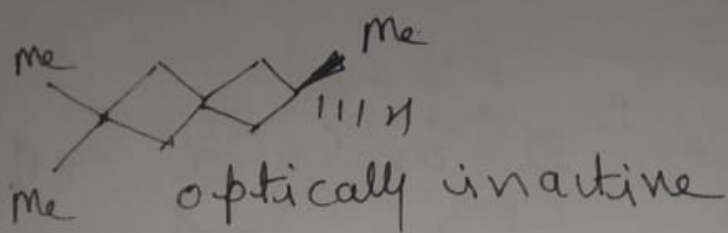
- 1) compound should have at least one chiral centre.



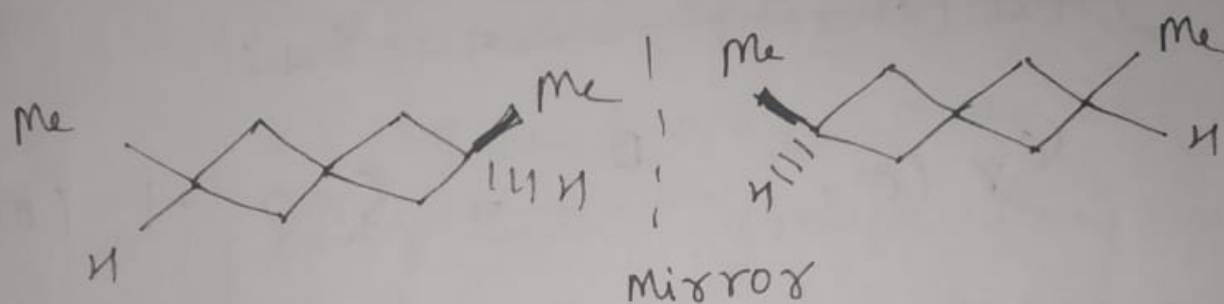
- 2) The mirror image of compound should not superimpose on it.



Cation

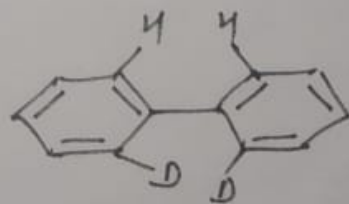
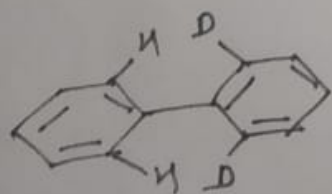


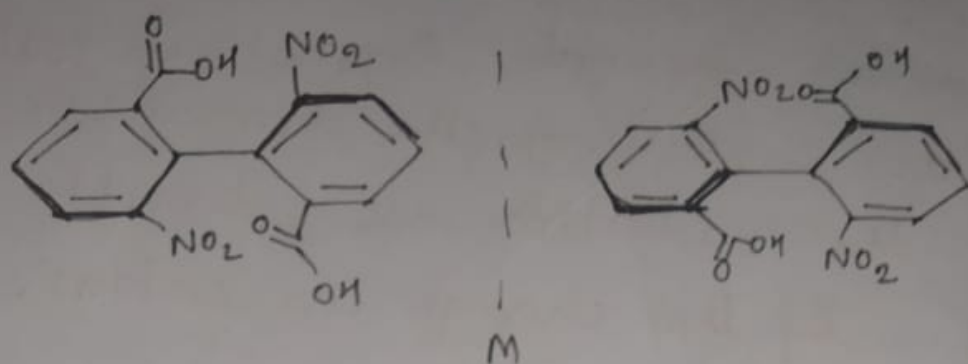
Spiranes are chiral and possess  $C_2$  symmetry. ~~They~~ They are asymmetric molecules.



Optical isomerism in biphenyl.

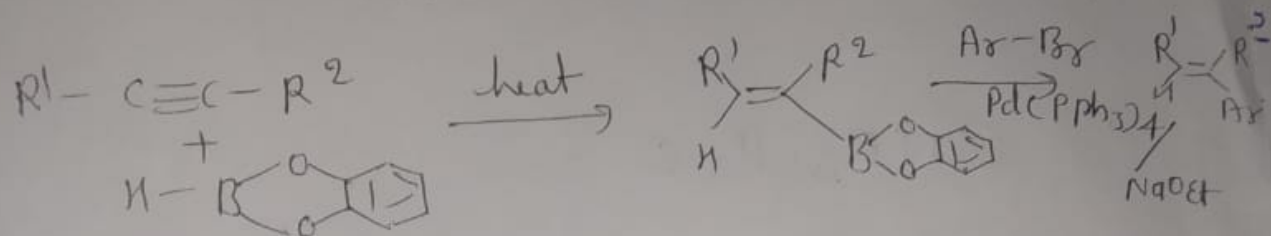
Optical isomerism ~~is a arises~~ in biphenyl arises from restricted rotation or hinderance.



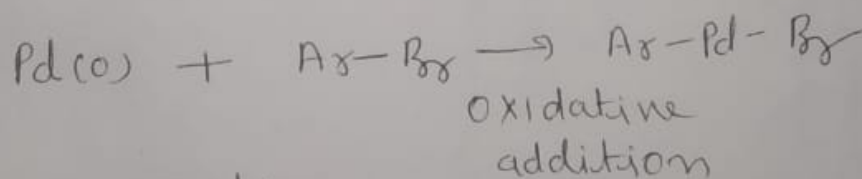
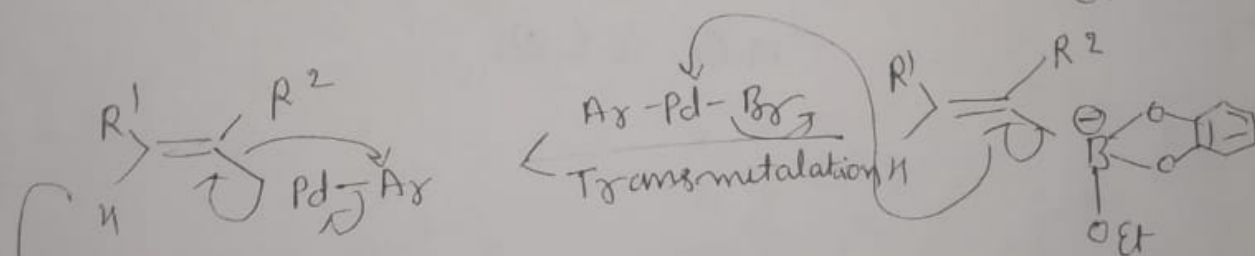
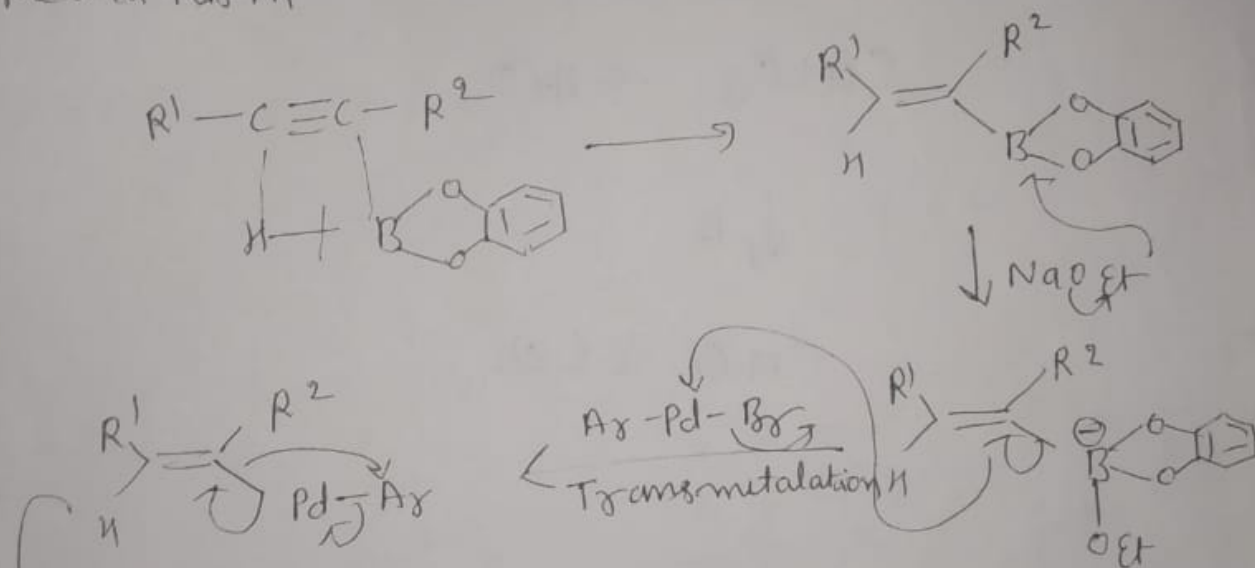


No free rotation is possible.  
 They are optically active.  
 -COOH and NO<sub>2</sub> are large  
 and bulky groups, they will  
 not allow free rotation of  
 two rings.

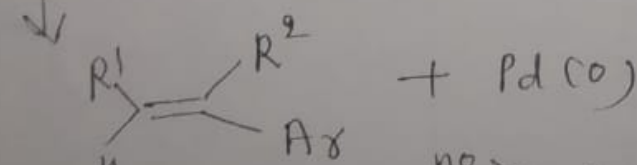
Suzuki Reaction  $\rightarrow$  Alkylation or arylation of alkynes with boronic ester and alkyl halide in presence of  $\text{Pd(0)}$  and  $\text{NaOEt}$  is known as Suzuki reaction



~~Mechanism~~ Mechanism  $\rightarrow$



Reductive elimination



Applications

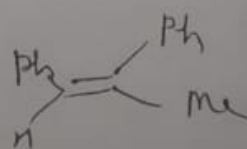
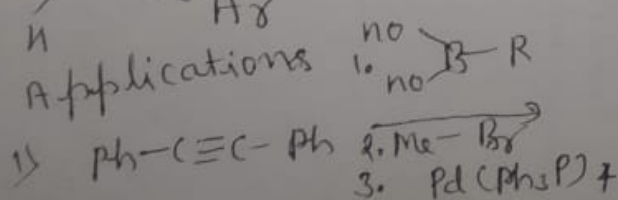
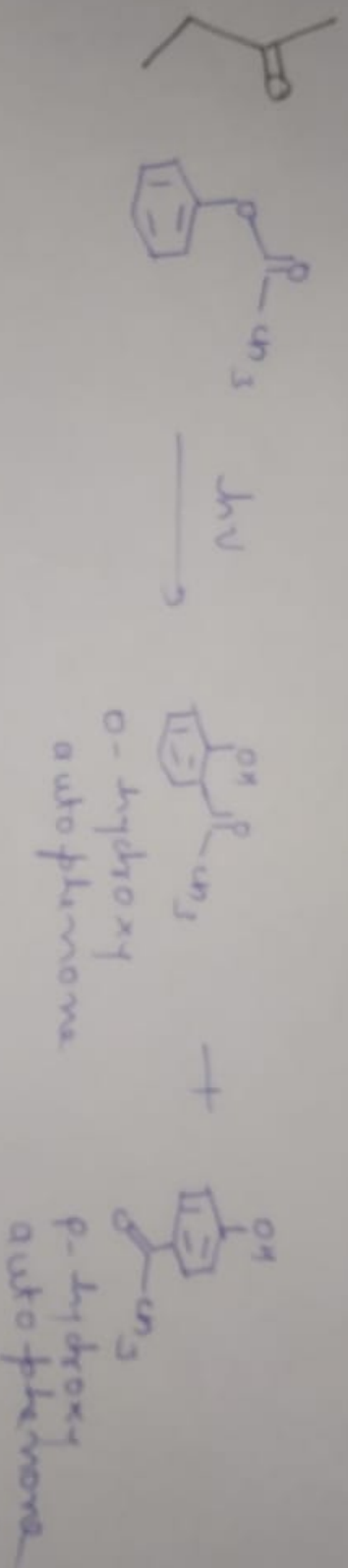
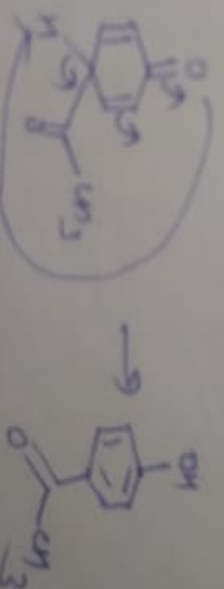
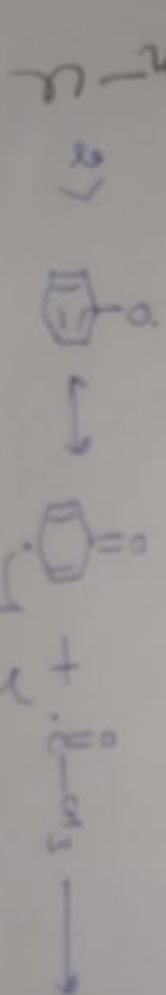
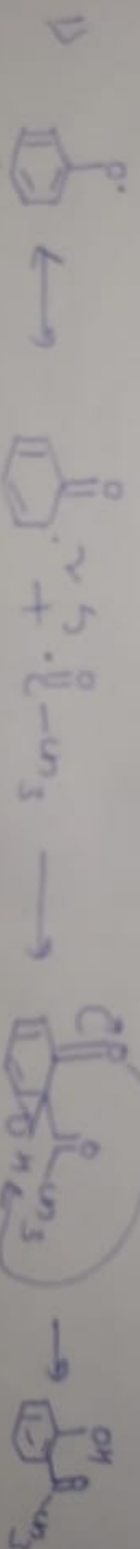
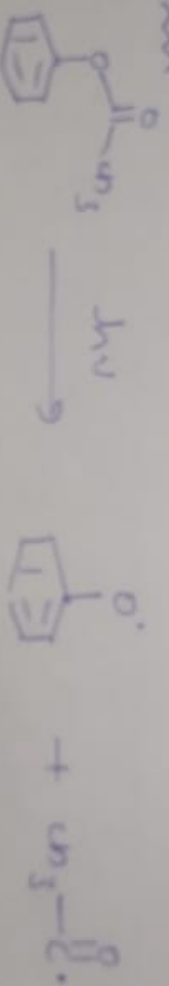




Photo Fries Rearrangement  $\rightarrow$  when Fries rearrangement takes place in presence of light, it is called photo Fries rearrangement.



Mechanism

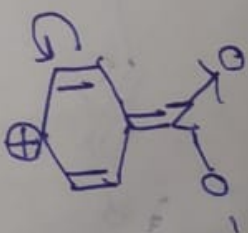
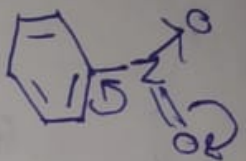


(31)

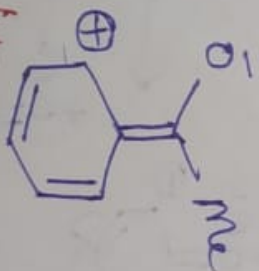
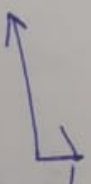
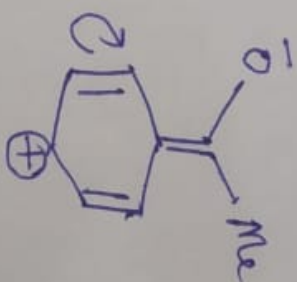
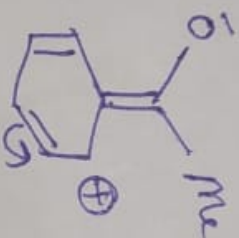
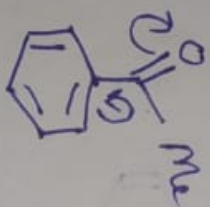
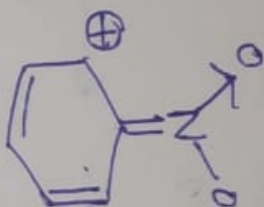
(32)



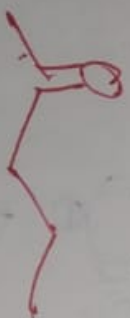
# Nitroene:



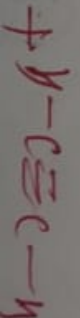
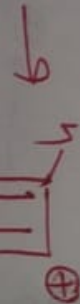
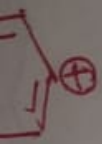
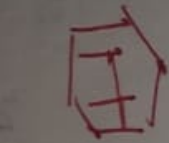
CH<sub>3</sub>-CH=CH-CH<sub>3</sub>

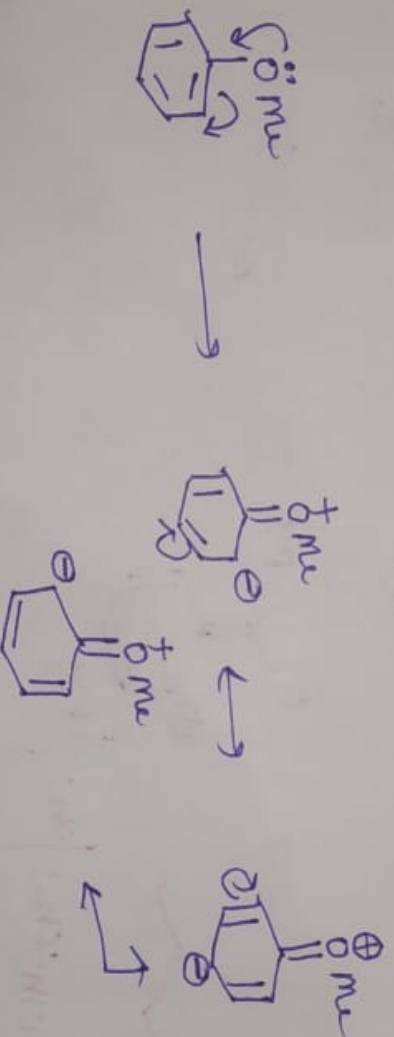
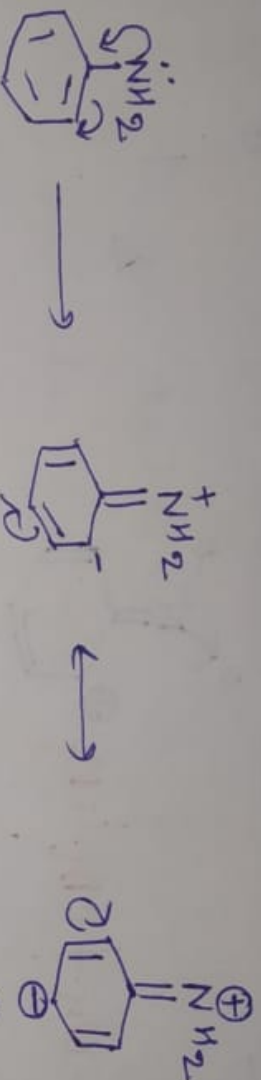
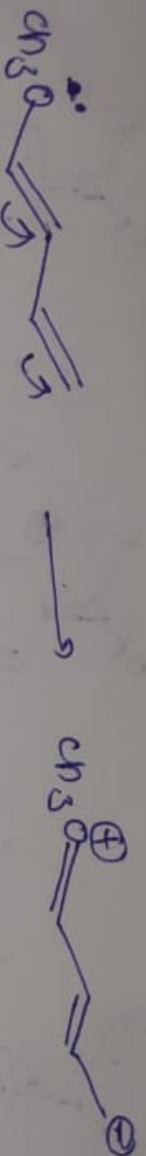


CH<sub>3</sub>-CH=CH-CH<sub>3</sub>

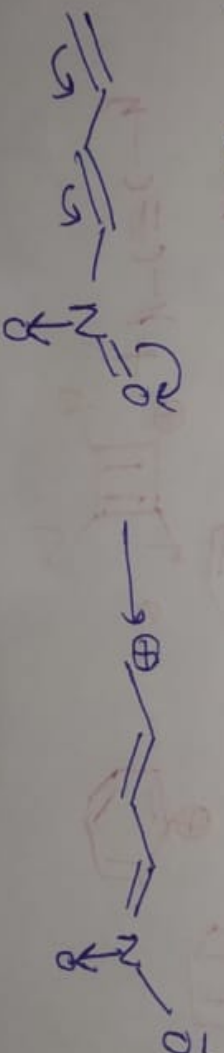


84  
7  
91



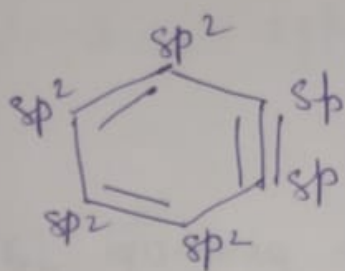


$M^-:$  when group attracts the lone pair of  $e^-$  from molecule. It is called  $m^-$  effect.



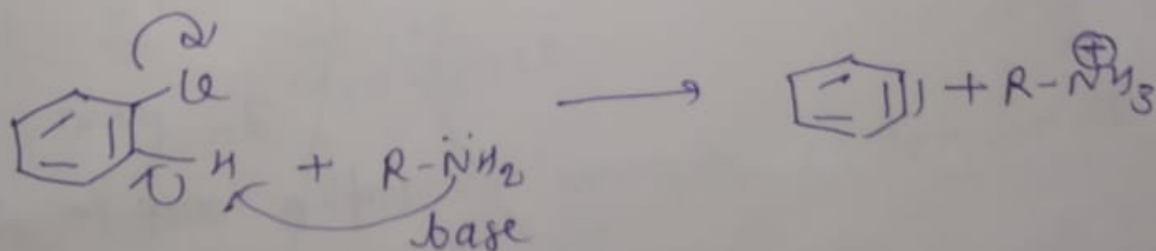


Benzynes: In benzyne, two carbons are in  $sp$  hybridization and other four are in  $sp^2$  hybridization

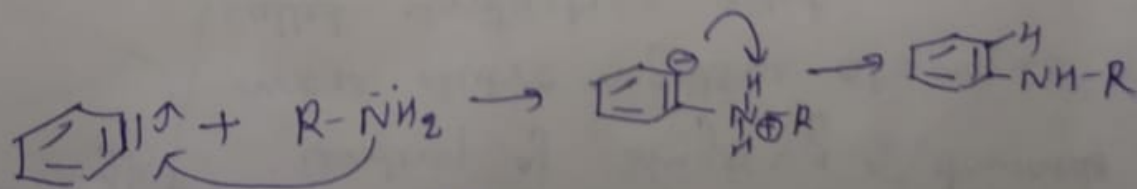


Formation of Benzyne:

The reaction of chlorobenzene with base to give benzyne.

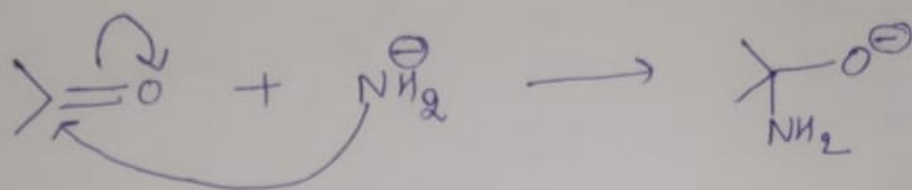


Reaction: Benzyne generally gives nucleophilic addition.





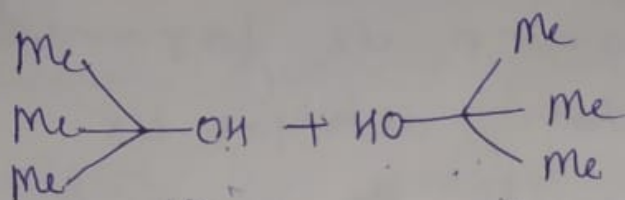
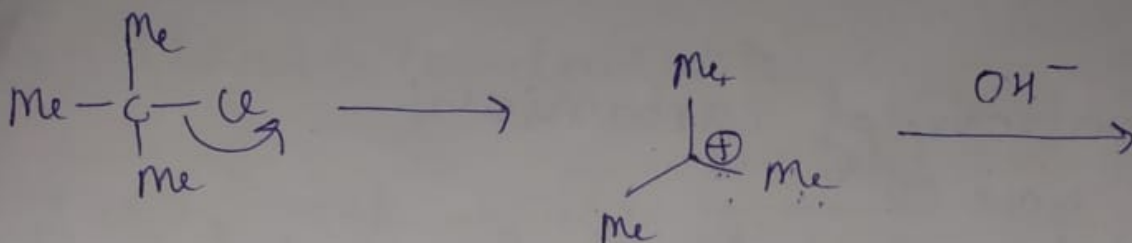
$E^- \rightarrow$  when attacking species are nucleophile. The  $e^-$  are transferred from nucleophile to substrate molecule. This type of effect is called  $E^-$  effect.



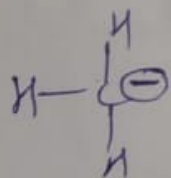
Mesomeric effect  $\rightarrow$  mesomeric effect is defined as the polarity produced in the molecule by interaction of two  $\pi$  bonds or between a  $\pi$  bond and lone pairs of  $e^-$  present on an adjacent atom.

It is of two types  
 $m^+$  and  $m^-$

1)  $m^+$ : when group or atom donate the  $e^-$  pair to the conjugated system. It is called  $m^+$



Carbanions: carbon species containing ~~not~~ negative charge are called carbanions. The carbanions are intermediates and have  $8e^-$  in the octet.



K.L  
2.5

$1s^2 2s^2 2p^3$

$2s^2$

$2p^3$

$\boxed{\uparrow\downarrow}$

$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

shape

G.S

$2s^2$

$2p^3$

$\boxed{\uparrow\downarrow}$

$\boxed{\uparrow\times}\boxed{\uparrow\times}\boxed{\uparrow\times}$   
H H H

E.S

↓

$\boxed{\uparrow\downarrow}\boxed{\uparrow\times}\boxed{\uparrow\times}\boxed{\uparrow\times}$   
H H H



$C+3H$

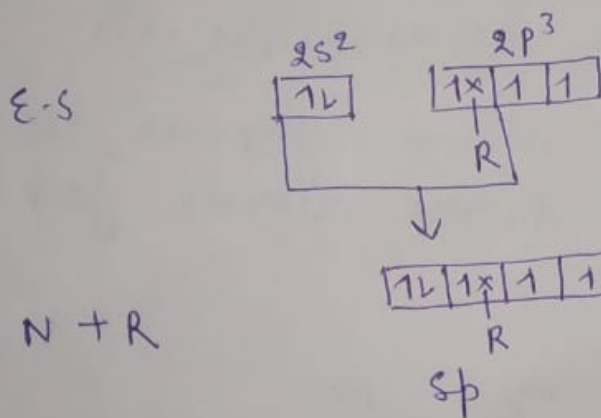
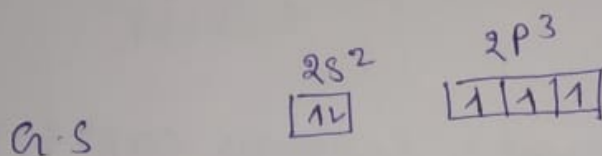
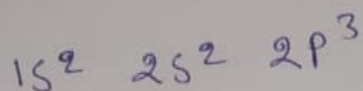
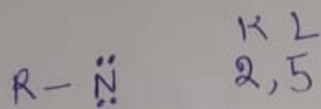
$sp^3$

Pyramidal shape

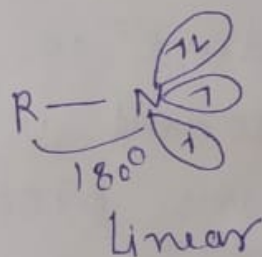
(4)



Nitrene: Nitrenes are intermediate and has six  $e^-$  in orbit.

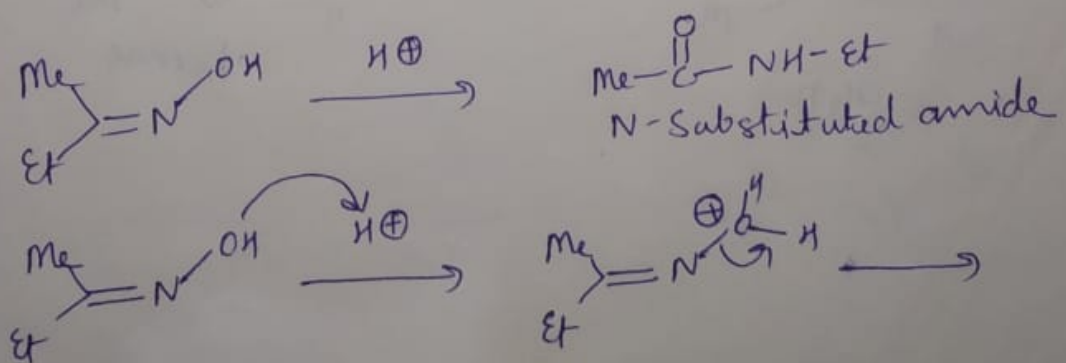


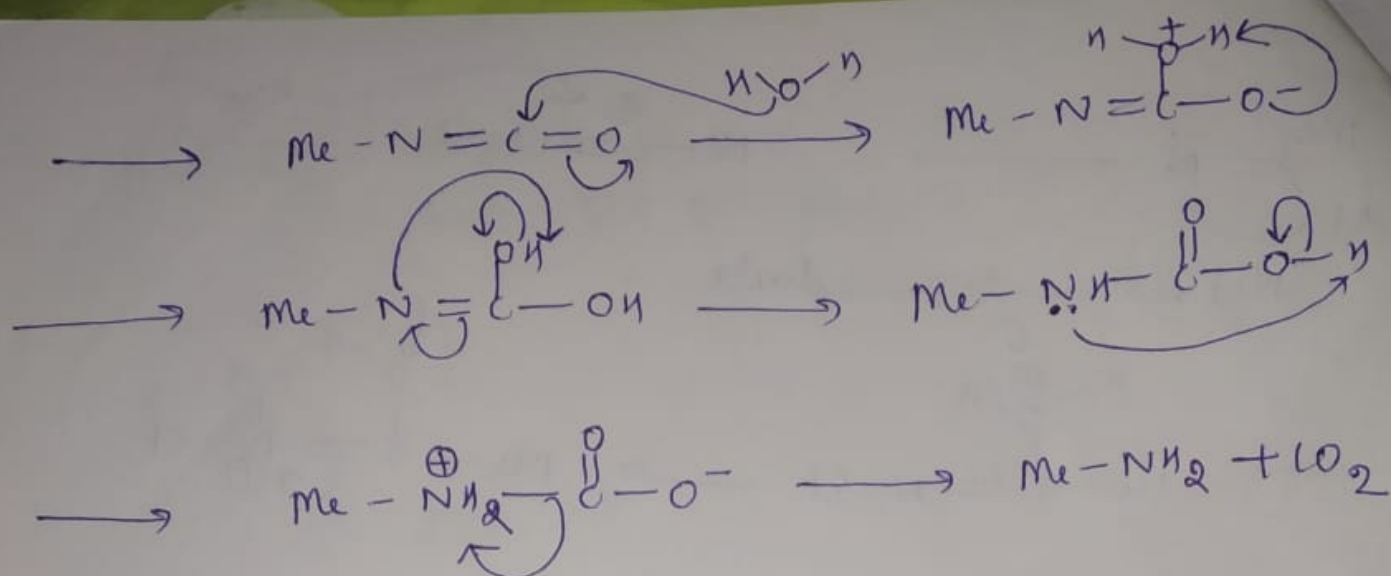
shape



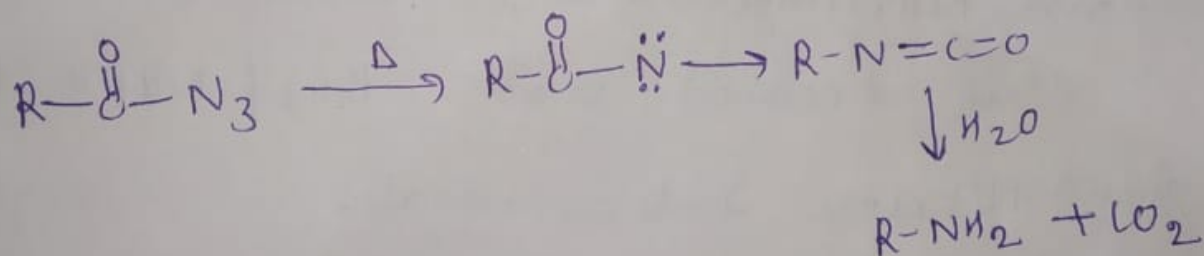
Formation of Nitrene:

Beckmann Rearrangement: Nitrene is formed when keto oxime is treated with acid.

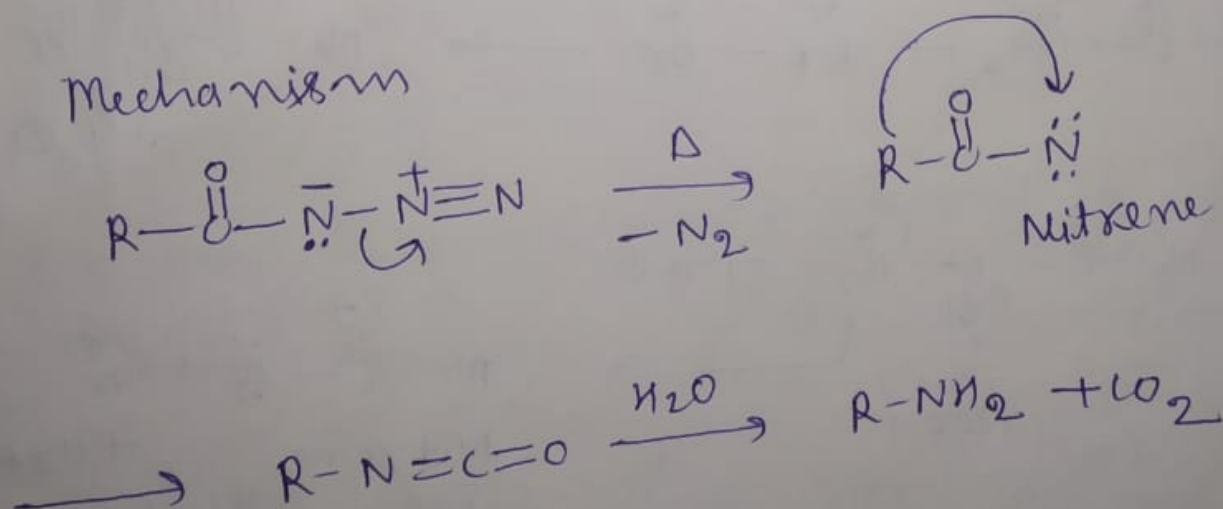




Curtius Rearrangement: Acid azide on heating to give nitrene.

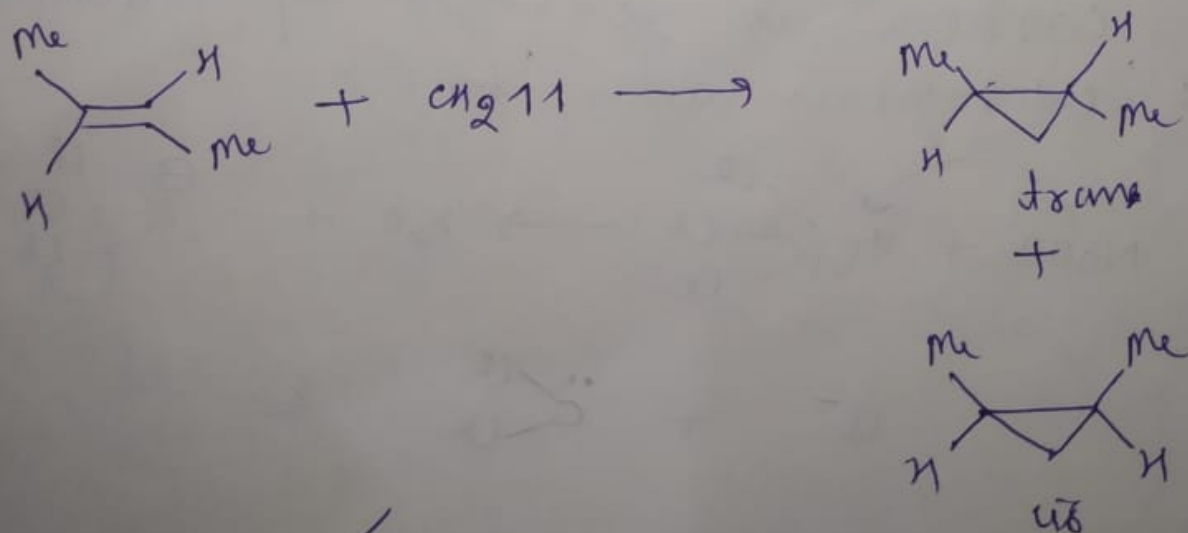
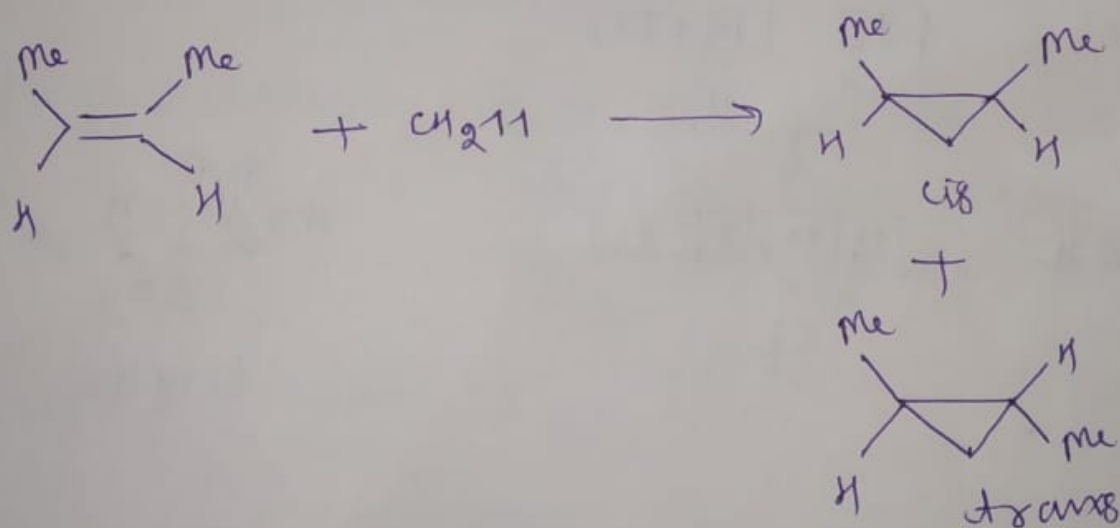


Mechanism



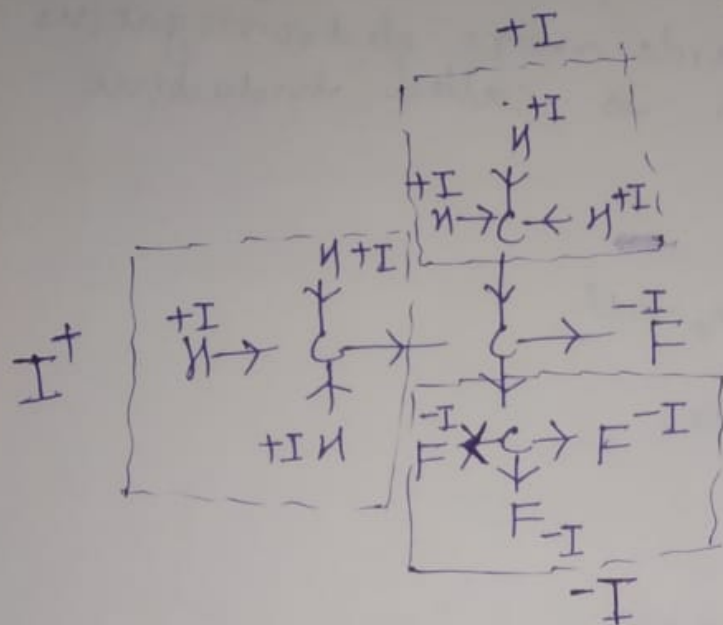
2) Triplet carbene: It is non stereo specific in nature.

cis or trans, both alkene give a mixture of cis and trans product.



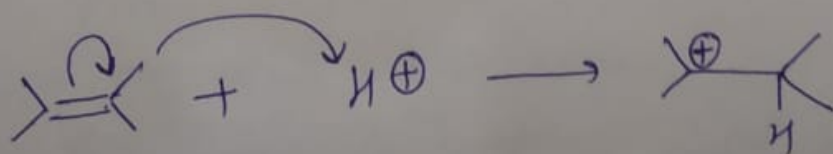


example of  $I^+$  and  $I^-$  effect



Electromeric effect: Separation of charge by attacking species is called electromeric effect. It is two types i.e.  $E^+$  and  $E^-$  respectively.

$E^+$   $\rightarrow$  Transfer of  $e^-$  toward positively charged species and attacking species are electrophile. It is called  $E^+$

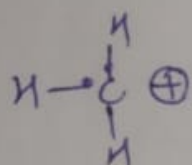


B.Tech. First year By B.

Purusottamsingh Nixanjan

Carbocations: The carbon species containing positive charge, are called carbocations.

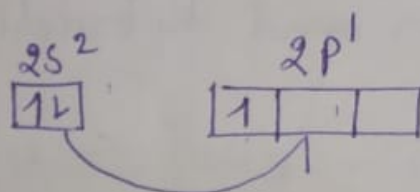
The carbocations are intermediates and have six electrons in the orbit.



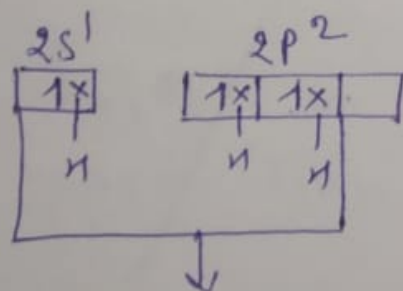
K 2  
2, 3

1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>1</sup>

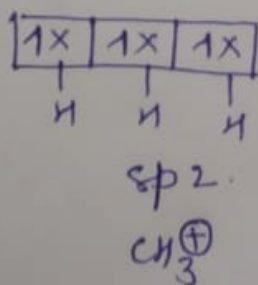
G.S



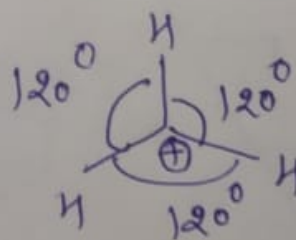
E.S



C + 3H



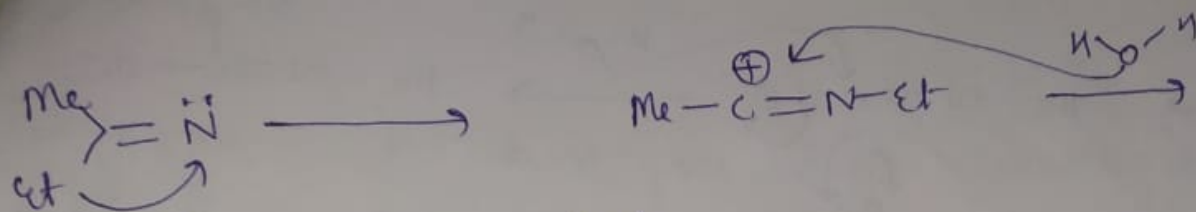
Shape



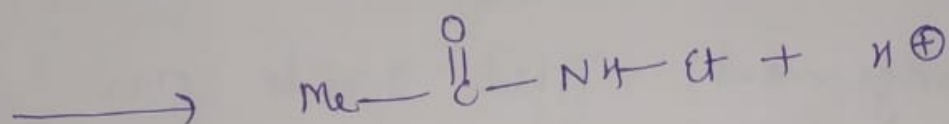
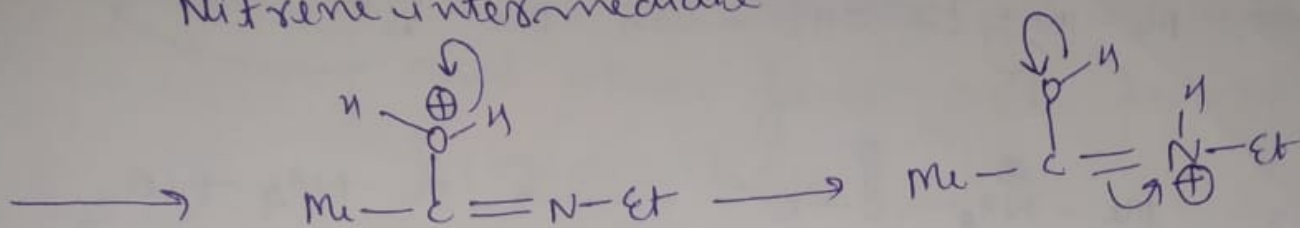
Trigonal planar

I 248

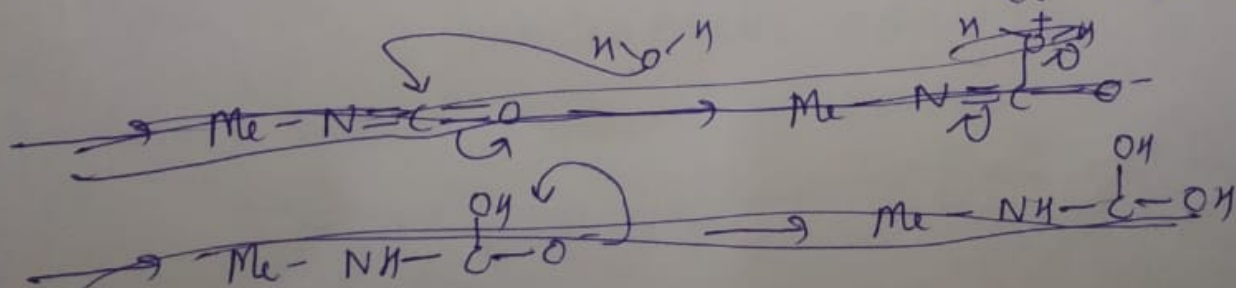
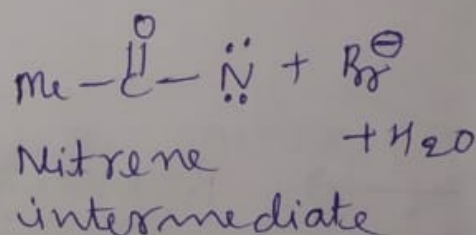
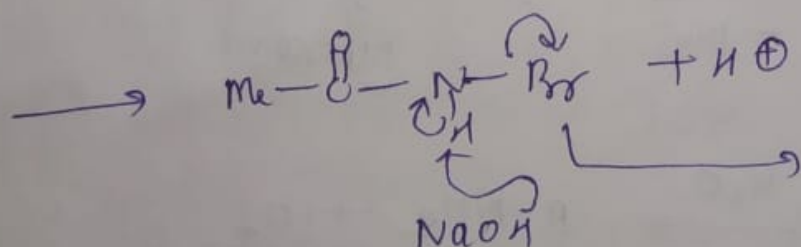
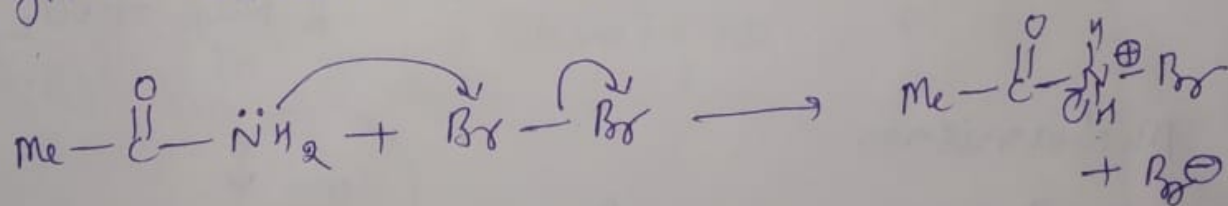
II. 209



Nitrene intermediate

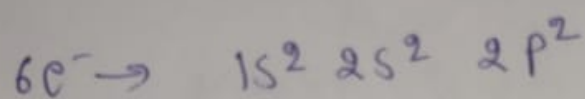
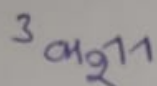


Hofmann Rearrangement: when an amide is treated with  $\text{Br}_2/\text{NaOH}$  to give Nitrene intermediate:

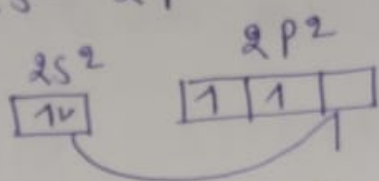




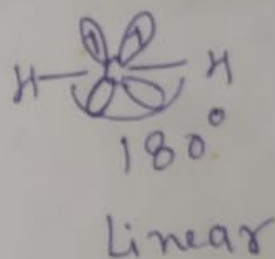
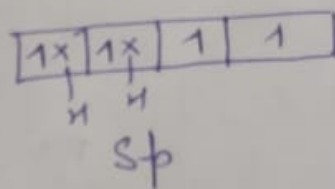
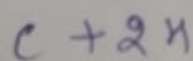
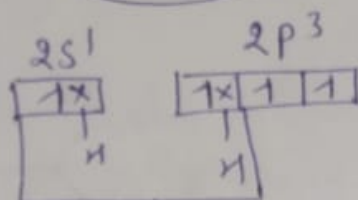
2) Triplet carbene: Both the  $e^-$  are in parallel spin and spin multiplicity is 3.



G.S

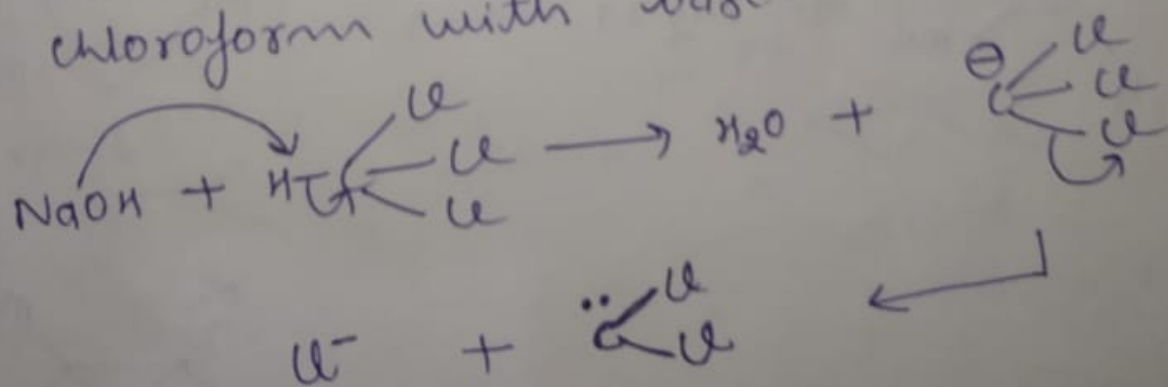


E.S

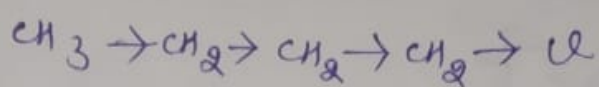


Formation of carbene:

1) carbene is formed by reaction of chloroform with base.



Inductive Effect: Tendency of shifting  $e^-$  towards more electronegative atom is called inductive effect.



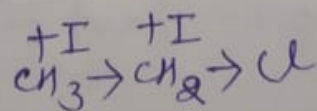
It is of two types

~~E<sup>+</sup> and~~

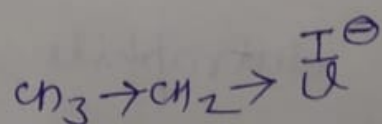
$I^+$  and  $I^-$

$I^+ \rightarrow$  ~~when a tendency of  $e^-$  is toward more electronegative~~

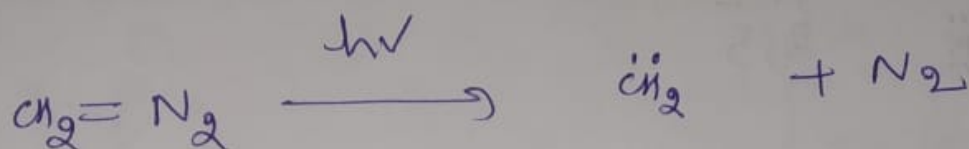
when atom push  $e^-$  toward more electronegative atom is called  $I^+$



$I^- \rightarrow$  when atom attracts  $e^-$  toward it. It is called  $I^-$



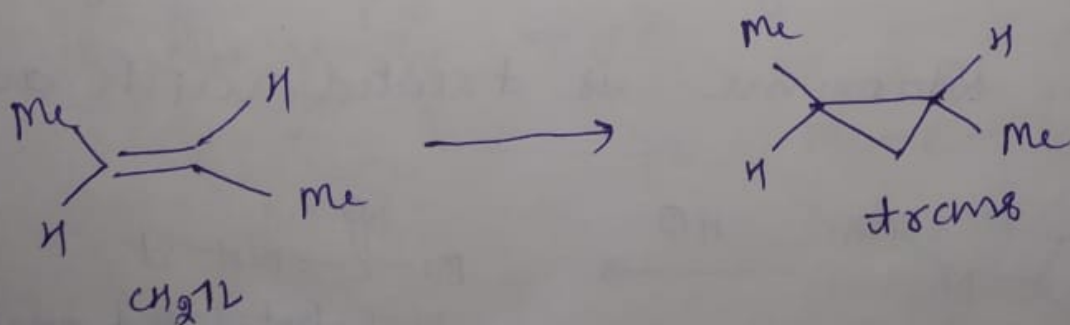
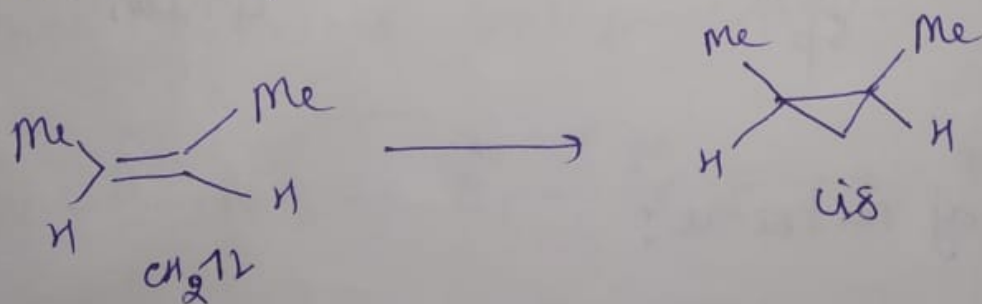
2) carbene is formed when diazo methane is irradiated with light



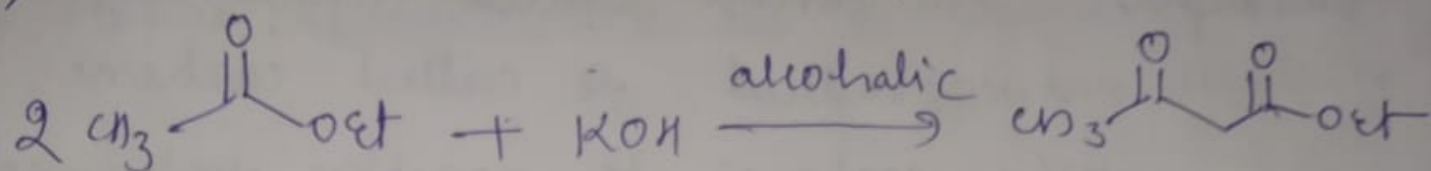
Reaction of carbene:

1) Singlet carbene: Singlet ~~carbene~~ carbene is stereospecific in

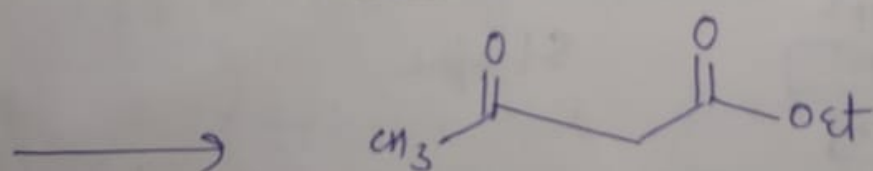
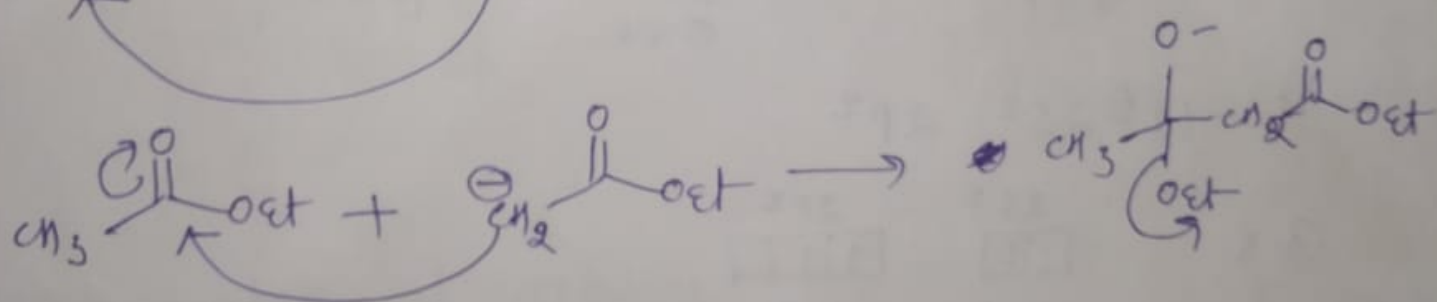
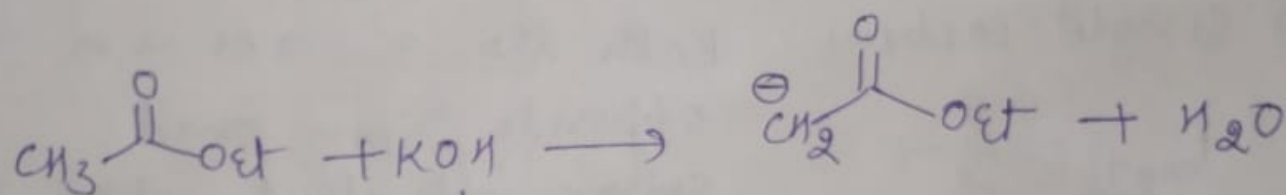
nature i.e. ~~cis~~ cis alkene forms cis product where as trans alkene forms trans product.



2) Claisen condensation:

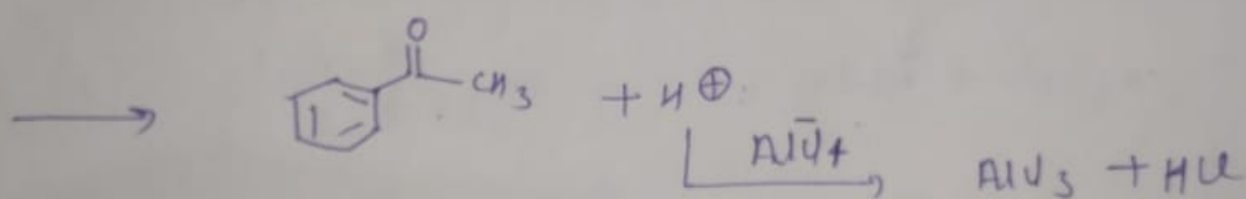
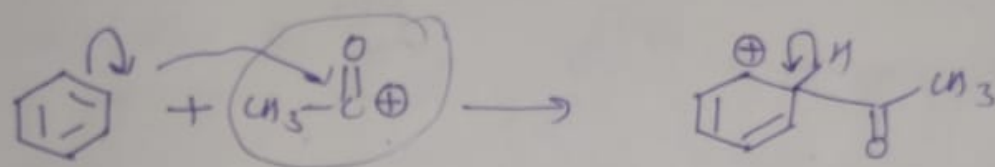
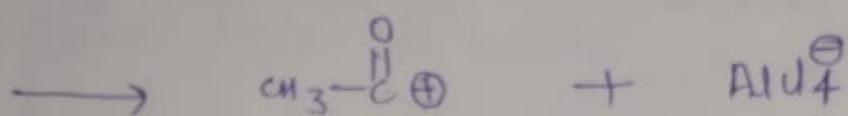
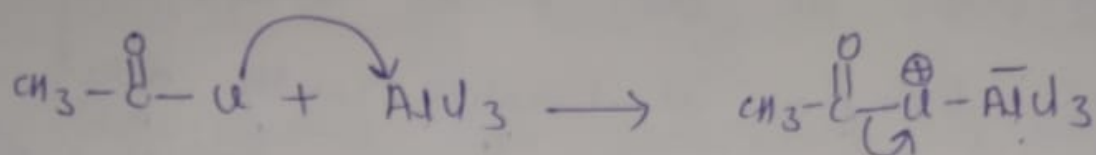
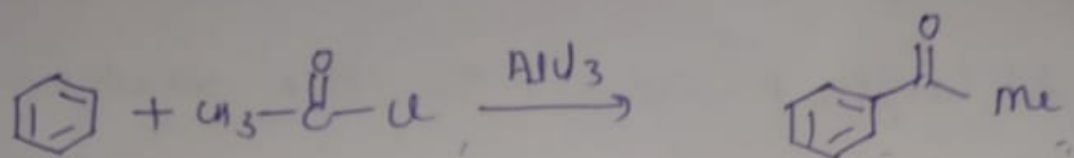


When two molecules of lower fatty esters are treated with strong base to give carbanion as a intermediate.

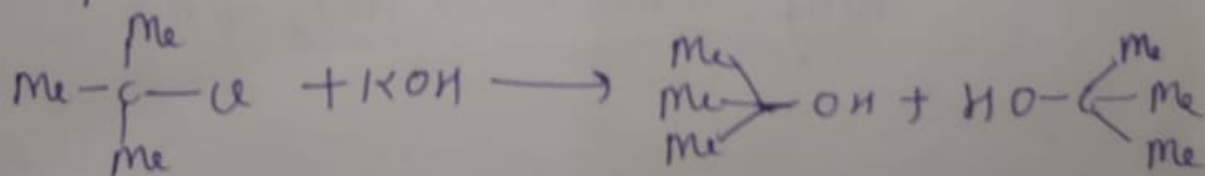




Acylation:

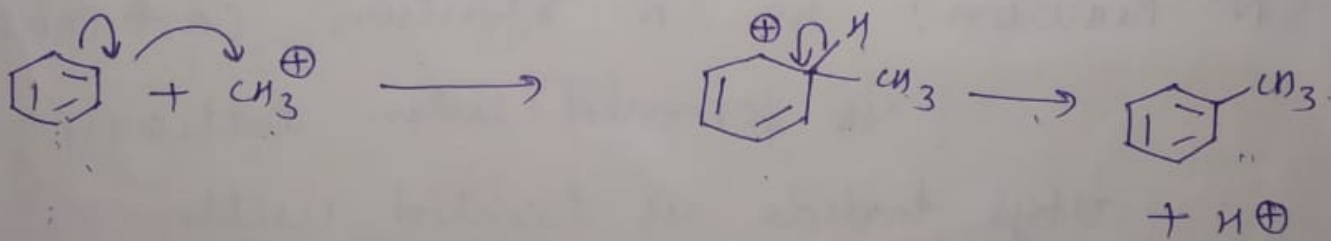
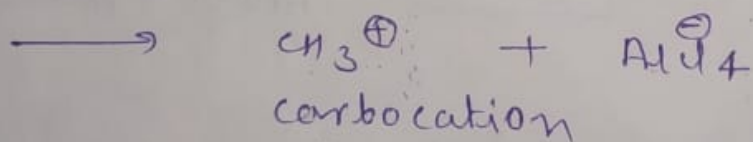
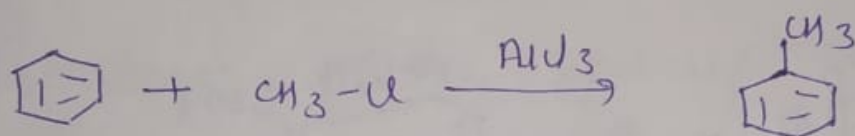


$\text{S}_\text{N}1$  Reaction: In  $\text{S}_\text{N}1$  reaction, carbocation is formed when tertiary alkyl halide is treated with aq. KOH



## Formation of carbocation:

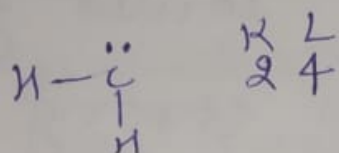
1) Friedel Craft Reaction: In this reaction, carbocation is formed as intermediate when benzene is treated with alkyl halide or aryl halide in presence of Lewis acid like  $AlCl_3$ .





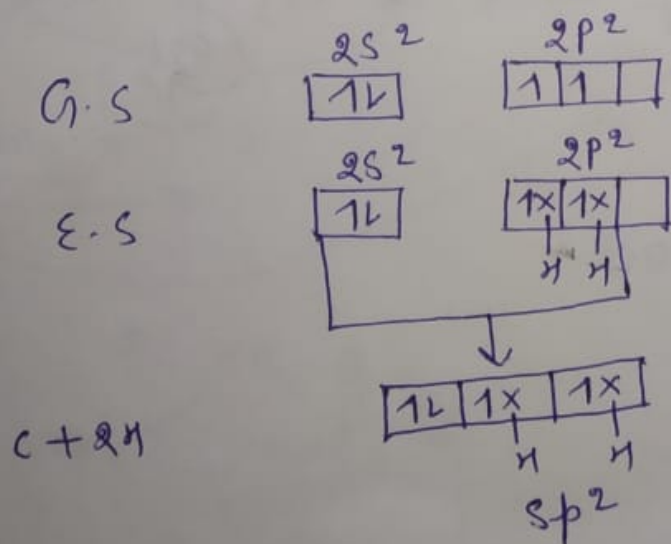
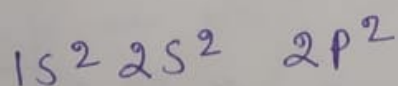
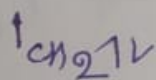
Carbene: The carbon species containing two radical is called carbene.

The carbene is reaction intermediate and has six  $e^-$  in octet.

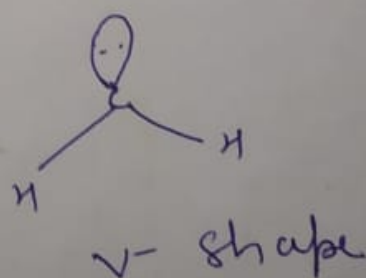


It is of two types.

- 1) Singlet carbene: Both the  $e^-$  are in opposite spin and spin multiplicity is one.



Shape



## Formation of carbanion!

1) Aldol condensation: In Aldol condensation, carbanion is formed as intermediate when aldehyde or ketone is treated with a strong base.

