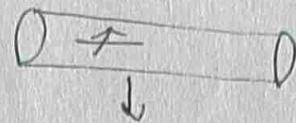


Optical Isomerism



Polarization of light
but
nudeprism



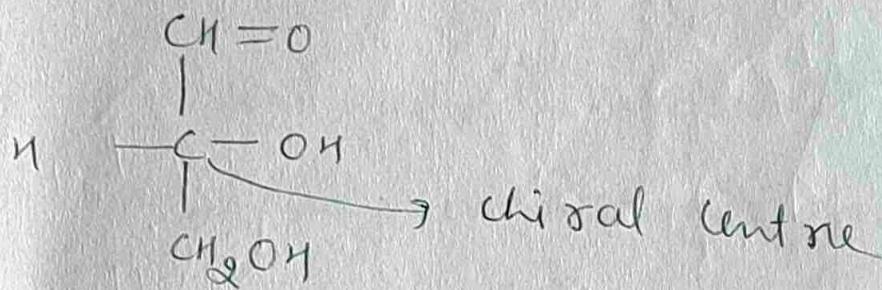
$\text{R} \neq \text{R}'$

Polarimeter

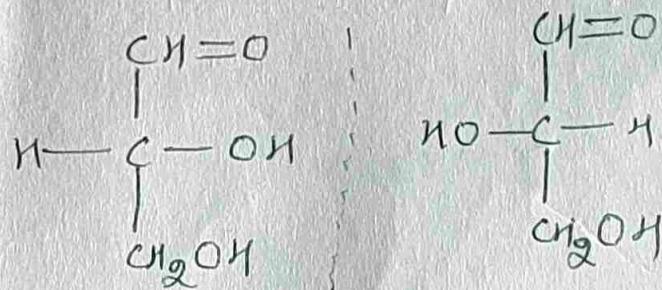
The compounds which rotates the plane of polarized light are called optical isomers and phenomenon is known as optical isomerism.

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.

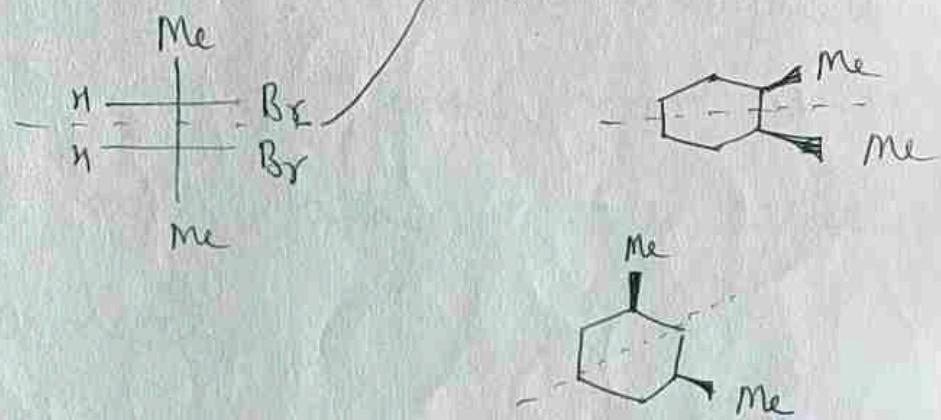
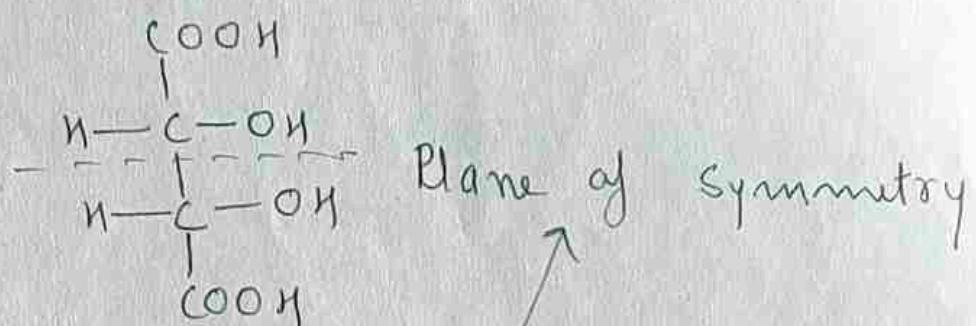


Not optically active

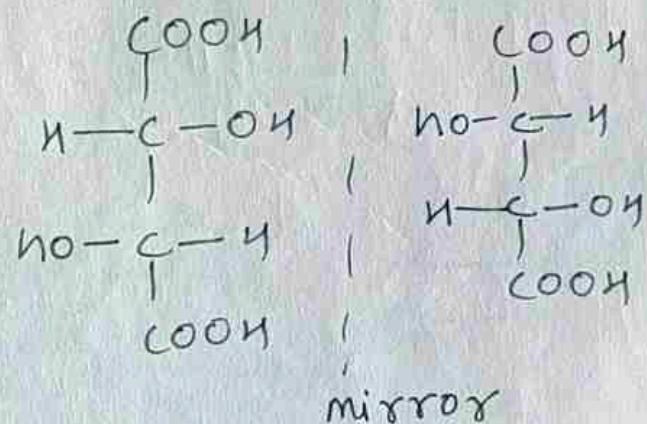
~~Not optically active~~

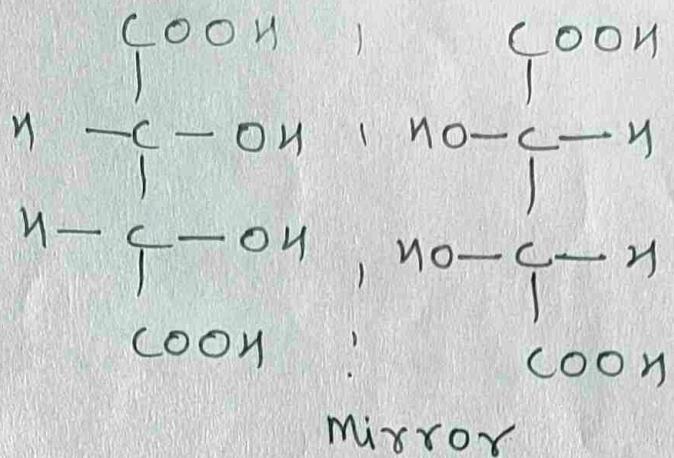
①

Compound should not have a plane of symmetry.

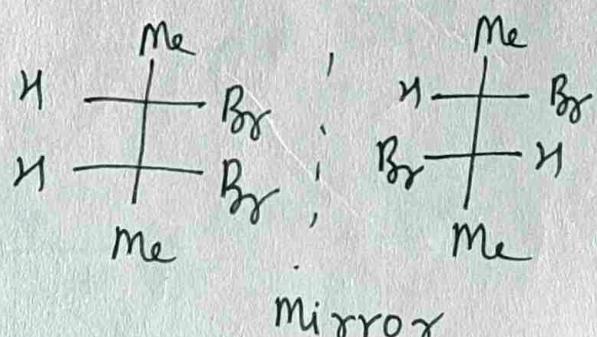
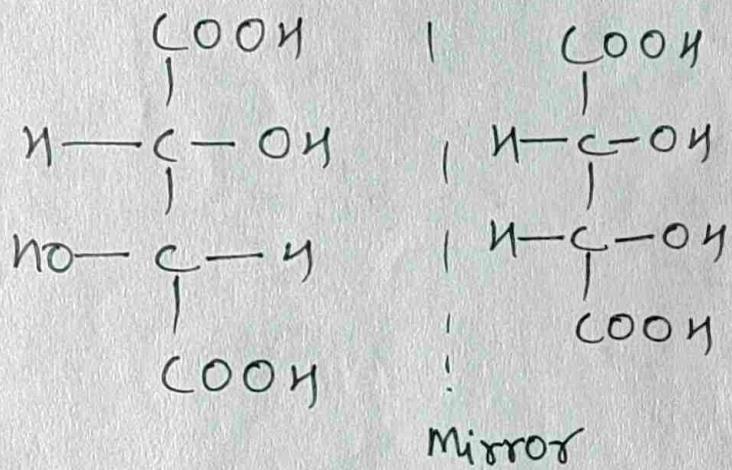


- Enantiomers \rightarrow Non superimposable mirror image \leftrightarrow is called enantiomer.



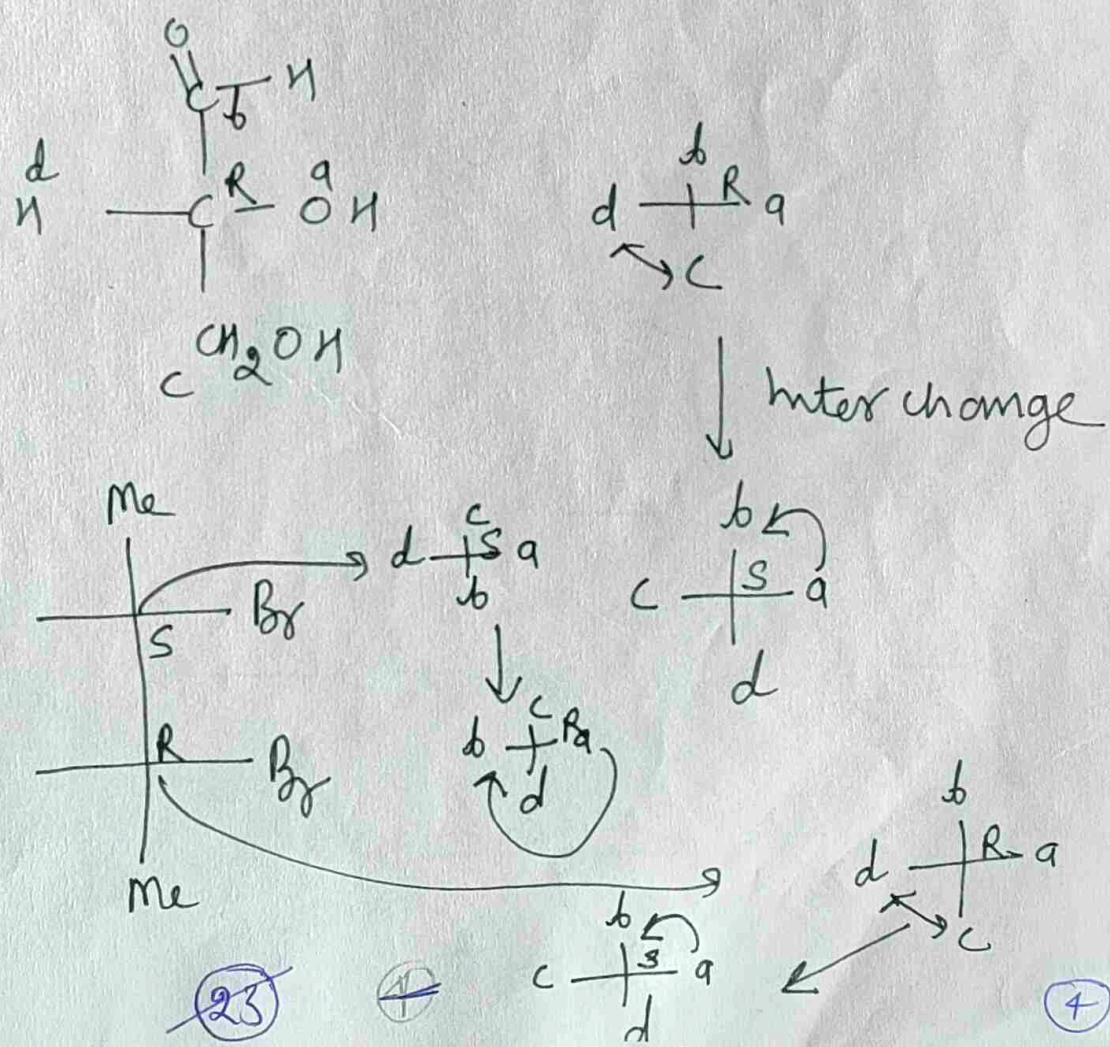


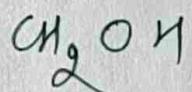
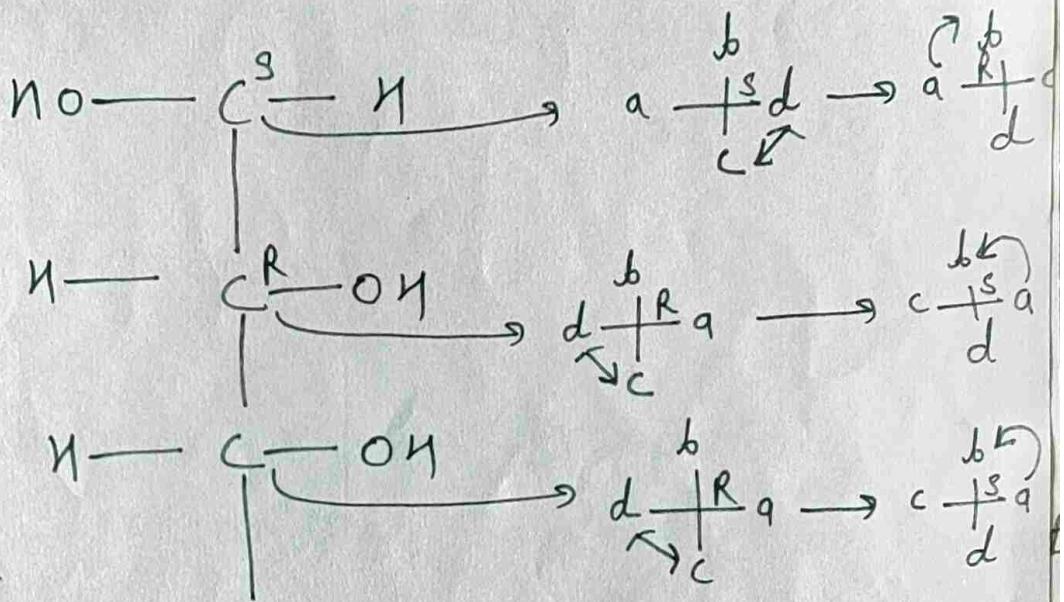
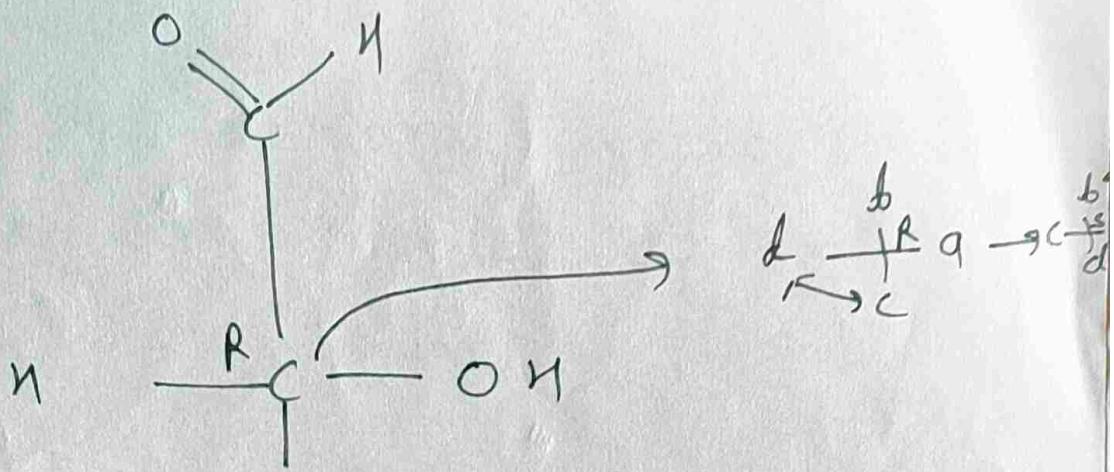
Diestereoisomers → Non-superimposable compounds which are not mirror image of each other are called diastereoisomers.



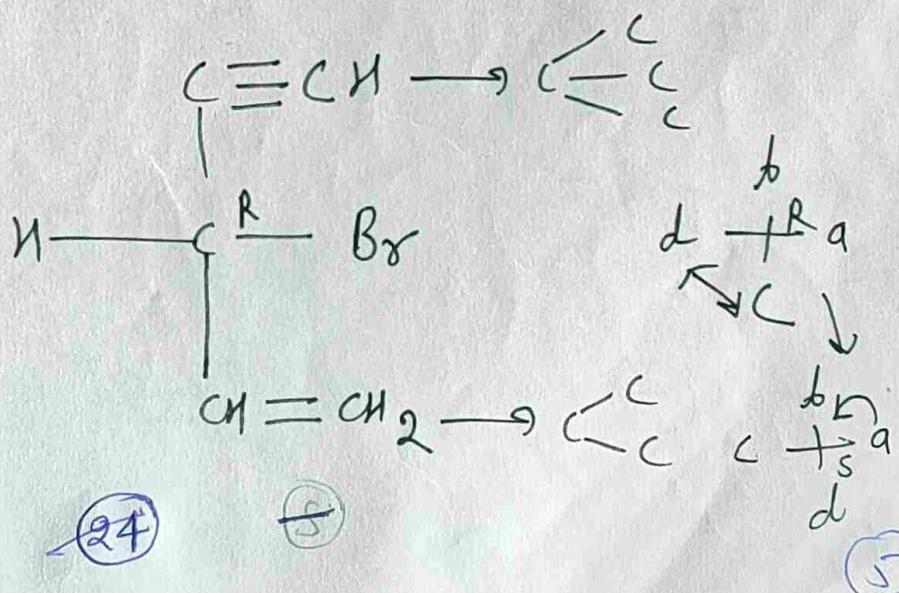
and S configuration or CIP rule
(Cahn, Ingold and Prelog's rule) :-

- 1) Select the ~~periority~~ of group according to atomic no or mass no.
- 2) The group of lowest ~~periority~~ should be away from observer.
- 3) Observe the rotation from a to b
 - i) clockwise \rightarrow R (Rectus)
 - ii) Anticlockwise \rightarrow S (Sinsister)





D-glucose



(24)

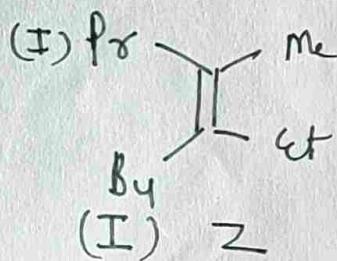
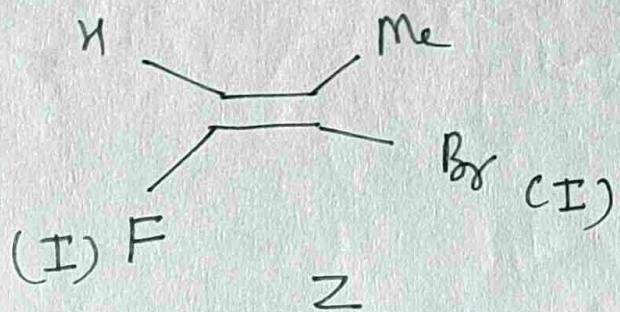
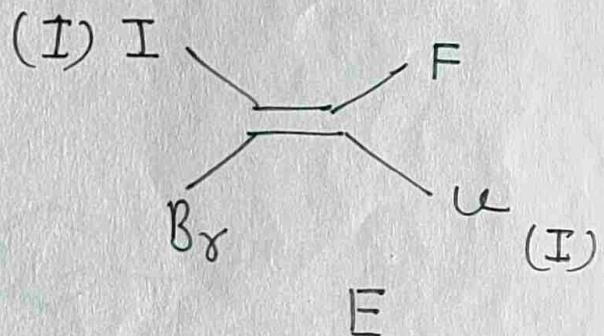
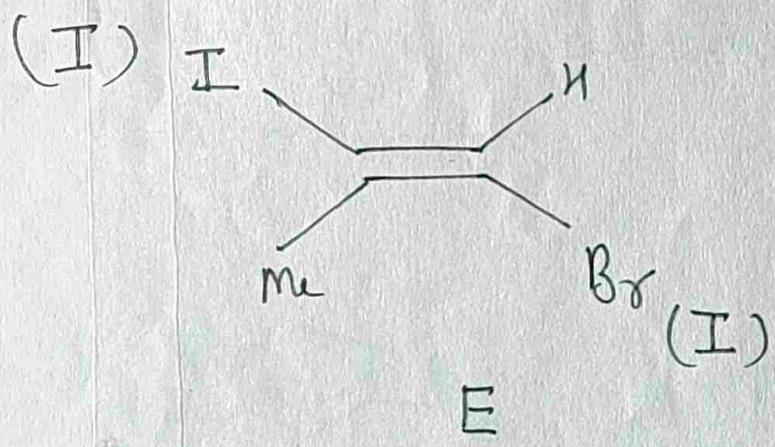
(S)

(5)

E and Z configuration →

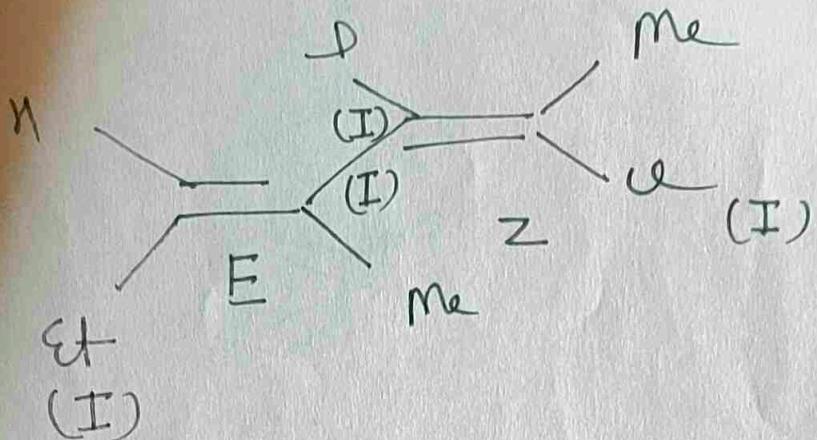
- when higher priority groups are on the same side, it is Z (Zusammen)
- when higher priority groups are on the opposite side, it is E (Entgegen)

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

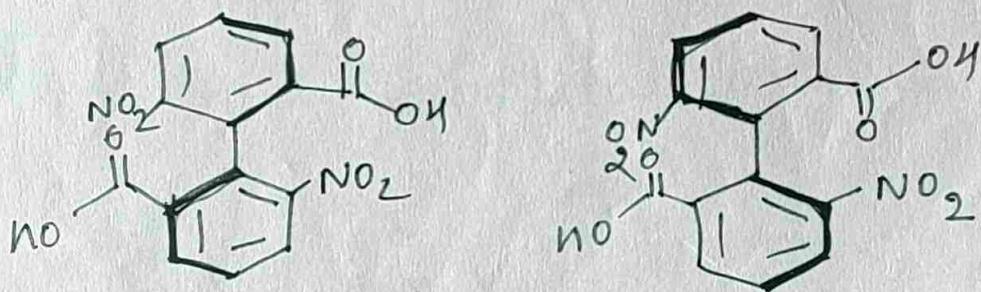


②6 ④ ②8

⑥



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

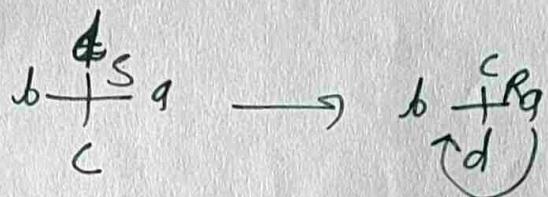
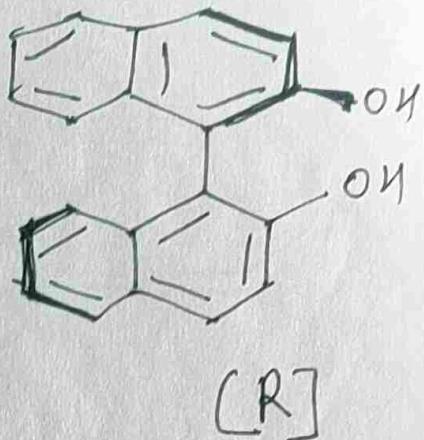
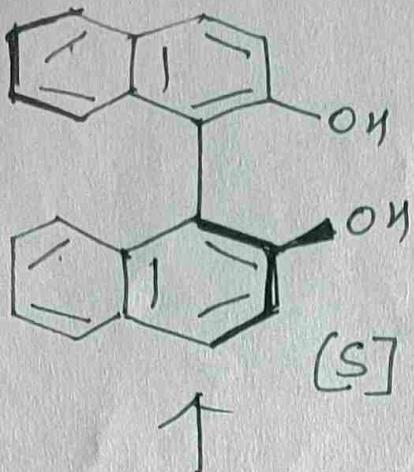


(24)

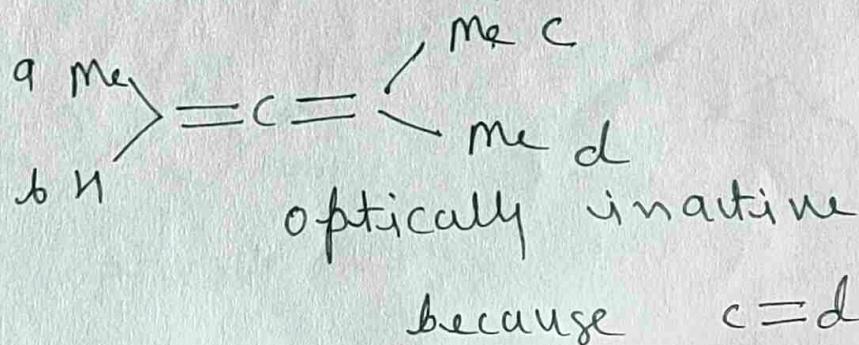
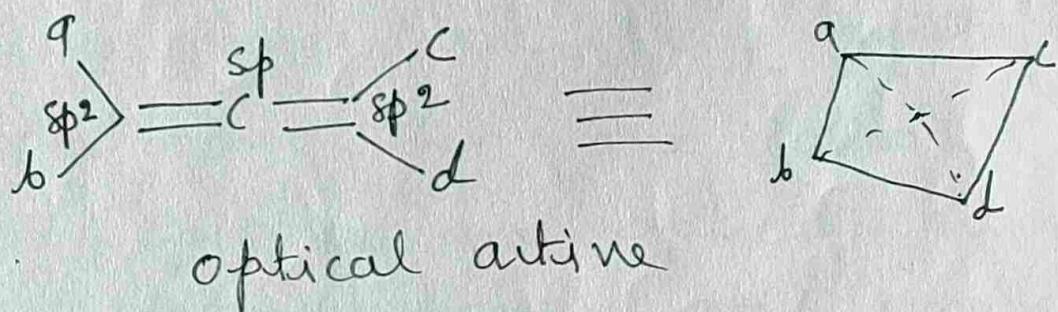
(25)

(26)

(27)



optical anti isomerism in Allenes \rightarrow
Allenenes show optical anti isomerism
if $a \neq b$ and $c \neq d$



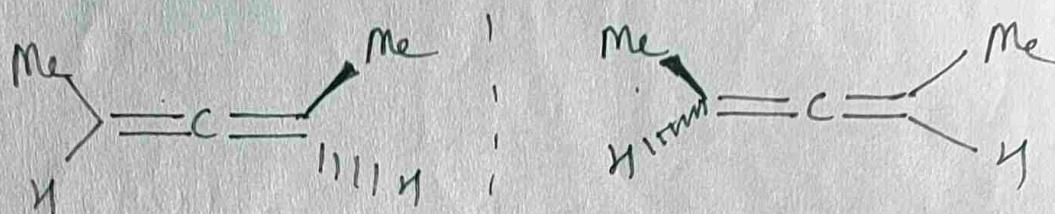
(29)

(8)

(27)

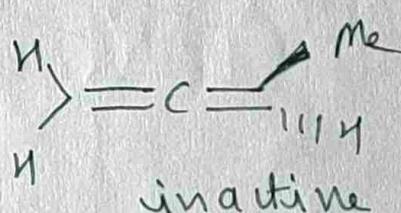
(8)

it is totally asymmetric molecule and it has C_1 symmetry.

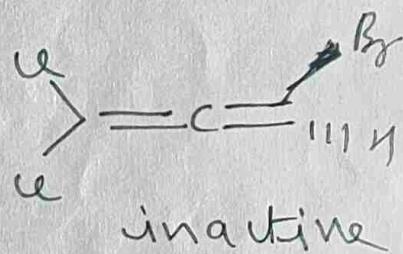


MIRROR

Non superimposable



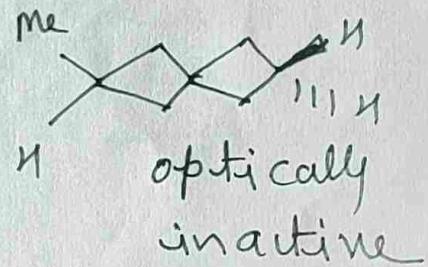
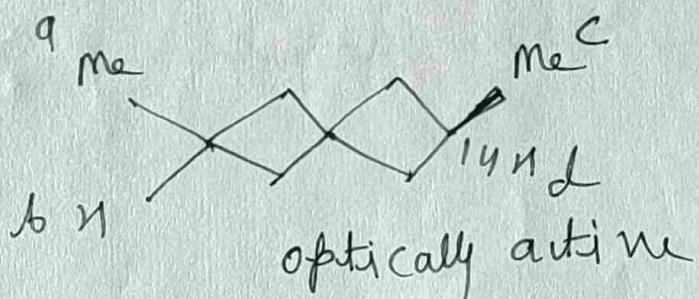
inactive

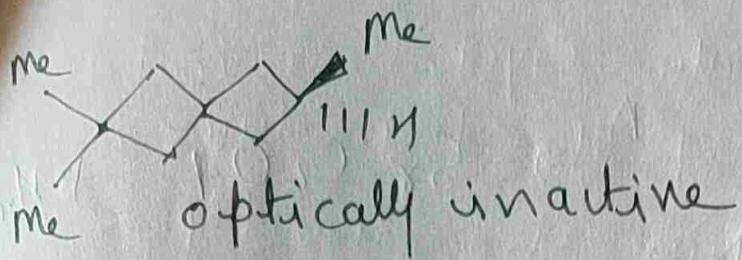


inactive

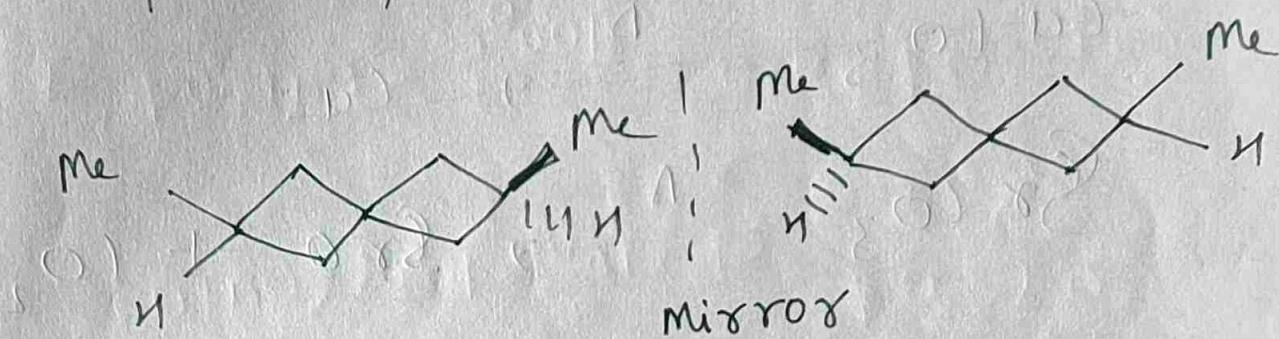
Optical isomerism in spiranes →

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 $c \neq d$.



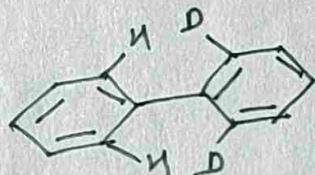


Spiranes are chiral and possess a symmetry. They are asymmetric molecules.

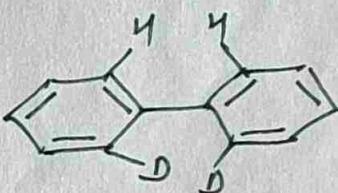


optical isomerism in biphenyl.

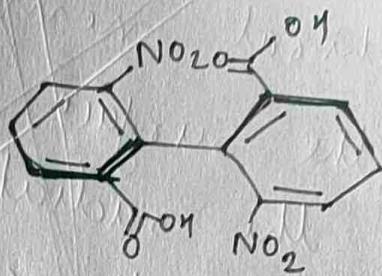
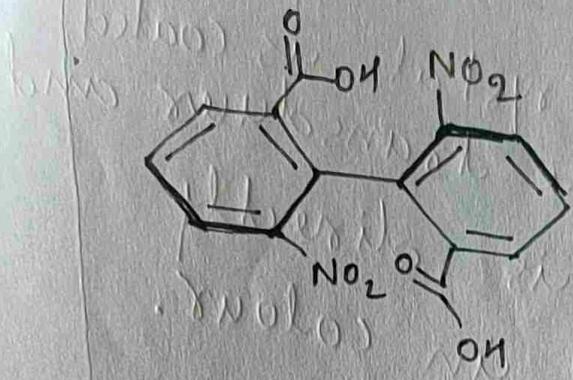
optical isomerism ~~is~~
in biphenyl arises from restricted
rotation or hinderance.



free rotation
optically inactive



free rotation
because - H atoms
are very
small atoms



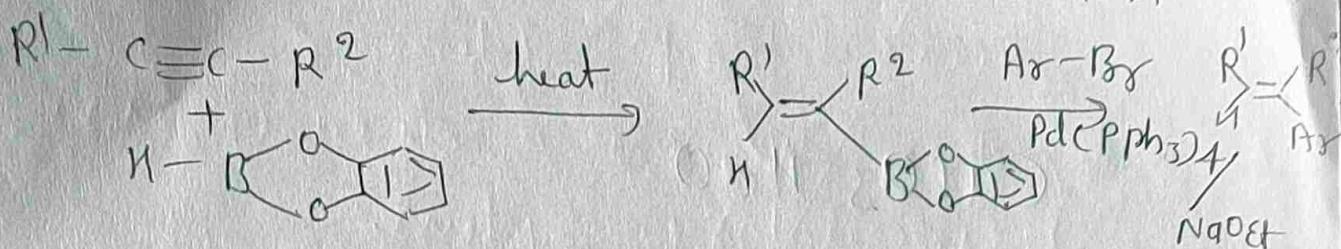
M

No free rotation is possible.

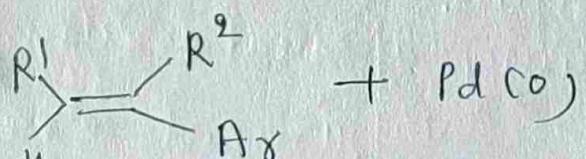
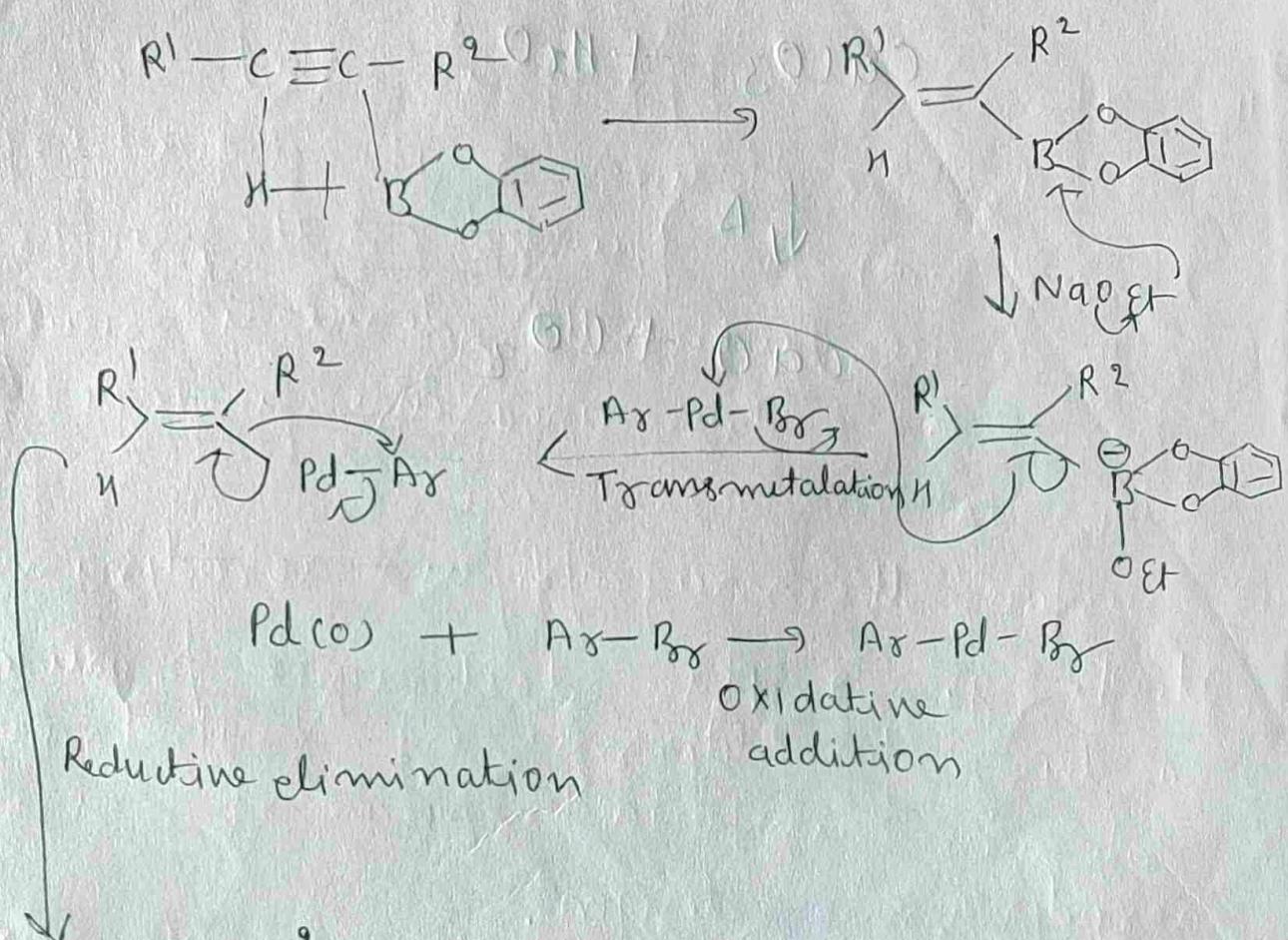
They are optically active.

-COOH and NO₂ are large and bulky groups, they will not allow free rotation of two rings.

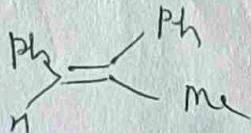
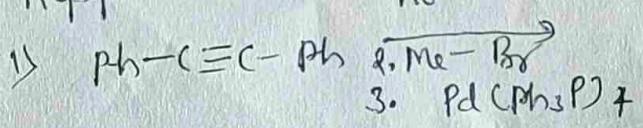
Suzuki Reaction \rightarrow Alkylation or arylation
 of alkynes with boronic ester and
 alkyl halide in presence of $Pd(O)$ and
 $NaOEt$ is known as Suzuki reaction



Mechanism Mechanism \rightarrow



Applications no $B - R$



(35)

(12)

(31)

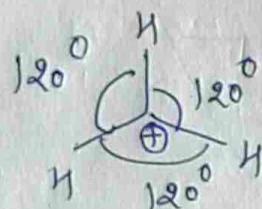
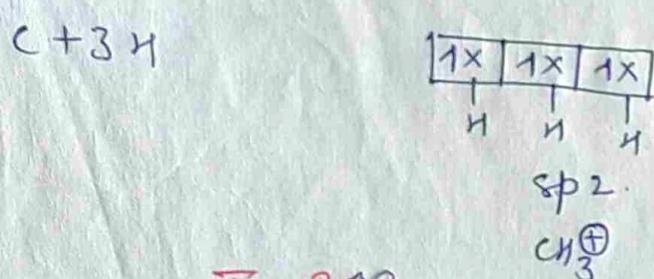
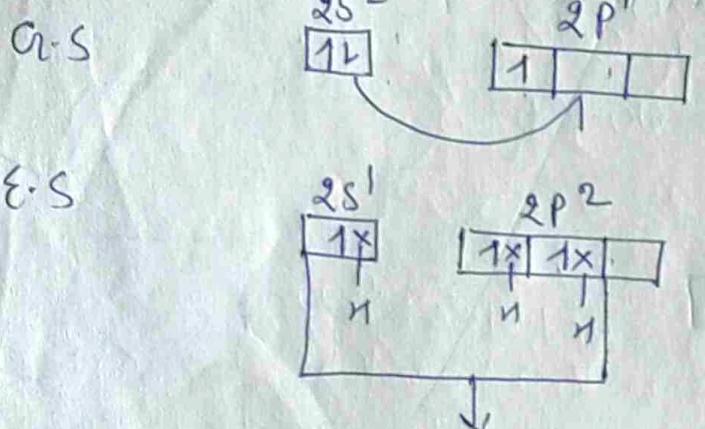
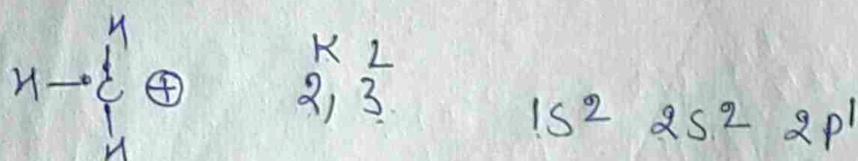
(12)

B.Tech. First year By | B.

Purnottam Singh Niramjam

Carbo cations The carbon species containing positive charge, are called carbo cations.

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

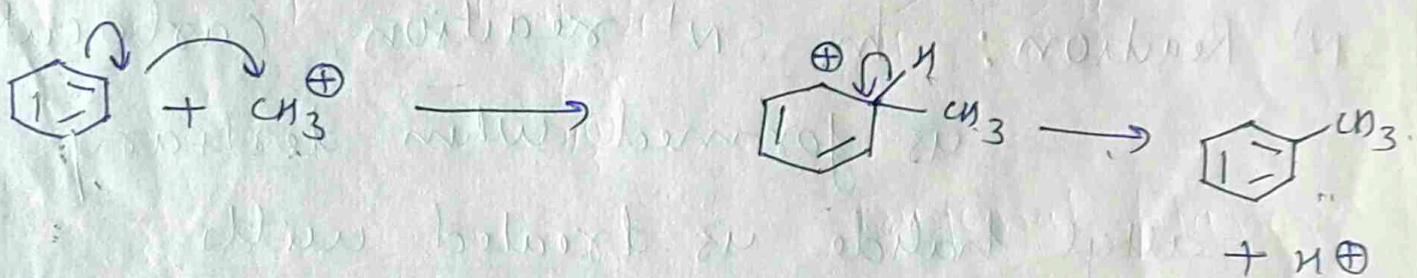
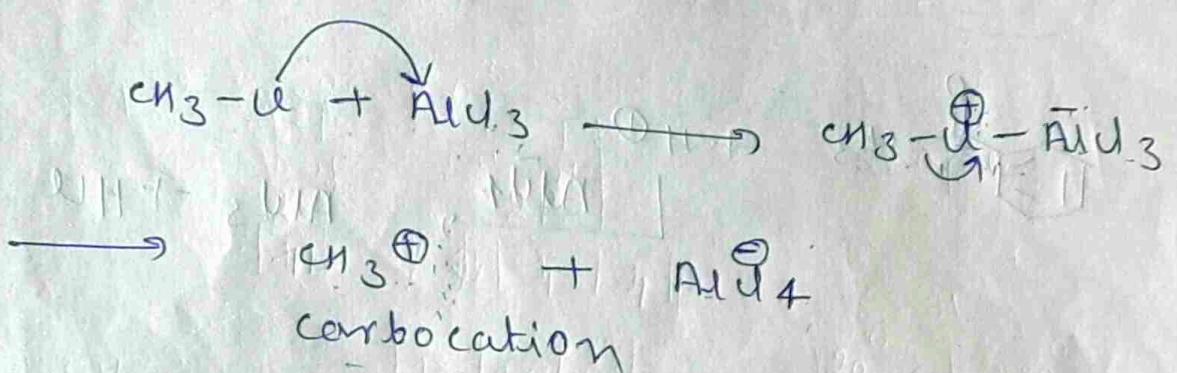
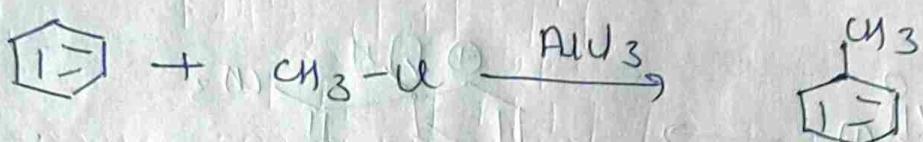


Trigonal planar

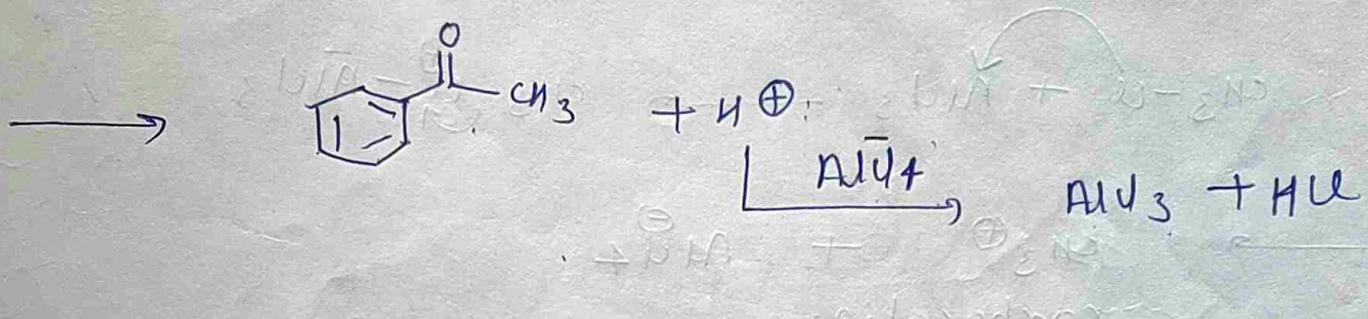
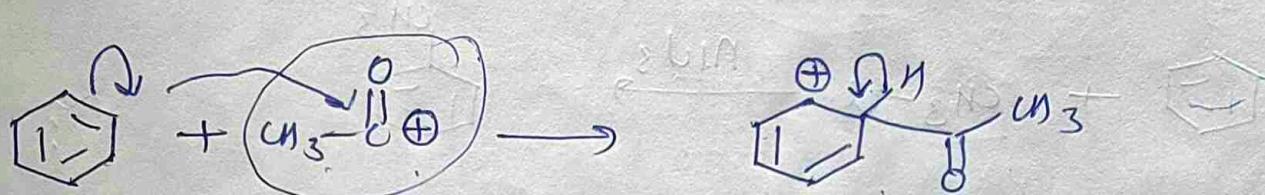
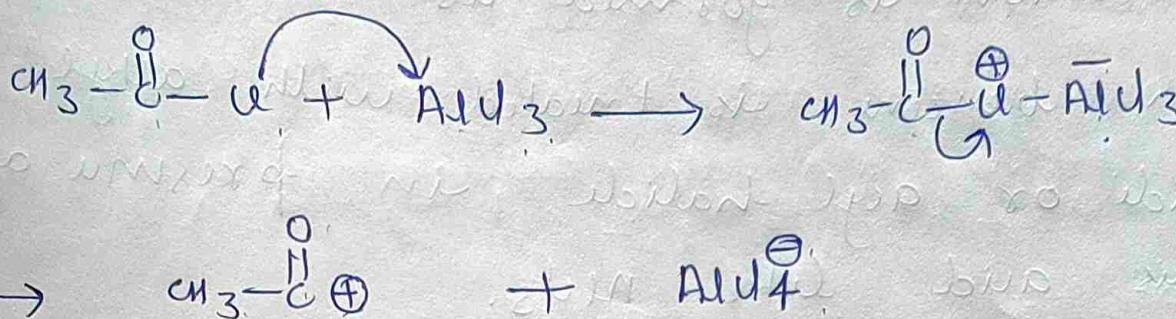
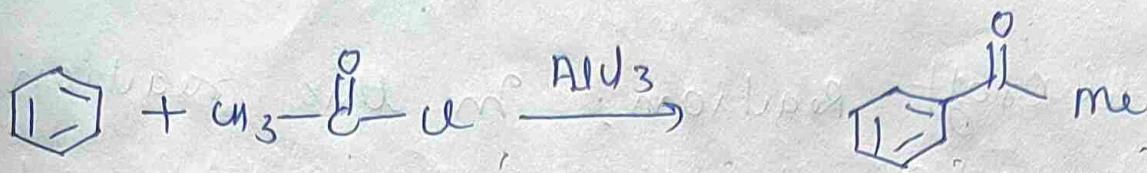
II - 209

Formation of carbocation:

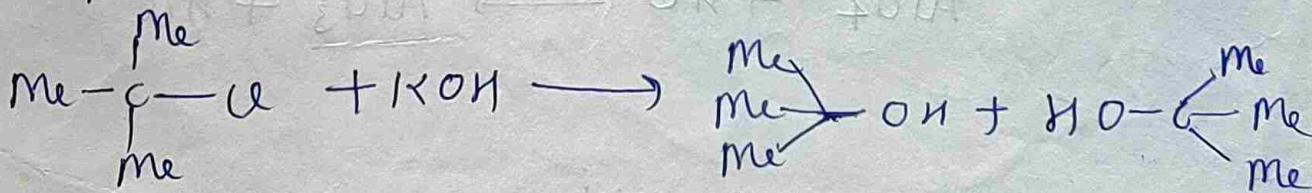
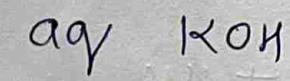
Q1) Friedel-Crafts Reaction: In this reaction, carbocation is formed as intermediate when benzene is treated with alkyl halide or acyl halide in presence of Lewis acid like AlCl_3 .



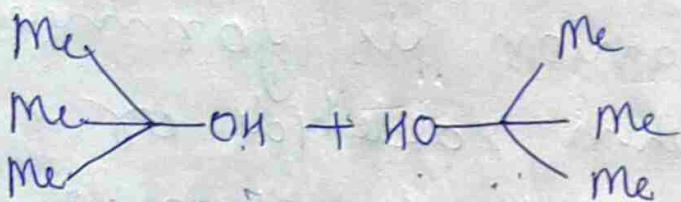
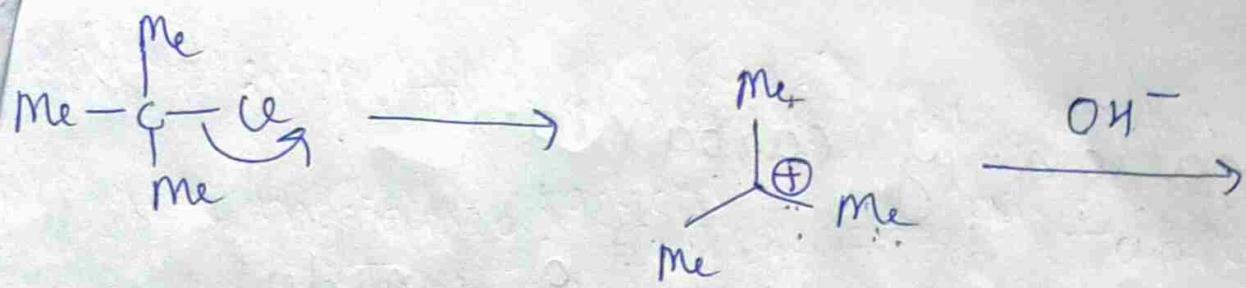
Acylation:



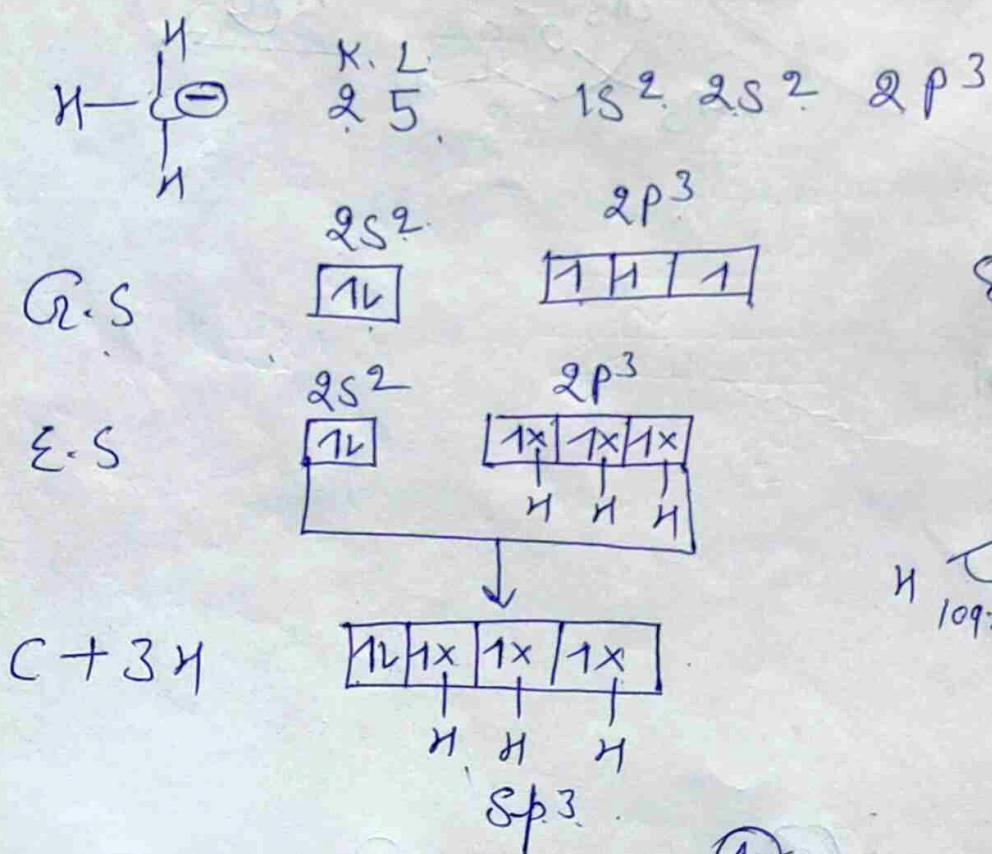
S_{N}^1 Reaction: In S_{N}^1 reaction, carbocation is formed when tertiary alkyl halide is treated with



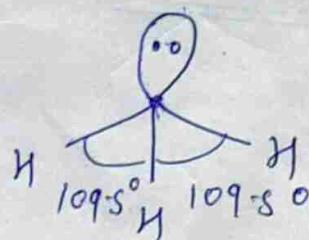
(3) (5)



Carbanions: carbon species containing net negative charge are called carbanions. The carbanions are intermediates and have 8 e^- in the octet.



Shape



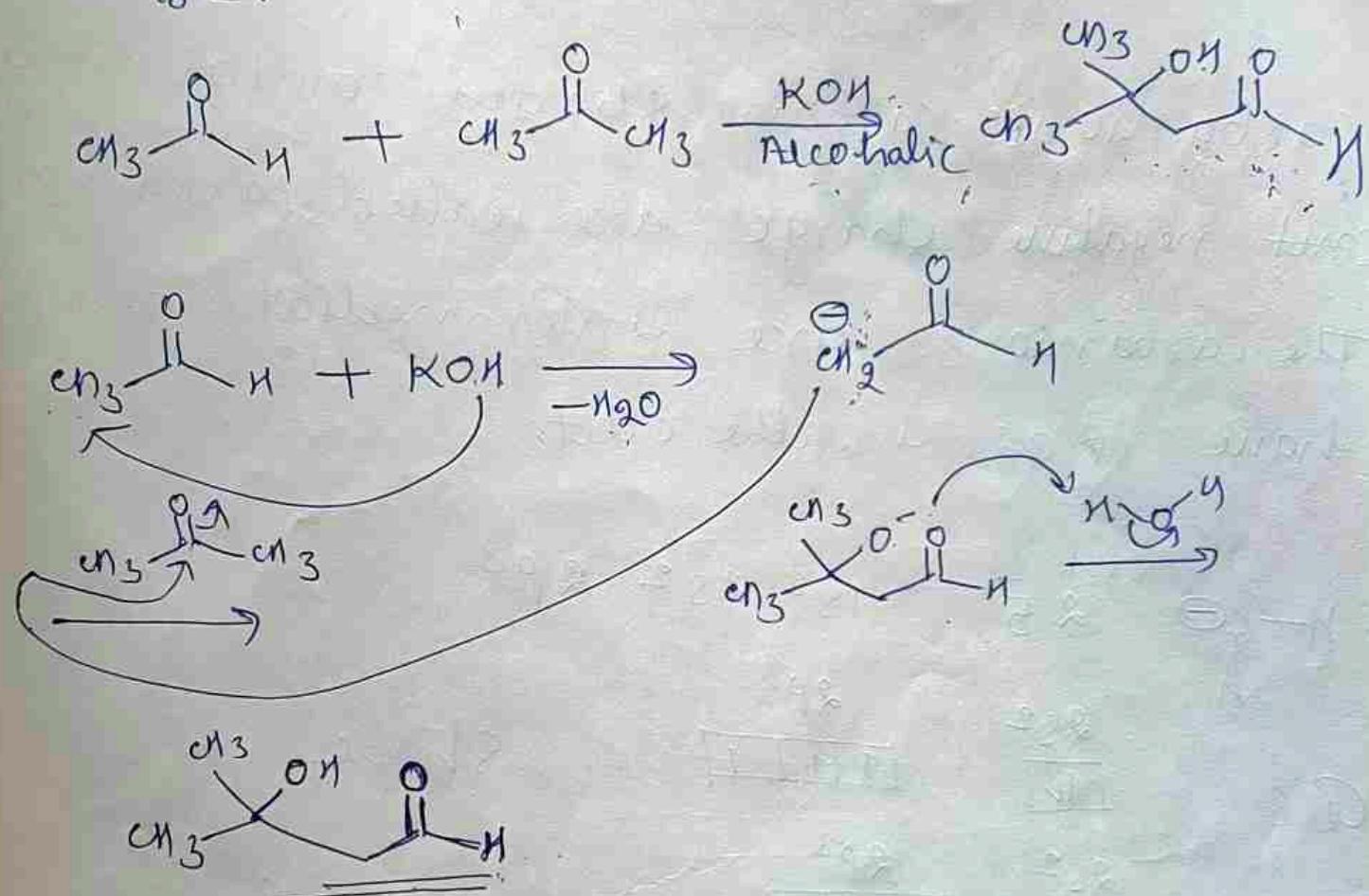
Pyramidal shape

(A)

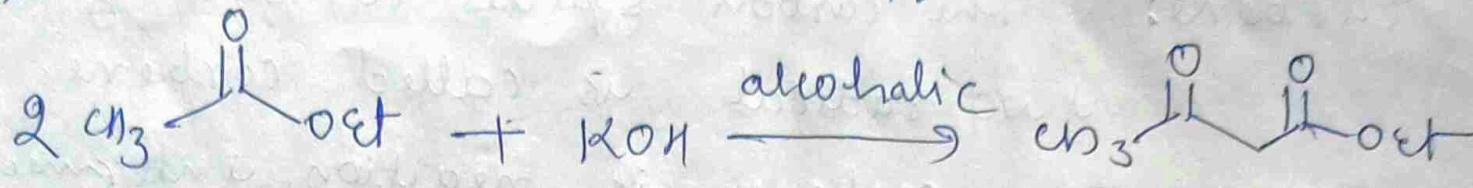
(16)

Formation of carbanion!

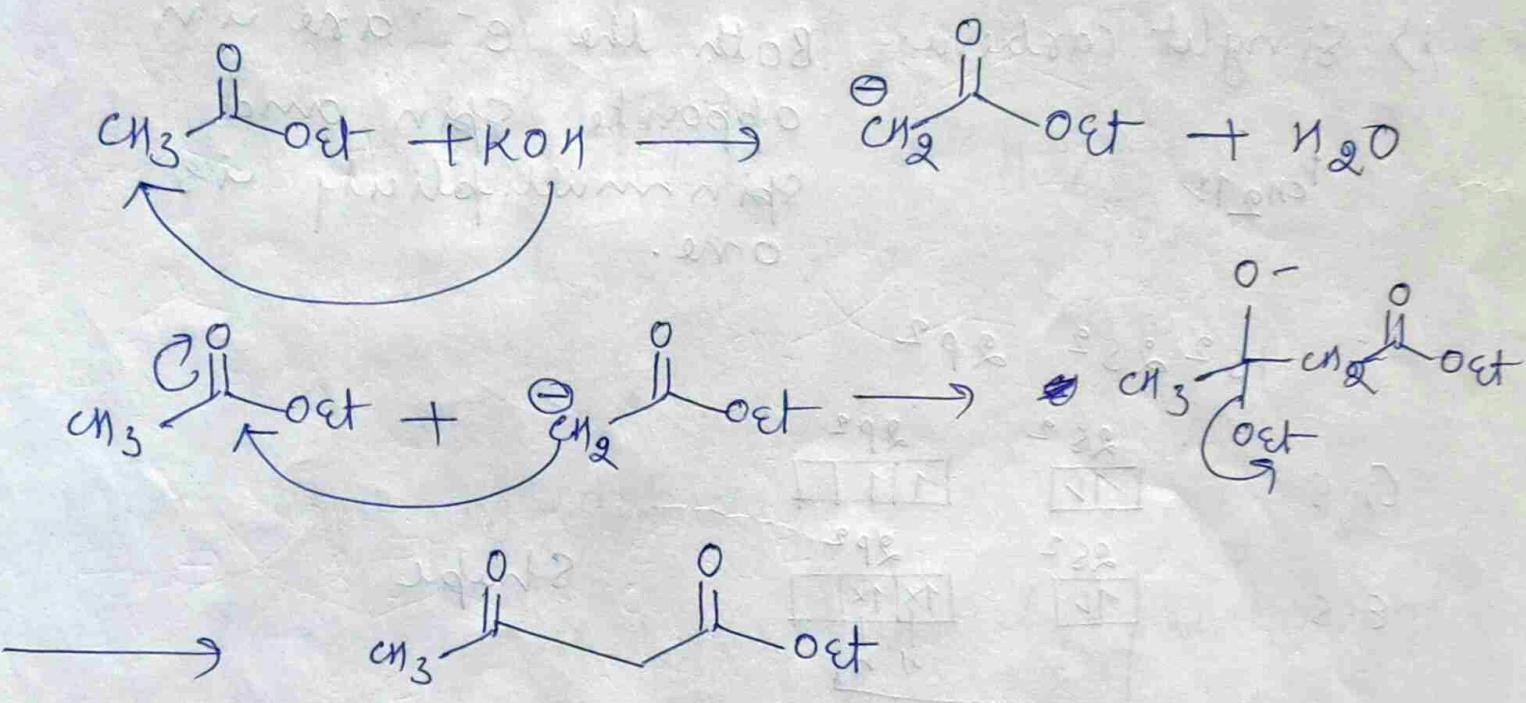
1) Aldol condensation: In Aldol condensation, carbanion is formed as intermediate when aldehyde or ketone is treated with a strong base.



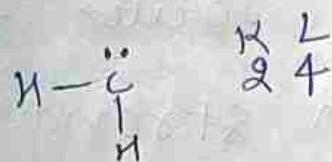
> Claisen condensation:



When two molecules of low molecular weight esters are treated with strong base to give carbanion as an intermediate.

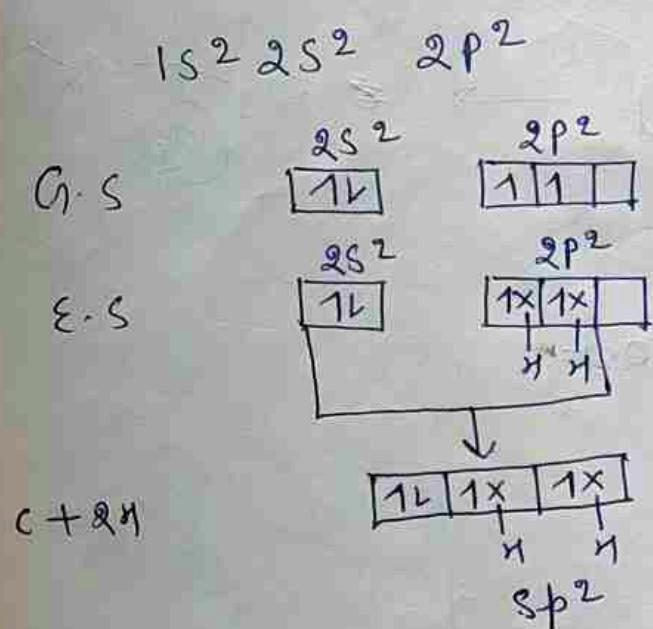


Carbene: The carbon species containing two radical e^- is called carbene. The carbene is reaction intermediate and has six e^- in octet.

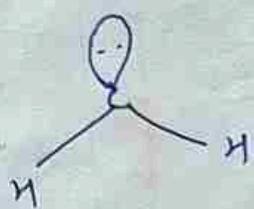


It is of two types:

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

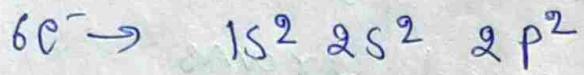
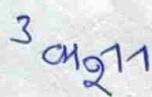


Shape

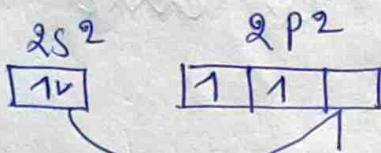


V-shape

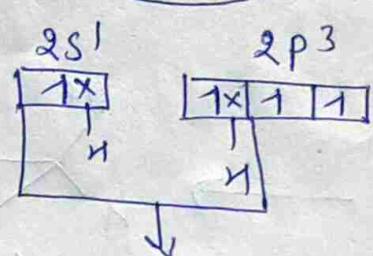
> Triplet carbene: Both the e^- are in parallel spin and spin multiplicity is 3.



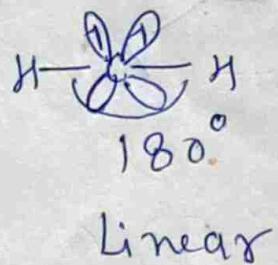
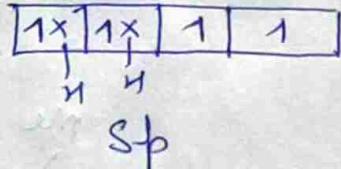
G.S



E.S

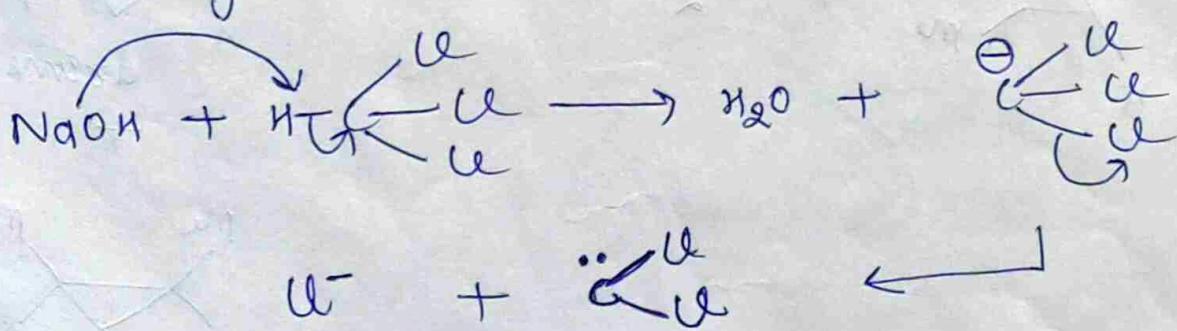


$\text{C} + 2\text{H}$



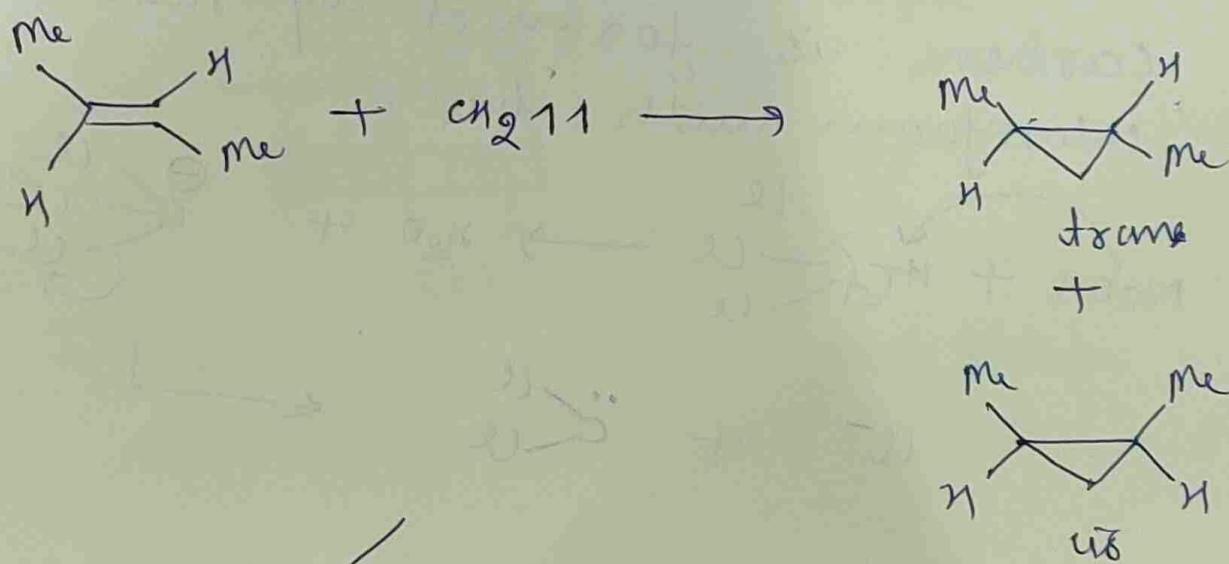
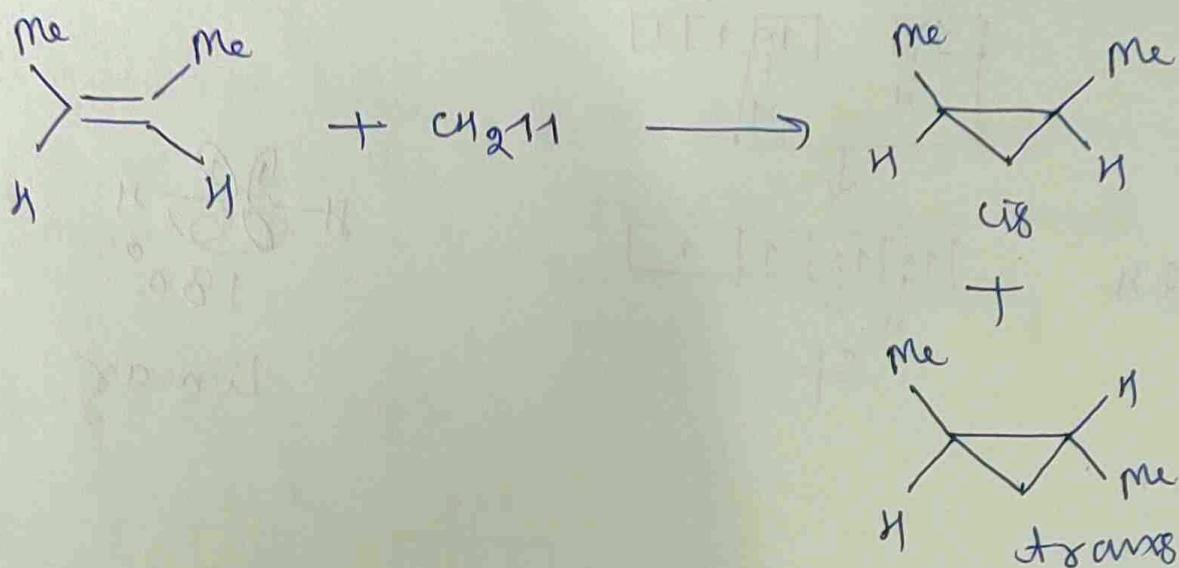
Formation of carbene:

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

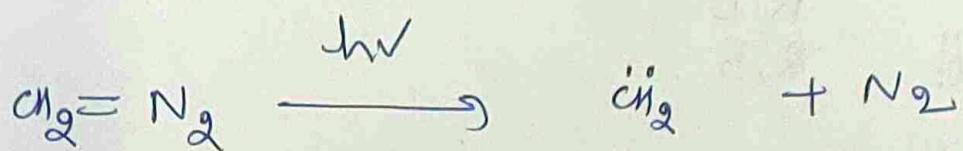


2) Triplet carbene: It is nonstereo specific in nature.

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

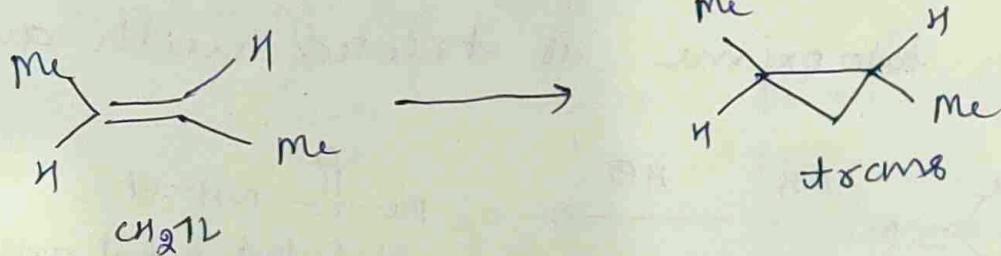
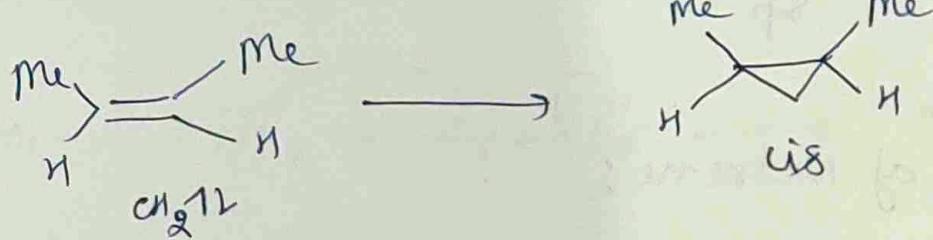


2) Carbene is formed when diazo methane is irradiated with light

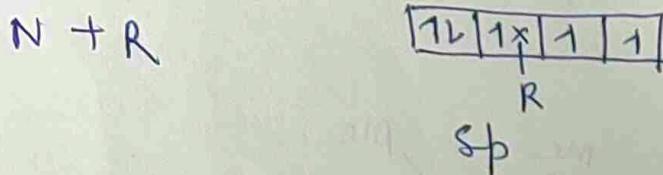
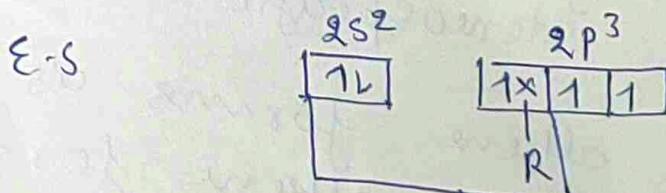
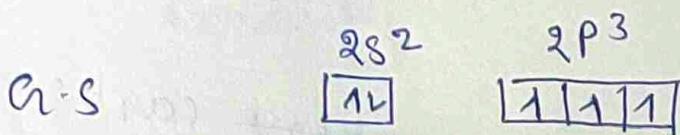
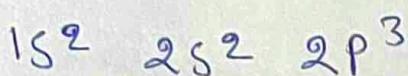


Reaction of carbene:

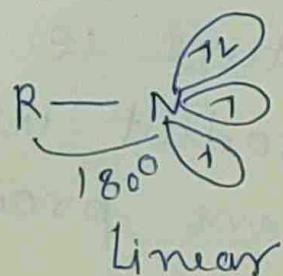
1) Singlet carbene: singlet carbene carbene is stereospecific in nature i.e. it is alkene forms cis product whereas trans alkene forms trans product.



Nitrene: Nitrenes are intermediate and has six e⁻ in octet.

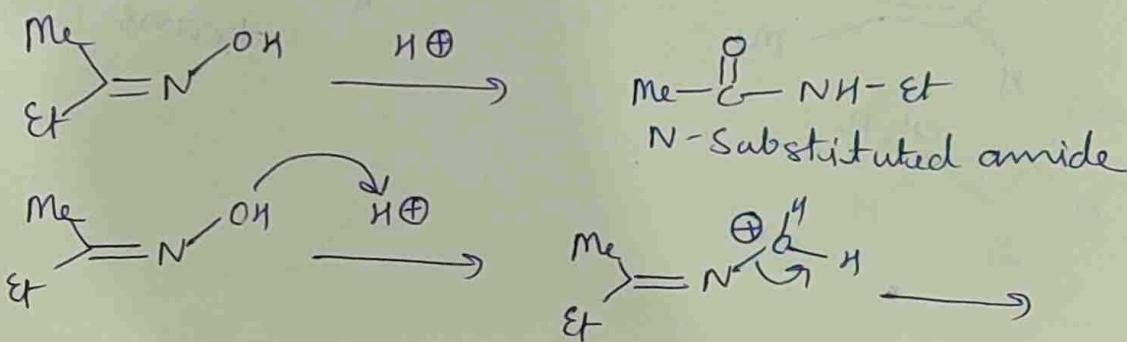


shape



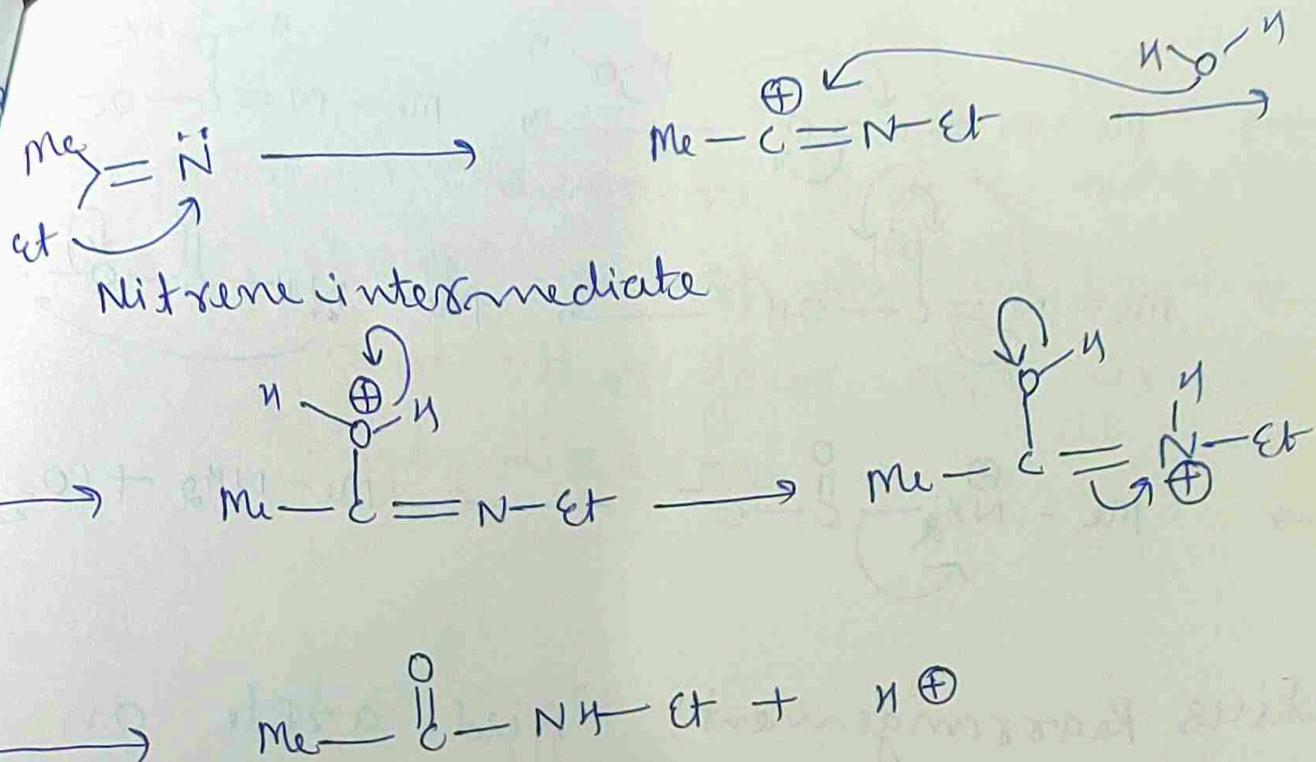
Formation of Nitrene:

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

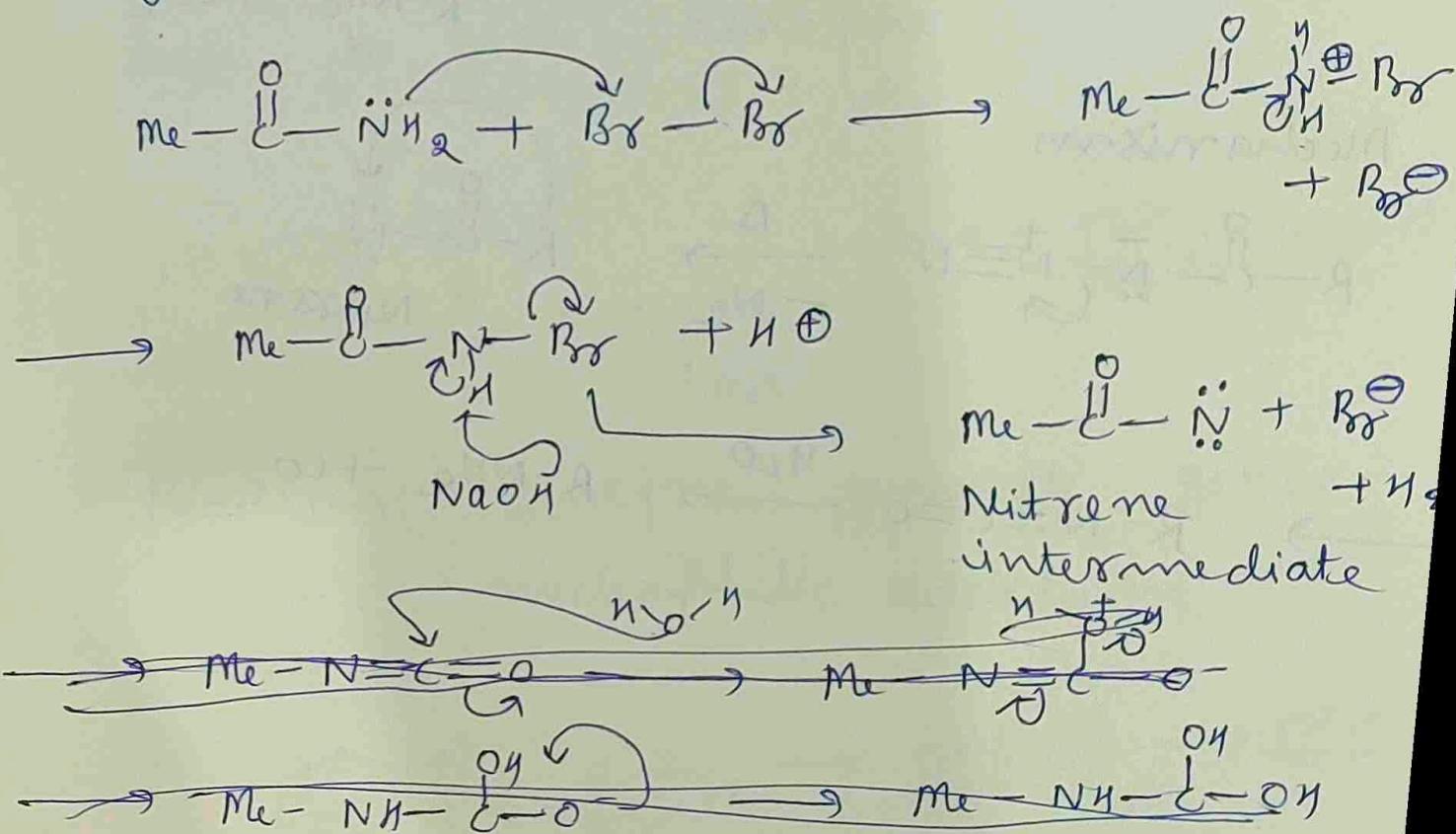


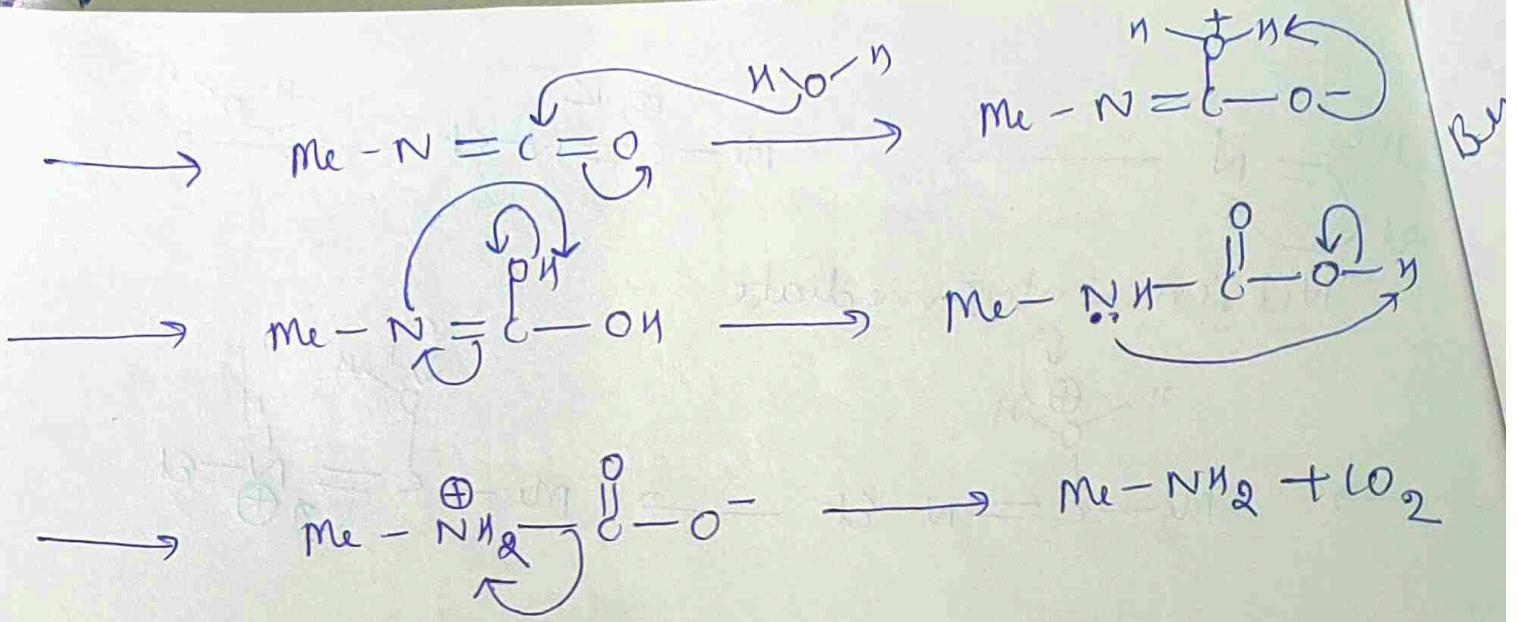
(11)

(23)

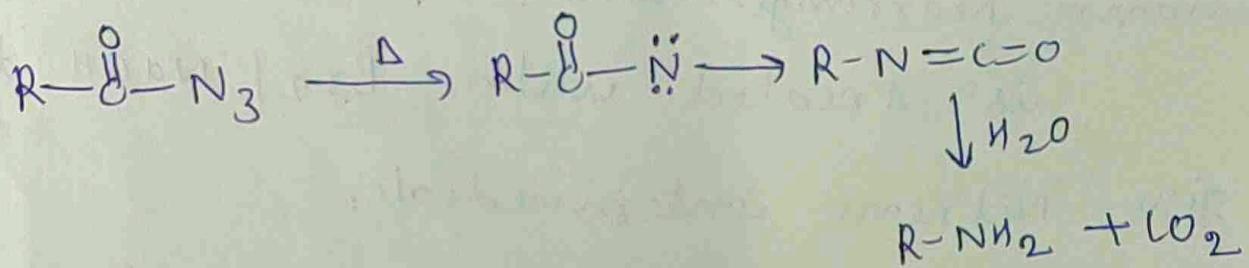


Noymann Rearrangement: When a carbamide
 is treated with Br_2/NaOH to
 give Nitrene intermediate:

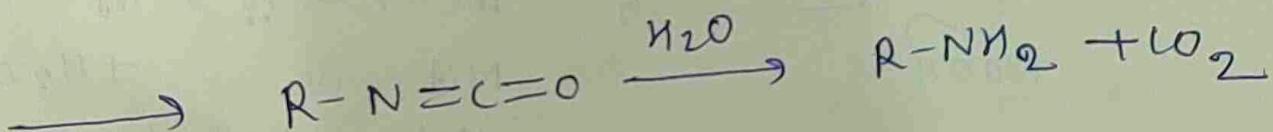
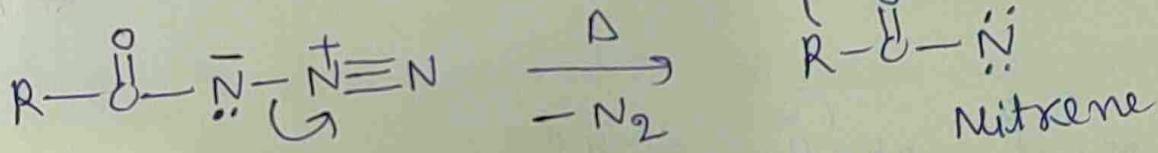




Curtius Rearrangement: Acid azide on heating to give nitrene.



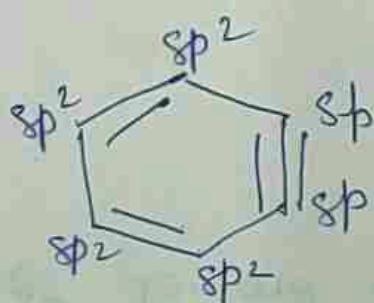
Mechanism



(13)

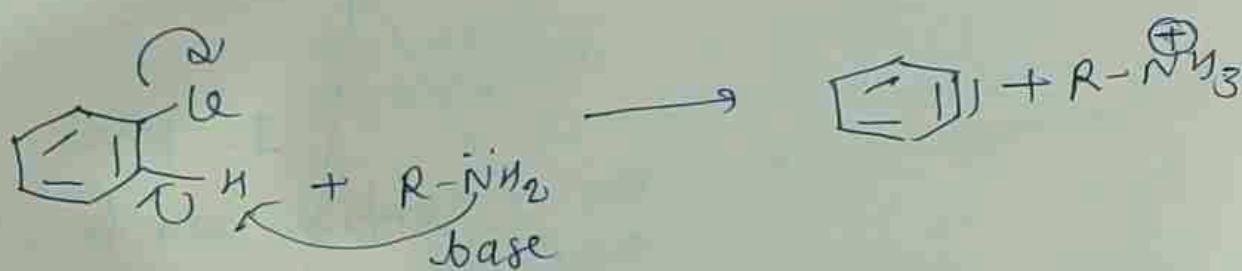
(25)

Benzyne: In benzene, two carbons are in sp^2 hybridization and other four are in sp^2 hybridization.

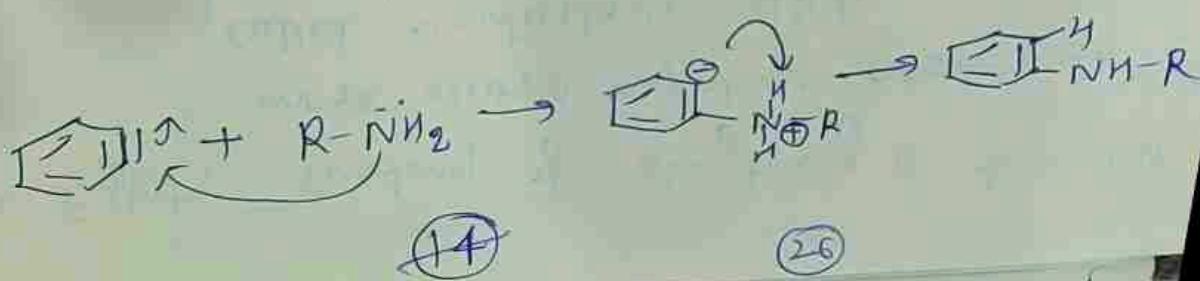


Formation of Benzyne:

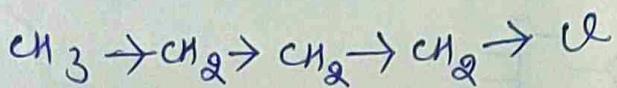
The reaction of chlorobenzene with base to give benzyne.



Reaction: Benzyne generally gives nucleophilic addition.



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



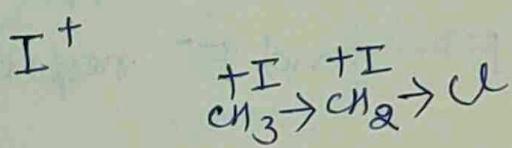
It is of two types

~~P+~~ atom



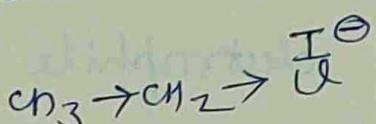
I^+ ~~when \rightarrow tendency of e^- is toward more elec~~

when atom push e^- toward more electronegative atom is called

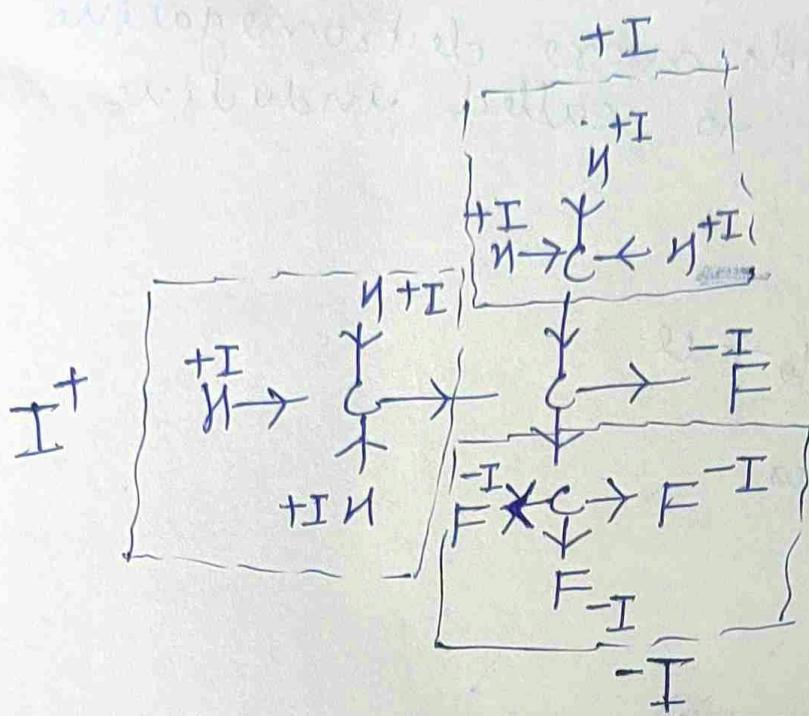


I^- ~~when \rightarrow atom attracts e^- toward it.~~

It is called I^\ominus

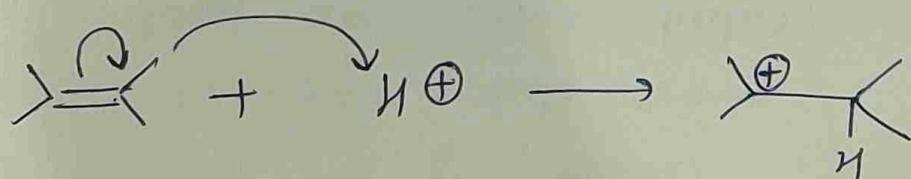


example of I^+ and I^- effect

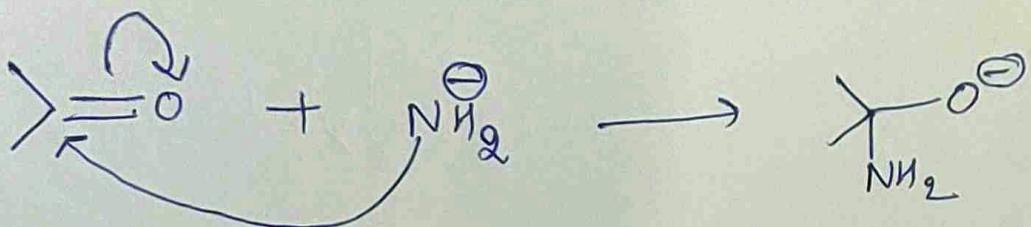


Electromeric effect: Separation of charge by attacking species is called electromeric effect. It is two types i.e. E^+ and E^- respectively.

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



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

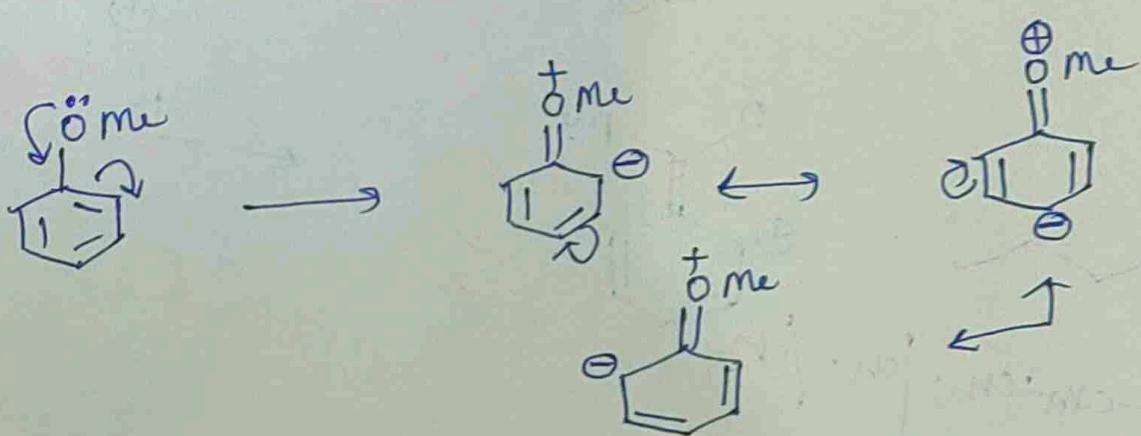
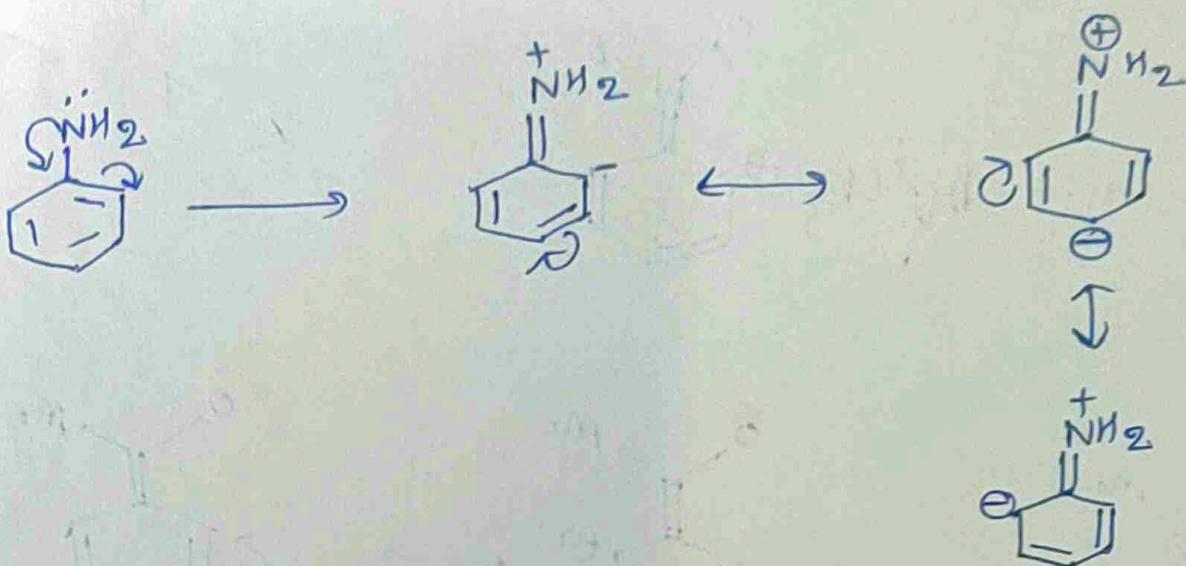


Mesomeric effect \rightarrow mesomeric effect is defined as the polarity produced in the molecule by interaction of two pi bonds or between a pi bond and lone pair of e^- present on an adjacent atom.

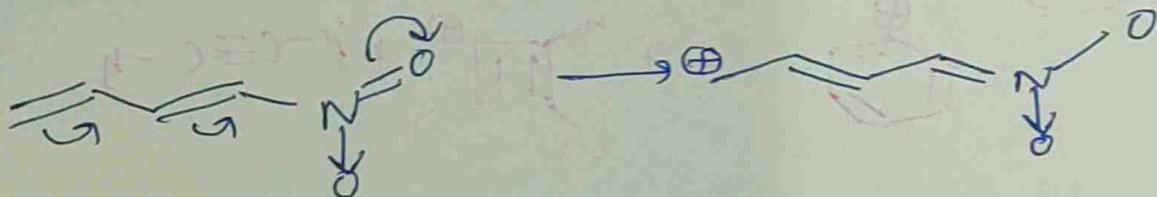
It is of two types

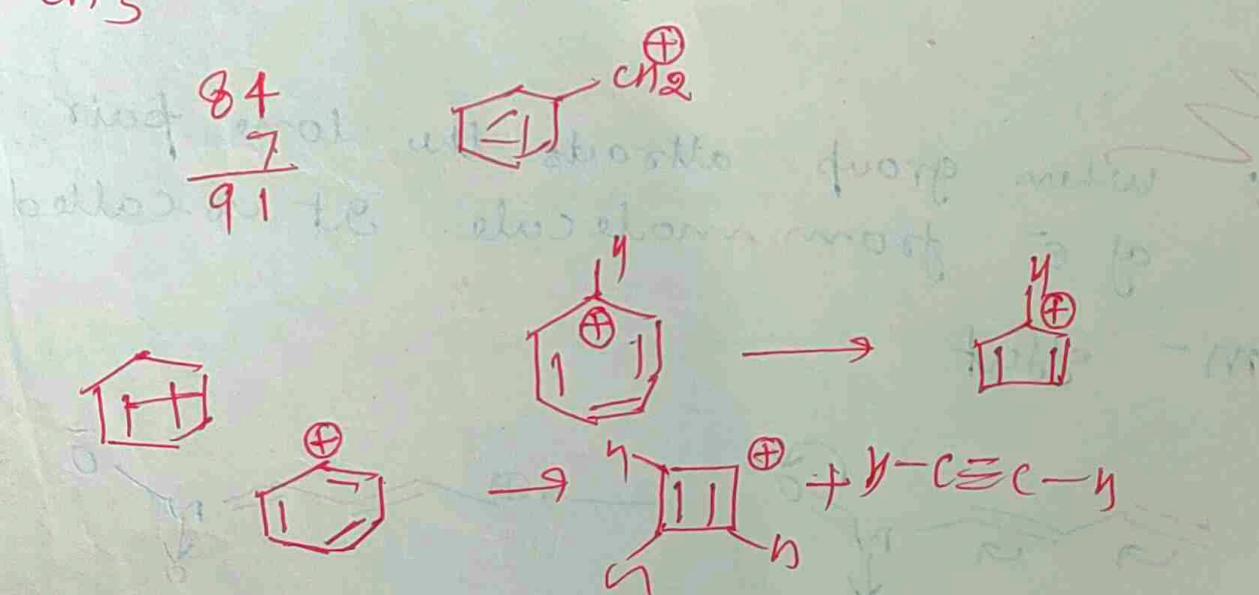
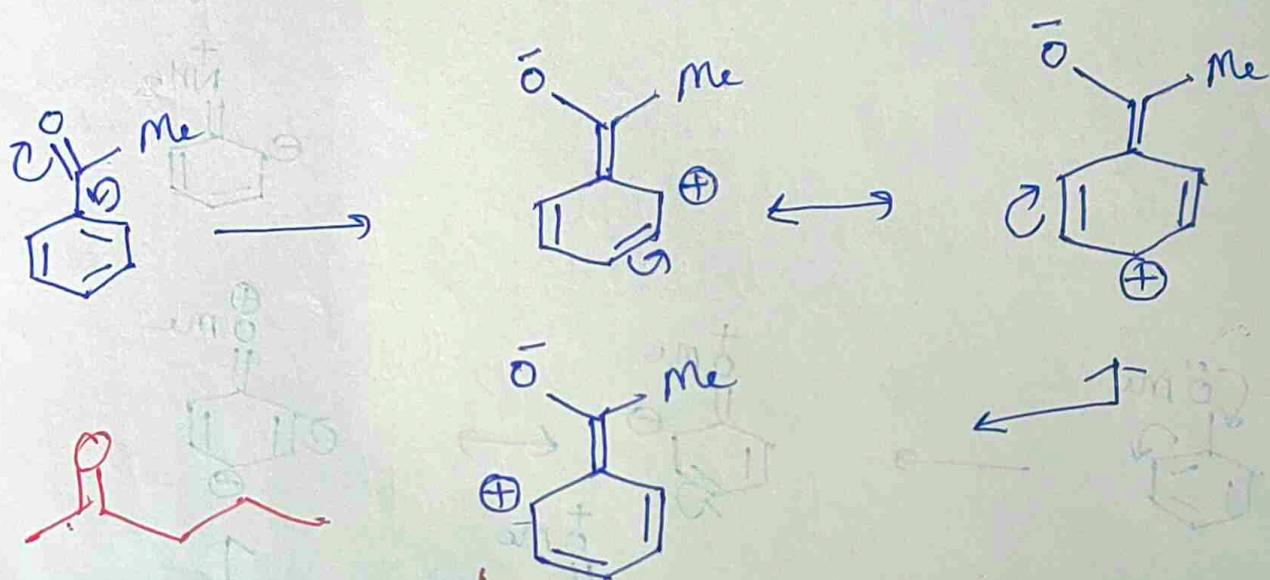
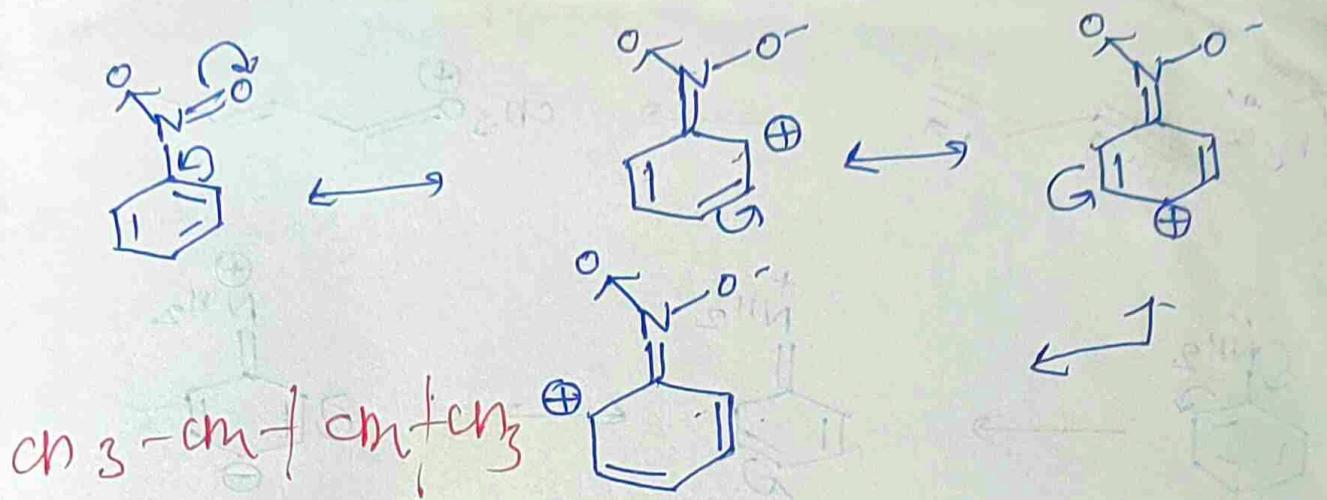
m^+ and m^-

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



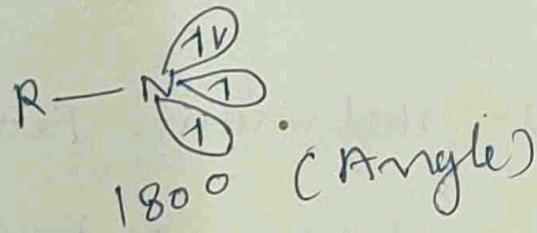
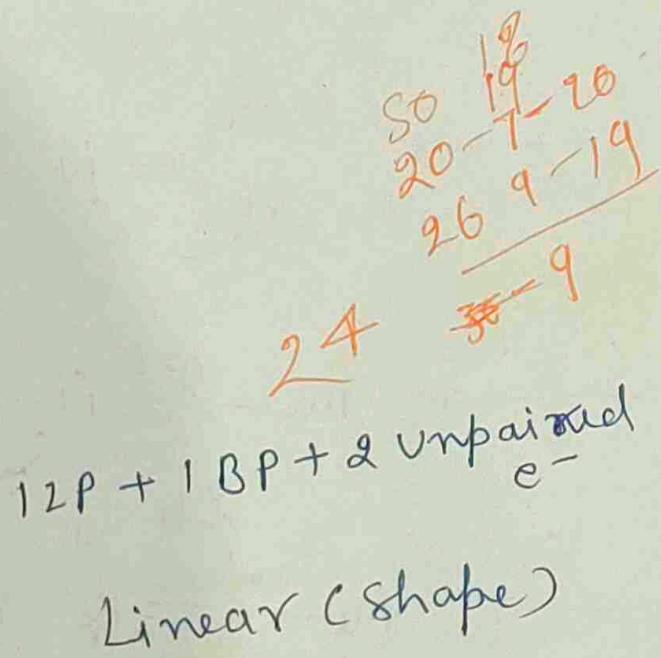
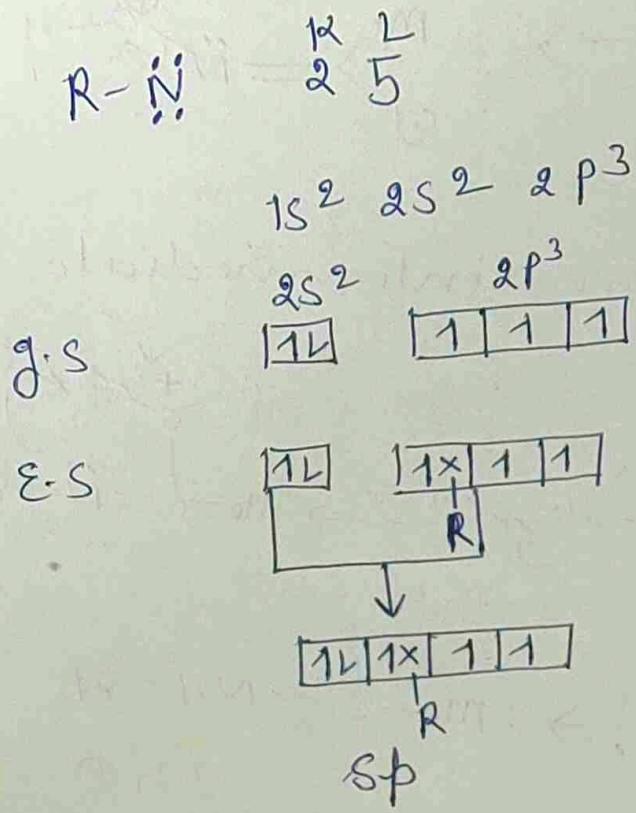
m⁻: When group attracts the lone pair of e⁻ from molecule. It is called m⁻ effect





Nitrene:

It is electron deficient and has 6 e⁻ in octet. Nitrene is formed as intermediate in many reactions.

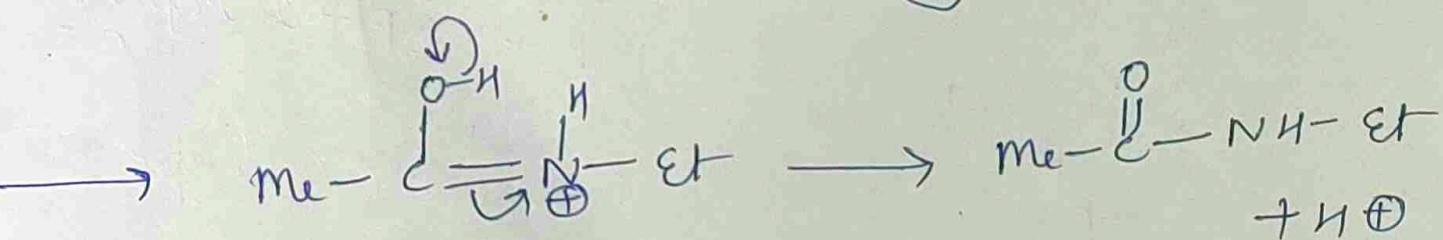
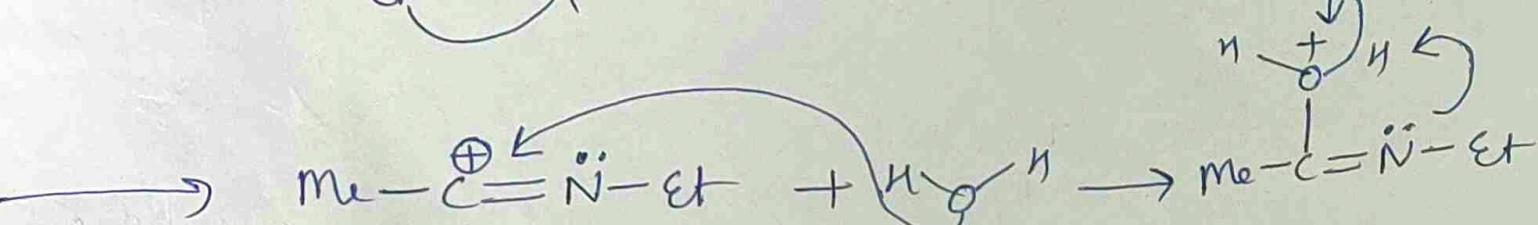
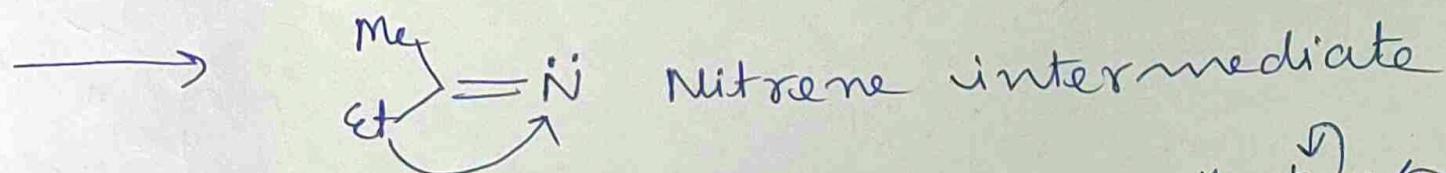
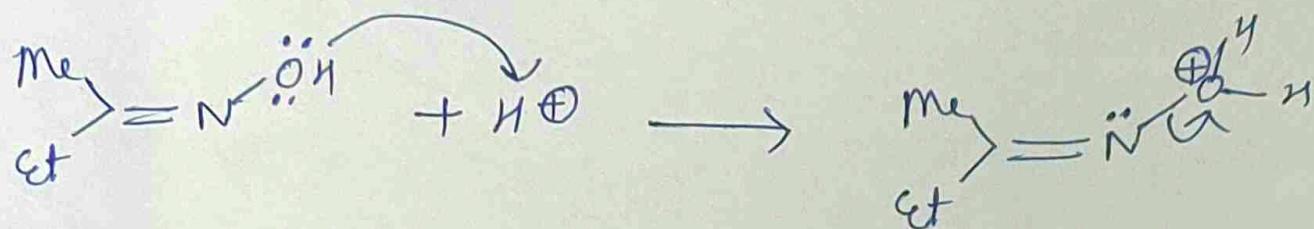


Formation: ~~when chloroform is treated with NaOH/KOH~~
~~Alts~~
~~when di-~~

KOH

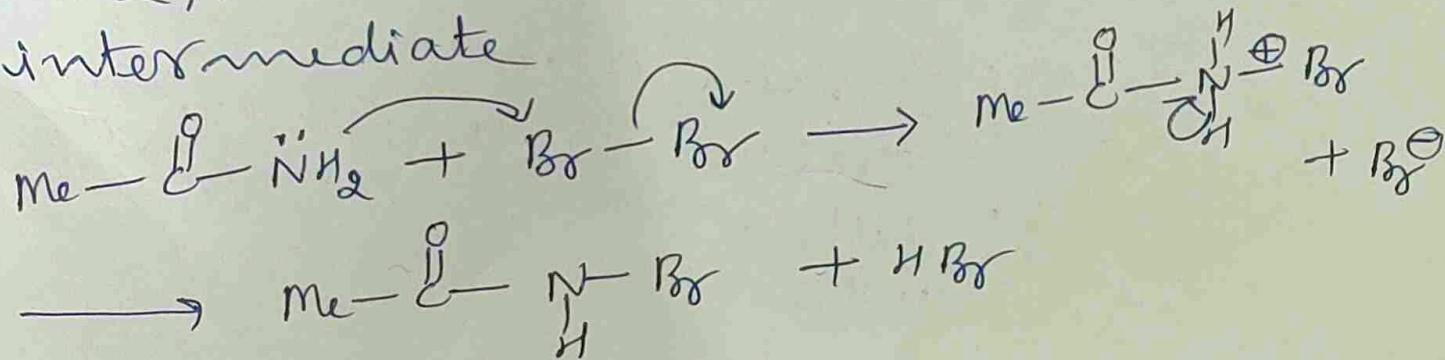
Formation of Nitrene -
Beckmann Rearrangement:

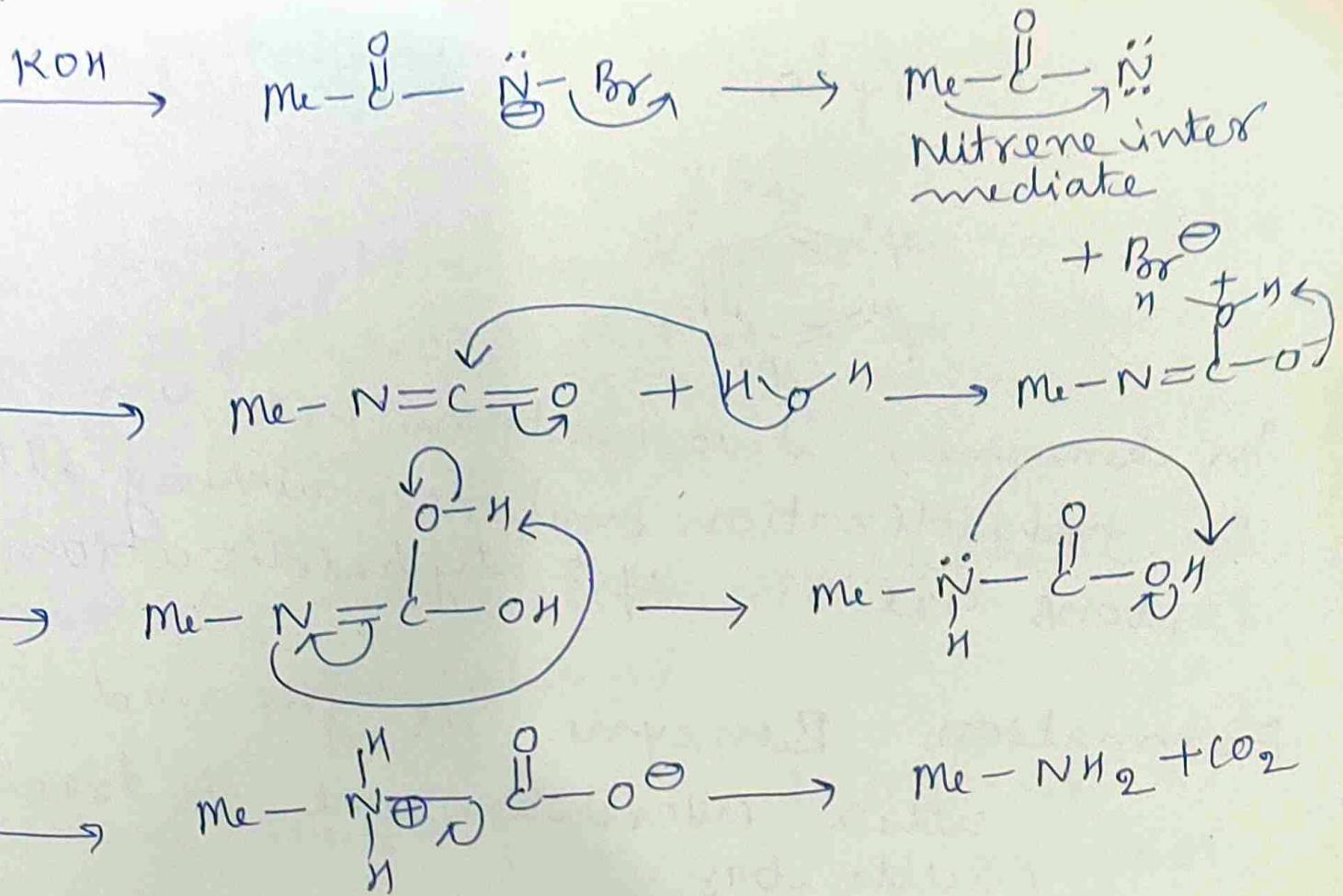
- 1) When ketoimine is treated with acid to give nitrene intermediate.



- 2) Hofmann Rearrangement -

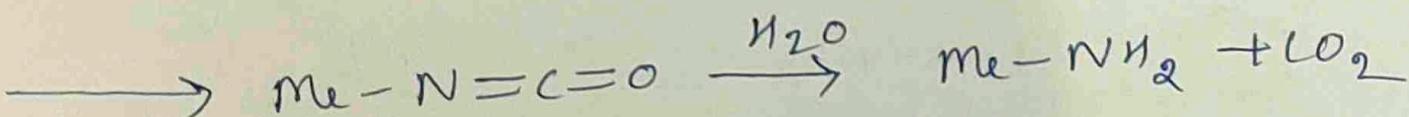
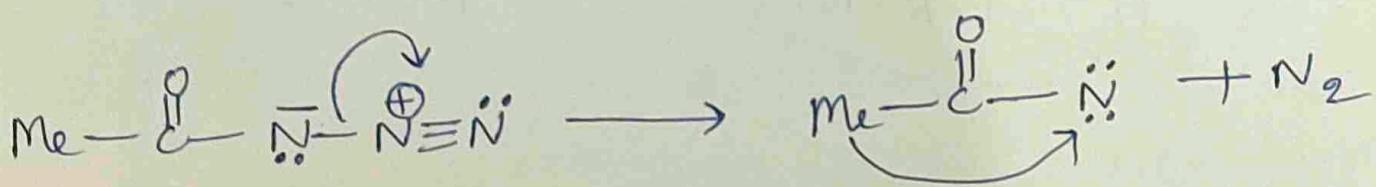
when autamide is treated with Br_2/KOH to give ~~is~~ nitrene intermediate





3) Curtius Rearrangement -:

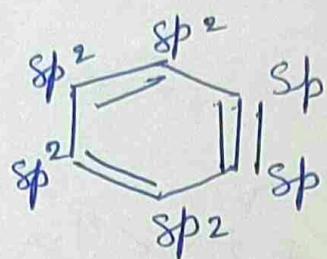
When amid azide is ~~treated~~ heated to form nitrene intermediate.



Examples of Nitrene intermediate

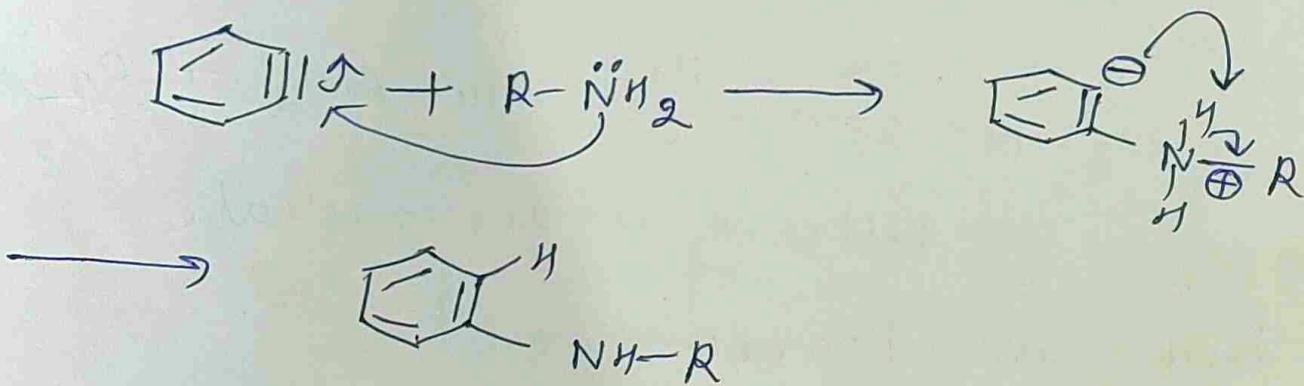
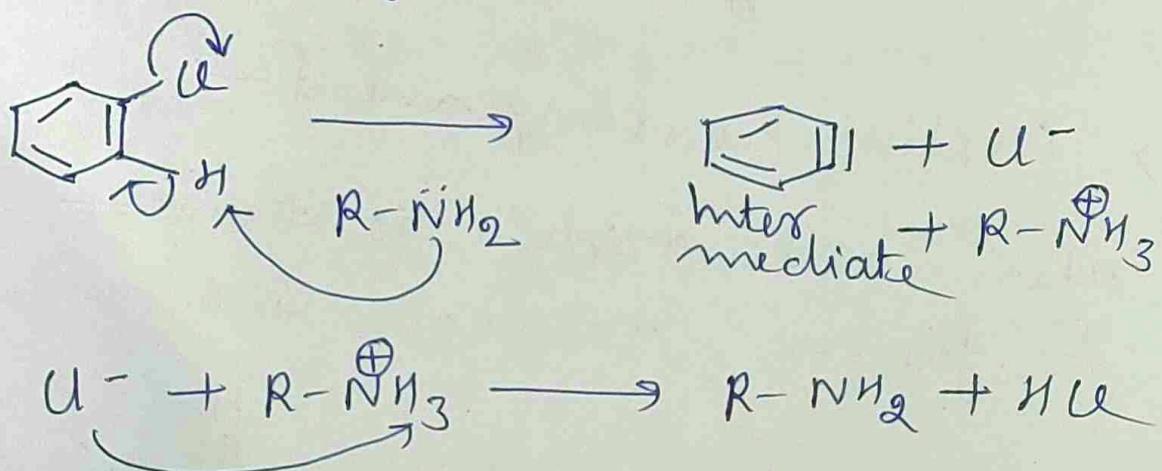
- 1) Beckmann Rearrangement
- 2) Hofmann "
- 3) Curtius "
- 4) Schmidt "

Benzyne:



In benzyne, two carbons are in sp hybridization and remaining all carbons are in sp^2 hybridization.

Formation: Benzyne is formed when chlorobenzene is treated with base.



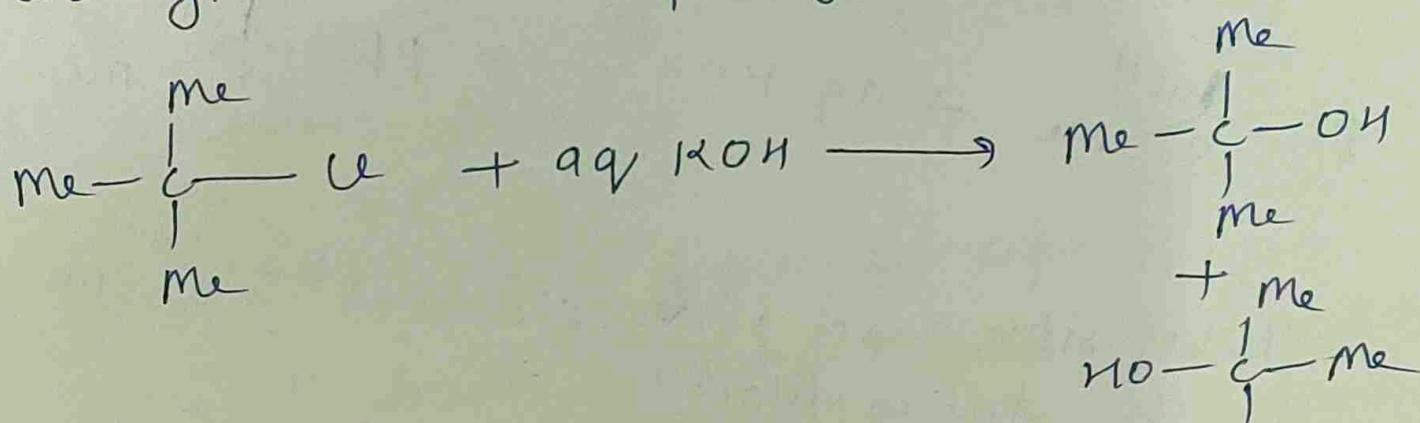
Nucleophilic Substitution

Replacement of group or atom by nucleophile is known as nucleophilic substitution. It is of two types.

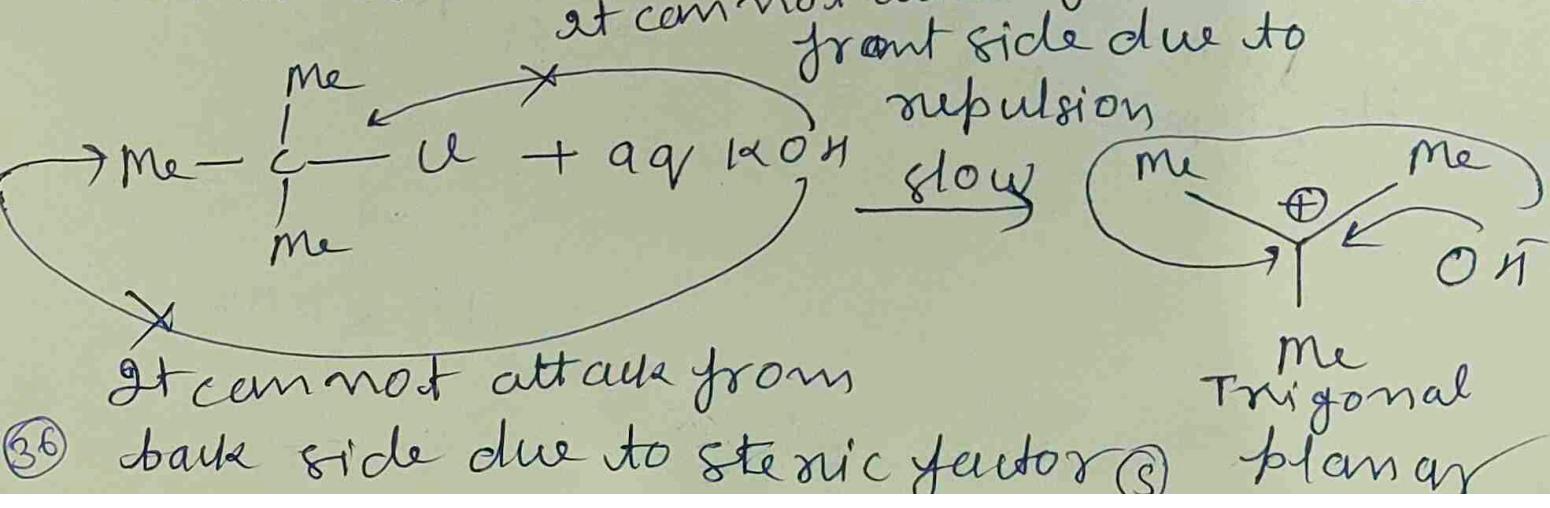
1) S_N1 and 2) S_N2

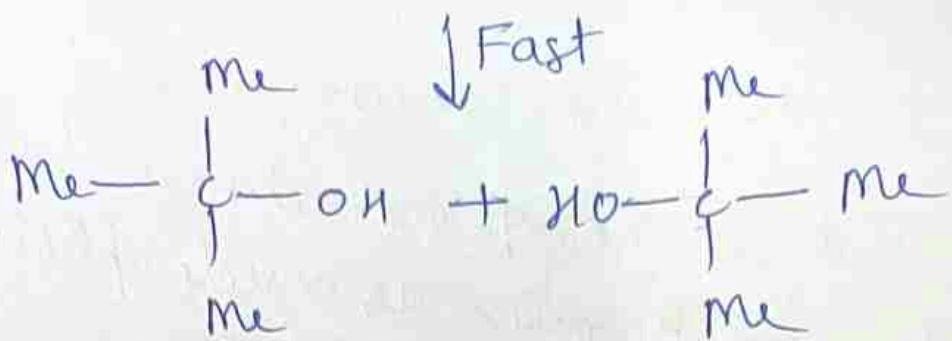
1) S_N1 (Unimolecular nucleophilic substitution)

When tertiary alkyl halide is treated with aq KOH or aq $NaOH$ to give tertiary alkyl ~~alcohol~~ alcohol.



Mechanism:-



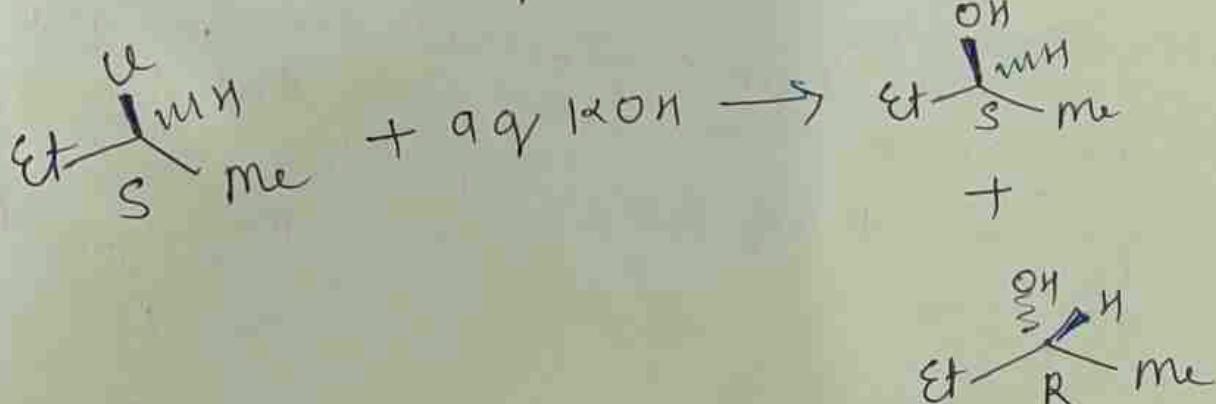
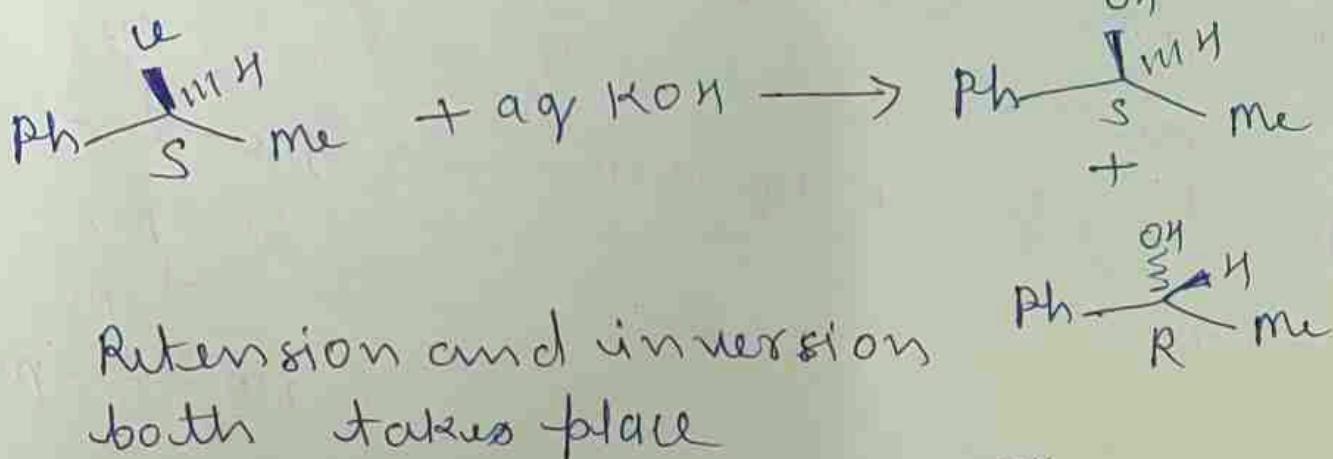


Slow step is rate determine step
as only one of alkyl halide
participate in reaction. ~~This step~~
~~This~~ is first order reaction.

$$\text{Rate} = [\text{Me}_3\text{C}-\text{I}]^1 [\text{OH}^-]^0$$

F.O.R

Example

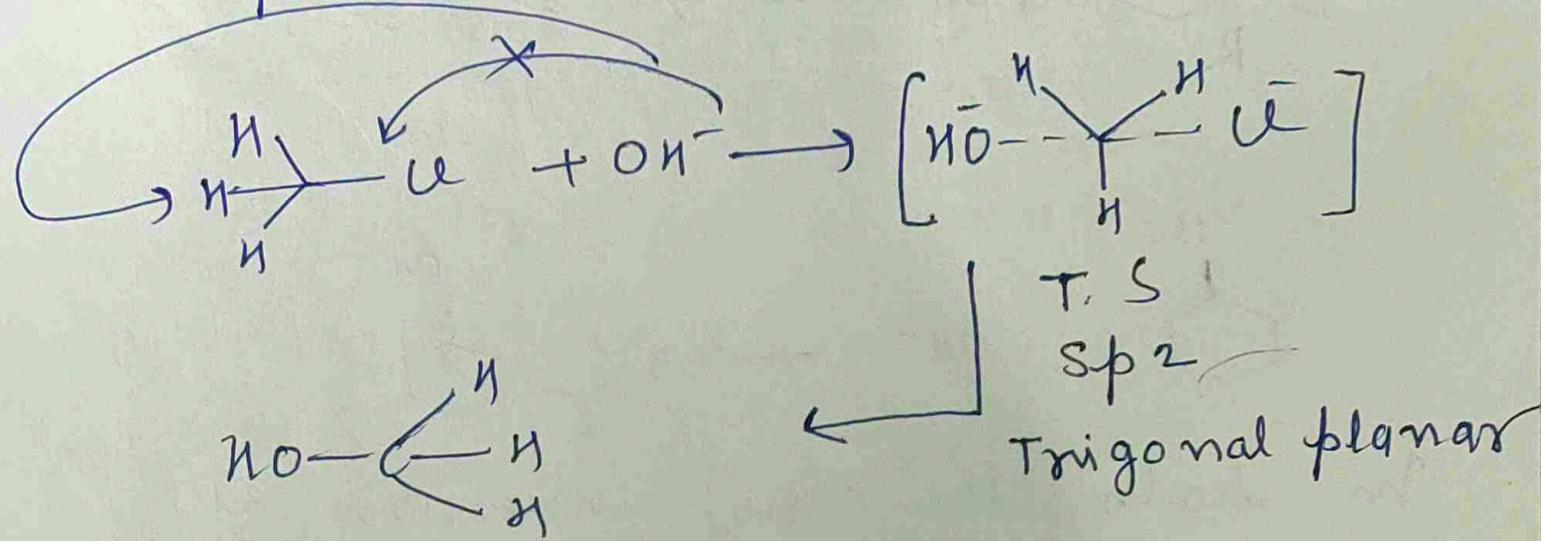


(6) (3)

S_N^2 (Bimolecular nucleophilic substitution reaction)

Generally primary alkyl halide gives S_N^2 reaction.

Nucleophile attacks from back side



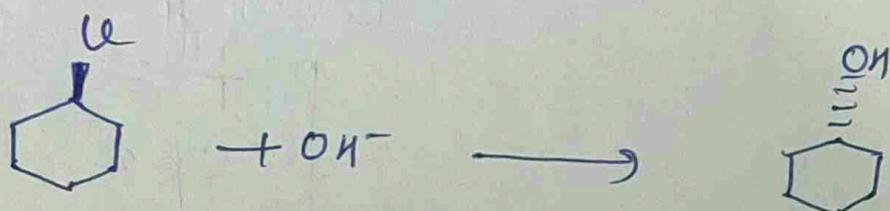
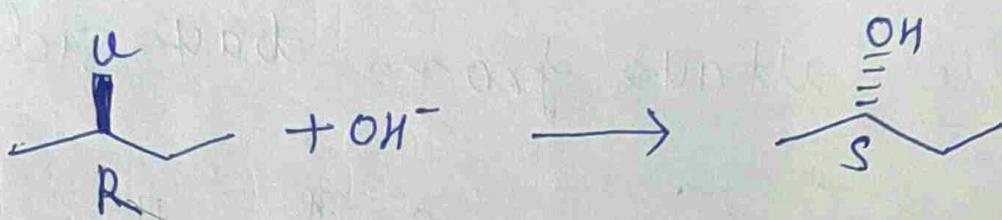
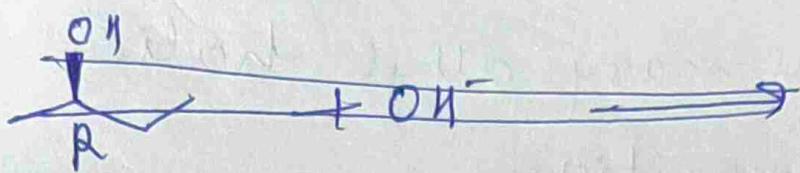
Inversion of configuration takes place.

Rate of Reaction depends upon conc of both reactant and product

$$R = [\text{CH}_3\text{I}]' [\text{OH}^-]'$$

S.O.R

Examples :-

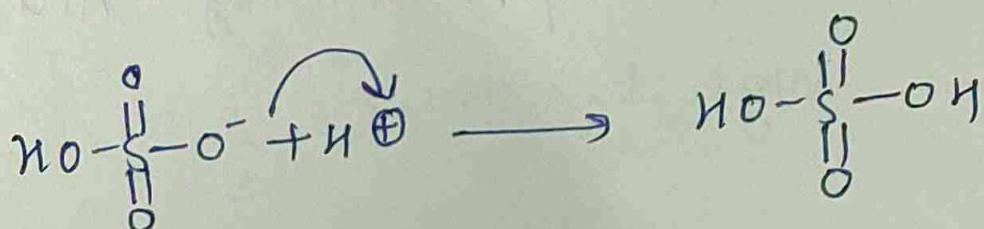
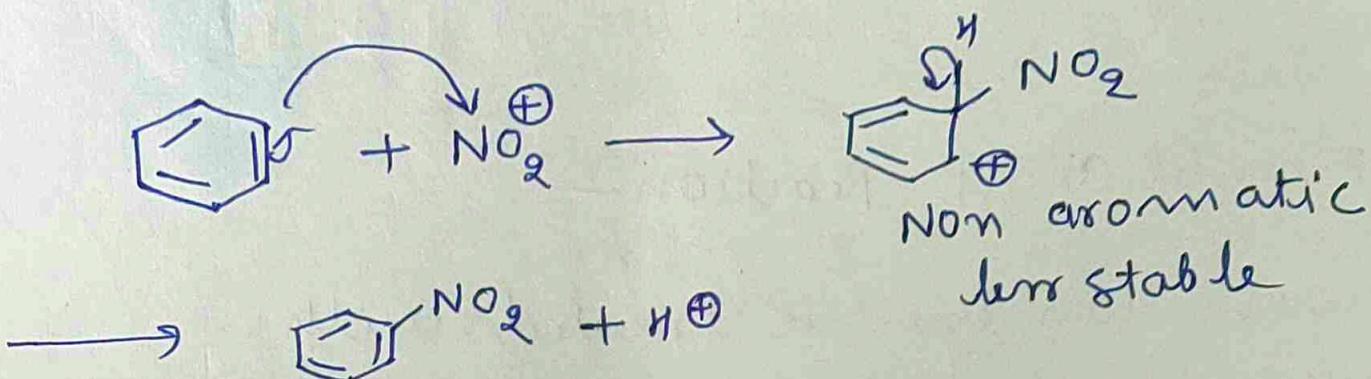
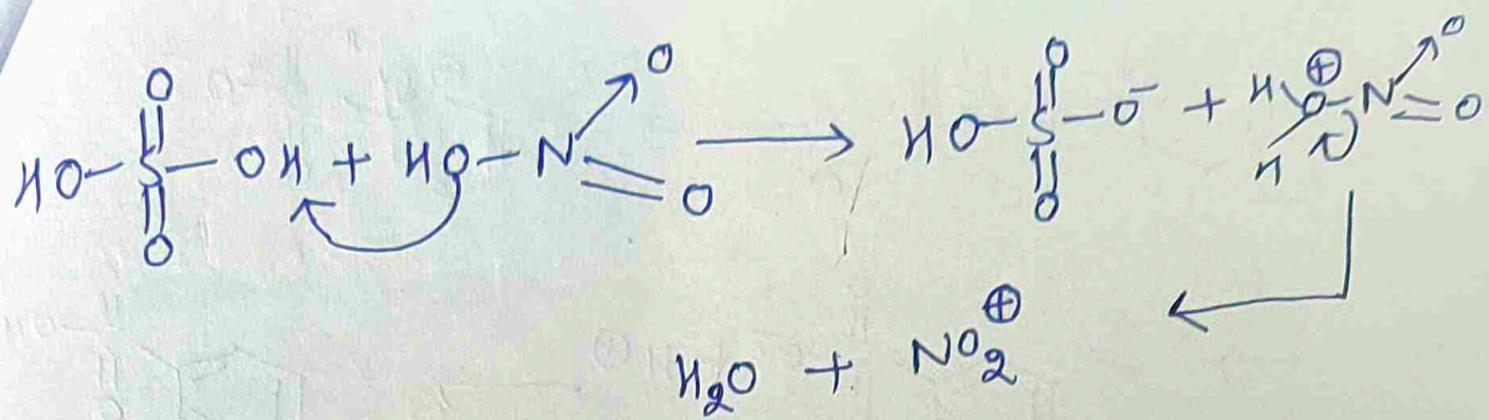


In both the cases, inversion of configuration takes place.

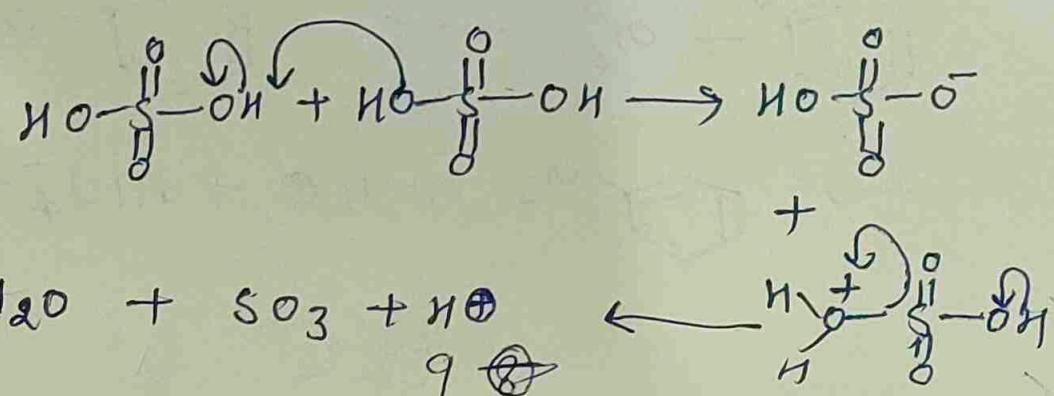
Aromatic electrophilic substitution Reaction :-

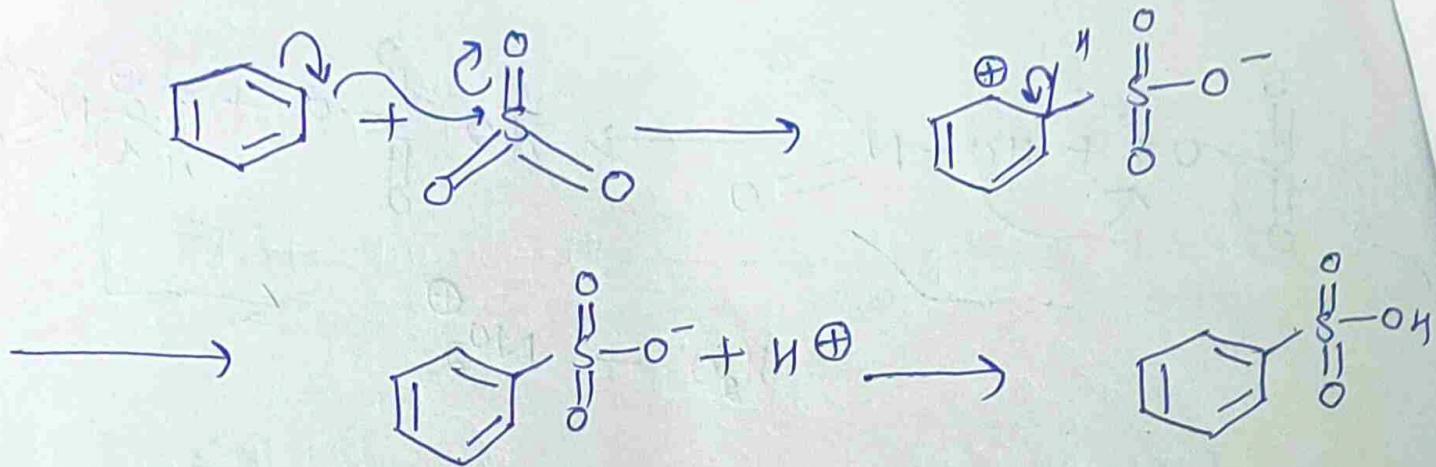
The replacement of # hydrogen atoms by electrophile is known as electrophilic substitution reaction.

- 1) Nitration:- When benzene is treated with HNO_3 / H_2SO_4 to give nitrobenzene.



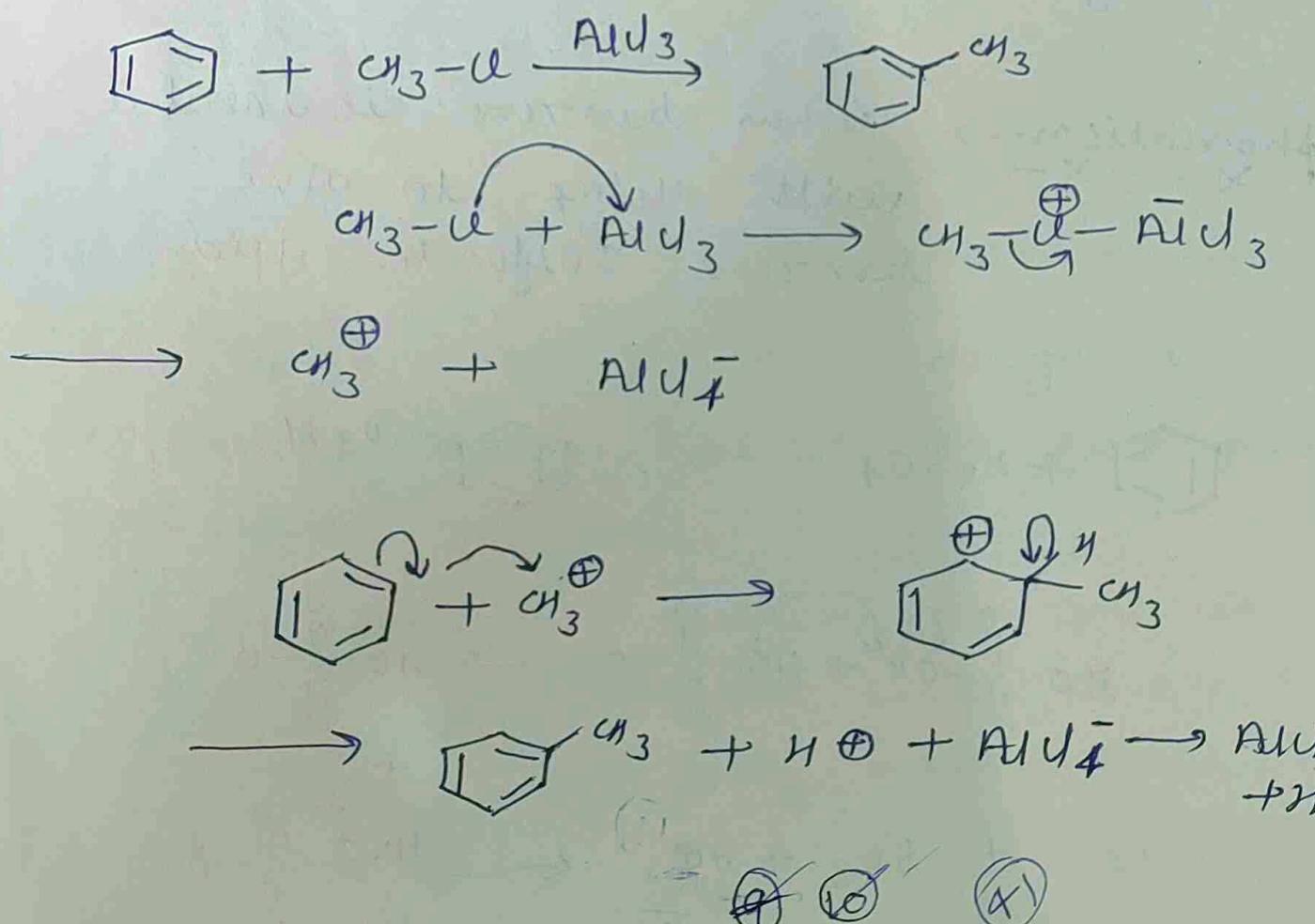
sulphonation → when benzene is treated with H_2SO_4 to give benzene sulfonic acid

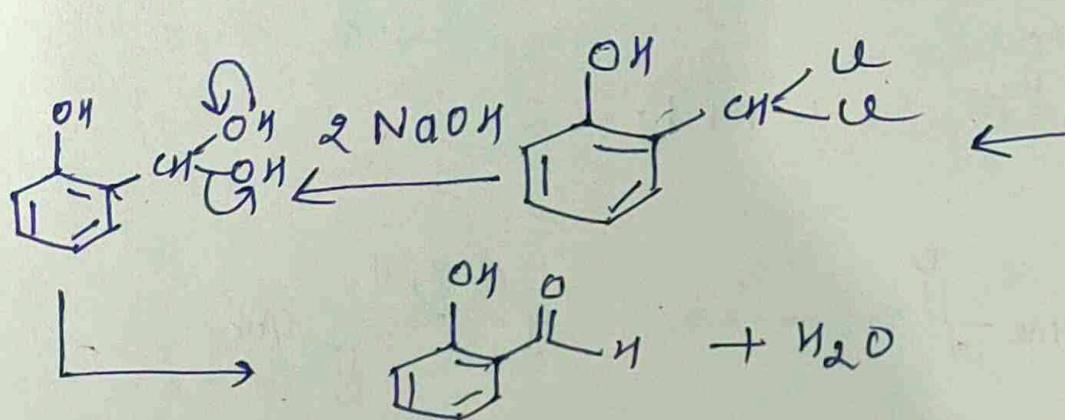
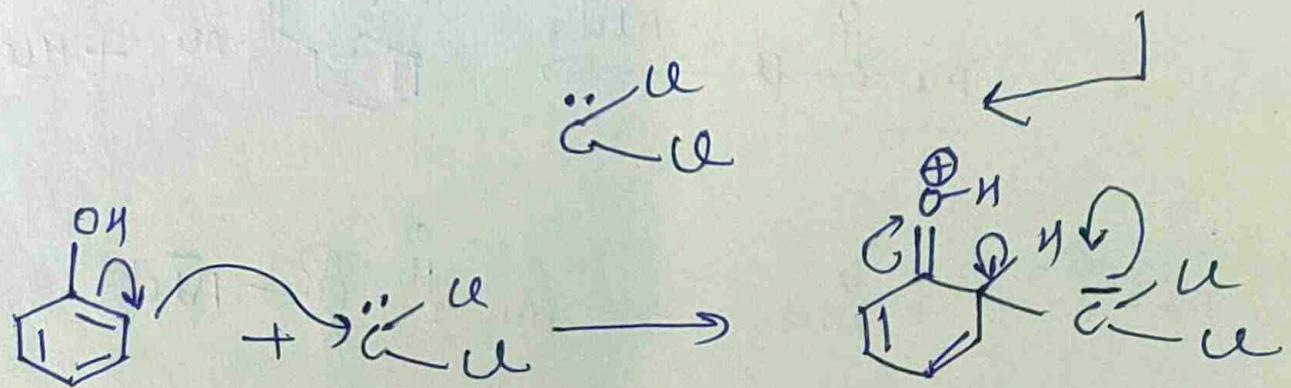
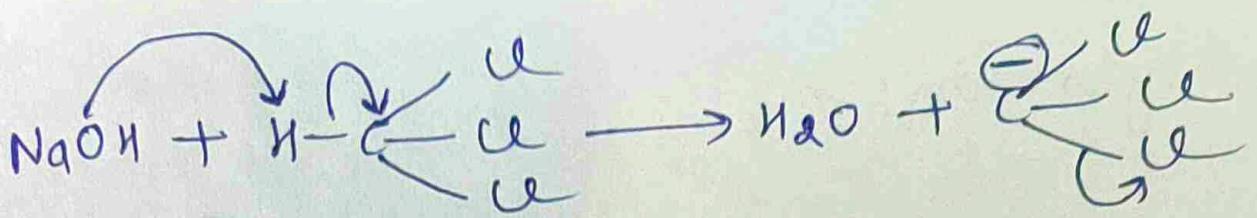




3) Friedel-Crafts Reaction :

When benzene is treated with alkyl halide in presence of AlCl_3 to form alkyl benzene.

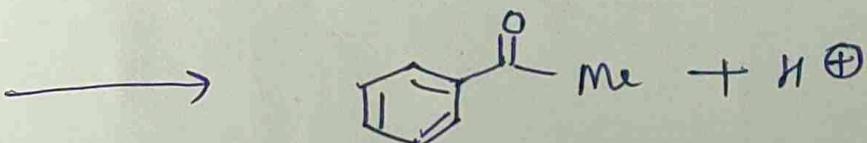
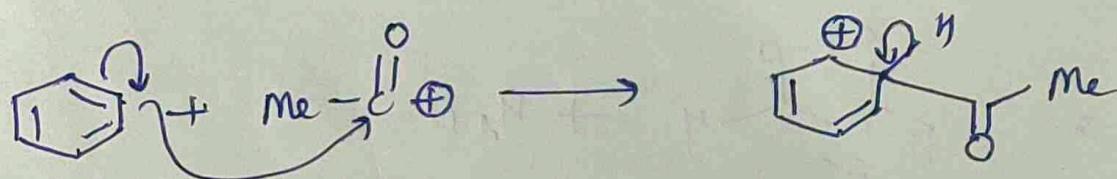
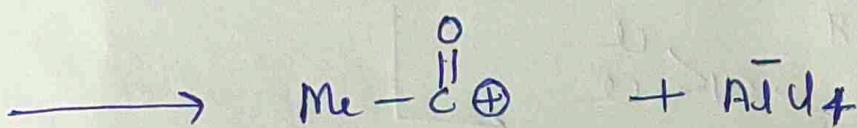
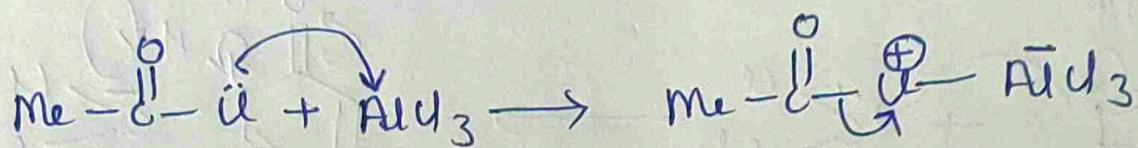
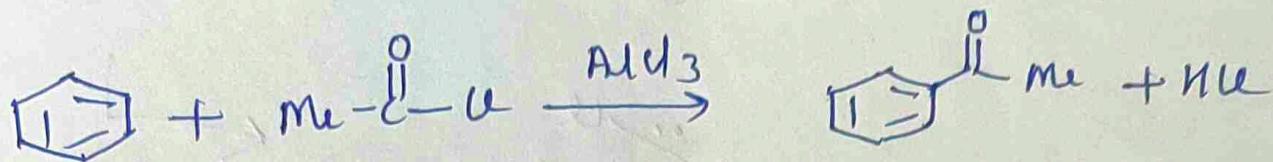




(42)

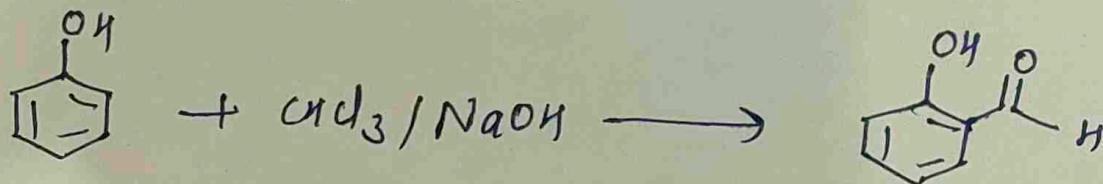
(+) (11)

Acylation: -



Reimer Tiemann Reaction: -

When ~~benzene~~^{phenol} is treated with $\text{CrCl}_3/\text{NaOH}$ to give Salicyldehyde.

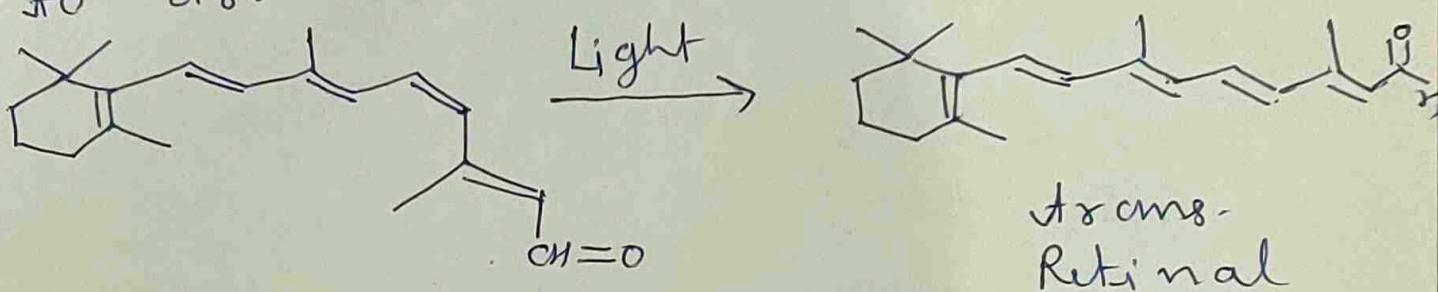


(P) (Q)

(A3)

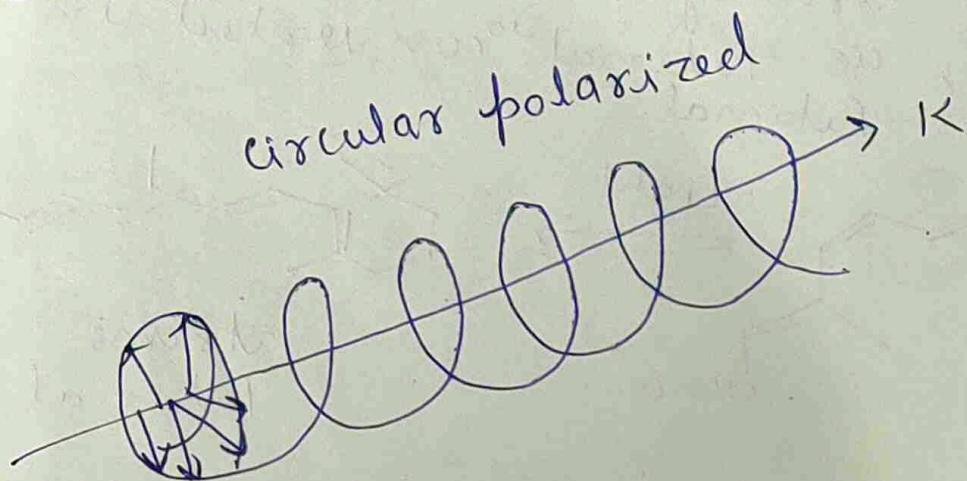
chemistry of vision

light strikes the eye and does something in the eye, and the brain receives a signal that something is there, the vision is possible because light strikes and carries out direct and uncomplicated purely chemical transformation. In this reaction, cis-Retinal is converted in to trans-Retinal.



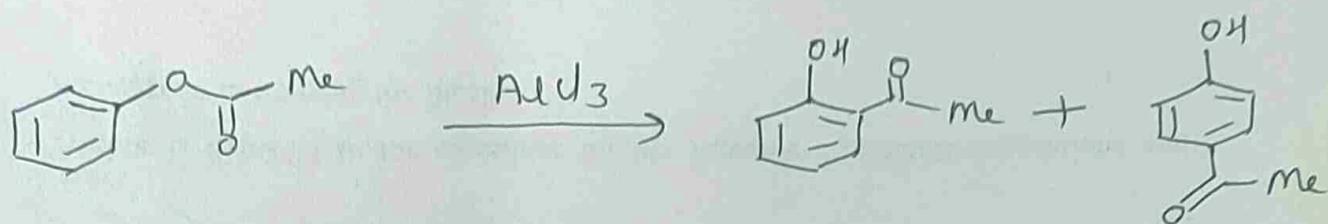
Circular Dichroism

circular dichroism an absorption spectroscopy, uses circularly polarised light to investigate structural aspects of optically active chiral media. It is mostly used to study biological molecules, their structure and interactions with metals and other ~~molecular~~ molecule

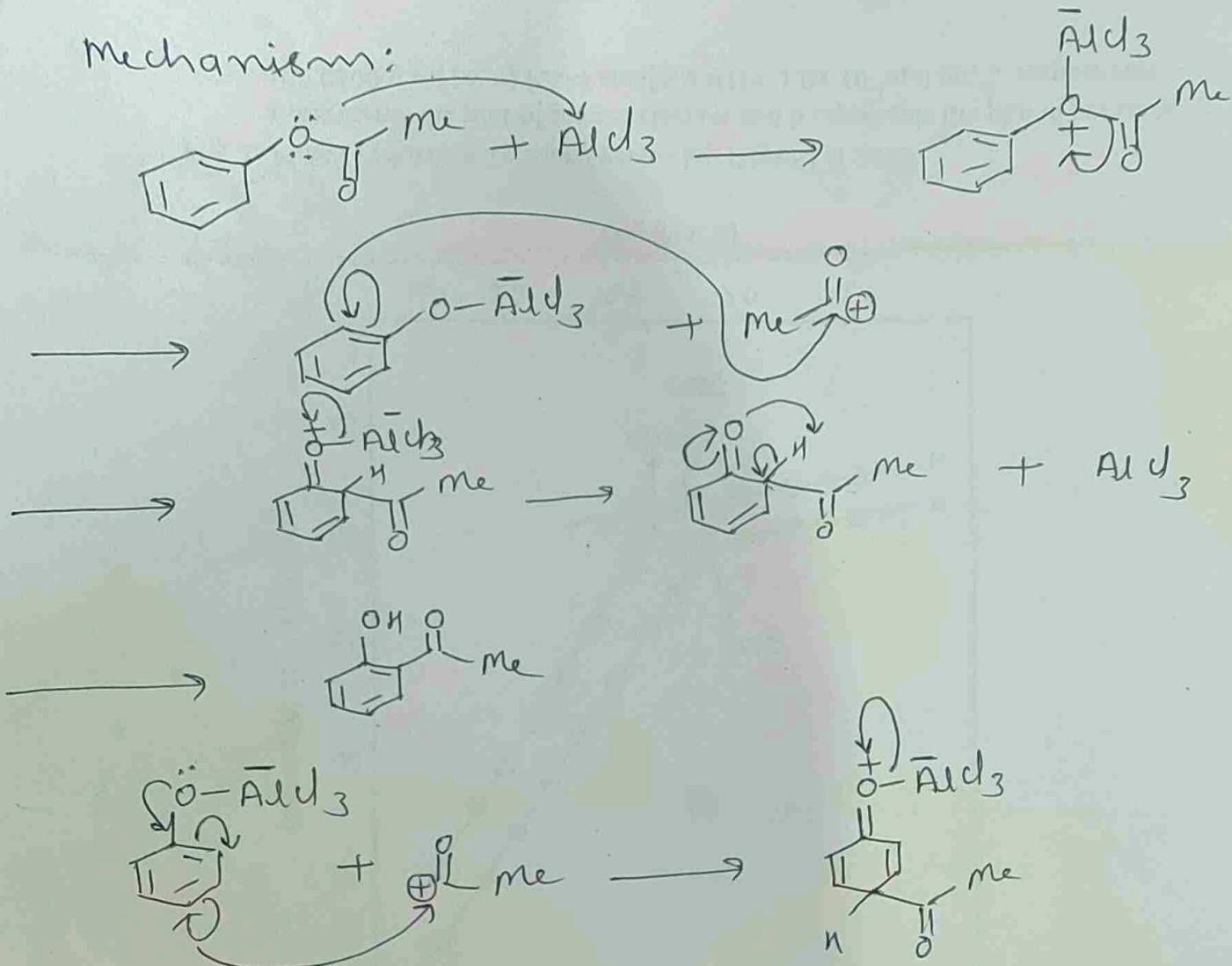


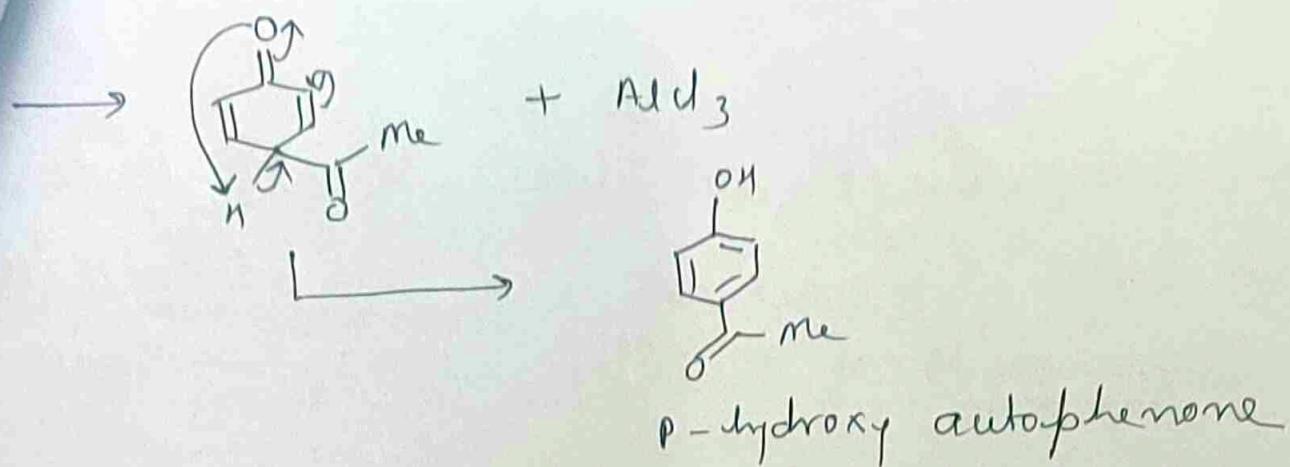
FRIES REARRANGEMENT

When phenyl acetate is treated with AlD_3 to give ortho and para hydroxy acetophenone is called Fries rearrangement



Mechanism:





Examples

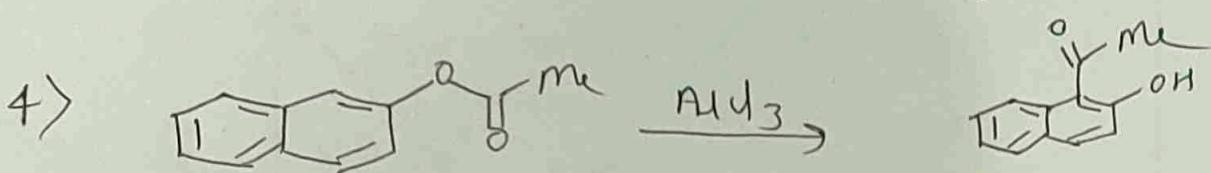
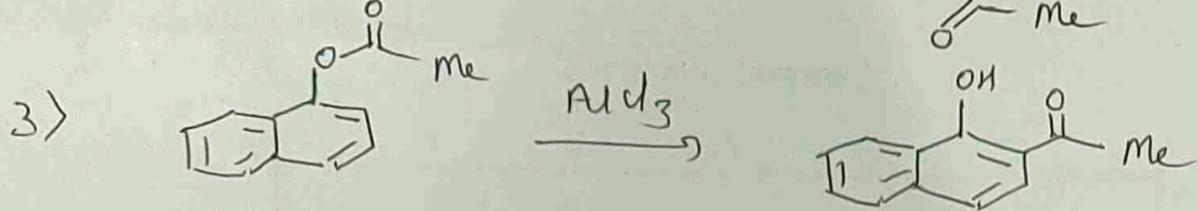
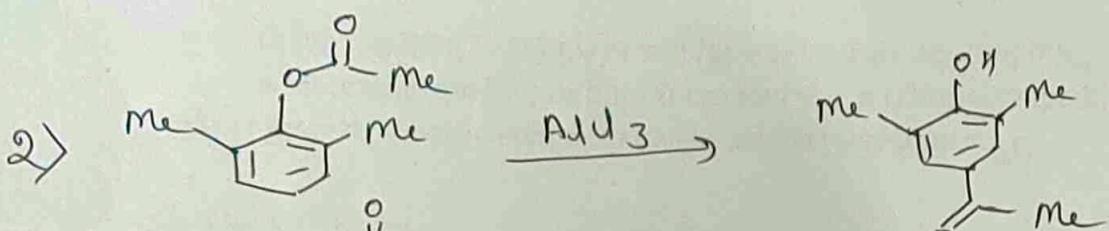
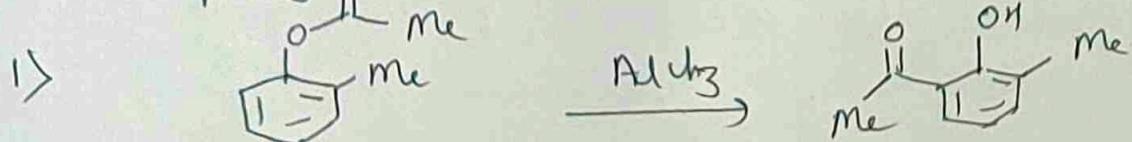
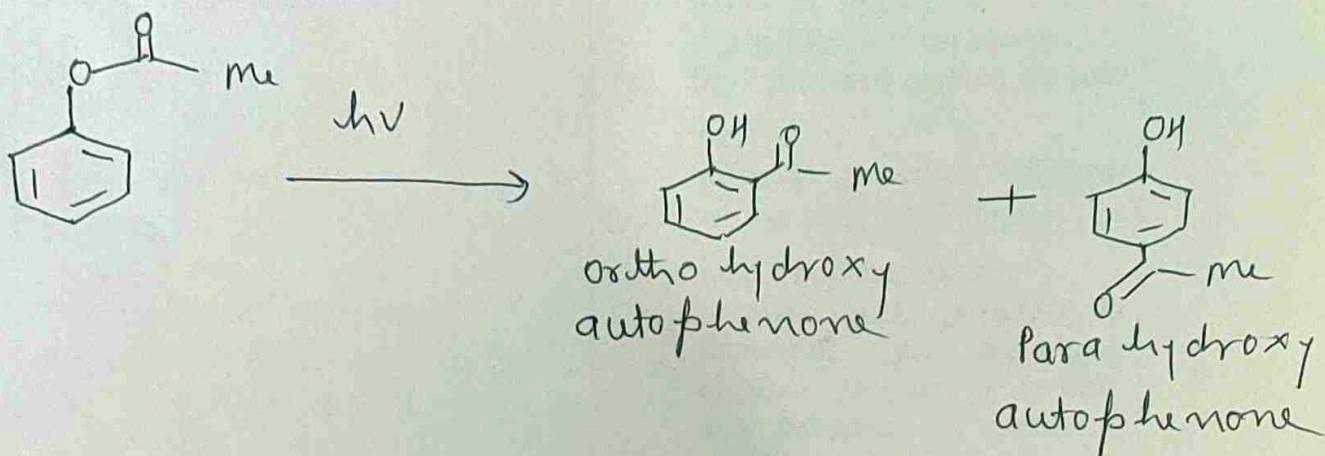
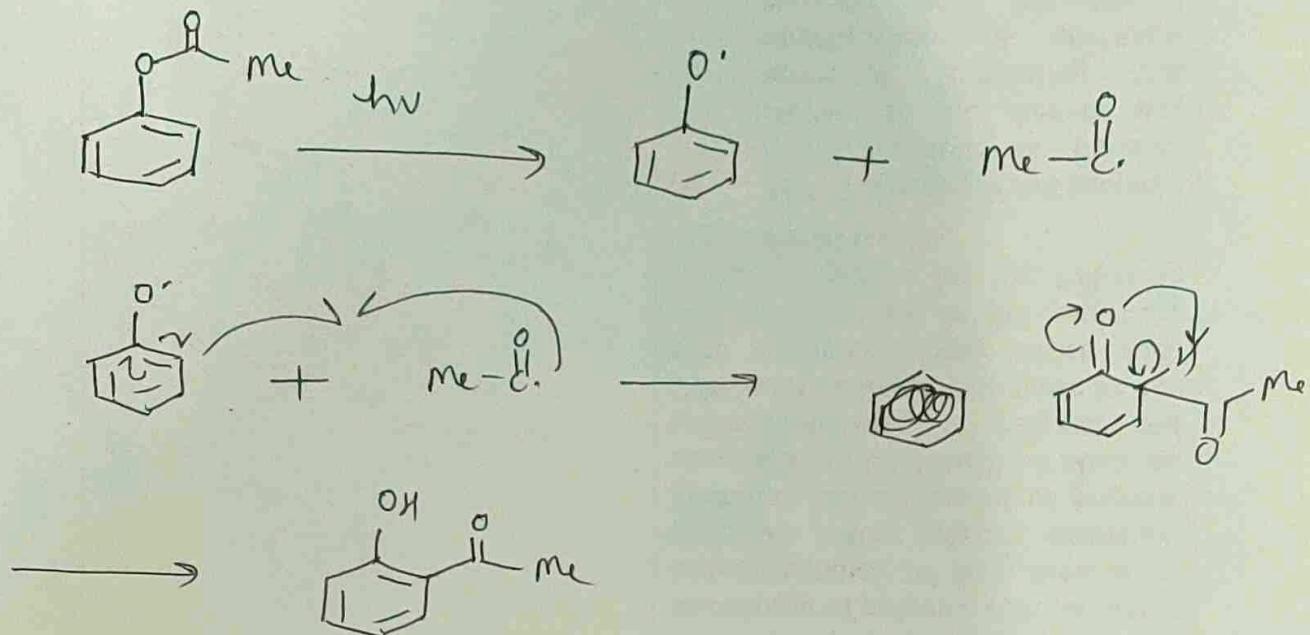


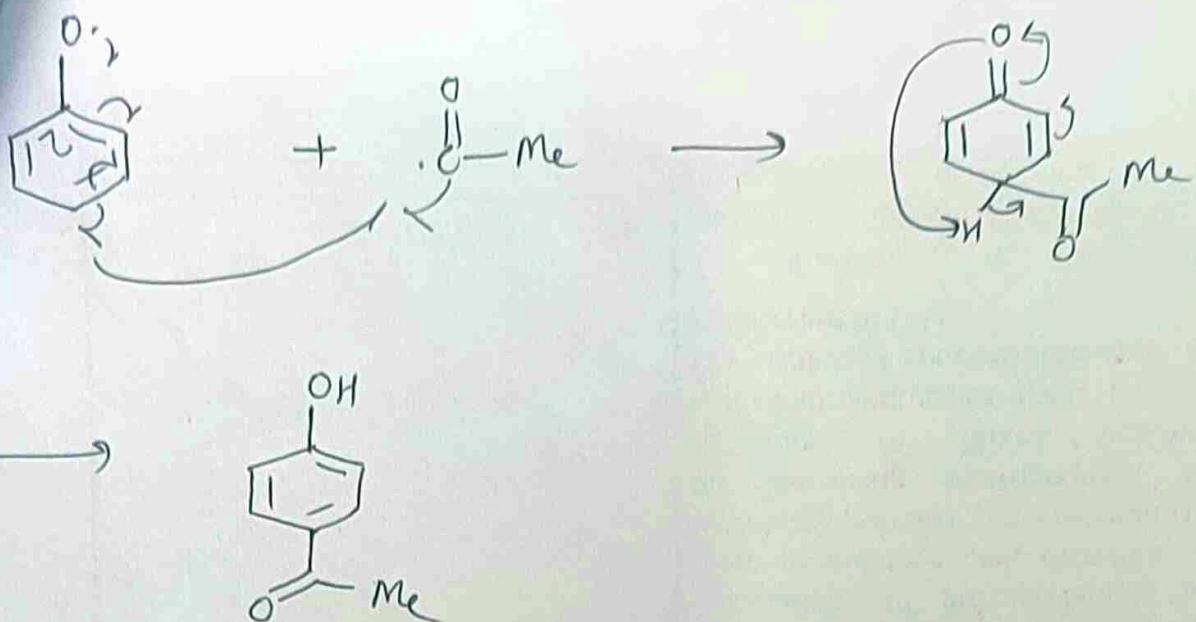
Photo Fries Rearrangement

When phenyl acetate is treated in presence of light to give ortho and para hydroxy acetophenone is called \rightleftharpoons Photo Fries rearrangement.

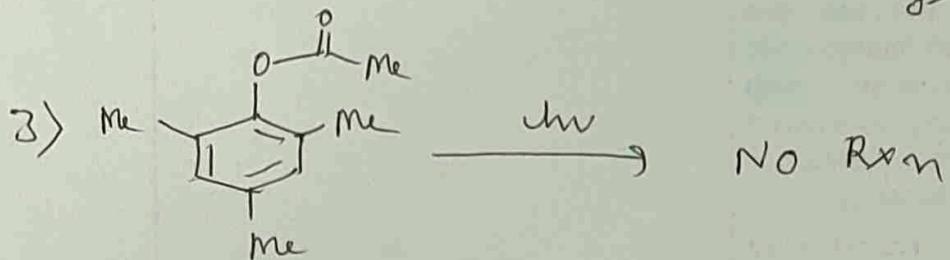
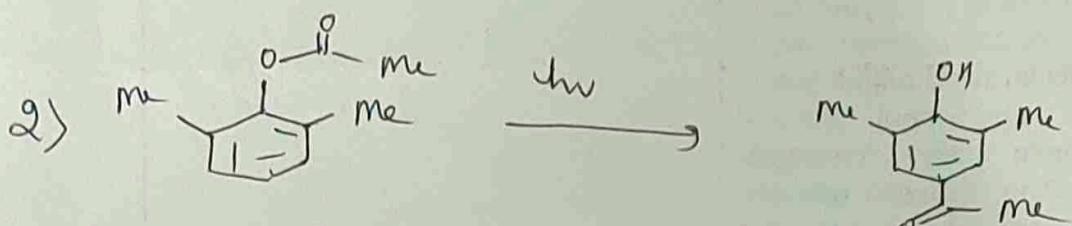
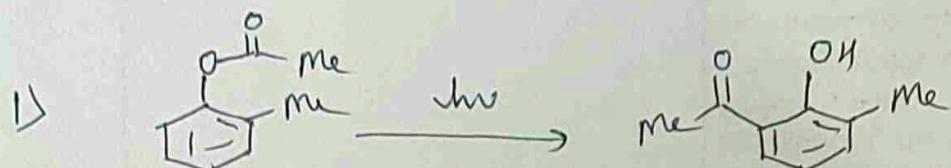


Mechanism





Example:

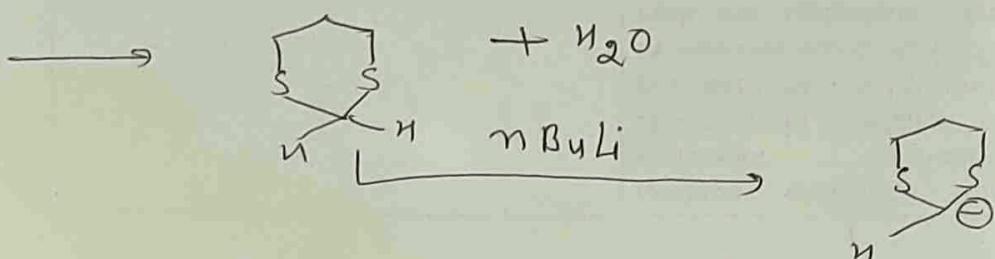
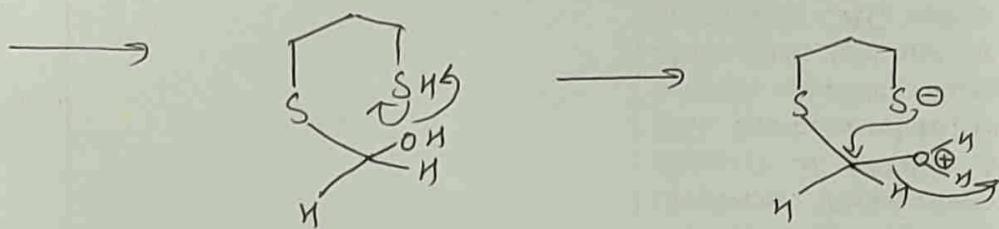
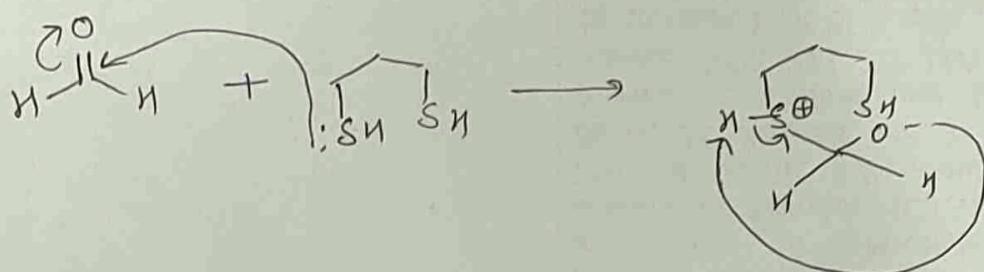
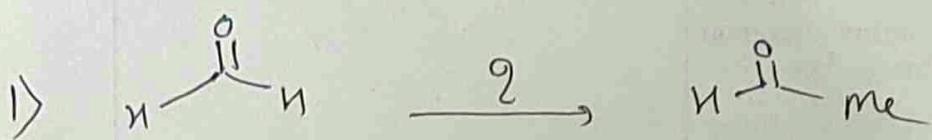
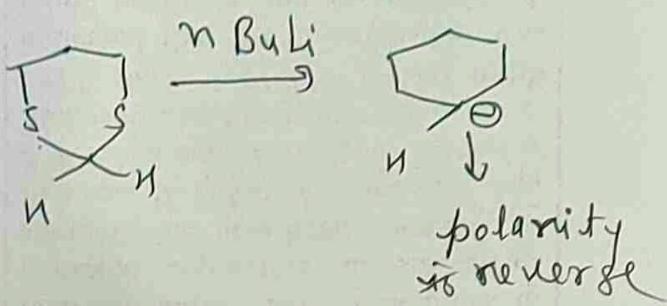
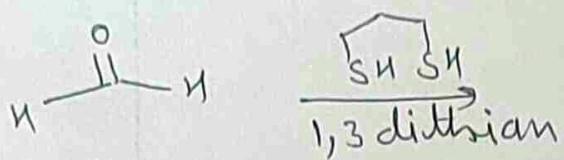


(49)

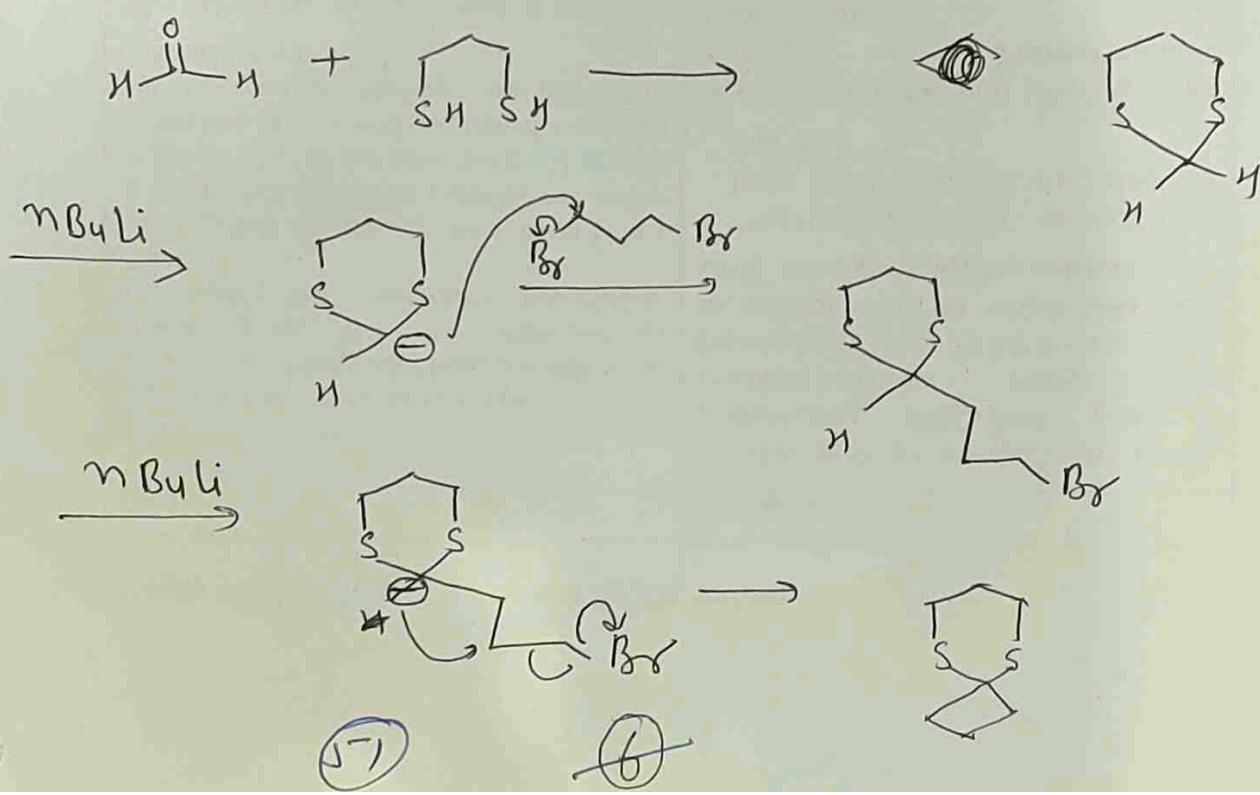
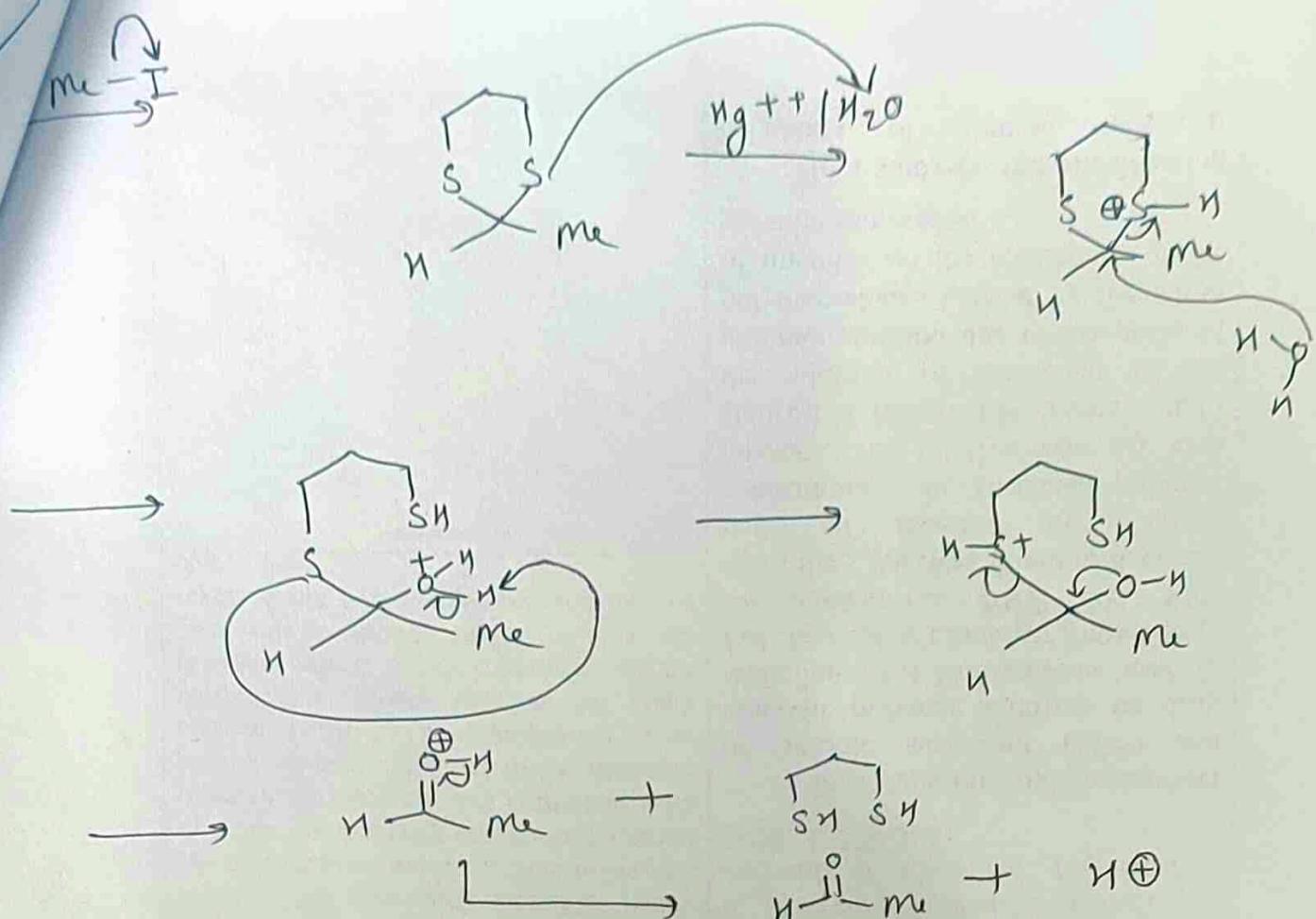
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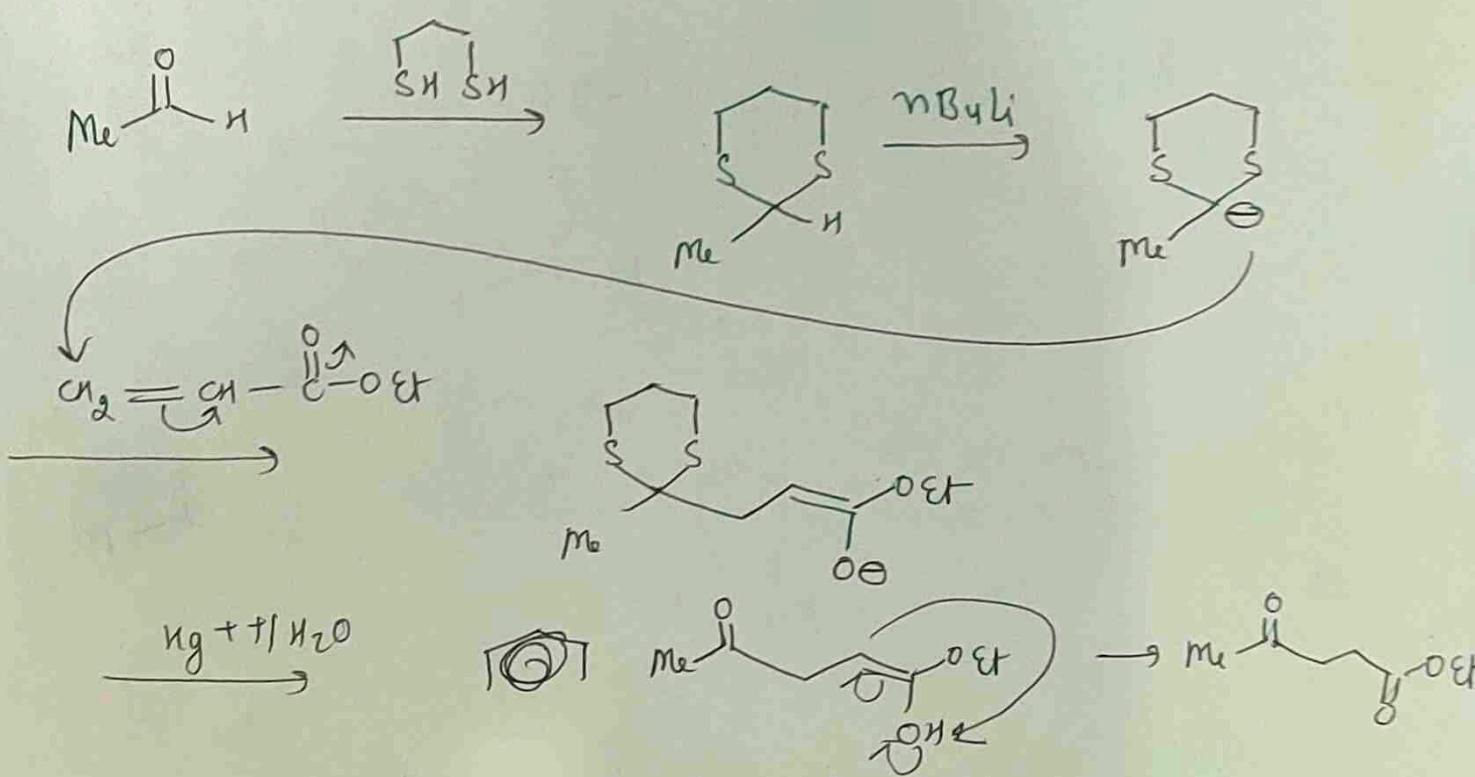
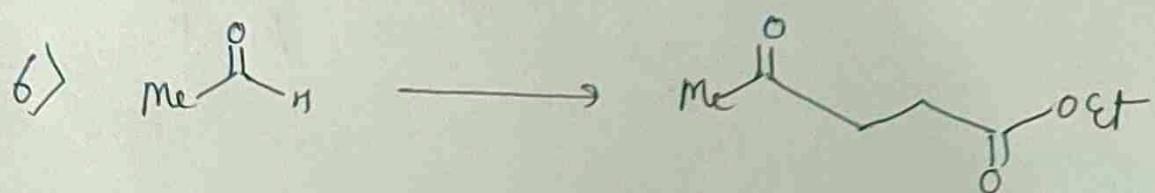
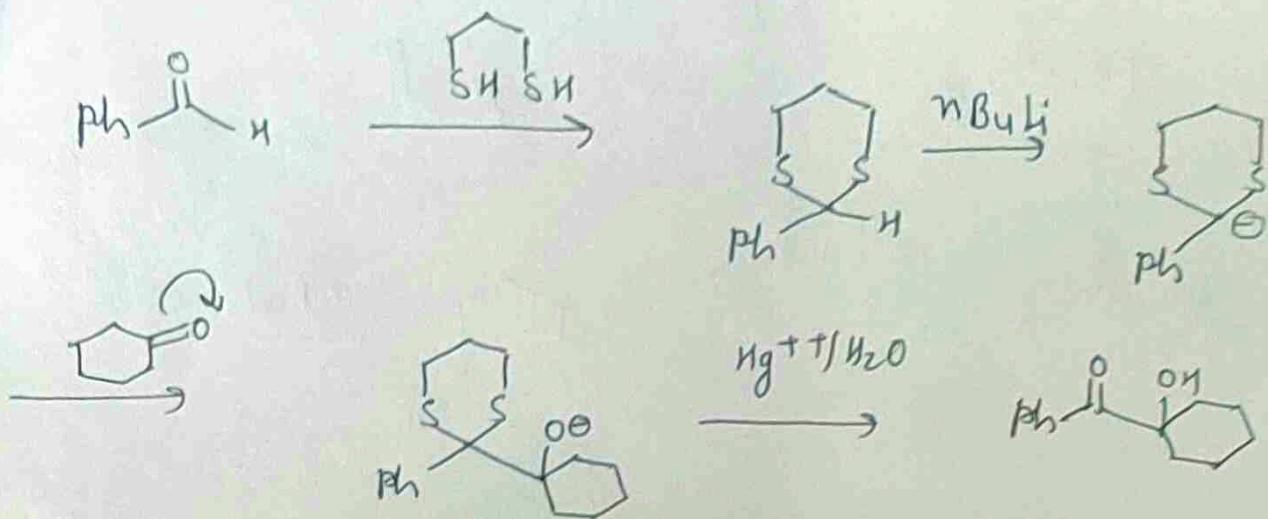
Umpolung:

Reversal of polarity is called Umpolung.



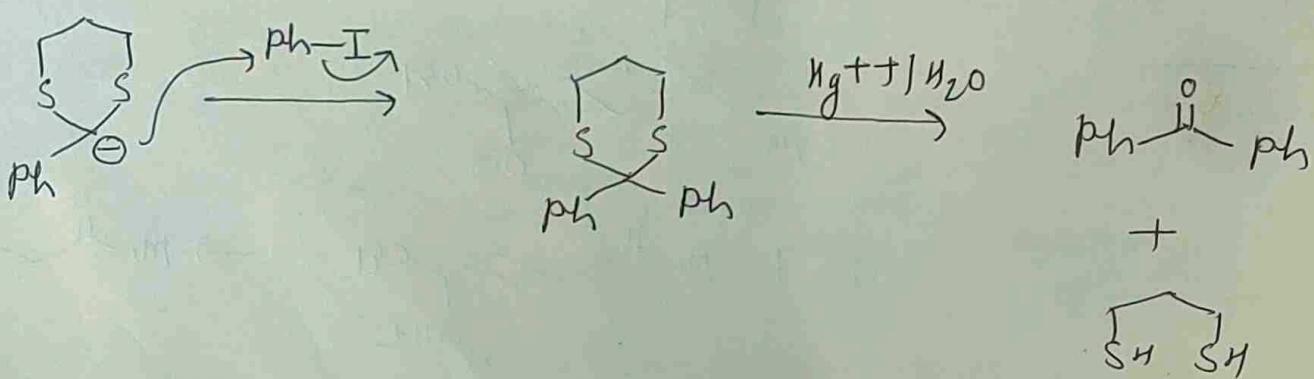
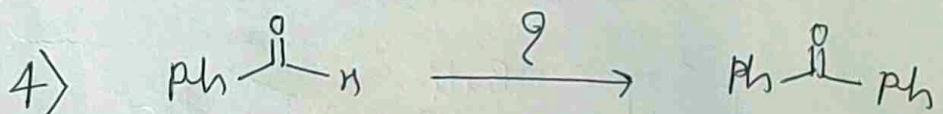
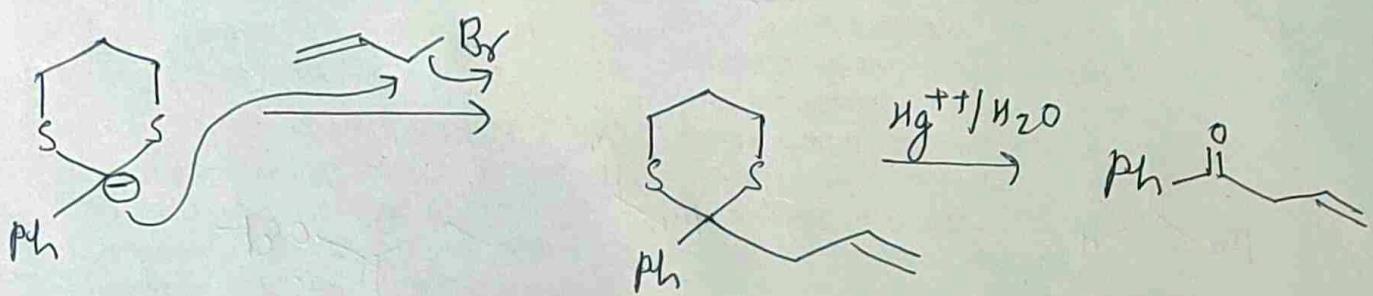
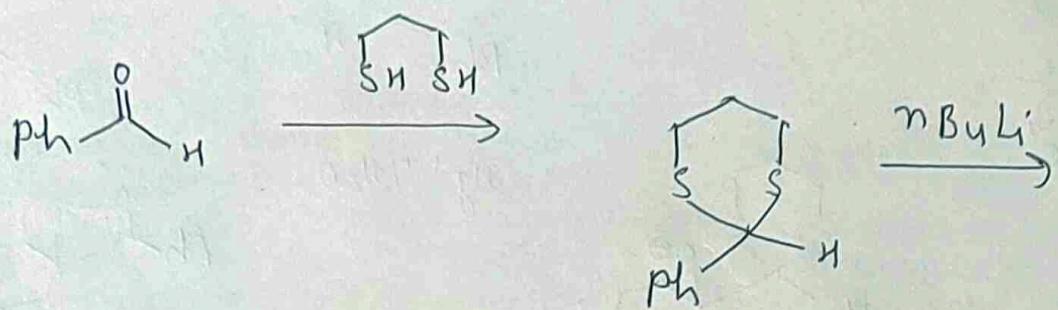
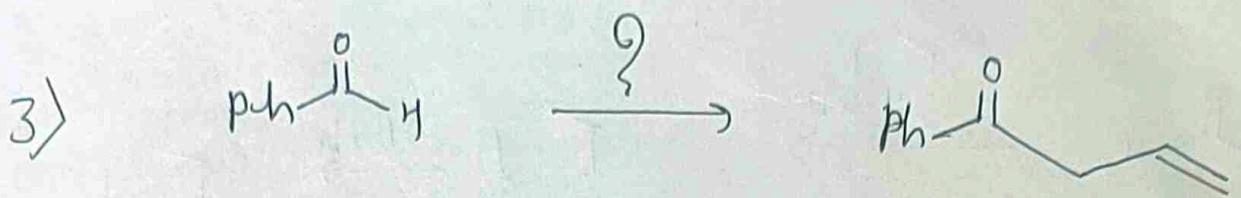
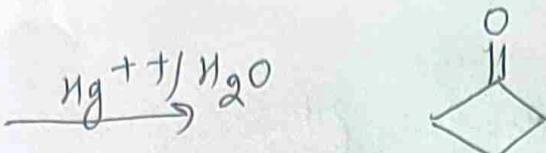
(S) (S)





(52)

(8)

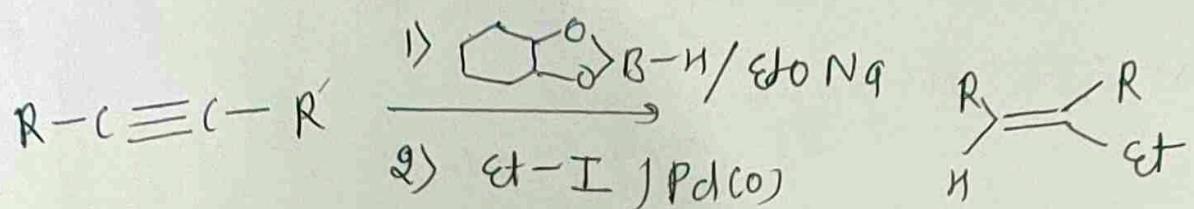


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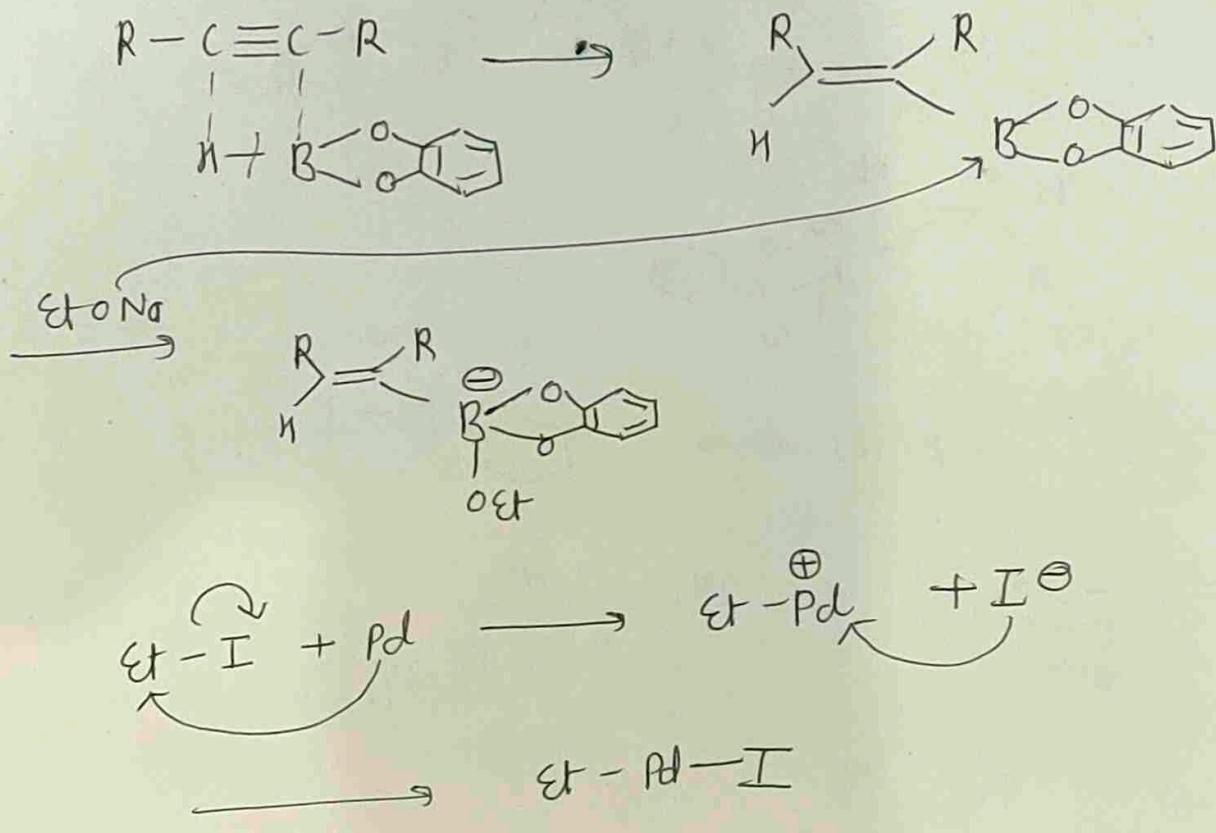
⊕

SUZUKI REACTION:

Alkylation or arylation of alkyne by boronic ester in presence of $\text{Pd}(\text{OAc})_4$ and base is called Suzuki reaction.

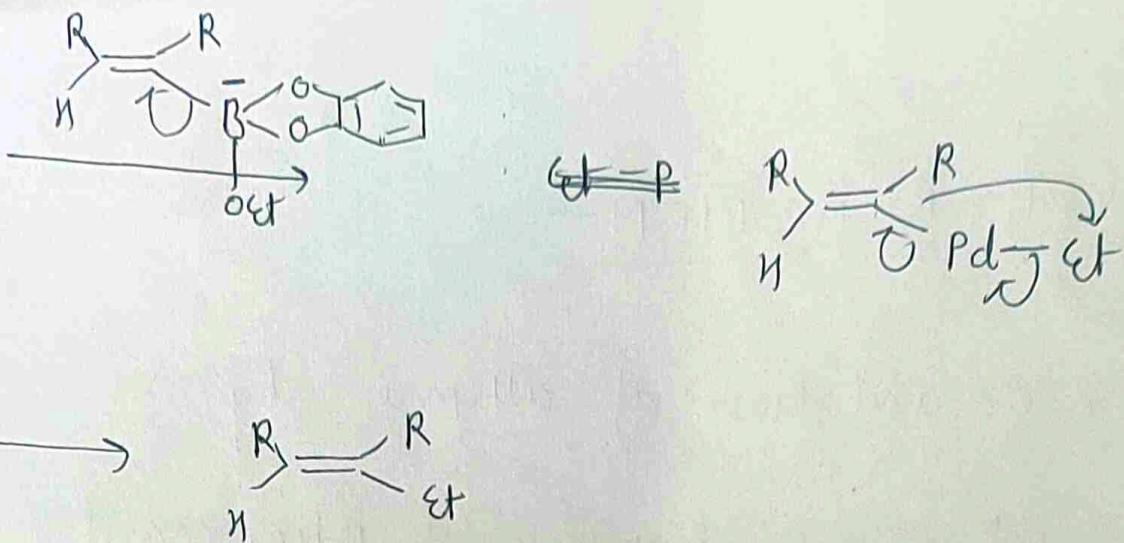


Mechanism +

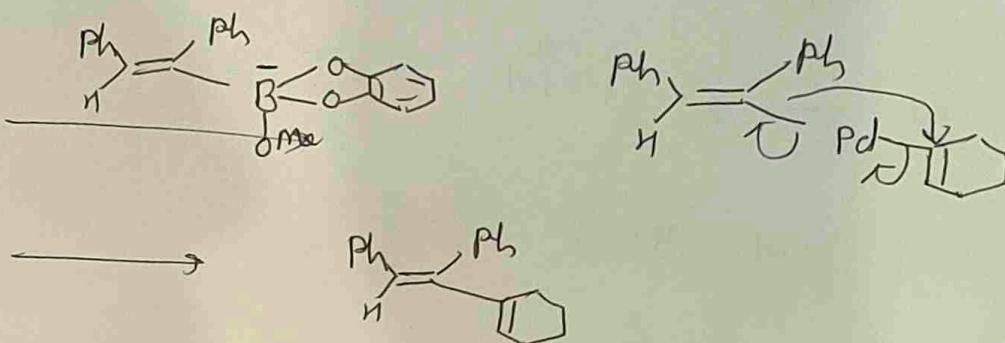
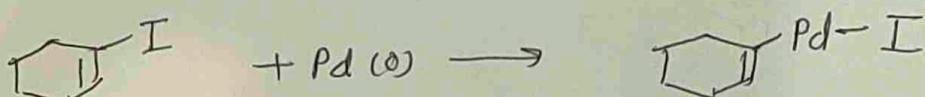
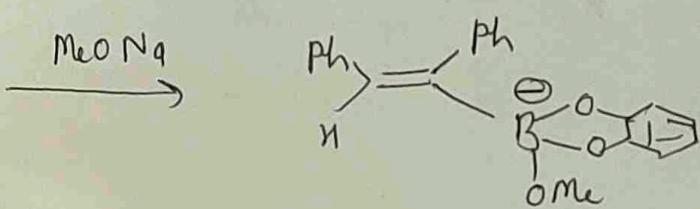
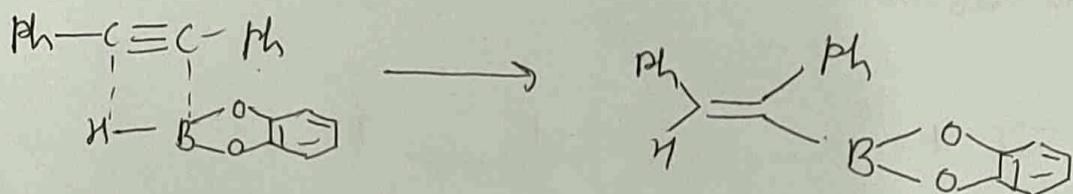
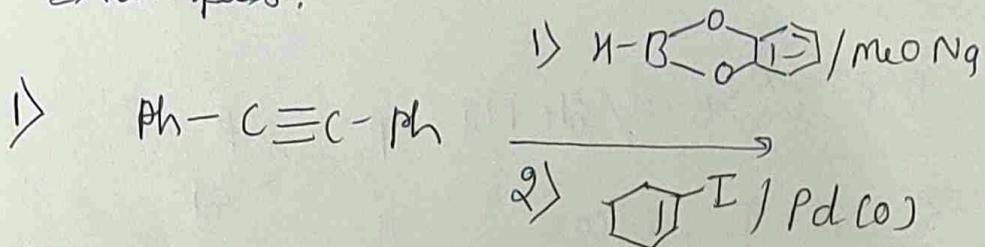


(54)

(9)

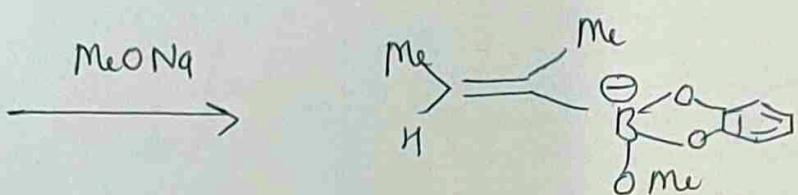
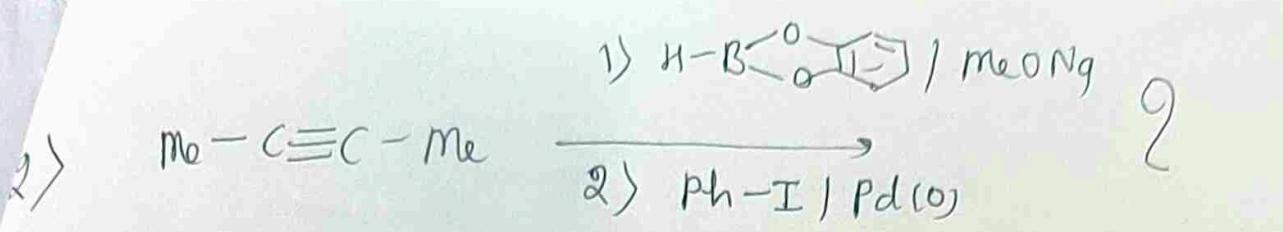


Examples:



(10)

(55)



Wagner-Meerwein rearrangement

It is a class of carbocation 1,2-rearrangement reactions in which a hydrogen, alkyl or aryl group migrates ~~to~~ from one carbon to α neighboring carbon.

