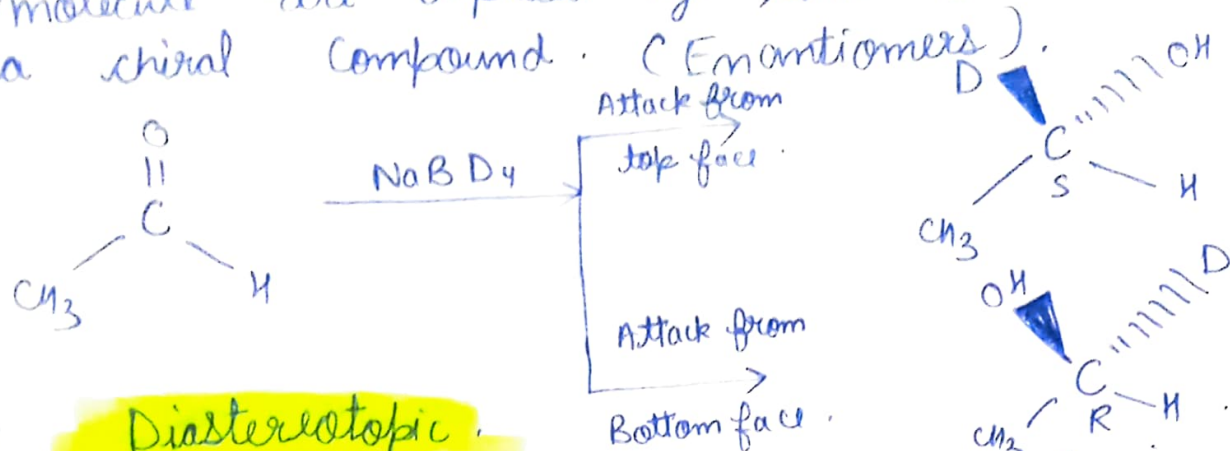


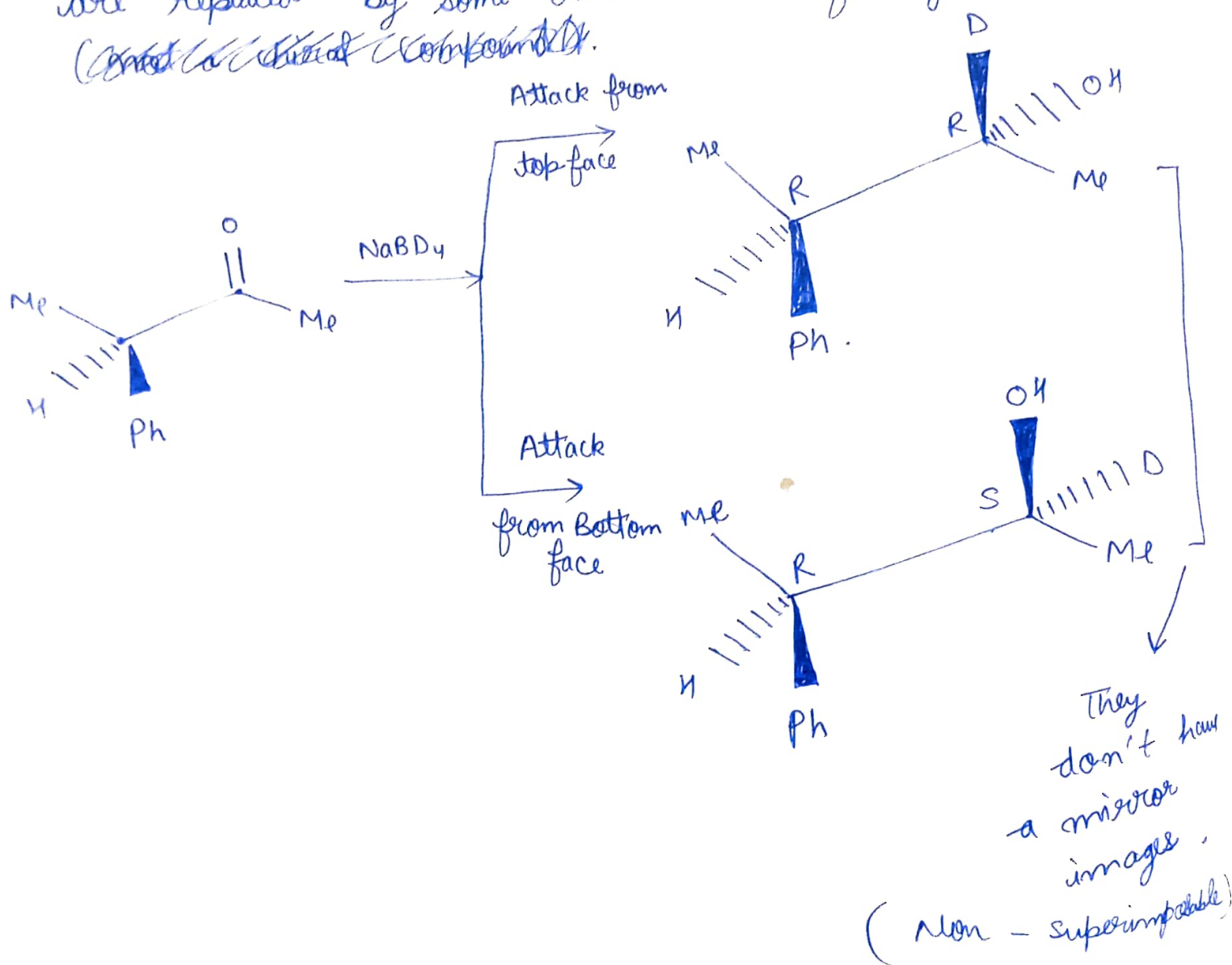
Enantiotopic

It is a term used when two substituents in a molecule are replaced by some other atoms forming a chiral compound. (Enantiomers).



Diastereotopic

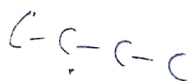
It is a term used when two substituents in a molecule are replaced by some other atoms, forming diastereomers (~~not a chiral compound~~).



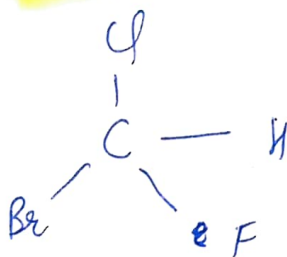
Asymmetric Synthesis:- It is synthesis of optically active product from optically inactive substrate with or without use of enantiomer.

Types:-
① Absolute asymmetric synthesis:- It is synthesis of optically active product from optically inactive substrate without using enantiomer (chiral molecule).

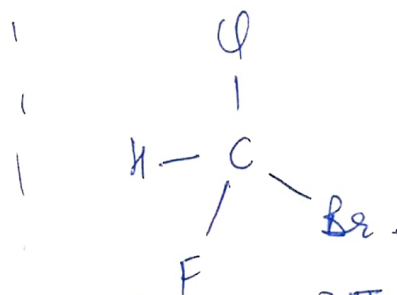
② Partial asymmetric synthesis:- It is synthesis of optically active product from optically inactive substrate by ~~not~~ using enantiomer (chiral).



Optical Purity:-



(Enantiomer) I



(Enantiomer) II

⇒ mirror image Non-Superimposable.

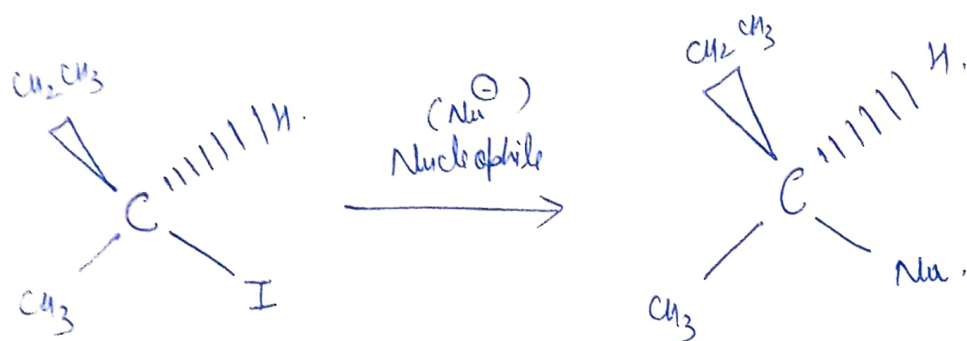
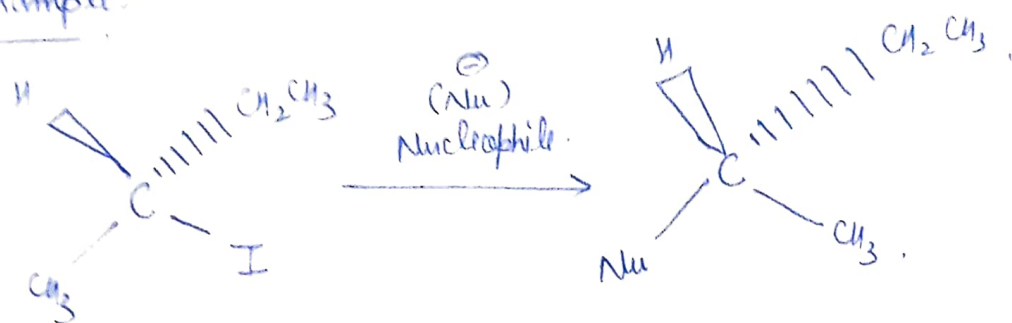
⇒ Sample that contain only one enantiomeric form (it may be I and II from example) are optically active.

Stereoselective and Stereospecific Reactions

Stereospecific

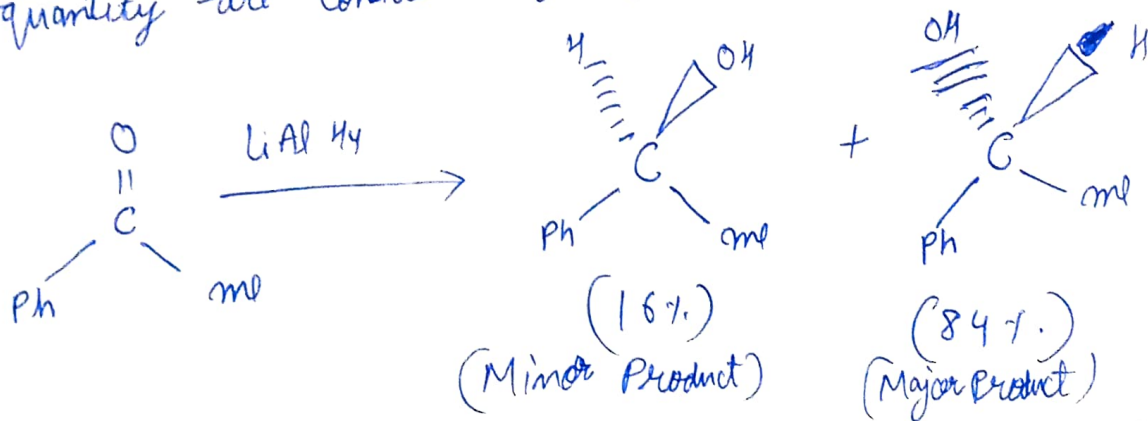
The stereochemistry of reactant completely determines the stereochemistry of product.

Example:-

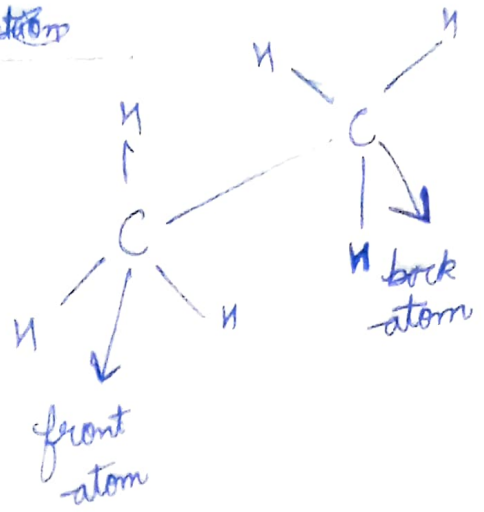
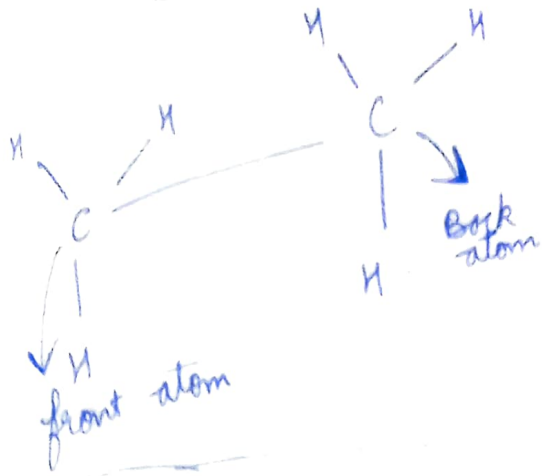


=> Stereoselective:-

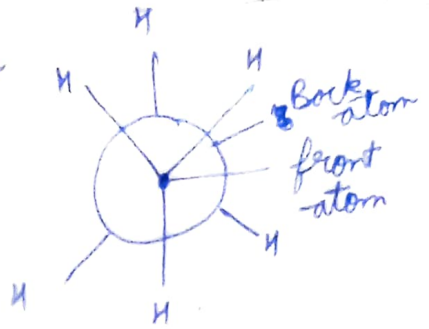
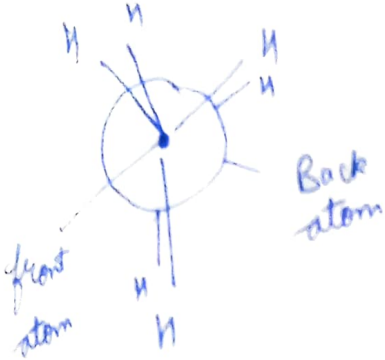
The Stereochemistry of Reactant can determine by the product which are major quantity are considered as stereoselective.



(Sawhorse Projection)
Newmann Projection



Newmann Projection



Eclipsed Conformation

Staggered Conformation

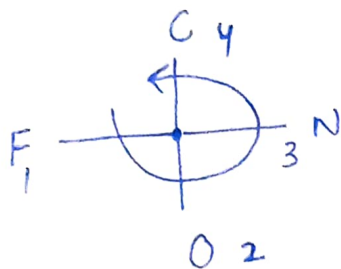
It helps to explain the 3-D structure of a molecule.

R and

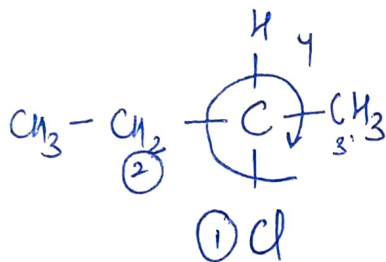
=>

R and S Configuration

- 1> Higher atomic number = Senior group.
- 2> Lower atomic number = junior group.

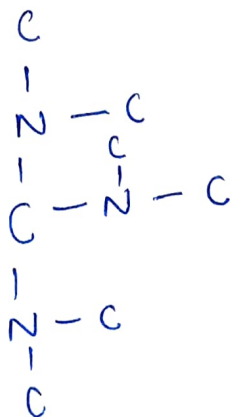
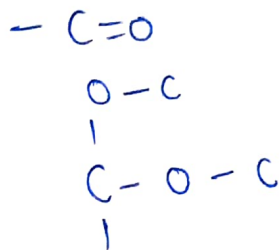


- 3> Atomic number is same then go to the 2/3/4th atoms till we find first Point of difference.

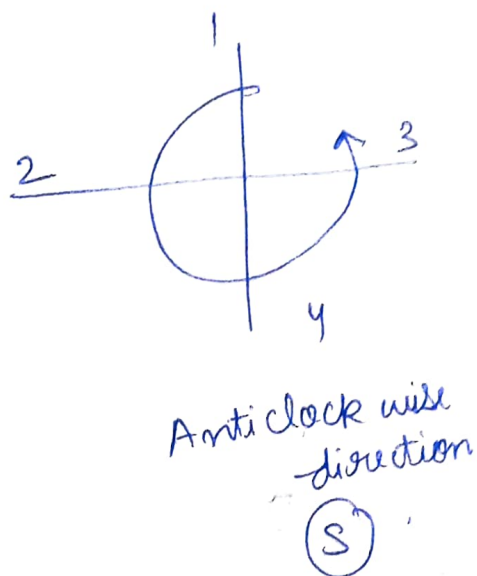
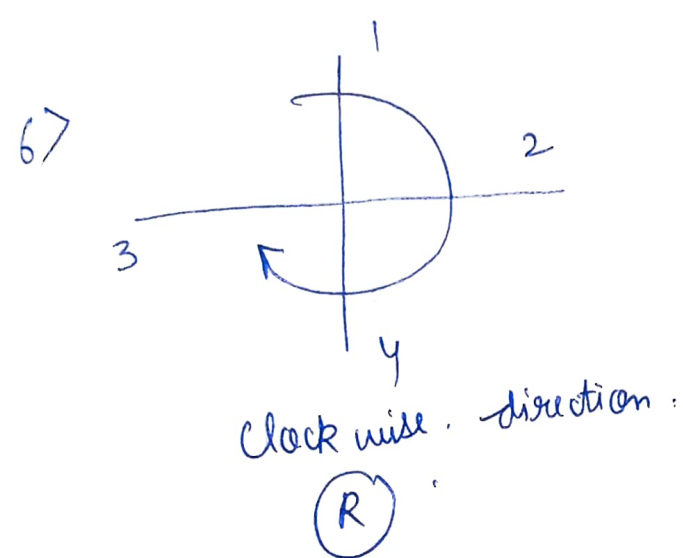


- 4> when first and second atoms of a group are connected through double bond or Triple bond then hypothetically it is considered that they are connected twice or thrice of each other.

Example $-C \equiv N$



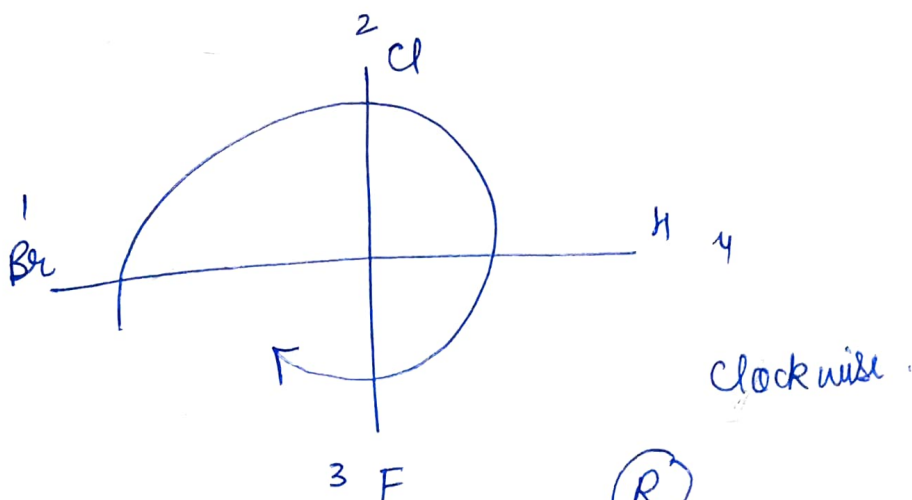
57 (Isotopes) higher mass number give to high Priority.
 $-T > -D > -H$



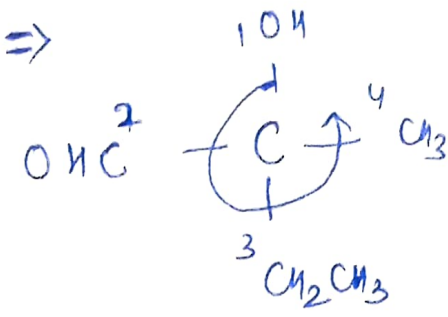
7> If Lowest Priority (4^{th} one) Present in vertical position. So the Configuration never change.

8> If Lowest Priority (4^{th} one) Present in horizontal position. So the Configuration Changes.

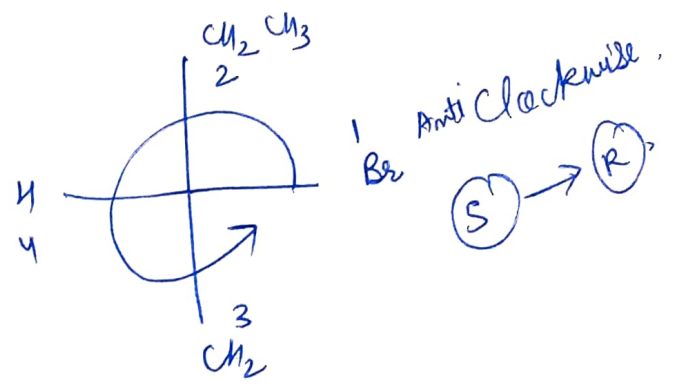
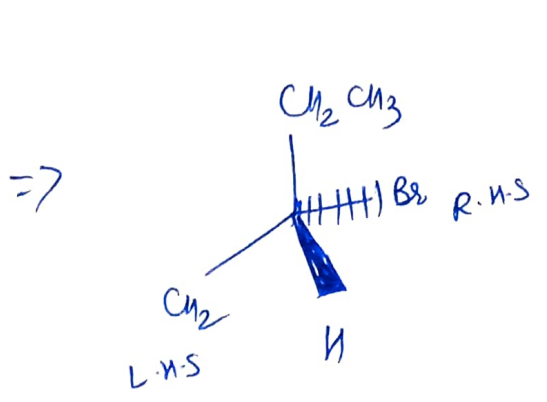
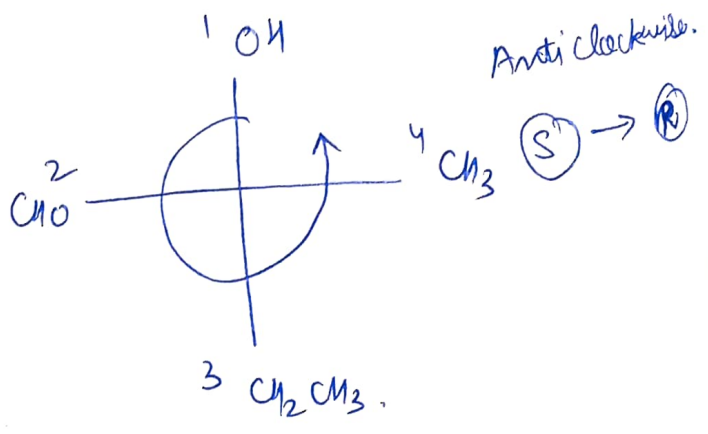
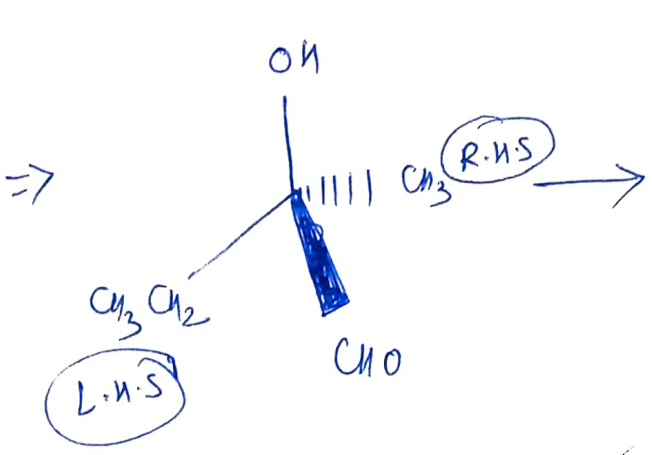
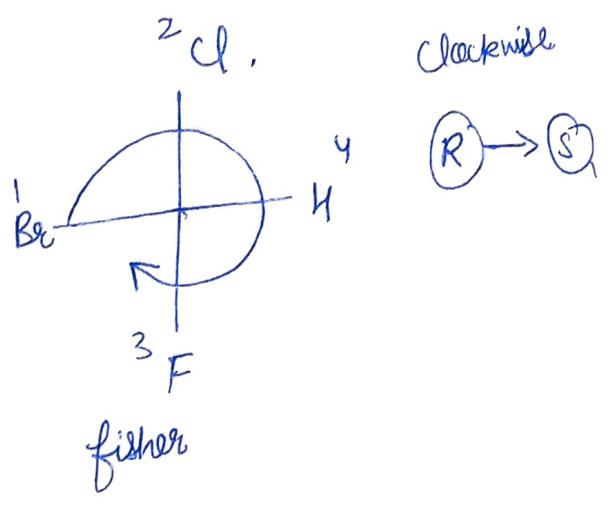
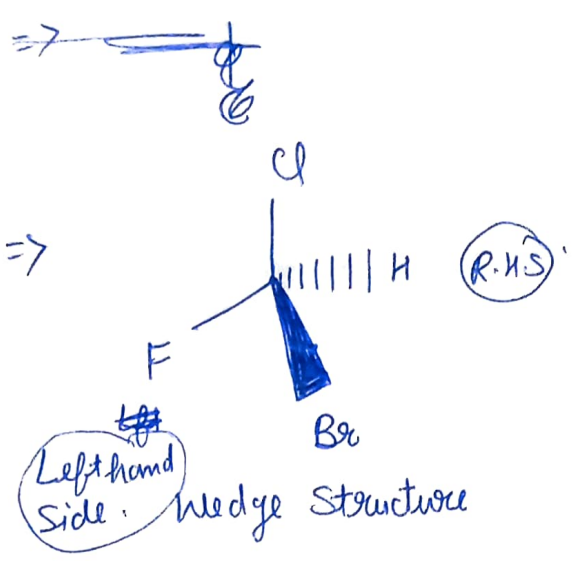
Example :-

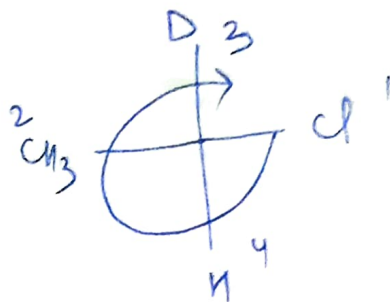
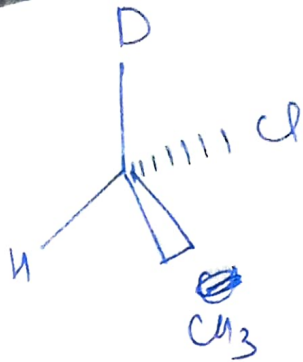


But 4^{th} in horizontal
 So change the Configuration
 $R \rightarrow (S)$

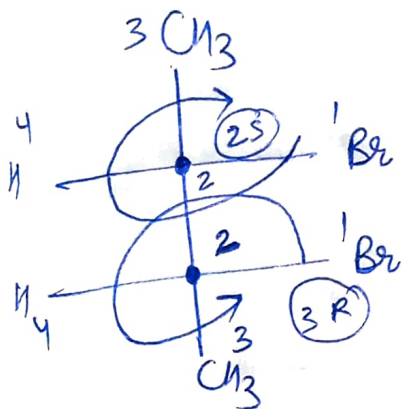


Anticlockwise
 (S) → (R)





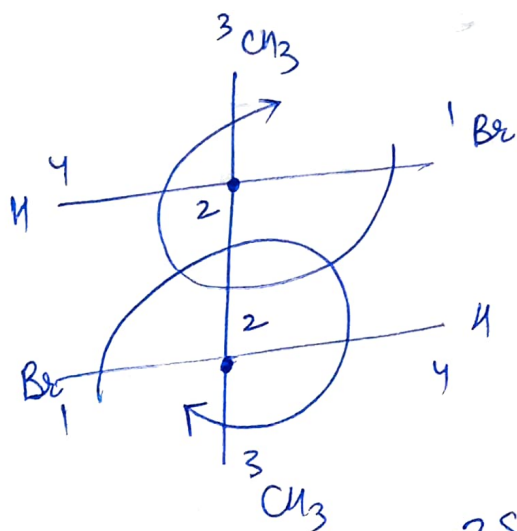
clockwise
(R)



Clockwise
(R) → (S)

Anticlockwise
(S) → (R)

~~2S, 3R~~
⇒ 2S, 3R



Clockwise
(R) → (S)

~~Anticlockwise~~
(R) ~~(S)~~ → ~~(R)~~ (S)

~~2S, 3R~~

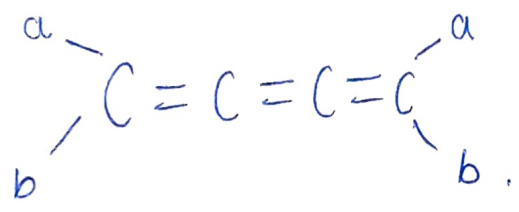
⇒ 2S, 3S

#

R and S
(Allenes, spirans, and Biphenyls).

=>

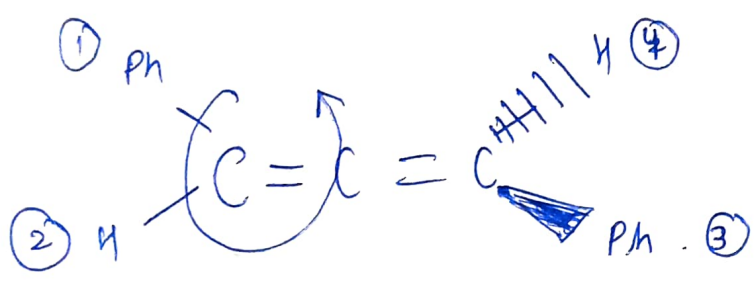
odd double bonds.



optically inactive
(Achiral)

They show geometrical isomers, E and Z

=>

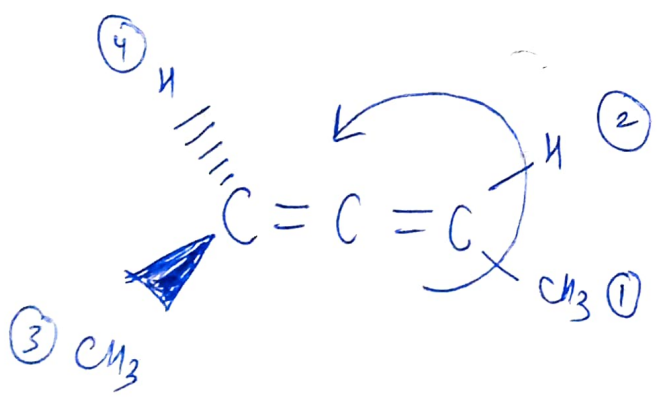


Anticlockwise.

(S)

and 4th group is below plane.

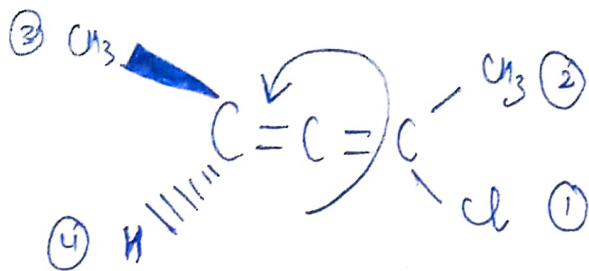
So, (S) will not change.



Anticlockwise.

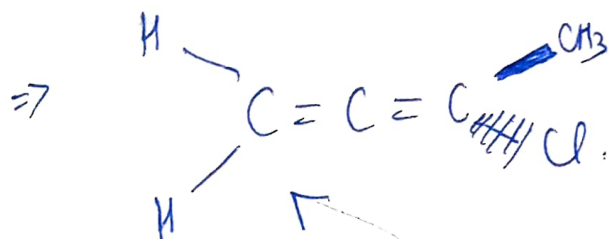
4th is below the plane.

(S)



Anticlockwise.
4th group is below
the plane.

(S)



($a \neq b$) = chiral

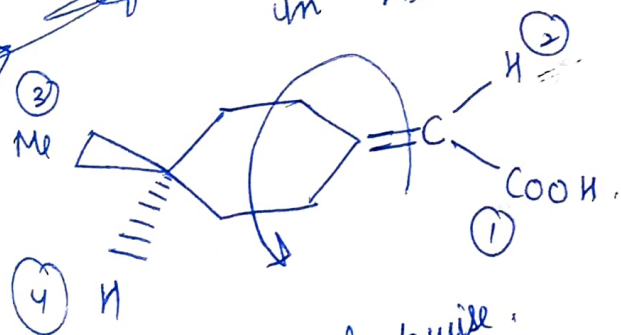
($a = b$) = Achiral

So, no Configuration.

#

Alkylidene cycloalkanes

⇒ If one double carbon is replaced by ring
in Allene is called Alkylidene cycloalkanes.



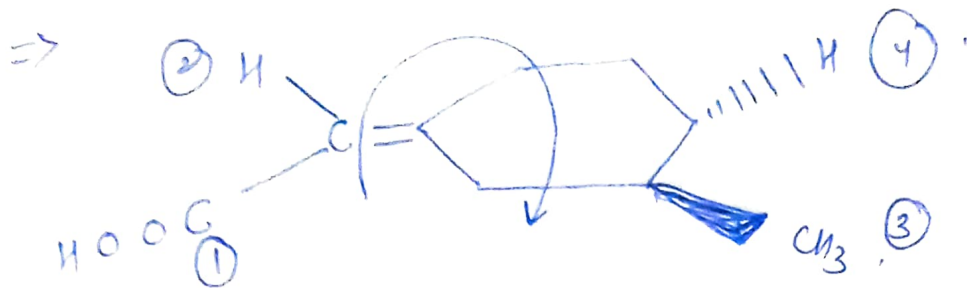
Anticlockwise.

(S)

(4th is
Below
the
Plane)

If the number of sum
of ring and double
bond carbon is
even $\Rightarrow$ it will be
chiral

if it will be
odd.
then E and Z

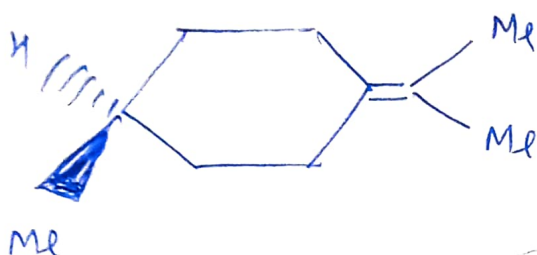


Clockwise.

(R)

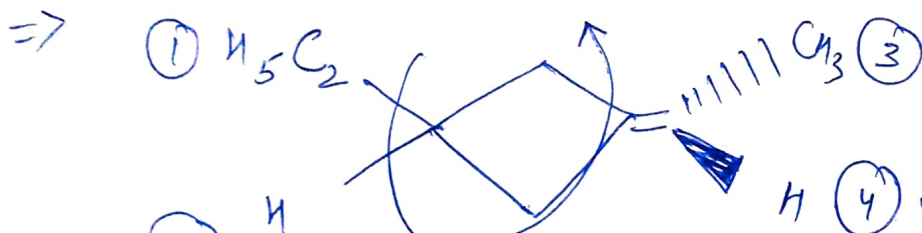
4th is below the plane

⇒



Here $a = b = \text{Achiral}$.

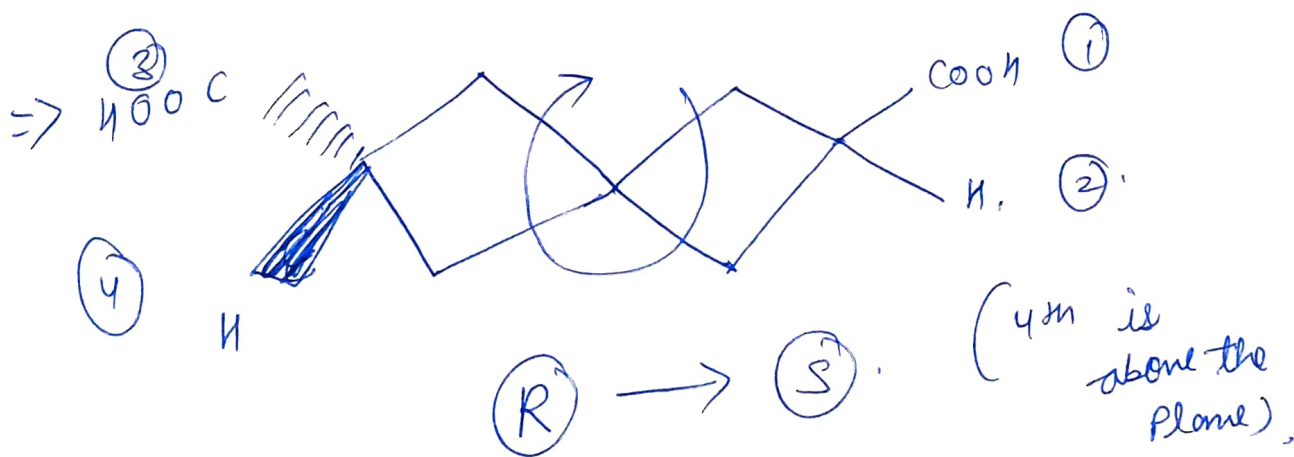
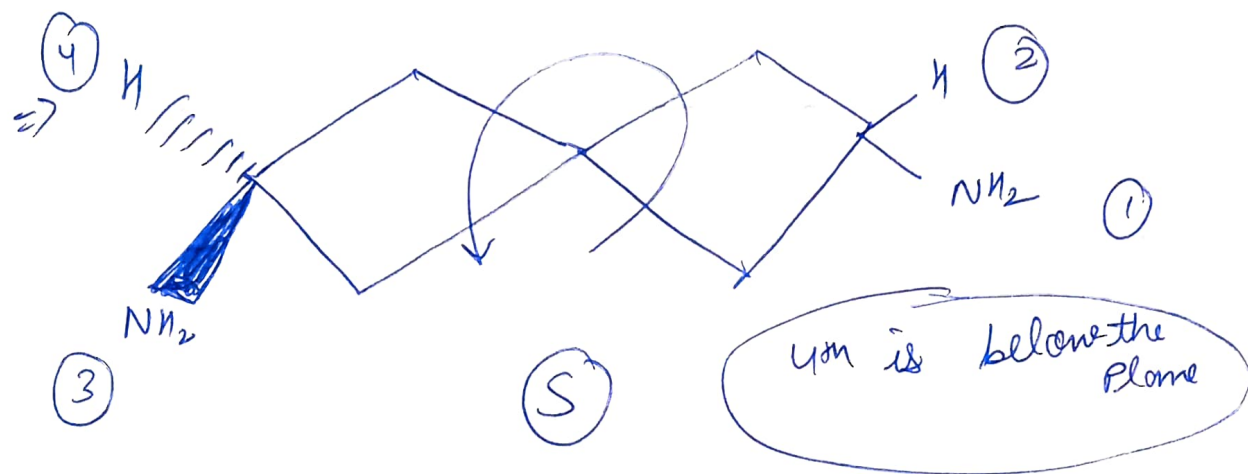
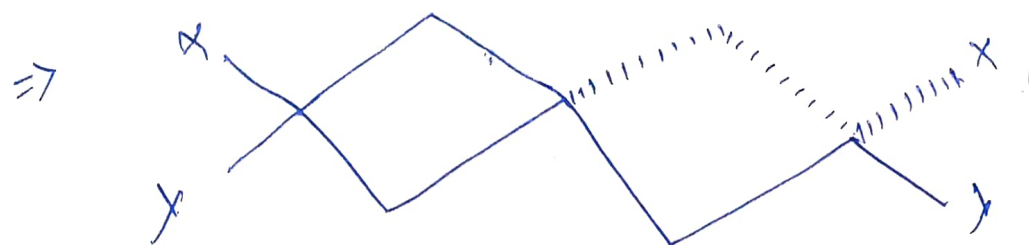
not Configure this compound



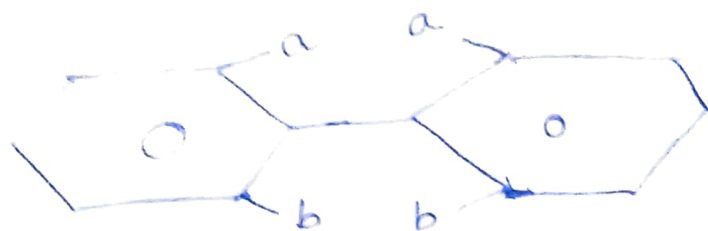
(S) → (R) [(4th) H is above the plane].

⇒ R and S Configuration in Spiranes

⇒ If in a compound the ~~then~~ the two double bonds are replaced by two rings is called Spiranes.



=> Chirality of Biphenyls. (R and S)



=> This biphenyl (Two benzene rings are bonded by a single bond).

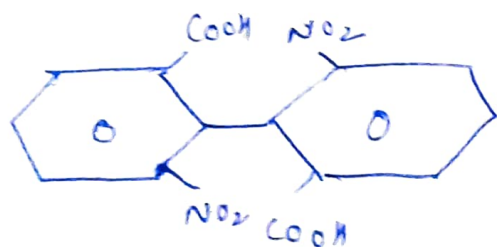
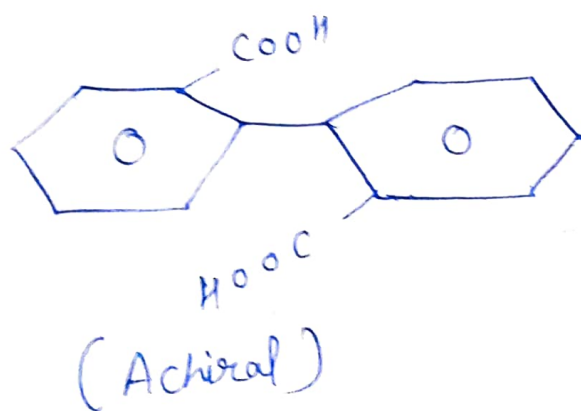
This Symmetrical (Achiral).

=>

=> But if O position contain Bulky group, and due to steric effect, ~~the~~ ^{one} ring ~~will~~ will rotate against another.

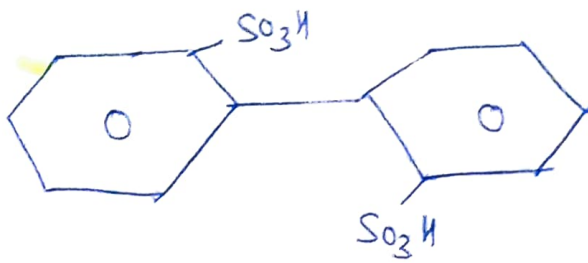
Then it will be $a \neq b$ Asymmetrical (Chiral).

=>

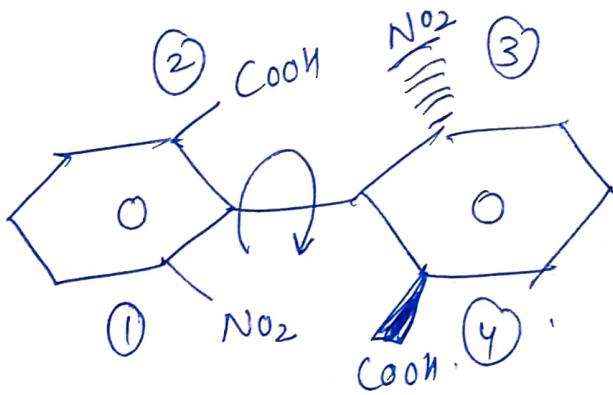
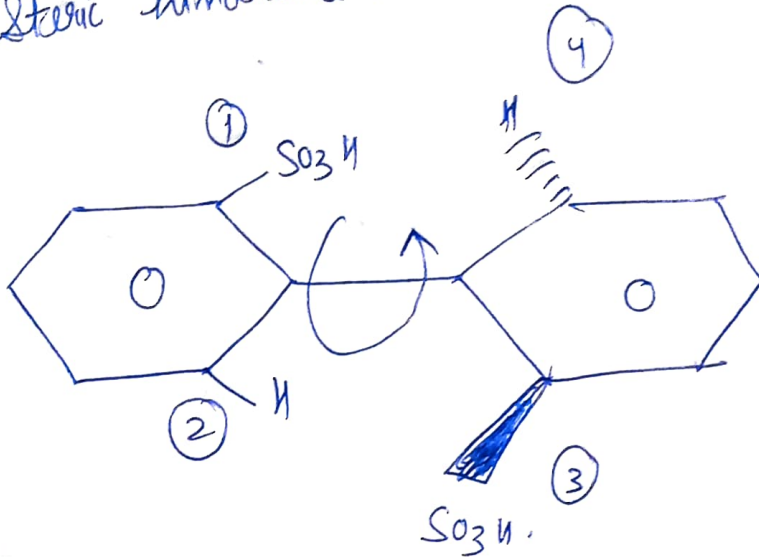


Due to Rotation.
(Chiral)

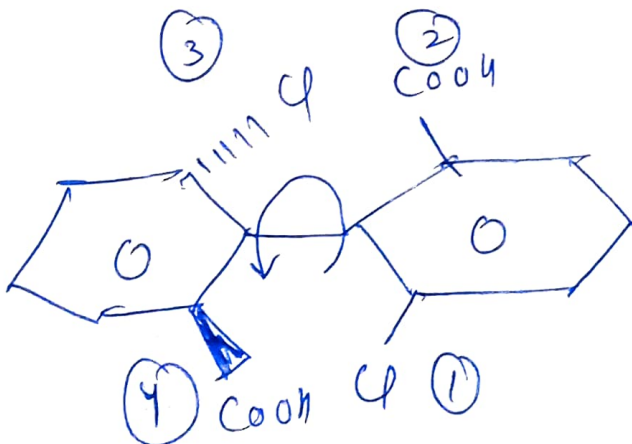
4 Bulky group
(the molecule is crowded and repulsion will take place)



$\Rightarrow$ SO_3H (Sulfonic Acid group) very large group. these two is enough for steric hindrance.



(R) $\rightarrow$ (S)
(4th Above the plane)



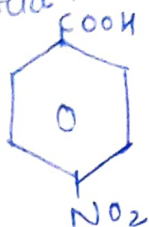
Hammett equation

The attached substituent in the reacting molecule affects the rate of the reaction.

The Hammett equation gives the quantitative relation of substituent effect of the reaction.

The meta and para substituted derivatives benzene are affected due to (electron withdrawing group or electron donating group)

Example NO_2 (electron withdrawing group), attached in benzoic acid



The acidic character of benzoic acid increases due to this substituent effect.

=>

$$\log k = \log k_0 + \sigma \rho$$

$k, k_0 =$ Constant

$\sigma =$ Experimentally determined Constant

It is a linear free energy equation of Hammett.

=> Significance of σ

σ measures the ability of substituent effect in benzoic acid. (Acidity increases or decreases).

(i) $\sigma (= 0) \Rightarrow$ There is no effect of substituent in Benzoic Acid.

(ii) $\sigma (+ve) \Rightarrow$ In this case the substituent is e^- withdrawing group. Acidic strength increases in benzoic Acid.

(iii) $\sigma (-ve) \Rightarrow$ In this case the substituent is e^- donating group. Acidic strength decreases in benzoic Acid.

$\Rightarrow$ Significance of ρ (Parameter).

If ρ is $(+ve)$ the equilibrium constant increases ~~of~~ of the substituent.

$\Rightarrow$ Limitations of Hammett equation:-

$\Rightarrow$ It fails for open-chain aliphatic derivatives.

$\Rightarrow$ Applications of the Hammett equation:-

$\Rightarrow$ 1) The Prediction of the PK_a value.

$$\log \frac{k}{K_a} = \rho \sigma$$

2) By using identify the acidic strength of the compound.

Taft equation

- => Taft proposed a method of extending linear free energy relationship of aliphatic system in which steric factor are important.
- => The Taft equation is a structure-reactivity equation that correlates field effect and steric effect.
- => The electronic nature of substituents will also have little effect on acid-catalysed hydrolysis of aliphatic esters. (mostly the effect is due to the substituents).

$$E_s = \log \left(\frac{k_{os}}{k_o} \right)_A$$

~~k~~ (s = steric effect)

k_s = Rate of ~~o~~ substituent

k_o = Rate of H (Parent ~~o~~ compound).

The general Taft equation

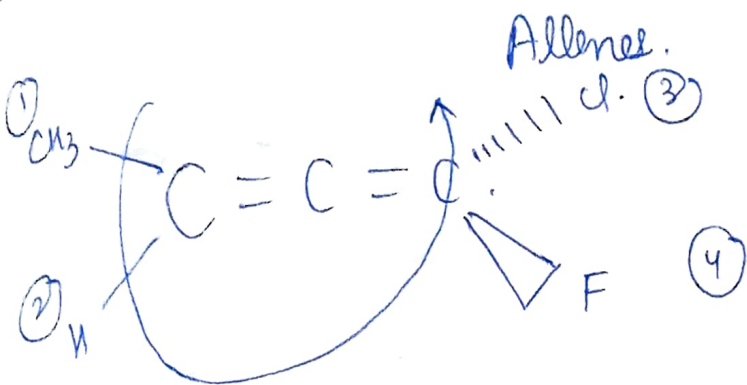
$$\log \frac{k_{os}}{k_o} = \sigma^* \rho^* + \delta E_s$$

σ^* = Polar substituent constant.

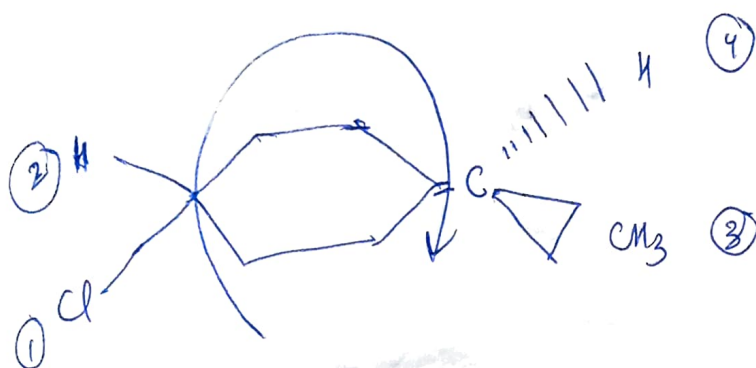
E_s = Steric substituent constant.

ρ^* = Sensitive factor ~~of~~ Polar effect.

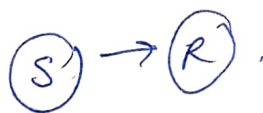
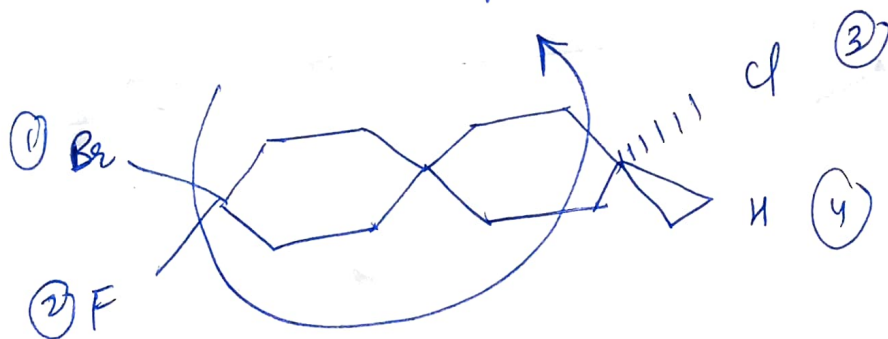
δ = Sensitive factor ~~for~~ of steric effect



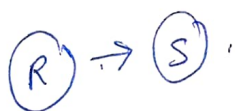
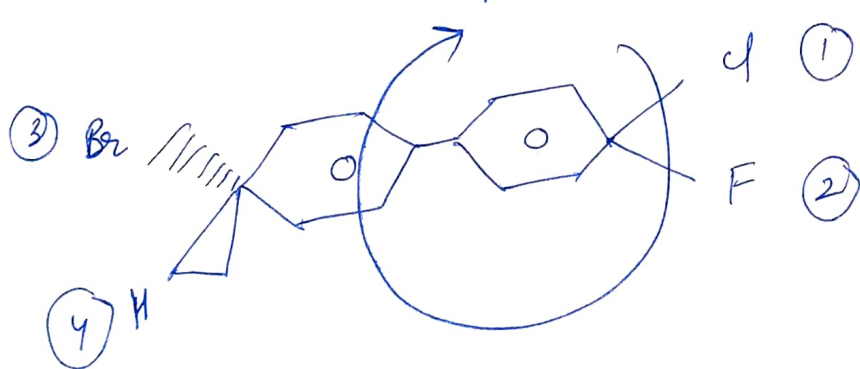
Alkyldiene cycloalkane,

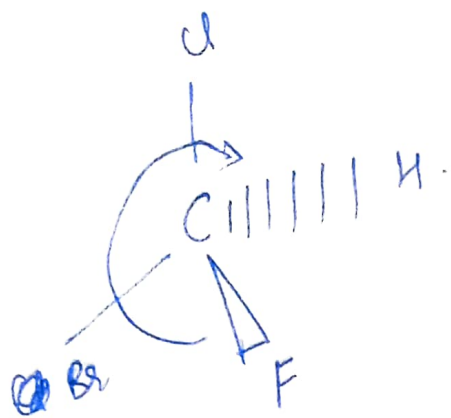


Spiroane.



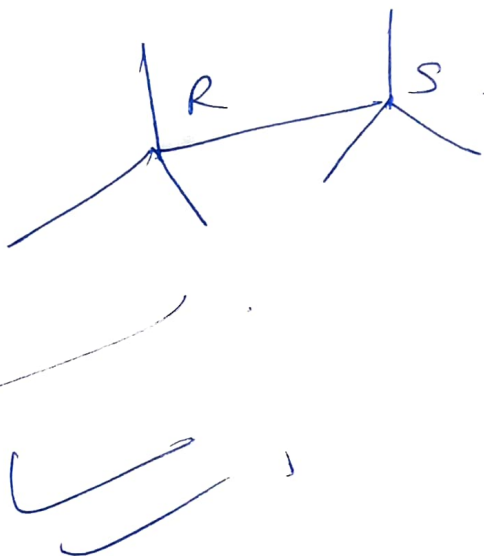
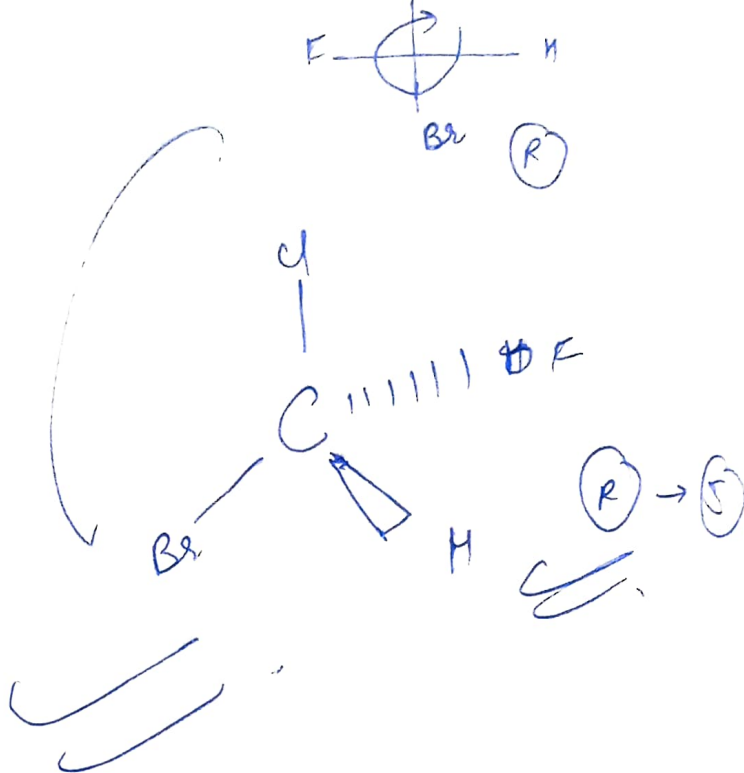
Biphenyl.





Enantiotopic

Diastereomers

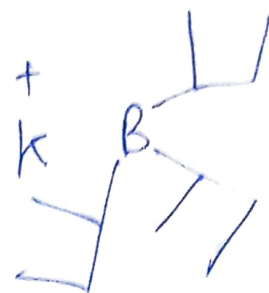
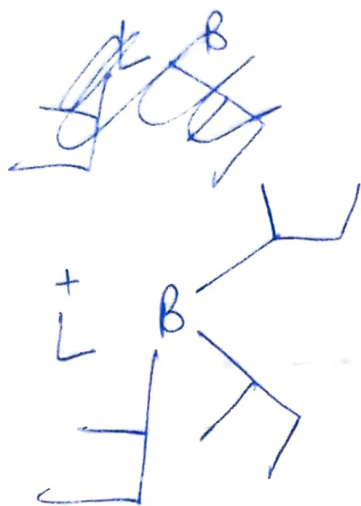


L- Selectride

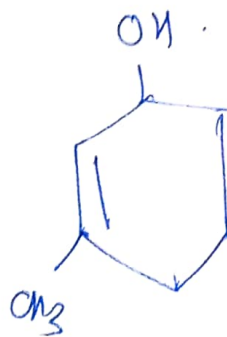
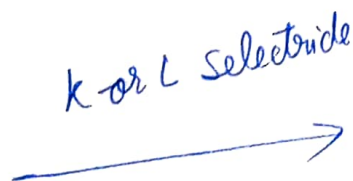
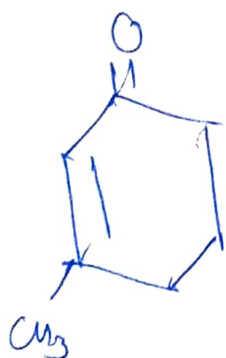
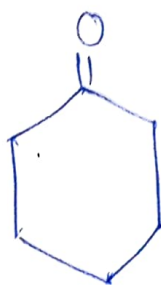
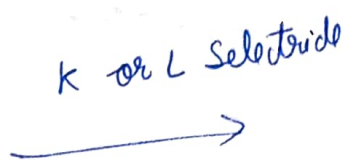
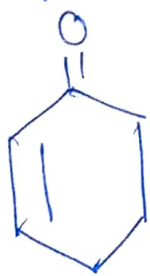
This reducing agent ~~is~~ is
of ~~the~~ Lithium

K- Selectride

This reducing agent
is of Potassium



Example

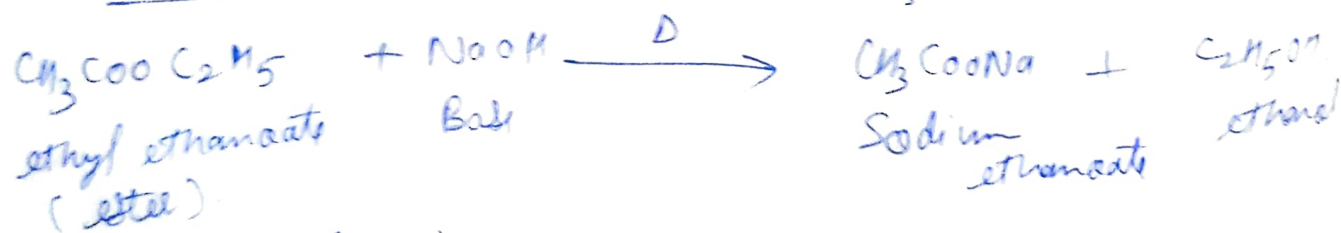


Winstein Eliehl equation

Curtin Hammett vs Hammett Principle :-

=> According this principle the Product Conformations of the reaction is independent on Conformations of Reactant but depend on the transition state energy & difference of the reactant conformations.

Saponification of ester.



Esterification:-

