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Isomerism

- Structural (Constitutional)
  - → chain
  - → positional
  - → functional
  - → metamerism
  - → tautomerism
- Stereoisomerism
  - Configurational
    - → optical
    - → geometrical.
  - Conformational

Structural Isomerism :-

Molecule with same MF but different structural formula are known as structural isomerism.

eg:- C_4H_{10}

$CH_3-CH_2-CH_2-CH_3$ (n-butane)

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3$ (iso-butane)

Chain Isomerism :-

→ Molecule having same MF.

→ F.G is same.

→ Main chain C- atoms is diffrent.

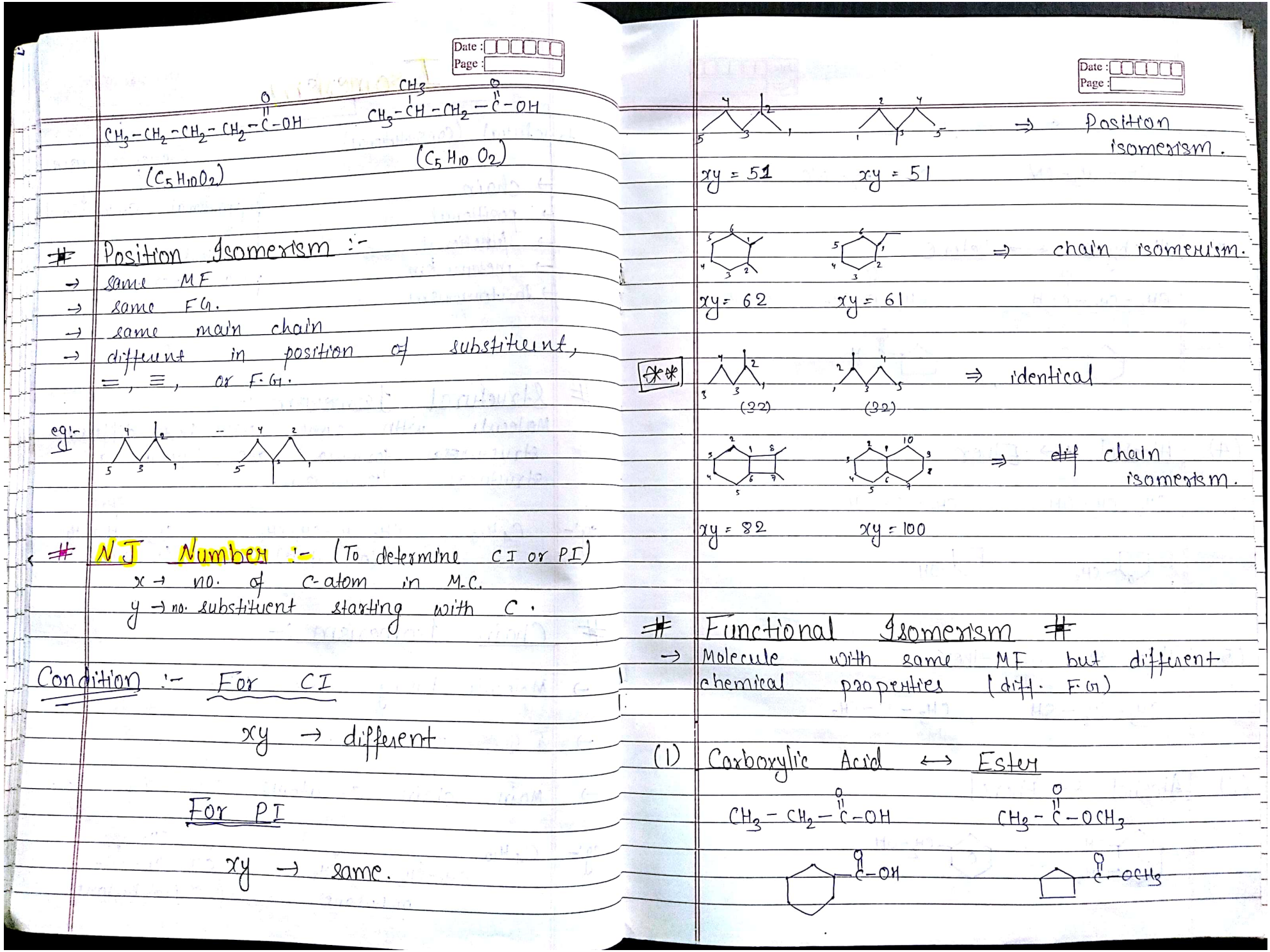
eg:- C_4H_{10}

$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$

n-butane

$\overset{1}{C}H_3-\overset{2}{\underset{CH_3}{\underset{|}{C}}}H-\overset{3}{C}H_3$

iso-butane

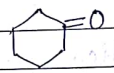
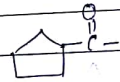


(2) Cyanide ⟷ Isocyanide

CH_3-CH_2-CN , CH_3-CH_2-NC

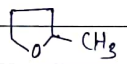
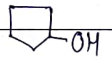
(3) Aldehyde ⟷ Ketone

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$, $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(4) Alcohol ⟷ Ether

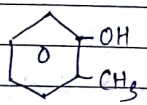
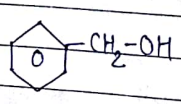
CH_3-CH_2-OH , CH_3-O-CH_3

(5) Thiol ⟷ Thio ether

CH_3-CH_2-SH , CH_3-S-CH_3

(6) Alcohol ⟷ Phenol

(7) Amine

$CH_3-CH_2-CH_2-\overset{H}{\underset{H}{N}}$ (1° amine)

$CH_3-CH_2-\overset{H}{\underset{CH_3}{N}}$ (2° amine)

$CH_3-\overset{CH_3}{\underset{CH_3}{N}}$ (3° amine)

Metamerism

Monovalent	* Bivalent / polyvalent *
-F	-S-
-Cl	-O-
-OH ✗	$-\overset{O}{\overset{\|}{C}}-O-$ ✓
-SH ✗	$-\overset{O}{\overset{\|}{C}}-$
$-NO_2$	$-\overset{\|}{N}-$
-Br	
-I	

Note: Metamerism is not applicable for monovalent

eg:- $CH_3-CH_2-\underset{\cdots}{O}-CH_2-CH_3$

$CH_3-\underset{\cdots}{O}-CH_2-CH_2-CH_3$

→ Metamerism

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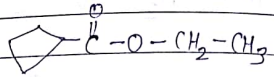
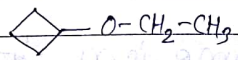
Note:- Metamerism arrises due to difference in attachment of different alkyl substituent across a bivalent / polyvalent atom or group.

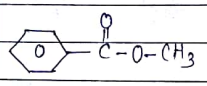
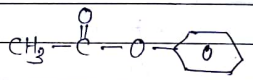
Que)

1) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-$  

⇒ Metamers.

2) CH_3-CH_2-O- 

⇒ identical

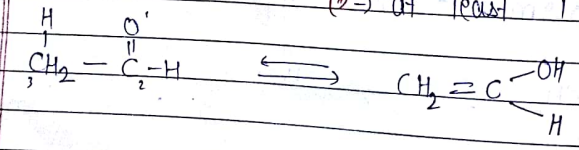
3)  

⇒ Metamers.

Tautomerism — Keto → enol

Condition :- (1) α-carbon → sp^3

(2) → at least 1 α-H



(2;3) → = 1 → H atom (of 3)

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* Tautomers are those type of isomer in which f.G is different.
* & with same M.F and can be converted to one another through a reversible process.
* Usually they are different in the position of an H atom.
* Tautomer usually present in the following functional group :-

carbonyl imine nitro nitroso

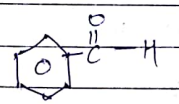
Que Which of the following comp. show tautomers and also write α-H.

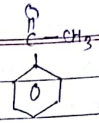
(1) $CH_3-\overset{O}{\overset{\|}{C}}-H$ α-H ⇒ 3

(2) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ α-H ⇒ 6

(3) $CH_3-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-H$ α-H ⇒ 1

(4) $H-\overset{O}{\overset{\|}{C}}-H$ X (α-C)X

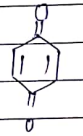
(5)  X sp^2 X

6)  α-H ⇒ 3

7) ph − C(=O) − ph ✗ ('sp³ X')

8) ph − C(=O) − CH₂ − C(=O) − ph α-H ⇒ 2

9)  α-H = 4

10)  ✗ (sp^3 X)

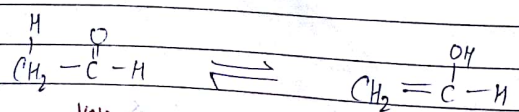
Dyad and Triad System

(1) DS

If the H-atom oscillates b/w 2 polyvalent atom linked together the system is dyad system.

Eg- H − C ≡ N ⇌ H − N ≡ C

(2) TS



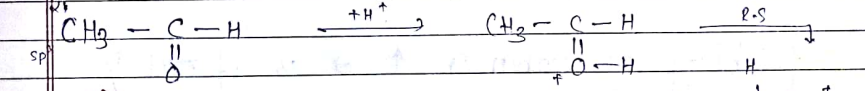
→ Tautomer are also functional isomer and exist in dynamic eqᵇ

→ By shifting of H-atom π-bond also change its position.

→ No. of e⁻ and lp in both tautomer always remains the same.

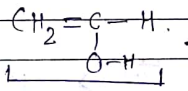
→ This process can be catalysed by acid as well as base.

* Acid Catalysed :- {depend on stability of alkene}

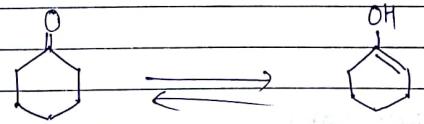


Mechanism

slow rds



Stability of alkene ↑ → % of enol ↑

Q) 

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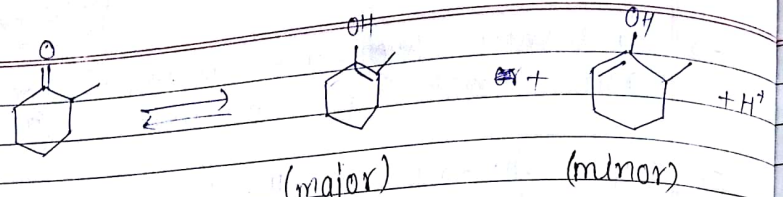
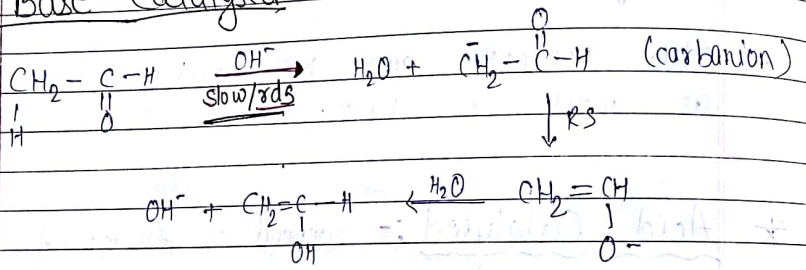
(Q)



(major) (minor)

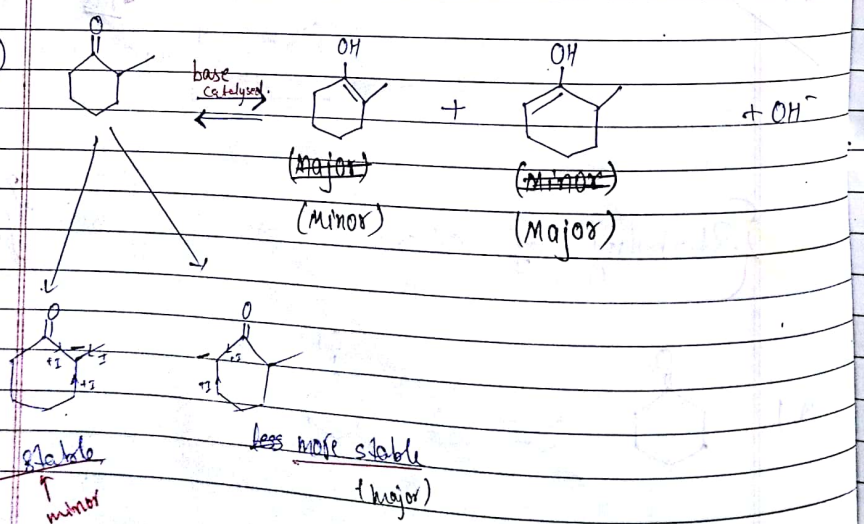
Base Catalysed

Mechanism



Stability of carbanion ↑ → % of enol ↑

(Que)



(Minor) (Major)

Less stable ← minor

less more stable → major

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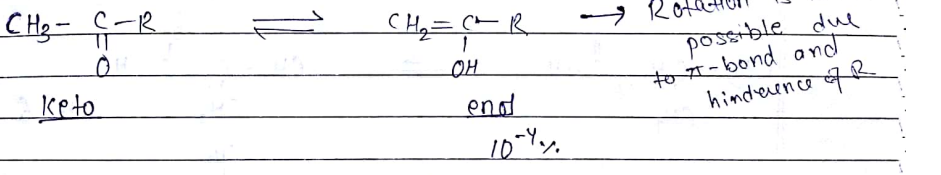
% age Enol Content

→ Enol content is the % age of enol in tautomeric mixture.

case (1) For Monocarbonyl compound :-



Keto — enol 10^{-4} %

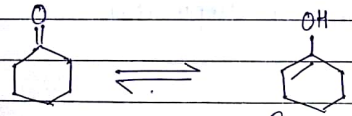
→ Rotation is not possible due to π-bond and hindrence of R

Reason :-

$>C=O$ $\quad$ $C=C$

$BE_{keto} > BE_{enol}$

So, stability → keto > enol

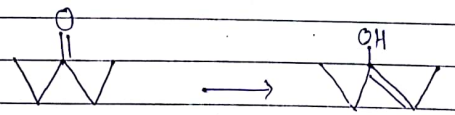


keto > enol

Rotation is possible

entropy ↑

stability ↑ → 1.2%



% keto > % enol

→ due to hinderence % ↓ (entropy ↓ stability ↓)

case(2)

(2) Enol content increases with increase in the stability of enol by resonance, hyperconjugation, H-bonding.

(Pure) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_3-CH=\overset{OH}{\overset{|}{C}}-H$ (enol 1)

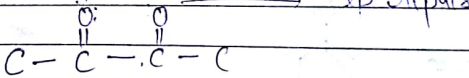
$\alpha H = 3$

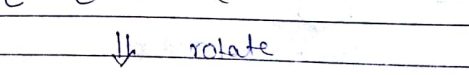
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons CH_3-\underset{CH_3}{\underset{|}{C}}=\overset{OH}{\overset{|}{C}}-H$ $\alpha H = 6$ (enol 2)

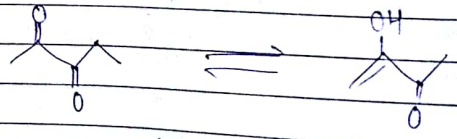
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH_3}} \rightleftharpoons (CH_3-\underset{CH_3}{\underset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-OH$ $\alpha H = 9$ (enol 3)

% $\Rightarrow$ enol 3 > enol 2 > enol 1

case 3 In adjacent diketone :-





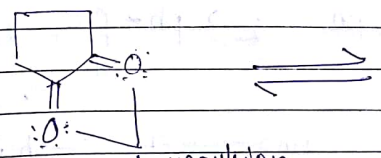


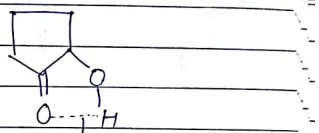
BE 1

no lp repulsion

$\therefore$ % keto > % enol

cyclic



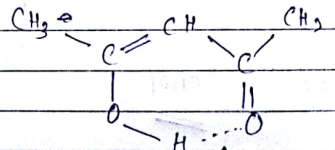


100%.

* (% enol > % keto)

case 4 For a carbonyl compound having AMG (active methylene group) % of enol content will be more bcz enol form intramolecular H-bonding. and also it will be stablised by resonance.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\underset{OH}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$



% enol > % keto

(active methylene compound)

Stability ↑ intramolecular H-bond. (6-membered ring)

Q) $ph-C(=O)-CH_2-C(=O)-ph \rightleftharpoons ph-C(OH)=CH-C(=O)-ph$ (% ↑)

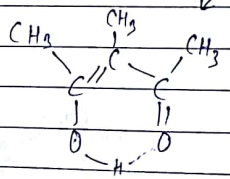
~~$ph-C(OH)=CH-C(=O)-ph$~~ ✗ ~~sp^2~~

reason → extended conjugation.

Q) $H-C(=O)-CH_2-C(=O)-H \rightleftharpoons H-C(OH)=CH-C(=O)-H$ (% ↑)

case 5 Steric Crowding :-

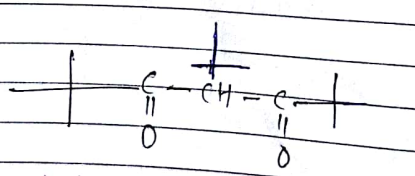
$CH_3-C(=O)-CH(CH_3)-C(=O)-CH_3 \rightleftharpoons CH_3-C(OH)=C(CH_3)-C(=O)-CH_3$



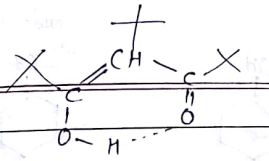
% keto > % enol

44%

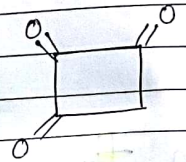
(due to repulsion / hindrance of CH_3 group.

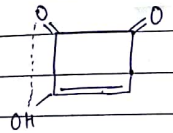
Que  0% enol why?

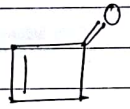
Ans bcz high steric hindrance in enol form

 → hindrance

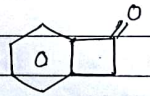
Que → 0% enol

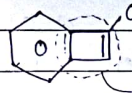
Que  100% enol why?

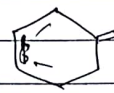
soln  aromatic → stability ↑

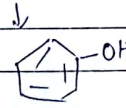
Que  0% enol why?

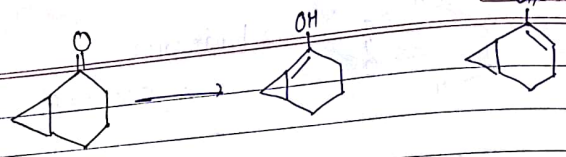
 → anti-aromatic → stability ↓

Que  0% enol why?

 → anti aromatic → stability ↓

Que  100% enol

 . aromatic → stability ↑



Ring - Chain Isomerism

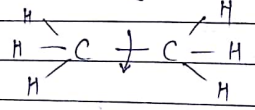
C-C=C △ (R.C.I)

C_3H_6 C_3H_6

Ring chain isomer are also functional isomer.

Conformational Isomer

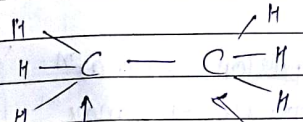
Rotation along σ bond.



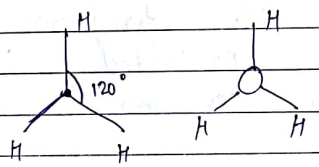
They are those 3D structures which are formed due to rotation about C-C bond or σ bond due to this there is no change in overlapping region.

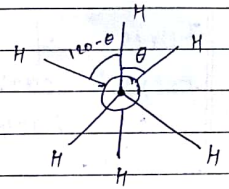
Newman Projection

$\{0^\circ < \theta < 60^\circ\}$



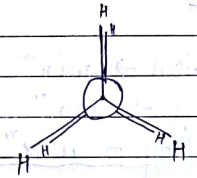
front carbon • Back carbon ○



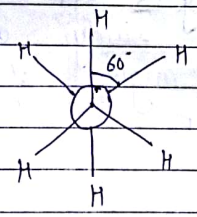


θ → torsional angle.

1) θ = 0° (eclipsed form)



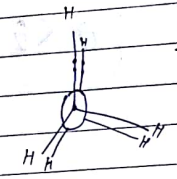
2) θ = 60° (max) (staggred form)



3) θ ≠ 0, θ ≠ 60 → Skew form

Torsional Strain

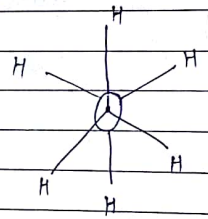
(*) $\theta = 0^\circ$



Repulsion → max^m
energy → max^m
stability → min^m

Force of repulsion b/w projected bond of front carbon and projected bond of back carbon known as torsional strain.

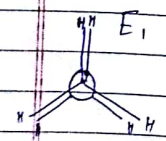
(*) $\theta = 60^\circ$



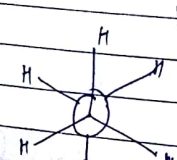
Repulsion → min^m
energy → min^m
stability → max^m

Conformational Analysis

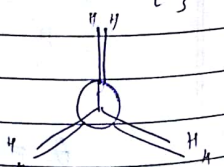
It is defined as the study of energy of molecule w.r.t. the angle of rotation (α).



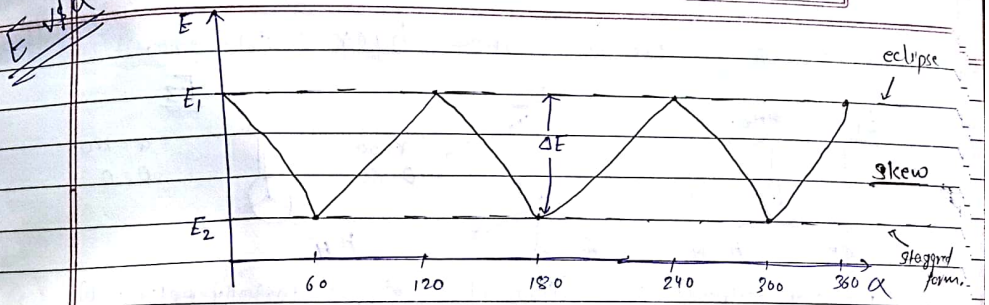
E_1
$\alpha = 0^\circ$
$\theta = 0^\circ$



E_2
$\alpha = 60^\circ$
$\theta = 60^\circ$



E_3
$\alpha = 120^\circ$
$\theta = 0^\circ$

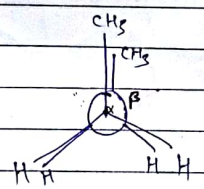


E_1 → eclipsed form
E_2 → staggered form
b/w $E_1 - E_2$ ⇒ skew.

ΔE → Difference of max^m and min^m energy known as rotational barier.

Vanderwaal Strain
(Steric strain)

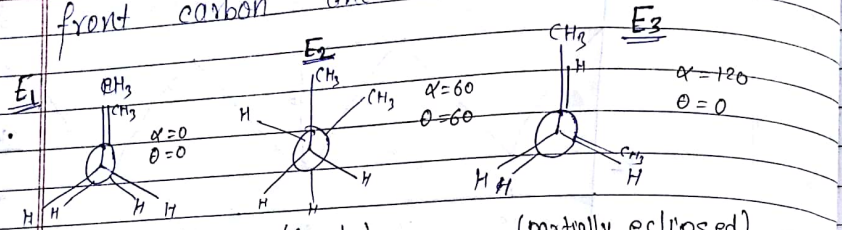
$CH_3 - \overset{\alpha}{CH_2} - \overset{\beta}{CH_2} - CH_3$ (α = front, β → back)



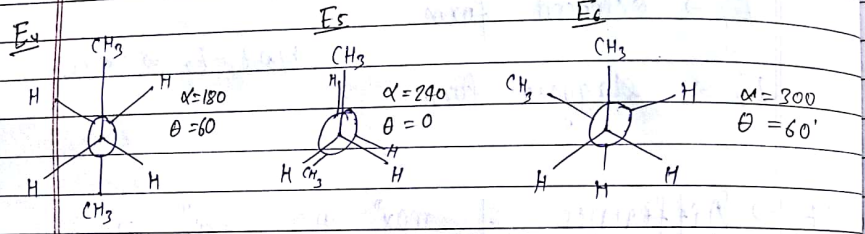
$\theta = 0^\circ$

Vanderwaal/steric strain is defined as the force of repulsion b/w atom or group of atom associated with

front carbon and back carbon.



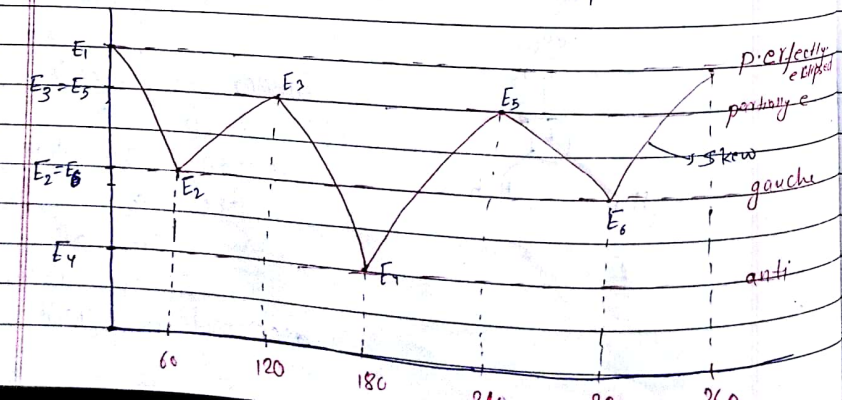
(perfectly eclipsed) (Gauche) (partially eclipsed)

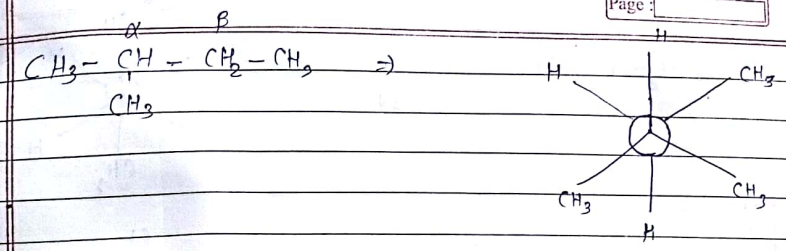


(anti) (partially eclipsed) (Gauche)

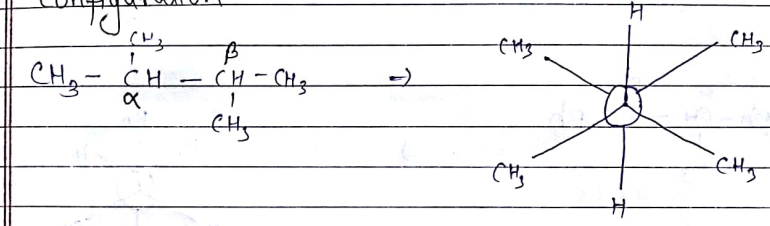
$$\{E_1 > E_3 = E_5 > E_2 = E_6 > E_4\}$$

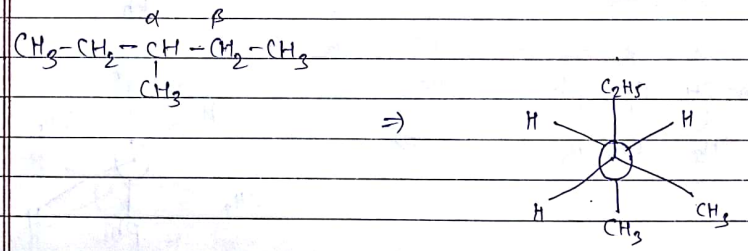
Stability anti > Gauche > partially eclipsed > perfectly eclipsed.

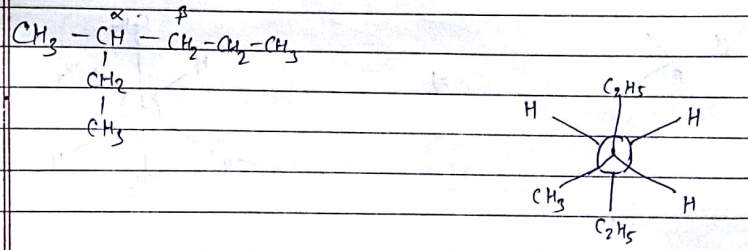




(Q) Identify most stable configuration (most stable)

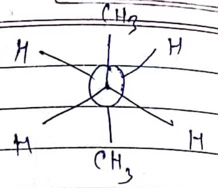




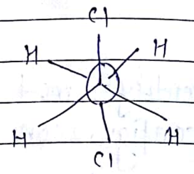


$\overset{\alpha}{CH_2}$ notation below marks α and β carbons.

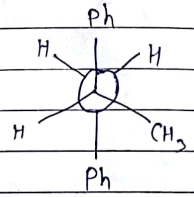
$CH_3-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-CH_3$ ⇒



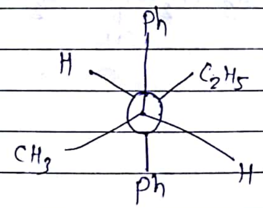
$\underset{\alpha}{CH_2}(Cl)-\underset{\beta}{CH_2}(Cl)$ ⇒

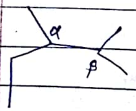


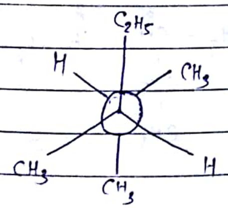
$Ph-\overset{\alpha}{CH}(CH_3)-\overset{\beta}{CH_2}-Ph$ ⇒

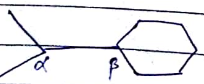


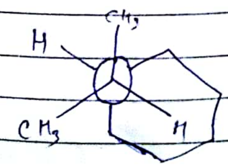
$Ph-\overset{\alpha}{CH}(CH_3)-\overset{\beta}{CH}(CH_2-CH_3)-Ph$ ⇒



 ⇒



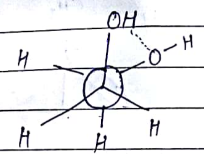




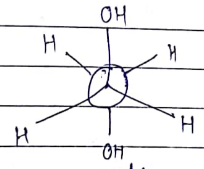
Gauche Effect :-

$\overset{\alpha}{CH_2}(OH) - \overset{\beta}{CH_2}(X)$ (X → -OH, $-\overset{O}{\overset{\|}{C}}-OH$, $-\overset{O}{\overset{\|}{C}}-OR$, -F etc)

(i) X → OH



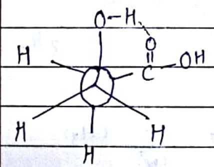
gauche



anti

Stability :- (Gauche > Anti) (due to H-bonding) → reason

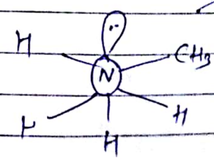
(ii) X → $-\overset{O}{\overset{\|}{C}}-OH$ ⇒ $\overset{\alpha}{CH_2}(OH) - \overset{\beta}{CH_2}(\underset{\overset{\|}{O}}{C}-OH)$



Gauche

* Gauche Effect *

$CH_3-\overset{\beta}{CH_2}-\underset{\alpha}{\ddot{N}}(H)-H$



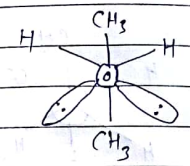
→ less repl. than in anti position

Most stable

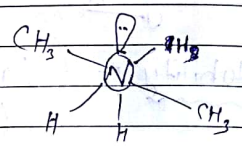
* lone pair and group में less rep. होता है compare to group-group में।

Most bulky substituent ~~att~~ occupies gauche position wrt lp this effect is known as gauche effect.

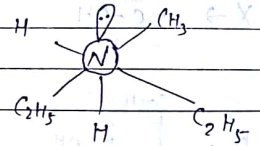
Q) $CH_3-CH_2-O-CH_3$ ⇒



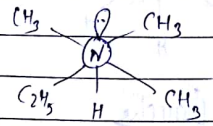
Q) $CH_3-CH_2-N(CH_3)(H)$ ⇒



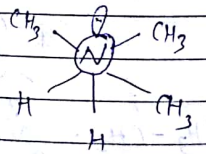
Q) $CH_3-CH_2-N(C_2H_5)_2$ ⇒



Q) $CH_3-CH(CH_3)-N(C_2H_5)_2$ ⇒



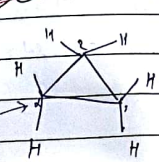
Q) $CH_3-CH(CH_3)-NH-CH_3$ ⇒

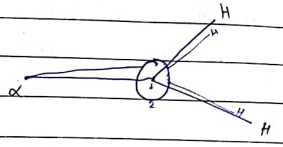


* Cyclic Conformation :-

cyclo propane

(Common carbon)





~~α = θ~~ free rotation is not possible

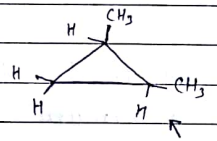
↓↓

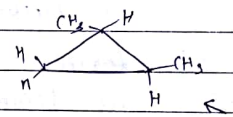
α ⇒ doesn't change.

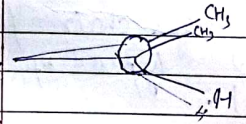
∴ $\alpha = \theta = 0^\circ$.

Que) Compare the stability of cis and trans form of 1,2-dimethyl cyclo propane.

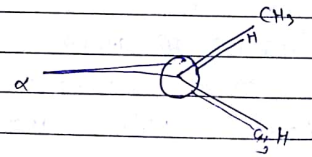
Soln







cis



trans

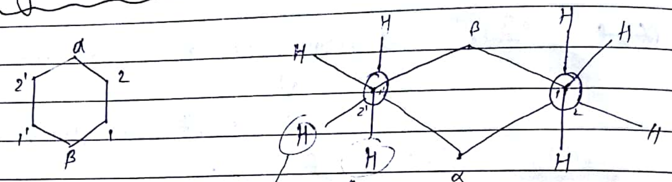
Stability :- trans > cis

↑

(more vandewaal Strain than trans form)

* Trans form in 1,2 dimethyl cyclopropane is more stable then cis form bcz trans form has minimum vandarwaal strain.

* Cyclo hexane :-



$\theta = 60^{\circ}$ (most stable)

equitorial (inclined) axial (verticle)

→ Chair form of cyclohexane is most stable form of cyclo hexane bcz of minimum torsional strain ($\theta = 60^{\circ}$).

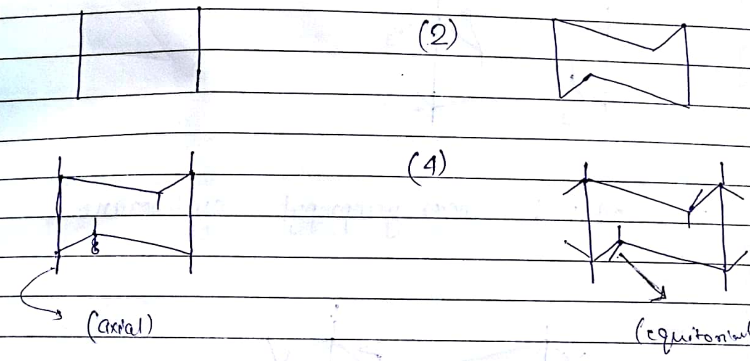
→ Every C-atom of cyclohexane chair form is associated with 2 types of bond (axial and equitorial).

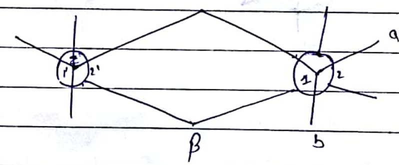
demerit → α और β का axial and equitorial bond पता नहीं चल रहा है

* Conventional Chair Form *

Steps :-

(1) (2) (3) (4)



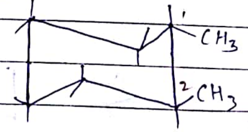


CH_3 (any subst.) → at equitoral position } less rep. ⇓ more stable

* Substituent placed on cyclohexane chair form will occupy equitorial position since equitorial is anti and axial is gauche.

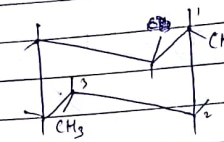
Q) Draw most stable of the following :-

1) 1,2 dimethyl cyclo hexane

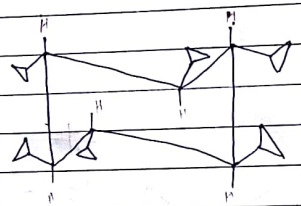


{Stability (equitorial > axial)}

2) 1,3 - dimethyl cyclohexane.

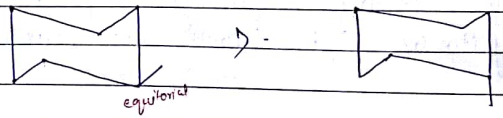


3) 1,2,3,-4,5,6 hexacyclopropyl cyclohexane.

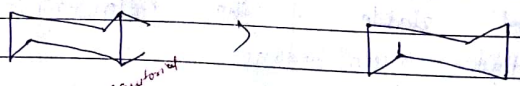


4) Compare the stability

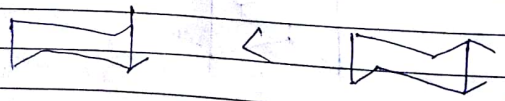
a)

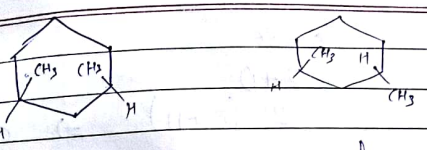


b)

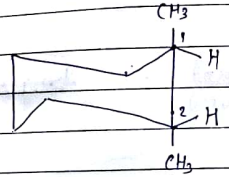


c)

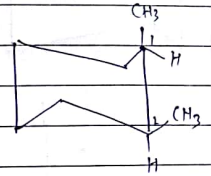




cis trans.



1a - 2a
1 + 0
= 1 (odd)
trans

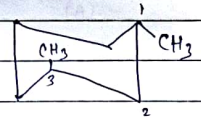


1a - 2e
1 + 1
= 2 (even)
cis

Note → position का difference निकालना है अगर दोनों same है (a-a)/(e-e) then add 0 नहीं तो अगर diff. है (a-e) तो add 1.

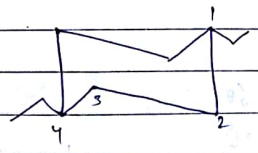
→ odd → trans even → cis.

Que)

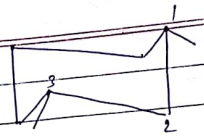


1e - 3a
2 + 1
3 (odd) ⇒ trans

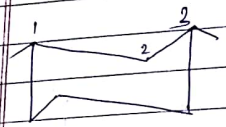
Que)



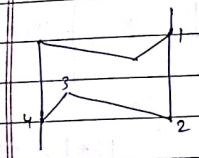
1e - 4e
3 + 0
= 3 (odd) ⇒ trans



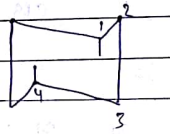
1e-3e
2+0
2 (even) ⇒ cis



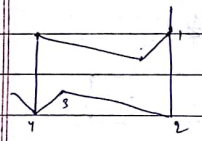
1e-2e
2+0
2 ~~(odd)~~ (even) ⇒ ~~trans~~ cis



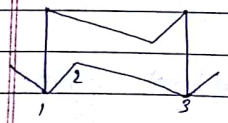
1a-4a
3+0
3 (odd) ⇒ trans



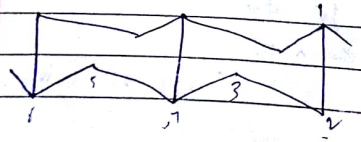
1a-4a
3+0
3 (odd) ⇒ trans



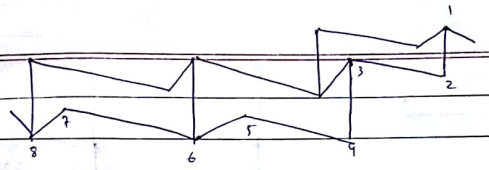
1a-4e
3+1
4 (even) ⇒ cis.



1e-3e
2+0
2 (even) ⇒ cis

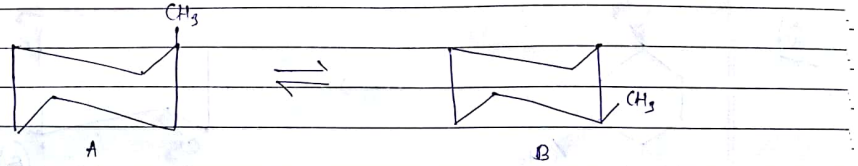


1e-6e
5+0
5 (odd) ⇒ trans



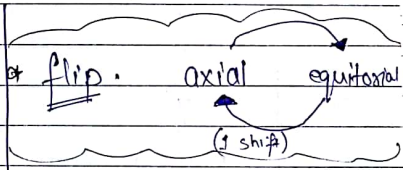
1e-8e
7+0
7 (odd) = trans

★ Eqb^m Constant ★



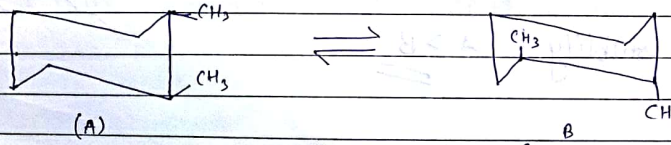
Stability ⇒ B > A

$K_{eq^r} \Rightarrow \frac{[B]}{[A]} > 1$



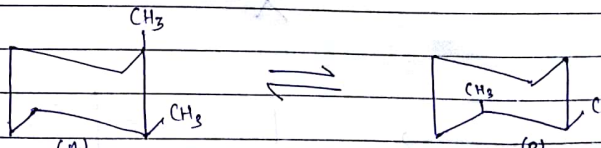
Que Calculate the eqb^m constant <1, >1 or =1

1)

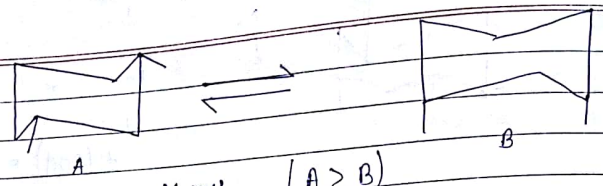


K > <1 {∵ A > B? Stability

2)

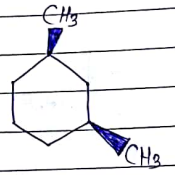


K = 1 {A = B? Stability

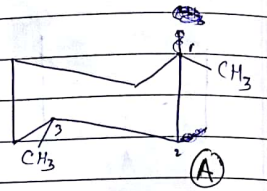


K ∝ 1/ (A > B)
stability

Q)



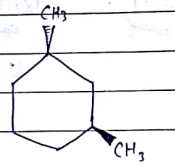
cis



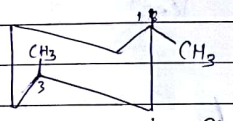
(A)

cis

Q)



trans

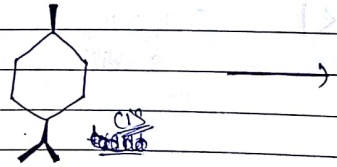


(B)

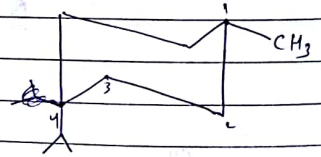
trans

Stablity A > B

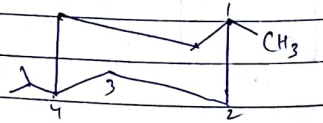
Q)



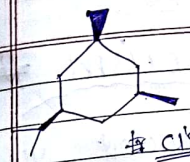
cis



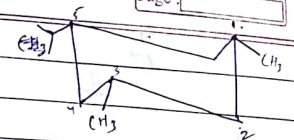
trans

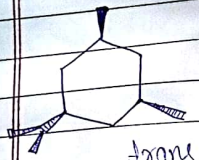


Q)

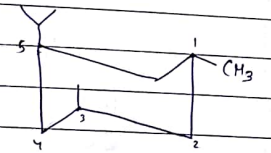


cis





trans



Relative Stability

Chair > Boat > Half chair

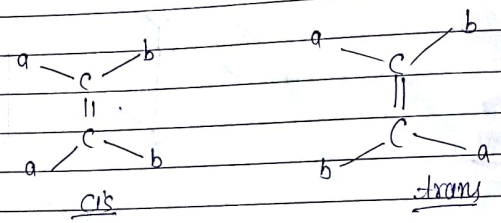
flip → flip →

Chair > twisted boat > boat > half chair

flip →

Geometrical Isomerism

GI are form due to restricted rotation in the presence of double bond.

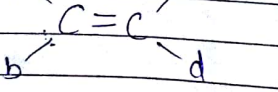


* GI are form due to restricted rotation about :-
1) double bonded system
2) substituted cyclo alkane
3) Cyclo alkene
4) diphenyl system
5) Rxn leading to GI
6) Resonating structure

(1). Double bonded System :-

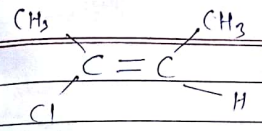
cis/trans — E/Z — syn / anti

* Cis - Trans :-

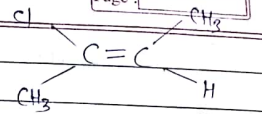


condition :- (i) double bond C=C
(ii) $a \neq b$
$c \neq d$

eg :-

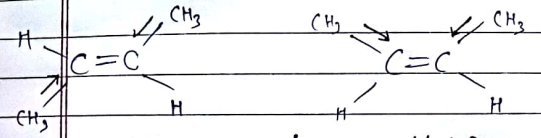


Cis's



trans

* Comparision of μ, BP and MP :-

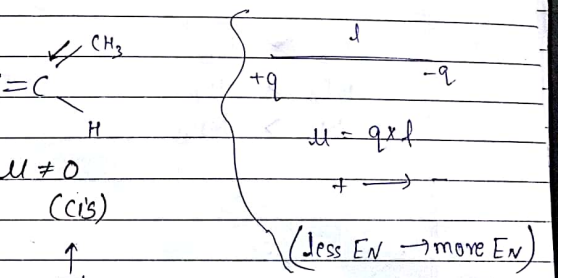


$\mu = 0$ (trans) < $\mu \neq 0$ (Cis's)

↑ Non polar — ↑ polar

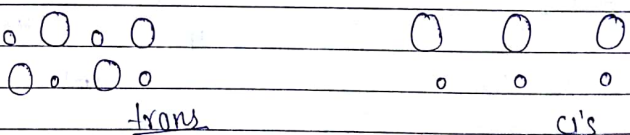
$(BP \propto \mu)$

$(BP_{cis's} > BP_{trans})$



μ↑ → dipole-dipole interaction ↑ → ↓ → BP ↑

MP → The temp. at which the crystal structure break



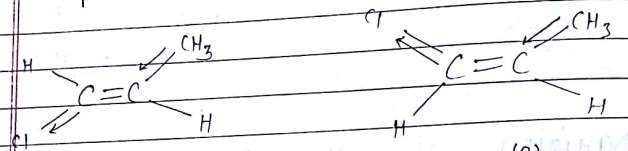
trans — cis's

↑ close packing than cis

always more energy required to break ⇒ MP ↑

$MP_{trans} > MP_{cis}$

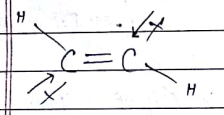
(Q) Compare μ, BP and MP :-



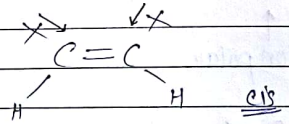
(A) trans

(B) cis

$\Rightarrow$ $\mu_A > \mu_B$
$BP_A > BP_B$
$MP_A > MP_B$

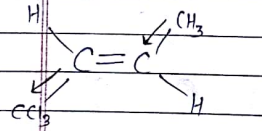


(A) trans

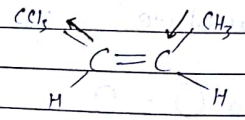


(B) cis

$\Rightarrow$ $\mu_B > \mu_A$
$BP_B > B.P_A$
$MP_B < MP_A$



(A) trans



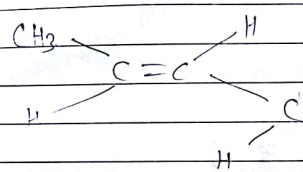
(B) cis

$\Rightarrow$ $\mu_A > \mu_B$
$B.P_A > B.P_B$
$MP_A > MP_B$

* Couting of GI :-

case I Unsymmetrical

$CH_3 - CH = CH - CH = CH - Ph$



C	T
C	C
T	T
T	C

✓ Total no. of GI = 2^n { n → no. of double bond showing GI

case 2

Symmetrical :-

$CH_3 - C = CH \div CH = CH - CH_3$

C	T
T	T
C	C

⇒ 3

T	C

X

✓ Total GI = $2^{n-1} + 2^p$

$p = \frac{n}{2} - 1$ (n → even)

$p = \frac{n-1}{2}$ (n → odd)

{ n → no. of = showing GI

Que) Find total no. of GI :-

Que) $CH_3-CH=CH-CH=CH-CH=CH-CH_3$

$n=3$ symmetrical

$p = \frac{3}{2} - 1 = 1$

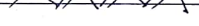
T. GI $= 2^{n-1} + 2^{p}$

$= 2^2 + 2 = 6$

Q) $ph-CH=CH-CH=CH-CH=CH-CH_3$

$n=3$

Total GI $= 2^n = 2^3 = 8$

Q) 

$\Rightarrow$ $n=3$ Total GI $= 2^3$

$= 8$

Q) $CH_3-CH=CH-CH=CH_2$

$n=1$

T. GI $= 2^1$

$= 2$

Q) $CH_3-CH=CH-CH=CH-CH=CH-CH=CH-Ph$

$n=4$

T. GI $= 2^4 = 16$

Q) $CH_3-CH=CH-CH_2-CH=CH-Ph$

$n=2$

T. GI $= 2^2$

$= 4$

Q) ~~$Ph-CH=CH-CH_2-CH=CH-CH_2-CH=CH-Ph$~~

~~$n=3$~~ ~~$p = \frac{n}{2} - 1$~~

~~$= \frac{2}{2} - 1 = 0$~~

~~T. GI $= 2^n + 2^p$~~ ~~T. GI $= 2^n$~~

~~$= 2^2 + 1$~~ ~~$= 2^3 = 8$~~

~~$= 4 + 1 = 5$.~~

Q) $Ph-CH=CH-CH_2-CH=CH-CH_2-CH=CH-Ph$

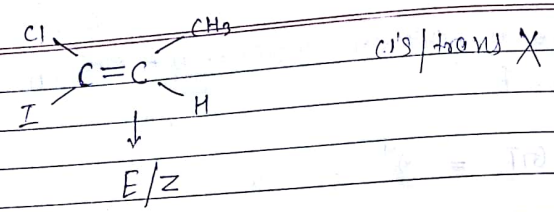
Symmetrical.

$n=3$ $p = \frac{n-1}{2} = \frac{3-1}{2} = 1$

T. GI $= 2^{3-1} + 2^1$

$= 4+2 = 6$

E → opp. Z - same.



cis/trans ✗

↓

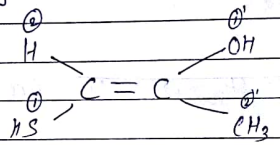
E/Z

(2) E/Z System :-

*) E/Z on the basis of CIP rule (Cahn Ingold Prelog)

Rule 1 Higher the at no gets higher priority.

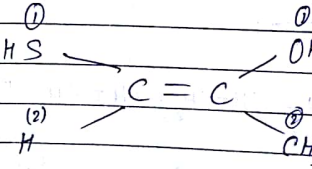
eg:



⇒ E

If the higher priority atom or group are on the opp. side of the double bond then the configuration is E.

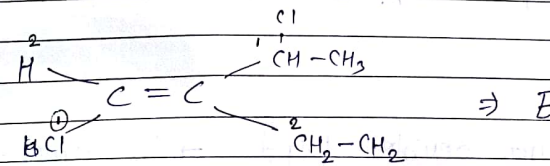
eg:



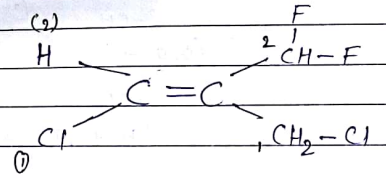
= Z.

Date :
Page :

Rule 2 If same group is present the apply Rule 1 on next atoms.

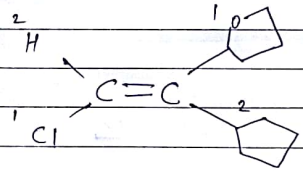


⇒ E



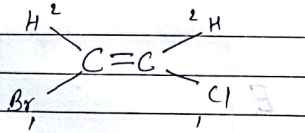
⇒ Z.

Q)



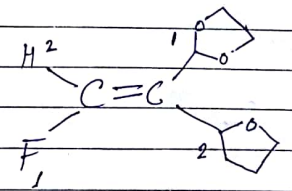
⇒ E

Que)

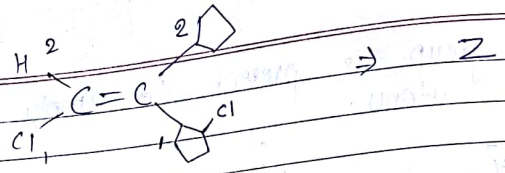


⇒ Z

Que)

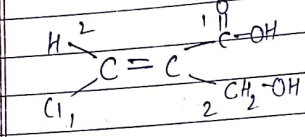


⇒ E

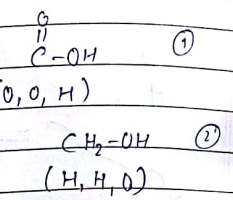


⇒ Z

Rule 3 count double bond → 2 times.

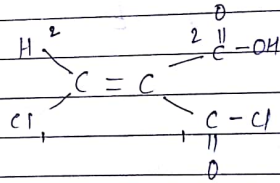


E

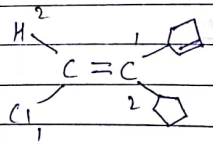


Triple bond count → 3 times

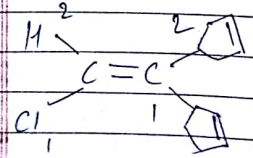
Q)



⇒ Z

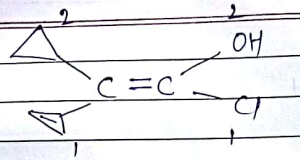


⇒ E



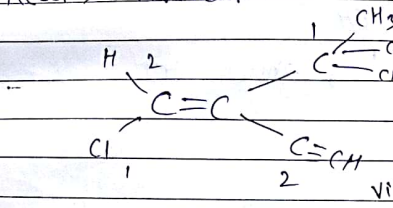
⇒ Z

oxime → (C=N-OH)



⇒ Z

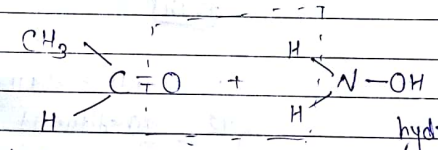
Rule 4 Real > Virtual



⇒ E

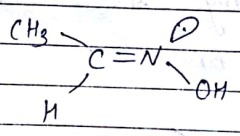
Syn - Anti :-

H-OH same side = syn
H-OH opp. " → anti

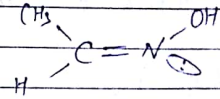


aldehyde — hydroxy amine

Δ

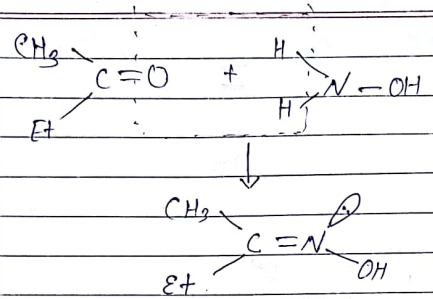


(Syn)



(anti)

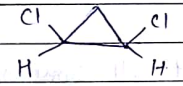
Name → aldo oxime.



(keto oxime)

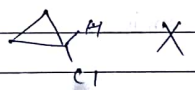
↳ shows GI.

Substituted Cyclo alkane



cis

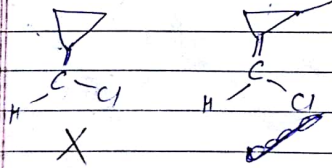
trans



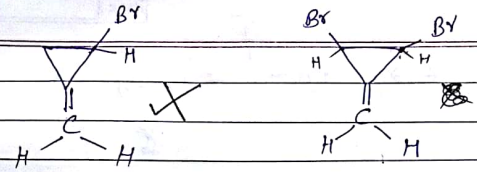
- 2 अलग-अलग C-atom पर substituent होना चाहिए।

Q) Which of the following shows GI.

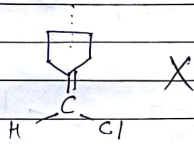
a)

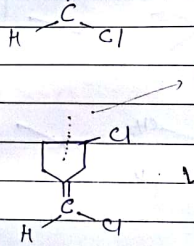


double bond.



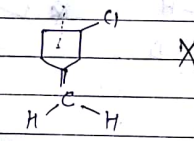
ring.

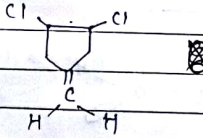




for double bond, bond ring

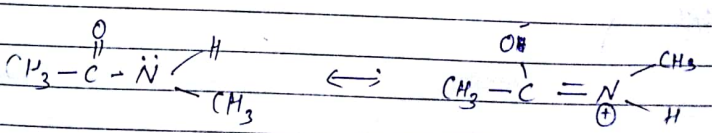
double bond.



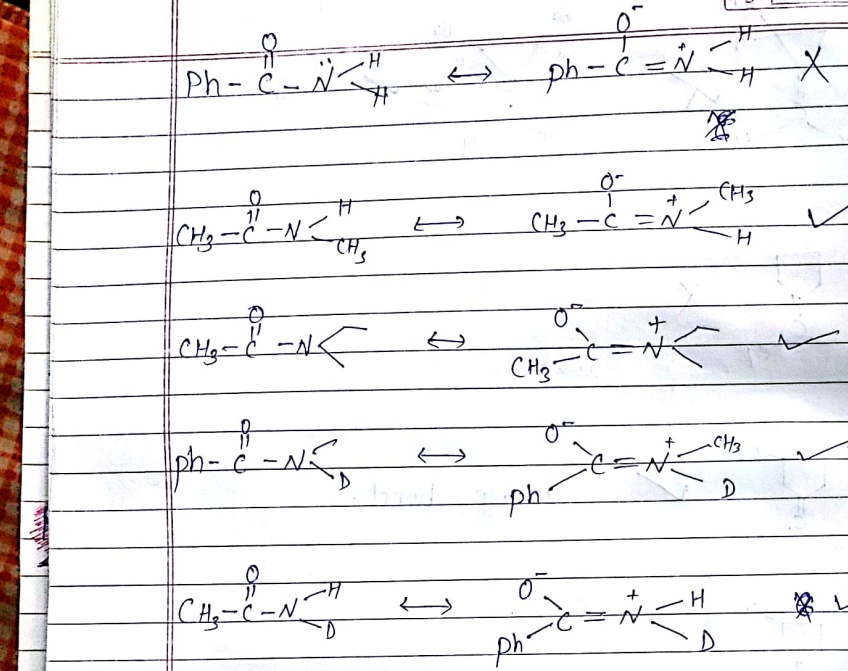


ring

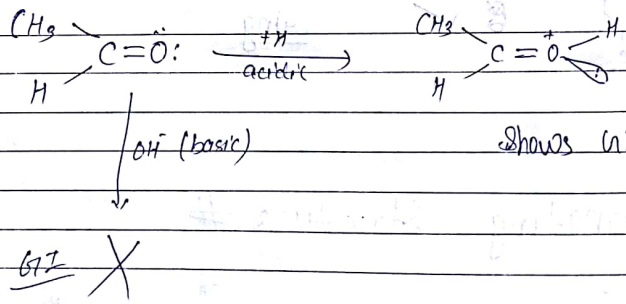
Resonating Structure



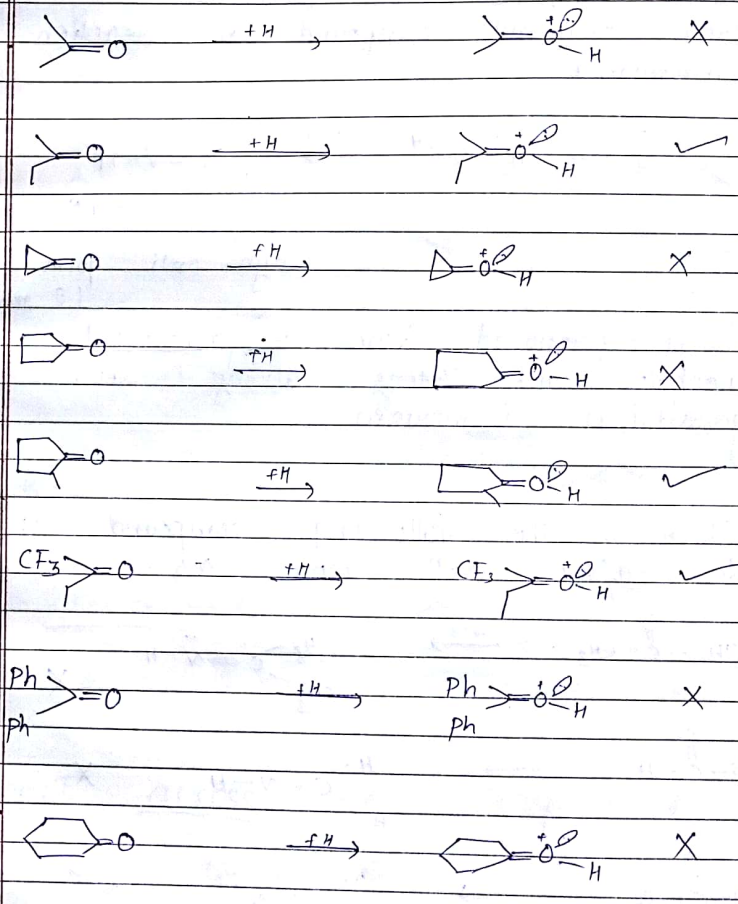
Shows GI



Chemical Rx^n leading to G.I

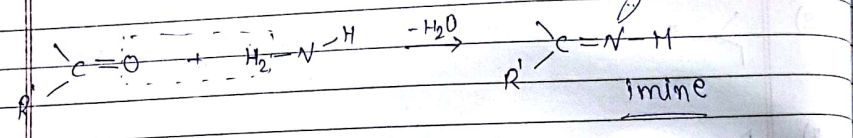


Que) Which of the following molecule. shows G.I in acidic medium.



Geometrical isomerism across Imine :- (C=N-H)

Imine compound are produced from carbonyl compound on reaction with ammonia

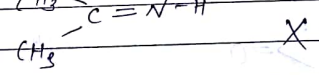


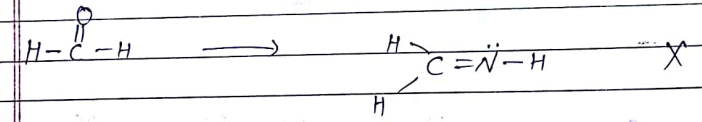
imine

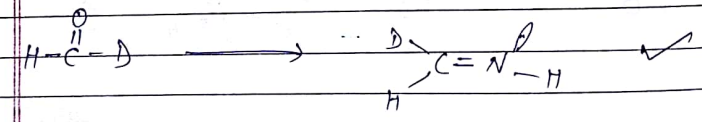
syn - anti form (2 group)

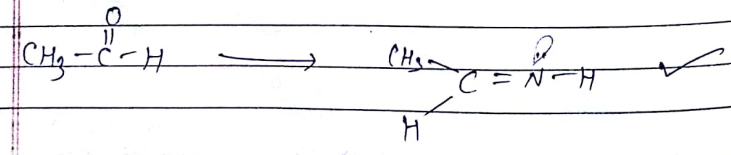
Note :- Imine prepared from unsymmetrical aldehyde and ketone always show geometrical isomerism

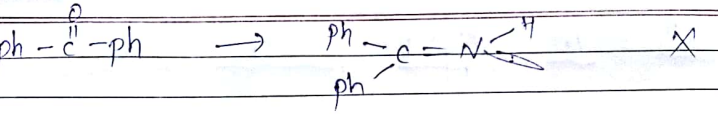
Que Which of the following compound show G.I after rxn with NH_3.

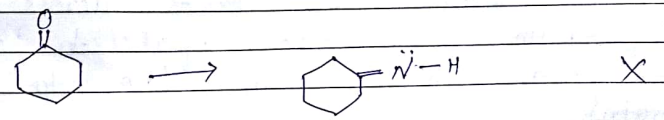
#1) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NH_3}$  ✗

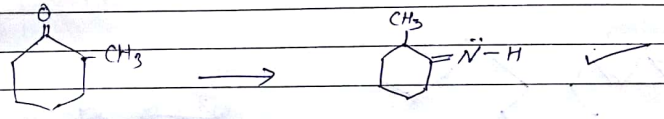
 ✗

 ✓

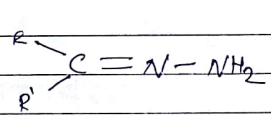
 ✓

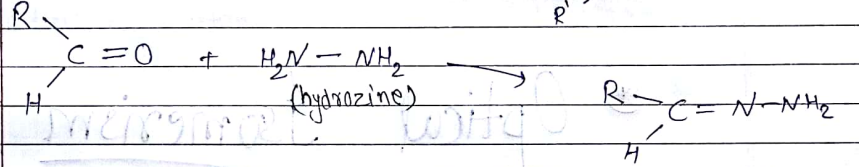
 ✗

 ✗

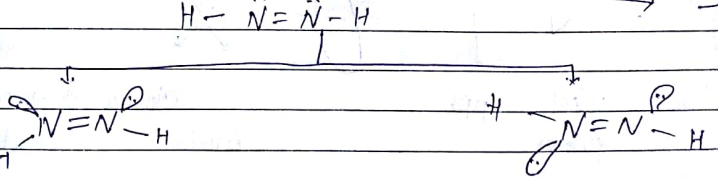
 ✓

G.I across Hydrazone :-





G.I across Azo Compound :- $-N=N-$

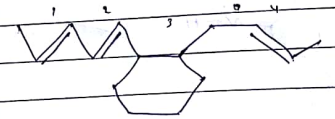


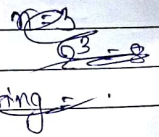
Syn

anti

GI in Cyclo Alkene across =

→ In cyclo alkene GI exist across double bond with ring size equal to or greater than 8 C-atom (due to ring strain)

Que 

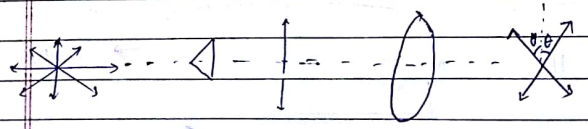


n = 4

$2^4 = 16$ //

✱ Optical Isomerism ✱

→ same M.F.
→ same structural formula.
But only differ in optical - activity.



ordinary light — nicol prism — ppl

Clockwise → dextro
anti- " → laevo

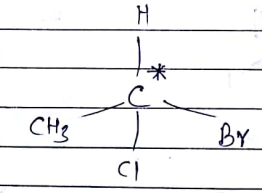
→ If rotation of ppl is clockwise then it is called dextrorotatory / (+) / d-form.

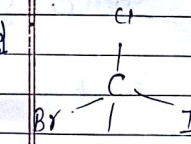
→ If rotation of ppl is anticlockwise then it is laevorotatory / (−) / l-form.

→ If no rotation of ppl → optically inactive (θ = 0°)

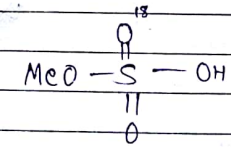
✱ Chiral Atom :-

→ Chiral atom must be sp^3 hybridised
⇒ All the 4 valency of the chiral atom must be satisfied by the diffuent atom or diffuent group of atom.



Qud 

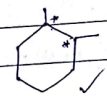
✓ Chiral

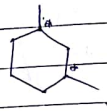


✓ Chiral

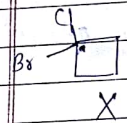
Date :
Page :

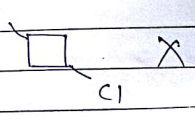
Que) In which of the following comp. chiral centre is present :-


✓ 2


✓ 2


✗


✗


✗

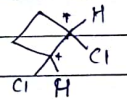

✓ (1)

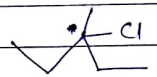
$CH_3 - \overset{*}{C}H(Cl) - CH_2 - CH_3$
✓ 1

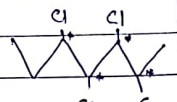

✓ 1

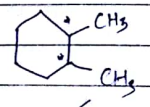

✓

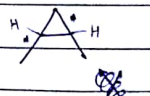
$CH_3 - \overset{*}{C}H(Cl) - \overset{*}{C}H(Br) - CH_3$
✓ 2


✓ 2


✗

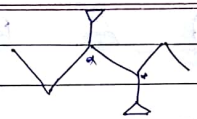

✓ 4

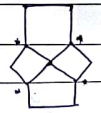

✓ 2


✓ 2

Date :
Page :


✓ (2)


✓ (2)

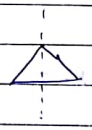

✓

Elements of symmetry

Types of symmetry :-

1) plane of symmetry (POS)
2) Centre of " (COS)
3) Axis " " (AOS)
4) AH. axis " " (AAOS)

1) Plane of symmetry :-

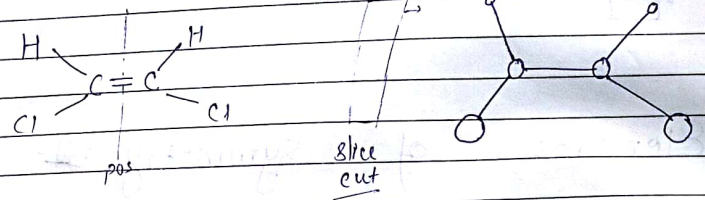


Plane of symm. is defined as an imagenday plane about which molecule can be divided into 2 equal parts such that both parts are identical and mirror image of each other.

Date :
Page :

eg:- A B C D E

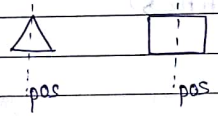
1) * Unsaturated :-



sp^2 (planar)

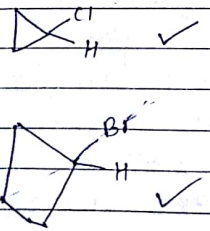
* Every planar molecule has minimum 1 pos (slice cut)

2) Cyclo Alkane :-



* without substituent pos is present

(i) Mono substituted cyclo alkane :

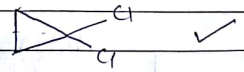


pos is present

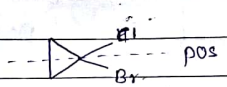
⇓

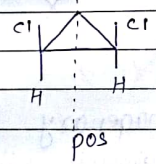
* {cut about substituent (Cl)

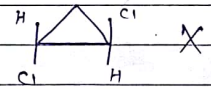
(ii) Disubstituted cycloalkane :



pos → cut about substitu

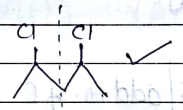


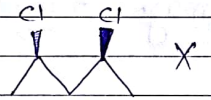


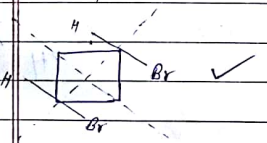


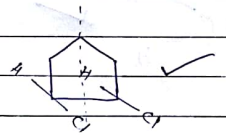
no pos

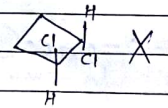
Que)

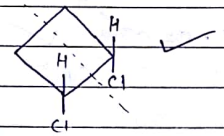




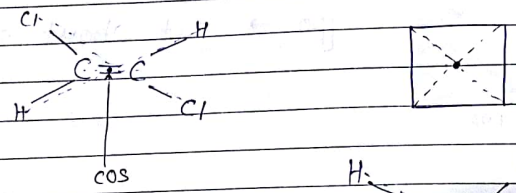




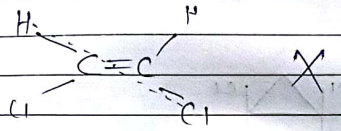




COS (Centre of Symmetry) :-



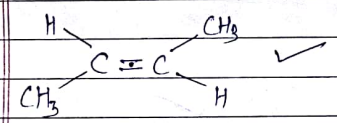
mirror image about point

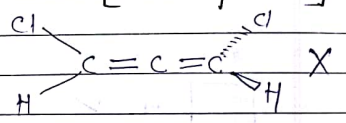


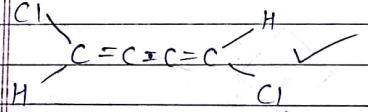
COS is defined as an imagenary point present in the molecule about which every atom has ~~ex~~ exactly identical mirror image.

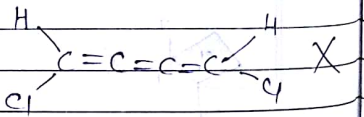
*[odd no. of C $\overset{\text{COS}}{\times}$]

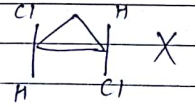
Que)

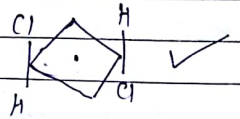




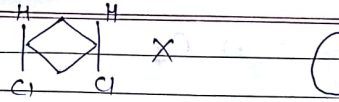


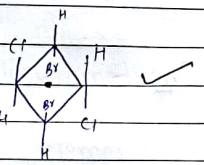


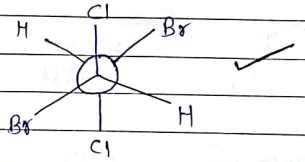




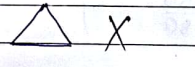
(odd no. of Carbon) $\times$

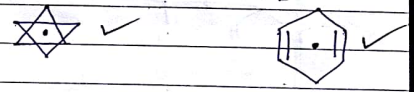




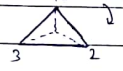


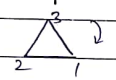
(b/w fc and be)

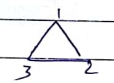




AOS (Axis of symmetry) :- (C_n)



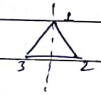




1 r axis

$n = \frac{360}{\theta}$

$n = \frac{360}{120} = 3$ C_3



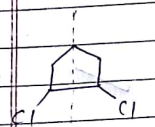
$n = \frac{360}{180} = 2$

C_2

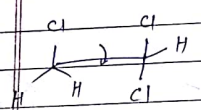
→ Axis of symmetry is defined as an imagenary axis about which if the molecule is rotated the structure repeat itself more than 1 time

{ if $n > 1$ → AOS is present }

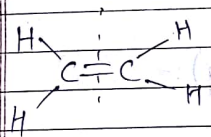
$n = \frac{360}{90} = 4 \Rightarrow C_4$



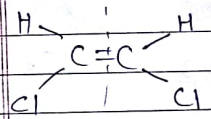
$n = \frac{360}{180} = 2 \Rightarrow C_2$



$\Rightarrow C_2 \quad \left(n = \frac{360}{180} = 2\right)$

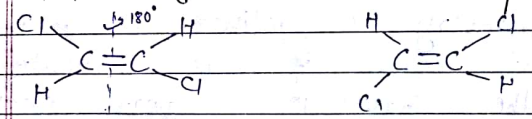


C_2

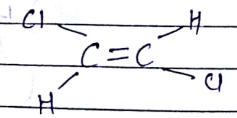


C_2

AAOS (Alternate Axis of Symmetry) :-



(A) (B)



(C)

A and C → ~~Symmetrical~~ identical then AAOs is present.

Disymmetry Molecule :-

The molecule or object in which min^m 2 elements of symmetry (cos and pos) are absent are called disymmetry molecule or object.

Asymmetric :-

When all elements of symmetry are absent then the molecule is said to be asymmetry.

Disymmetry and Chirality :-

All disymmetry molecule are chiral and optically active.

* Configuration :- (CIP)

(1) Assign priority on the basis of CIP.

(2) Ignore 4th priority.

(3) Rotation 1 → 2 → 3

(4)

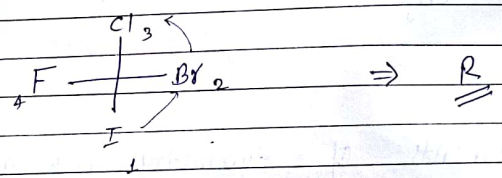
(4) Position of 4th priority

vertical → VCR

horizontal → HCS

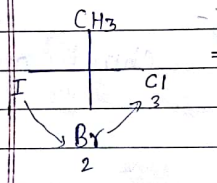
vertical clockwise → R

Horizontal clockwise → S

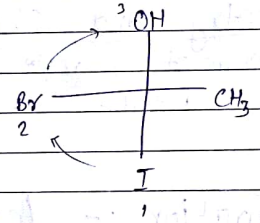


⇒ R

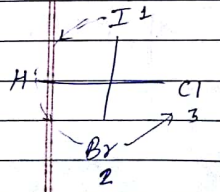
Que) Identify R-S configuration :-



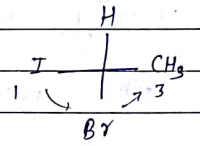
⇒ S



⇒ S

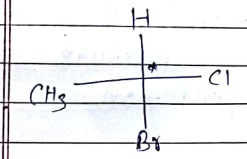


⇒ R

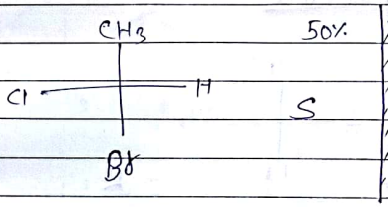


⇒ S

Molecule Containing Single Chiral Atom :-



POS X
COS X
→ optically active



(A) $\alpha = +20^\circ$

(B) $\alpha = -20^\circ$

A and B are enantiomers.

↳ optically active

A + B → Racemic mixture

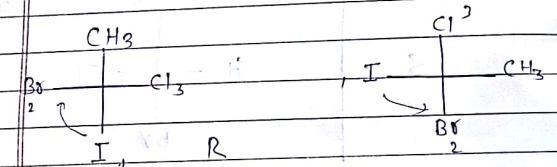
1) 50% d + 50% l
2) optically inactive.
3) external compensation

* Enantiomer → They are non-superimposible mirror image of each other. They produce equal and opp. rotation for ppl.

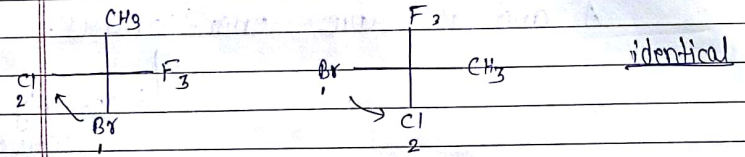
Date :
Page :

* **Racemic mix.** → It is a mixture of enantiomers in equal proportion. It is optically inactive mixture bcz of external compensation.

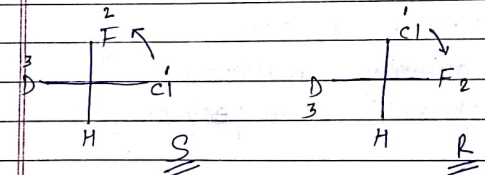
Relationship b/w molecule :-



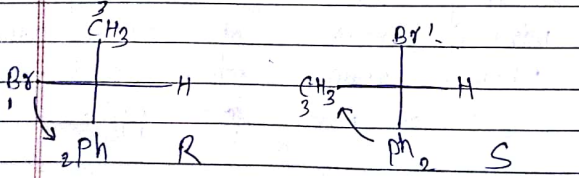
identical



identical

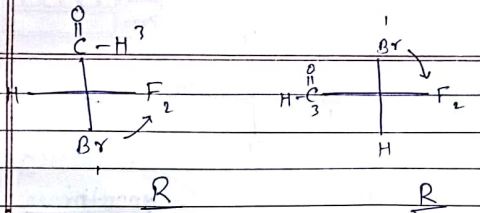


⇒ enantiomer

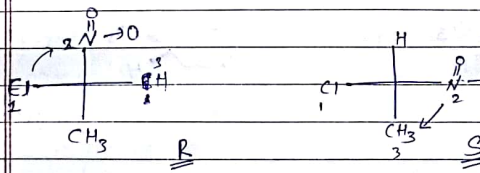


⇒ enantiomer

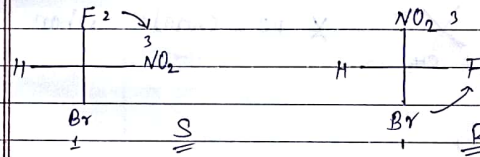
Date :
Page :



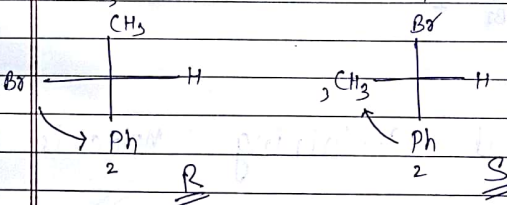
⇒ identical.



⇒ enantiomer

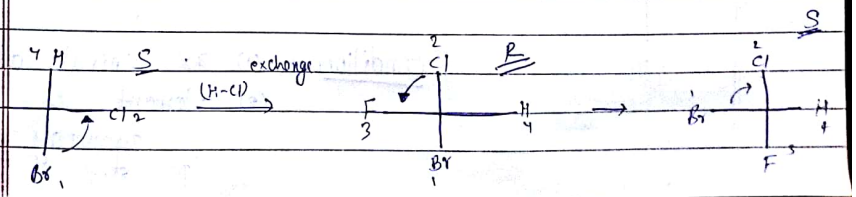


~~enantiomer~~ enantiomer

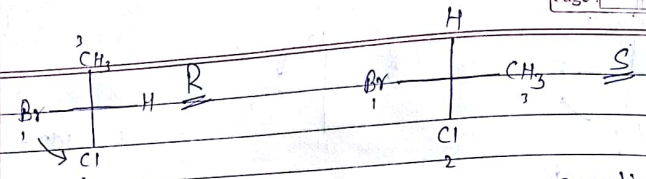


⇒ enantiomer.

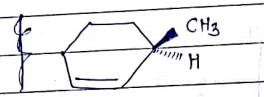
Trick add even no. of exchange → inverse
" " " " → identical



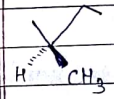
Date :
Page :

Que) 

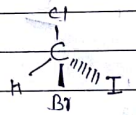
enantiomer



enantiomer

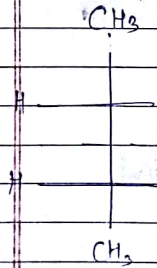


✗ no chiral carbon



enantiomer

Multiple chiral Containing Molecule

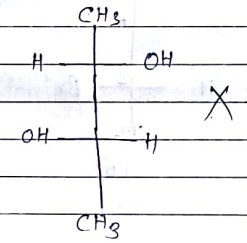


pos ⇒ Meso compound (optically inactive)

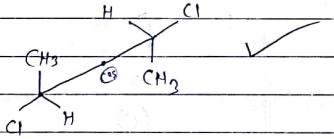
Condition → (1) ≥2 chiral atom
(2) element of symmetry is present (pos / eos)

→ Meso compound are those compounds which are optically inactive due to the presence of pos or cos and also contain chiral atom.

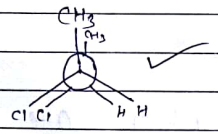
→ whatever rotation is produced by half part of the molecule is exactly cancelled by other half part of the molecule this is known as internal compensation.



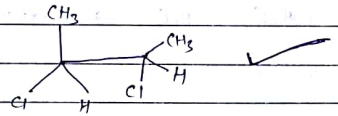
✗



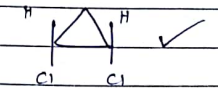
✓



✓



✓



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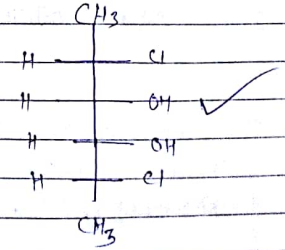

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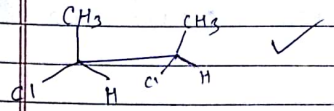
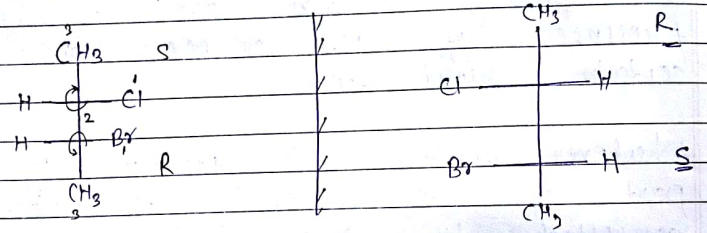


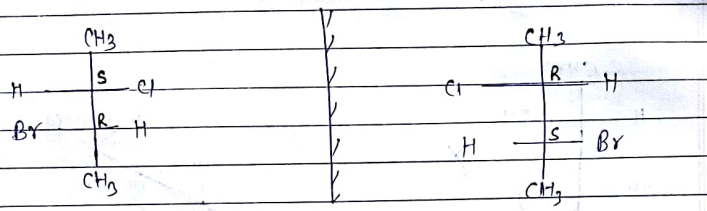
✓

Relationship b/w Molecules :-



(A)

(B)



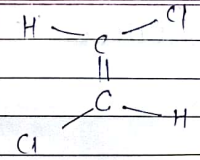
(C)

(D)

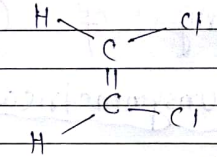
A, B → enantiomer C/D → enantiomer
A, C / B, C → distereomer

→ Distereomer are molecules which are ~~stereoma~~ isomer but not mirror image of each other.

→ All geometrical isomers which are not mirror images of each other are distereomers.



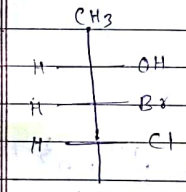
trans



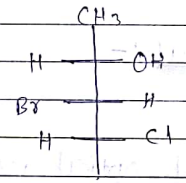
cis

Stereomers
mirror image ✗
↓
distereomer

Que) Identify relationship b/w molecules :-

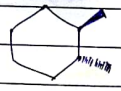


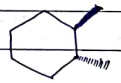
ph



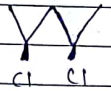
ph

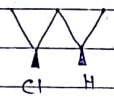
distereomer





distereomer





distereomers

Counting of Optical Isomers :-

Case 1 For Unsymmetrical :-

Total optical isomer = 2^n Meso = 0

" enantiomer pair = 2^{n-1}

optically active = 2^n

n → no. of chiral centre

eg:- $CH_3 - \overset{*}{C}H(OH) - \overset{*}{C}H(OH) - CH_2 - CH_3$

n = 2

TOI = $2^2 = 4$

TEP = $2^{2-1} = 2$

Case 2 For Symmetrical :-

① n → even

total optical isomer = $2^{n-1} + 2^{\frac{n}{2}-1}$

" optical active = 2^{n-1}

Meso = $2^{\frac{n}{2}-1}$

Ep = 2^{n-2}

$CH_3 - \overset{*}{C}H(Cl) - \overset{*}{C}H(Cl) - CH_3$

Ep = 1

OI = 2 + 1 = 3

Meso = 1

OA = 2

② n → odd

total optical isomer = 2^{n-1}

Meso = $2^{\frac{n-1}{2}}$

Optical active = $2^{n-1} - 2^{\frac{n-1}{2}}$

Ep = $\frac{OA}{2}$

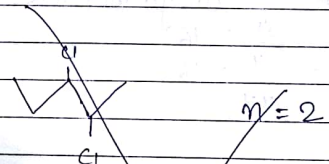
***

$CH_3 - \overset{*}{C}H(Cl) - \overset{+}{C}(H)(Cl) - \overset{*}{C}H(Cl) - CH_3$

n = 3

pseudo chiral carbon.

Que



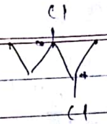
n = 2

TOI = $2^{2-1} + 2^{\frac{2}{2}-1} = 3$

OA = $2^{2-1} = 2$

Ep = $2^{2-2} = 1$

Meso = $2^{\frac{2}{2}-1}$

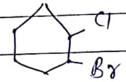
Que) 

unsymmetrical $n = 2$

$OI = 2^2 = 4$

$OA = 2^n = 4$

$Ep = 2^{2-1} = 2$

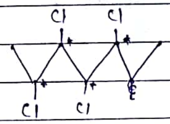
Que) 

$n = 2$

$OI = 2^2 = 4$

$OA = 2^2 = 4$

$Ep = 2^{2-1} = 2$

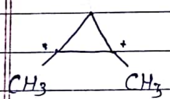
Que) 

$n = 4$ unsymmetrical

$OI = 2^4 = 16$

$OA = 2^4 = 16$

$Ep = 2^{4-1} = 8$

Que) 

$n = 2$ symmetrical

$OI = 2^{2-1} + 2^{\frac{2}{2}-1}$

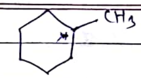
$= 3$

$OA = 2^{2-1} = 2$

$Meso = 2^{\frac{n}{2}-1}$

$= 2^{\frac{2}{2}-1} = 1$

$Ep = 2^{2-2} = 1$

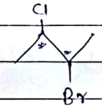


$n = 0$ unsymmetrical.

$OI = 2^0 = 1$

$OA = 2^0 = 1$

~~$Ep = 2^{1-1} = 1$~~

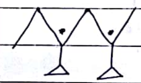


$n = 2$ unsymmetrical.

$OI = 4$

$OA = 4$

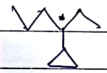
$Ep = 2^{2-1} = 2$


$n = 2$ unsymmetrical

$OI = 4$

$OA = 4$

$Ep = 2^{2-1} = 2$

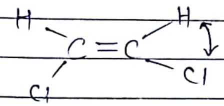

$n = 1$ unsymmetrical

$OI = 2^1$

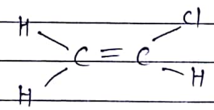
$OA = 2$

$Ep = 2^{1-1} = 1$

Stereocentre



(A)



(B)

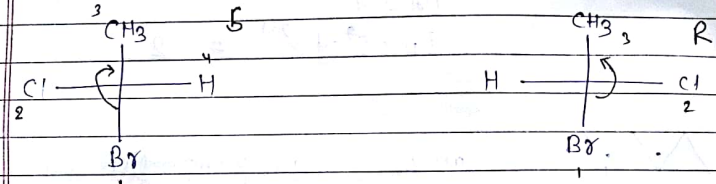
* Molecule का वह atom जिसके about group को exchange करने पर SI मिले उसको stereocentre कहते हैं।

$CH_3 - CH = CH - CH = CH - CH_3$ ⇒ 4

$CH_3 - CH = CH - CH = CH_2$ ⇒ 2

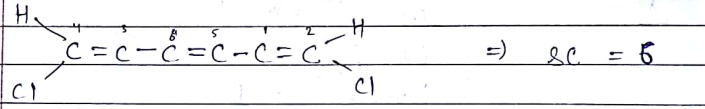
GI show X

only * GI show होगा → stereocentre होगा

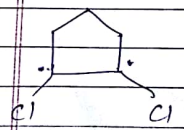


* → every chiral centre is a stereocentre.

Q)



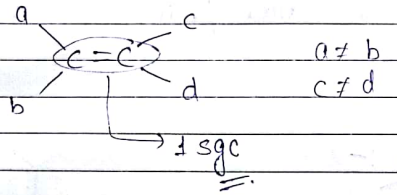
⇒ SC = 5



⇒ SC = 2

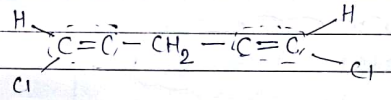
Stereogenic Centre

It is a point or a location for an atom present in the molecule which can generate a pair of stereoisomer.



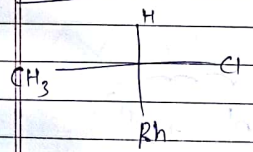
$a \neq b$

$c \neq d$



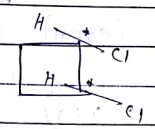
⇒ 2 sgc //.

* Chiral Centre → point



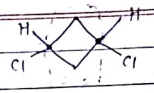
Every chiral centre is a sgc.

⇒ 1 sgc.



SC = 2

sgc = 2 //



sgc = 1
sc = 2

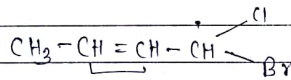
* chiral → sgc → point ka about
* chiral X → sgc → area / ring ka about.

* Stereo Isomer :-

case A Unsymmetrical :-

total SI = 2^n

n → sgc

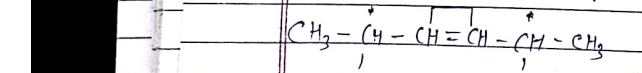


n = 2

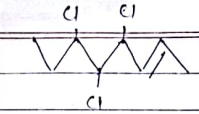
case B Symmetrical :-

total SI = $2^{n-1} + 2^p$

$$\begin{cases} p = \frac{n}{2} - 1 & \text{(even)} \\ p = \frac{n-1}{2} & \text{(odd)} \end{cases}$$

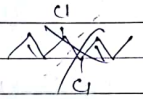


n = 3 p = 1

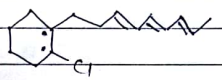
Que 

n = 84 unsymmetrical.

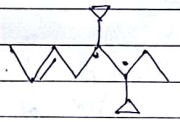
TSI = 2^4 = 8x2 = 16



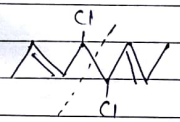
n = 4 ~~symmetrical~~
~~TSI = 2^4 = 16~~



n = 5 unsym.
TSI = 2^5 = 32



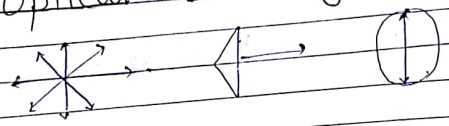
n = 3 unsym.
TSI = 2^3 = 8

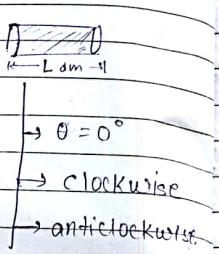


n = 4 p = 4-1 = 1

(Symmetrical) TSI = $2^{4-1} + 2^1$
= 8 + 2 = 10

Optical Activity





POS/COS present
optically inactive
$\theta = 0$

POS/COS absent
OA
$\theta \neq 0$

$\theta \propto L$
$\theta \propto C$
$\theta \propto CL$
$\theta = \alpha CL$

L → length of polarity
C → conc^n of sol^n
α → specific angle of rotation

→ α → depends on intensity of light

Que a) C = 0.1 gm/mL L = 30 dm θ = +20° (dextro)

sol^n $\alpha = \frac{\theta}{CL} = \frac{20}{30 \times 0.1} \Rightarrow 6.67°$

b) If the length of the tube is doubled and conc^n is become to 0.04 g/mL then caculate θ.

sol^n $\theta = 6.67 \times 0.04 \times 2 \times 30$
$= 6.67 \times 2.4 \Rightarrow 16.008$ (dextro)

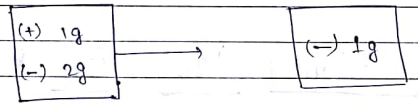
Clock → +ve
anti " → -ve

Q2 An aq. sol^n of 2-butanol with conc^n 0.01 g/mL and length = 20 cm and θ = +10°
Calculate the following
a) α for dextro form
b) if 100 mL of 0.01 g/mL (+) 2-butanol is mixed with 200 mL of 0.01 g/mL (−) 2-butanol. Calculate θ.

sol^n a) $\alpha = \frac{10}{0.01 \times 20 \times 10^{-1}} = 500°$

b) $\theta = \alpha CL$

Mass of (+) butanol = 1g
" " (−) " = 2g



conc^n = $\frac{1}{300}$

$\theta = \alpha C L$ L = 20 cm = 2 dm.
$= 500 \times \frac{1}{300} \times 2$ α = 500°

θ = −3.3° (anticlockwise)
(l-form)

Date :
Page :

Enantiomeric Excess (EE) / Optical Purity (OP)

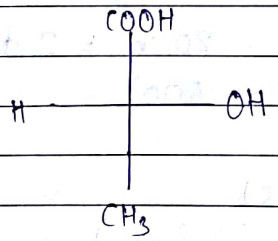
d	l	Racemic mix.	ee/op
100%	0%	0%	100%
80%	20%	40%	60%
50%	50%	100%	0%
30%	70%	60%	40% (-) (l-form)

$$ee = \frac{|d-l|}{|d+l|} \times 100$$

Racemic mix. = 100 − e.e.

* Fisher Projection *

* $CH_3\ CH(OH)\ COOH$



- Max^m C-atom lie in vertical line
- Higher priority C containing func^n group at top position.