Isomerism

Isomers — Comps. with same molecular formula, but diff. phy. & chem. proprts.
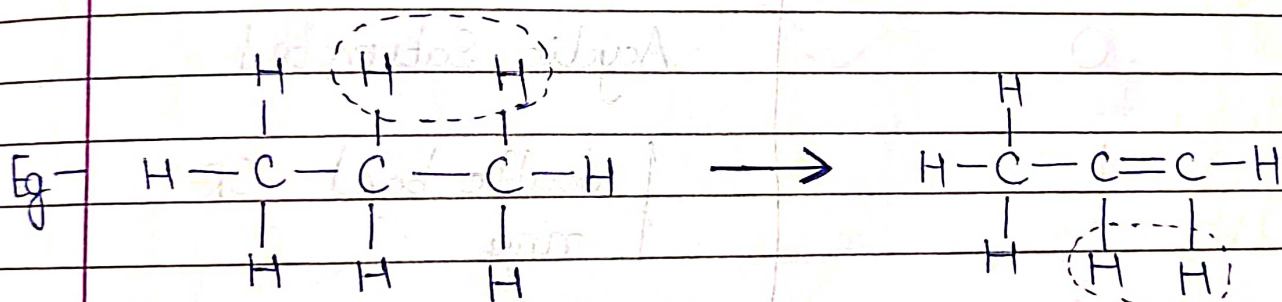
```
                    ┌──────────────┐
                    │  Isomerism   │
                    └──────────────┘
        ┌────────────────────┴────────────────────┐
┌──────────────┐                          ┌──────────────┐
│  Structural  │                          │    Stereo    │
└──────────────┘                          └──────────────┘
        │                                          │
  ─ Chain                              ┌────────────────────┐
  ─ Position                           │   Confirmational   │
  ─ Functional                         └────────────────────┘
  ─ Metamerism                             ─ Rotation around C—C
  ─ Tautomerism                            ─ Amine Inversion

                                       ┌────────────────────┐
                                       │   Configuration    │
                                       └────────────────────┘
                                           ─ Geometrical
                                           ─ Optical
```
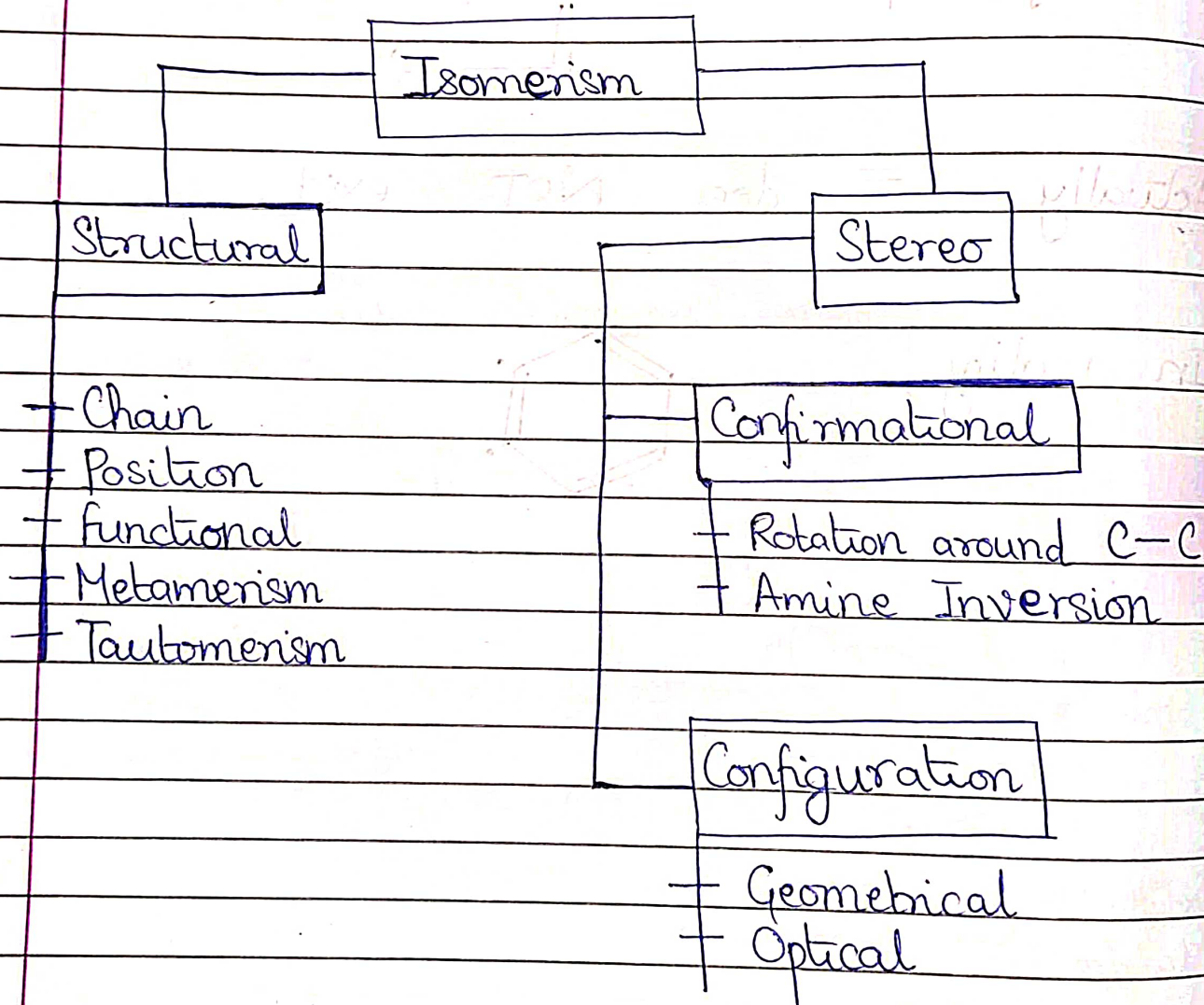
Steroisomers — Same IUPAC name, diff. spatial arrang-ement
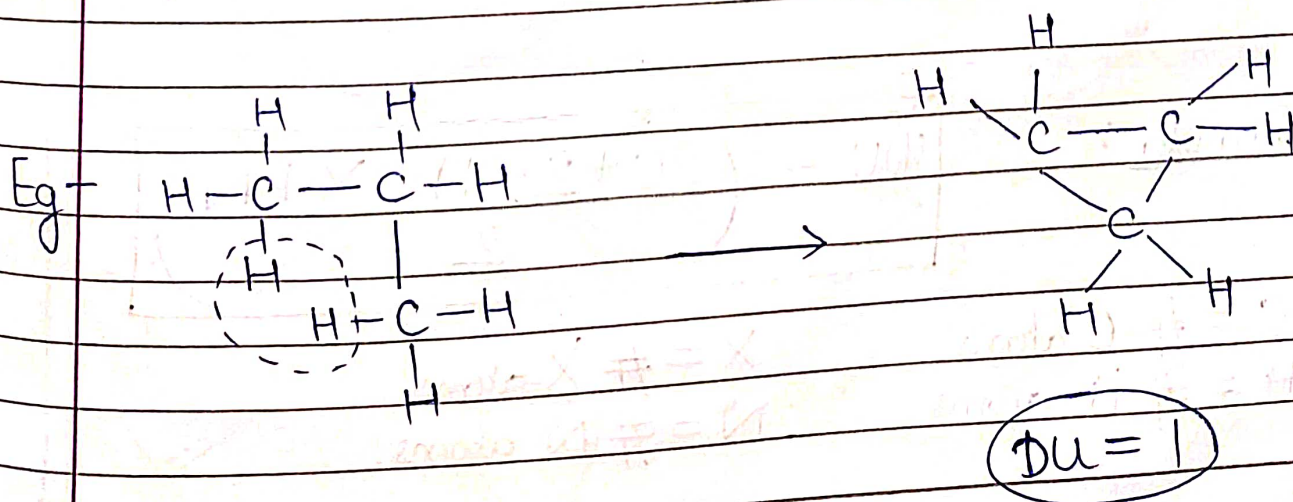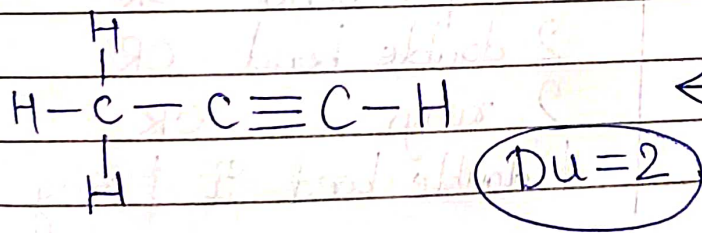
Degree of Unsaturation (DU)

Also called __Double Bond Equivalent__ (DBE) or __Hydrogen Deficiency Index__ (HDI)

It is index to find no. of H_2 molecules removed from any species.

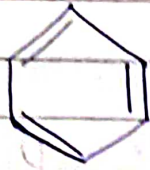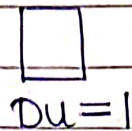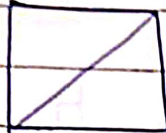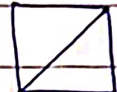$\star$ (It is measured wrt. ACYCLIC SATURATED Molecule.)

Eg-

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C=C-H$$

$$\underset{\underset{\displaystyle H \quad H}{|\quad|}}{}$$

(Du = 1)

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C\equiv C-H$$

(Du = 2)

Eg-

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\underset{\displaystyle H}{|}}{\overset{\displaystyle H}{|}}{C}}{C}}-H \longrightarrow$$

$$H-\overset{|}{C}-H$$

(Du = 1)

Eg —

$$DU = 3 + 1 = \boxed{4}$$

⟍ due to ring

due to //

Eg —

DU=1 → DU=2

☆

DU	Possibility
0	Acyclic Saturated
1	1 double bond OR 1 ring
2	1 triple bond OR 2 double bond OR 2 rings OR 1 double bond & 1 ring

formula : $\boxed{DU = \left(\dfrac{2C+2-H-X+N}{2}\right)}$

C = # C atoms   X = # X atoms

H = # H atoms   N = # N atoms.

Q) find no. of all possible structural isomers of —

1) C_3H_4 $\qquad$ DU = 2

2) C_4H_8 $\qquad$ DU = 1
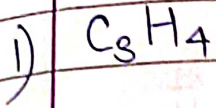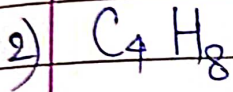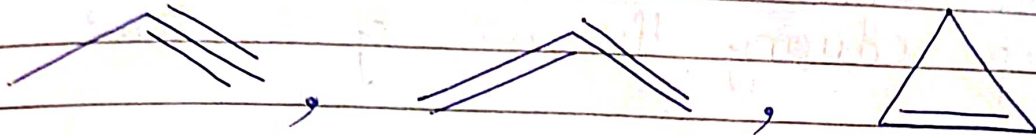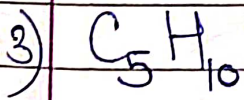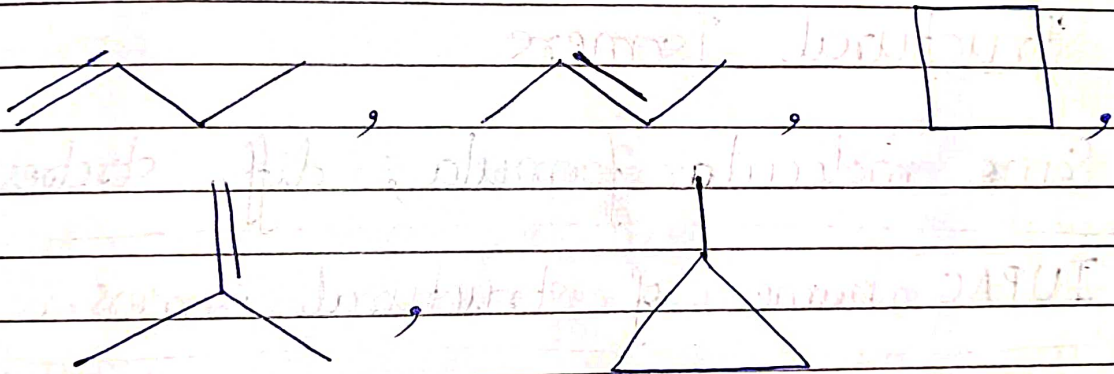
3) C_5H_{10} $\qquad$ DU = 1
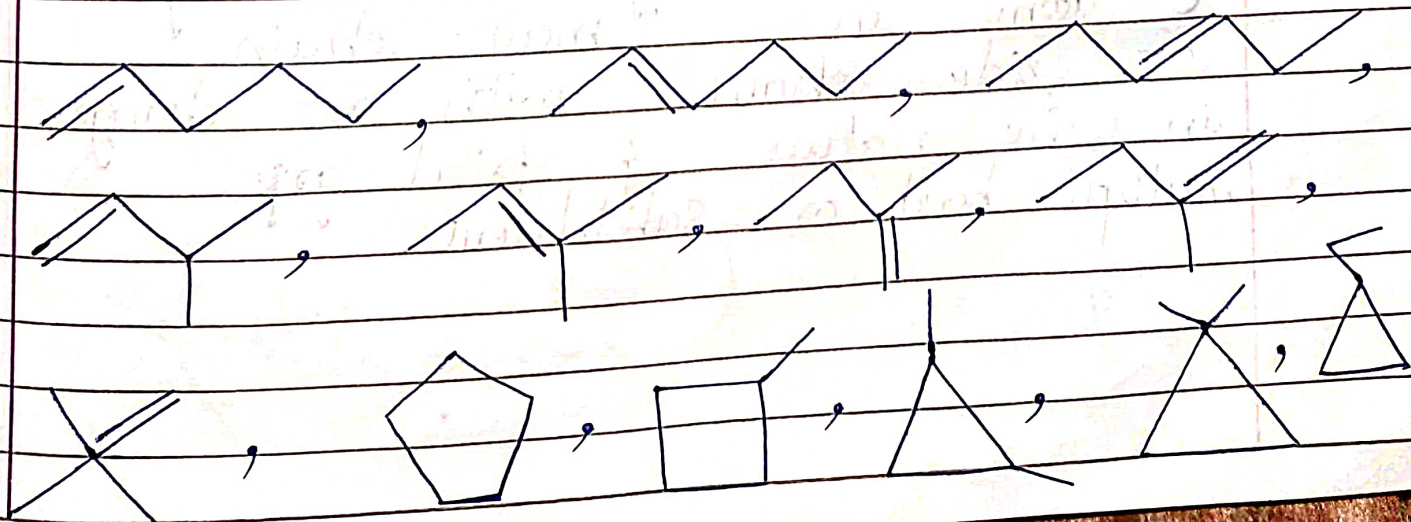
☆ Count systematically !

first acyclic, then cyclic.

Start with max. C atom chain &
keep reducing the no. of C atoms.

Structural Isomers

Same molecular formula; diff. strctres.

☆ IUPAC name of structural isomers is diff.

1) Chain –

Arises due to diff. in no. of
C atoms in main chain
or side chain, with no change
in the nature of fx'nal grp,
multiple bond, or substituent.
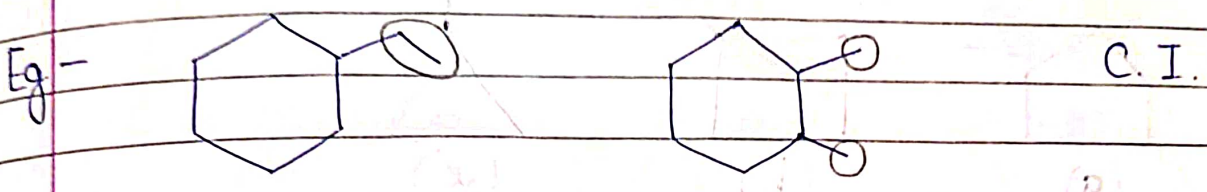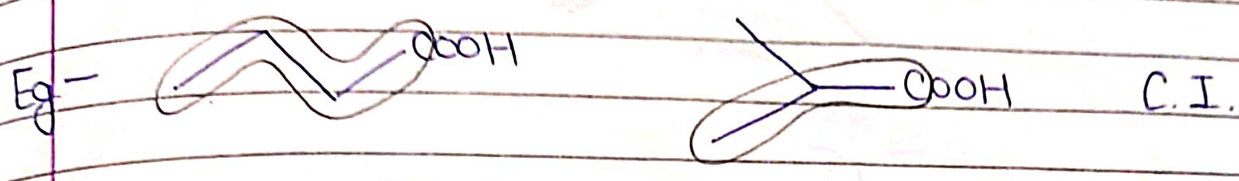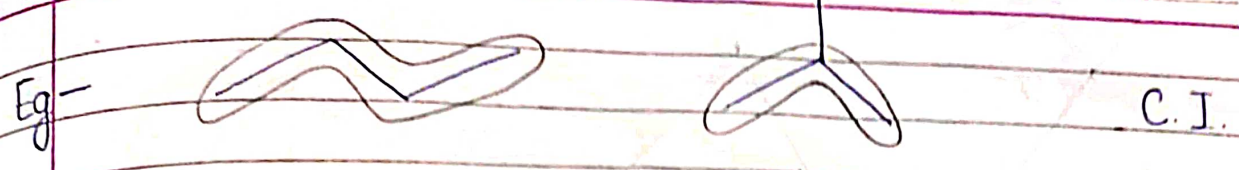
Eg -   C.I.

Eg -   C.I.

Eg -   C.I.

2) Position -

Arises due to ~~change~~ diff. in posn. of fxⁿal grp, multiple bond or substituent, with no change in main/side chain, nature of fxⁿal grp, multiple bond or substituent.

Eg -   P.I.

Eg -   C.I.

Eg -   P.I.

Eg —

C.I.

Eg —

(a)   (b)   (c)

(d)   (e)
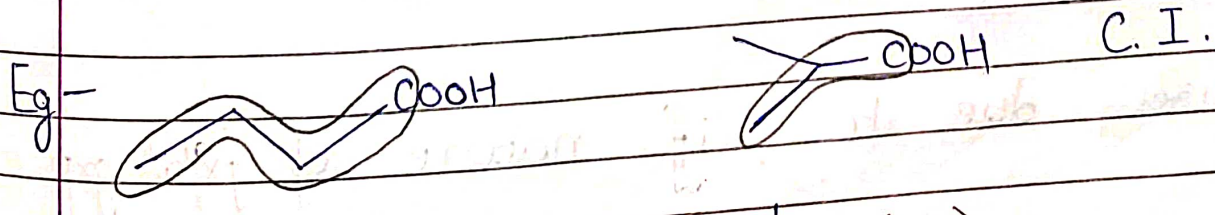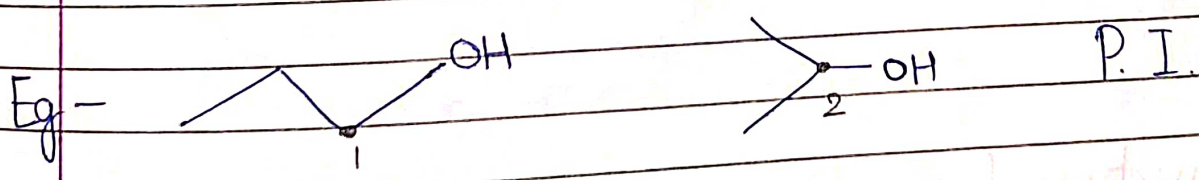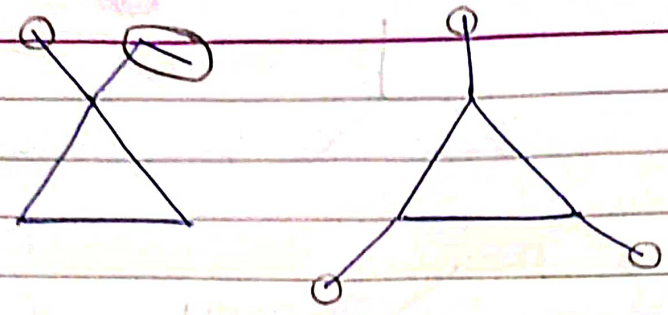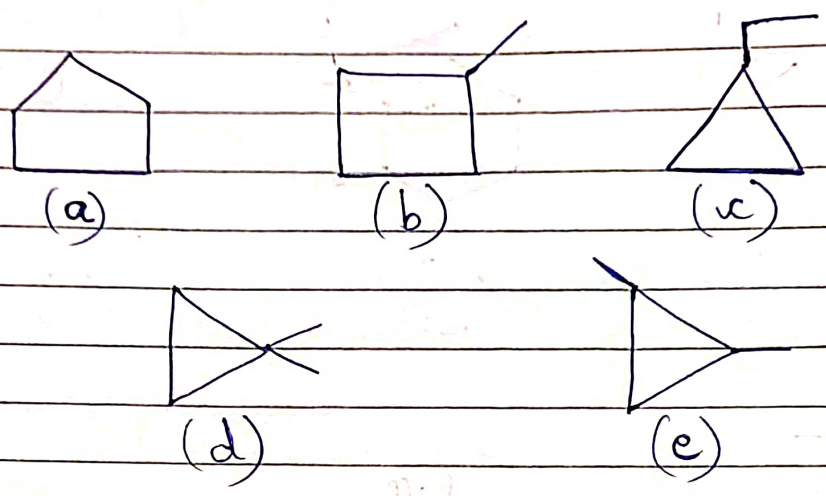
C.I : (a, b) ; (a, c) ; (a, d) ; (a, e)
(b, c) ; (b, d) ; (b, e)
(c, d) ; (c, e)

P. I :   (d, e)

3) Functional —

Arises due to diff. nature of fᵪⁿal grp.

Eg —

Alcohol   Ether

F. I.

Eg —
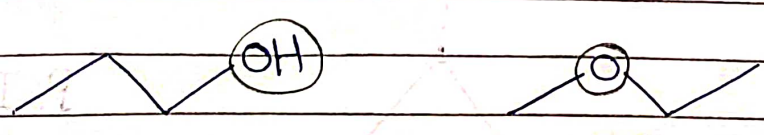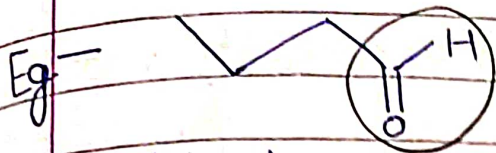
Aldehyde   **Ketone**   F.I.
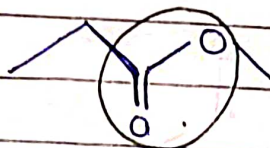
Eg —

Carboxylic Acid   **Ester**   F.I.

Eg —

$1°$ $2°$ $3°$

Amine   **Amine**   **Amine**   F.I.

Eg —

Nitro   **Nitrite**   F.I.

Eg —

**Ring**   • **Chain**   Ring chain F.I.

Eg —
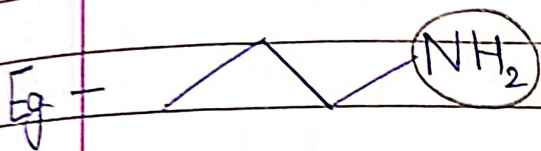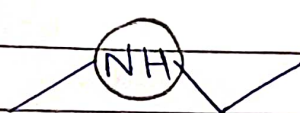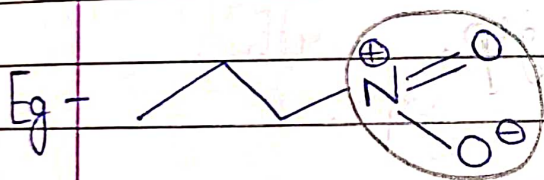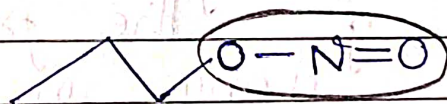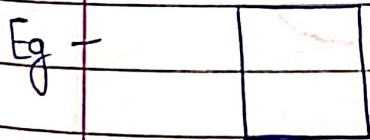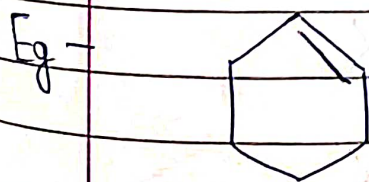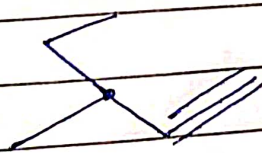
Ring   **Chain**   Ring chain F.I.

Q) How many esters are there with mol formula

1) CH_3O_2 $DU = 1$

I double bond
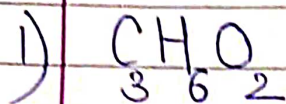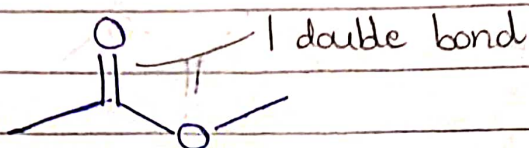
4) Metamerism —

~~This~~ ~~is~~ Arises due to unequal distribution of substituents on either side of the fx^{n}al grp, with no change in fx^{n}al grp, multiple bonds, substituents.

⭐ All **NON TERMINAL** fx^{n}al grps show Metamerism.

— O — ✓   — S — ✓

— OH ✗   — SH ✗

— CO — ✓   — COOH ✗

— NH$_2$ ✗   — NH — ✓

$$-\overset{\overset{\displaystyle O}{\|}}{C}-O- \quad \checkmark$$

$$\underset{\diagup N \diagdown}{|} \quad \checkmark$$

$$-SO_3H \quad \times$$

$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O- \quad \checkmark$$

$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}- \quad \checkmark$$
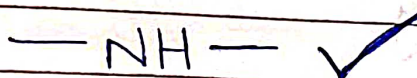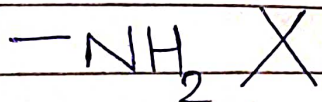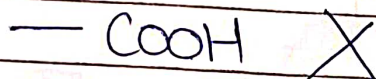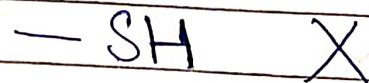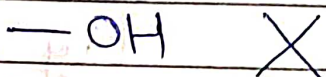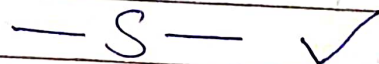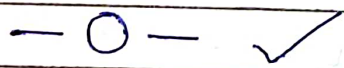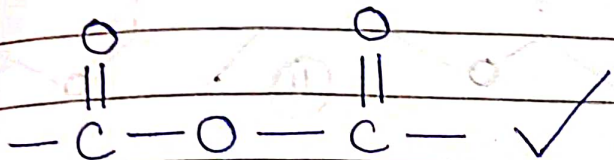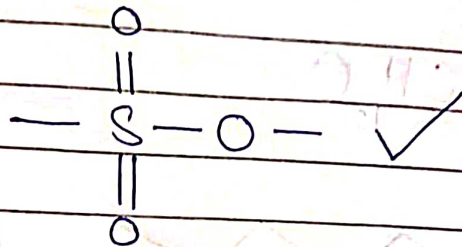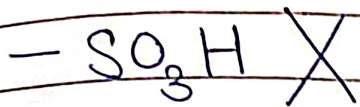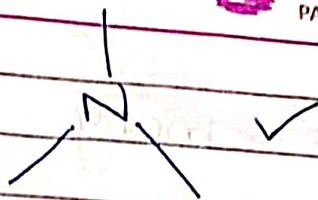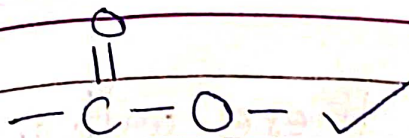
How many alcohols are there with mol formula—
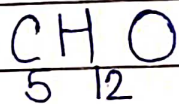
$$CH_5O_{12} \qquad DU = 0.$$
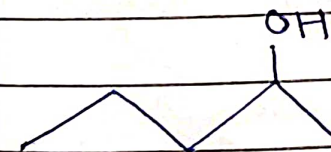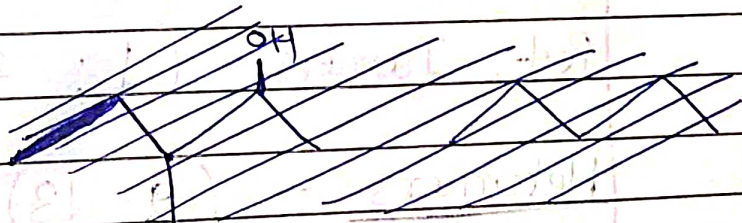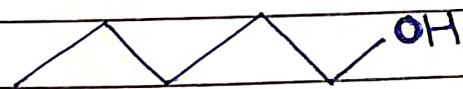
③
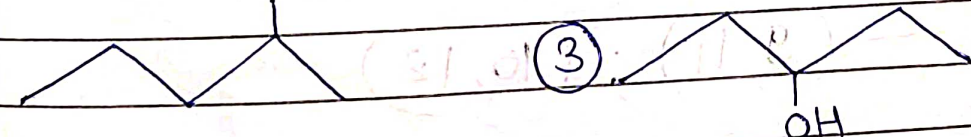
④
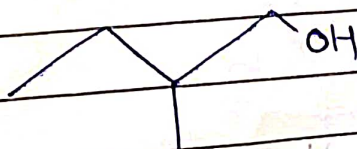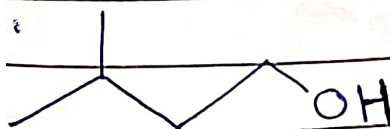
⑦
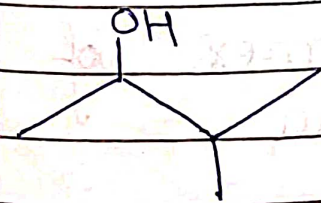
⑧
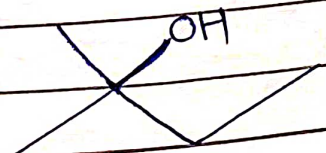
Q) How many ethers are there with mol. formula-

1) $C_5H_{12}O$ $DU = 0$

(9)   (10)   (11)

(13)   (12)

(14)
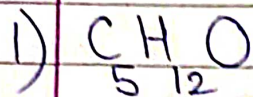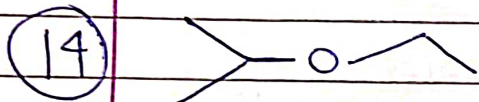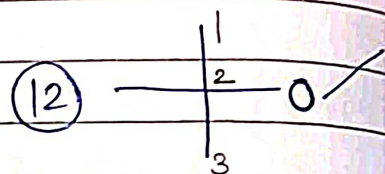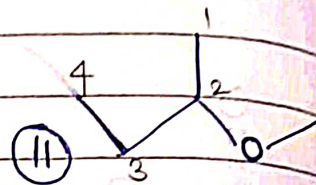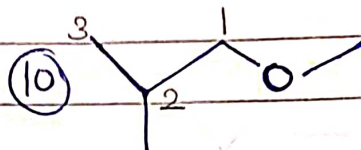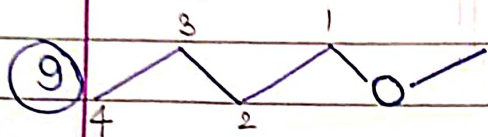
Eg/

Chain Isomers — (1; 5, 4, 6, 7, 8)

Post. Isomers — (1 ; 2, 3)

Metamers — (9, 13)

☆ Post Isomers — (9, 11) ; (10, 12)

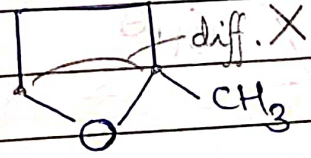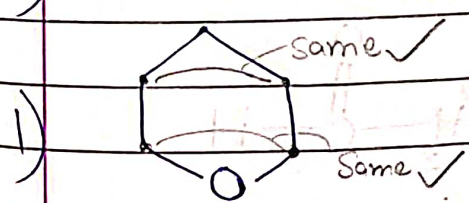Q) Write all possible structral isomers of alkanamide with mol. formula

$C_5H_{11}NO$

(18)

Q) find type of isomers

1)
   same ✓
   Same ✓
   diff. X
   CH₃

   M.I.,
   C.I.

2)

   f.I.

3)

   M.I.,
   P.I.
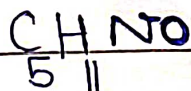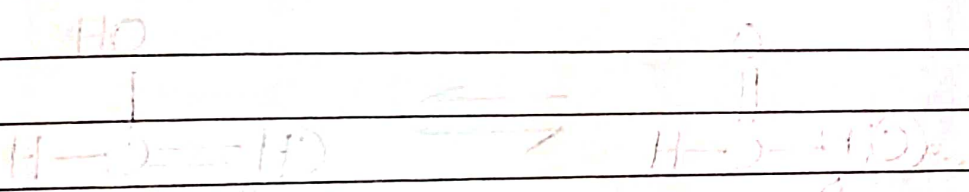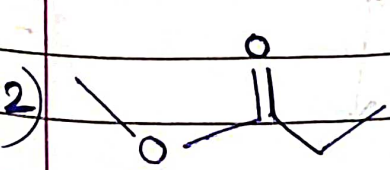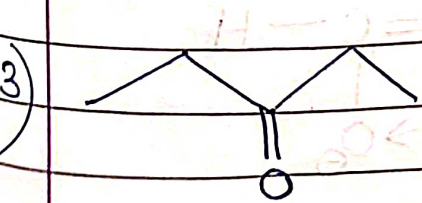
4) [structure: CH₃CH₂CH(CH₃)—NH— with positions 3,2,1]   [structure: (CH₃)₂CH—NH with positions 1,2,3]   P. I.
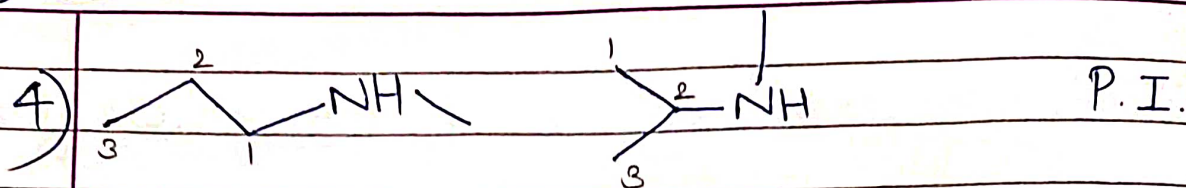
5) Tautomers —

The isomerism in which 2 isomers change into one another with great ease s.t. they exist together in dynamic eq.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \rightleftharpoons CH_2=\overset{\overset{\displaystyle OH}{|}}{C}-H$$

α C atom

Aldo/Keto   enol
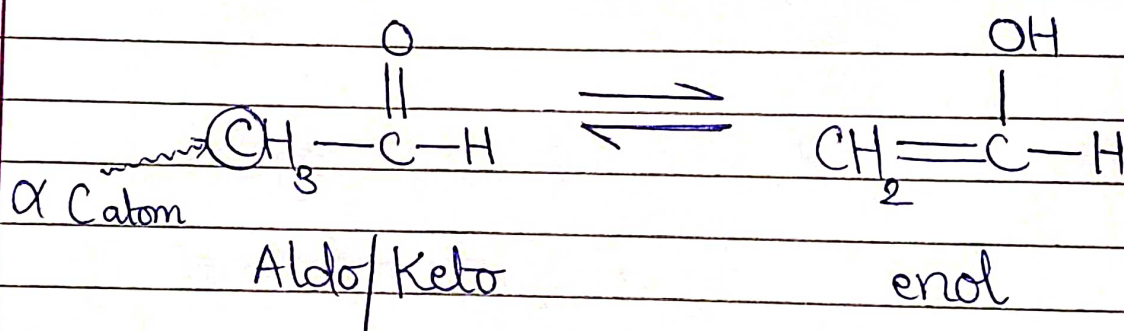
Mechanism (in Basic Medium) —
Reason :

$$\underset{acidic\ H}{CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H} \quad \xrightarrow{\ OH^{\ominus}\ } \quad \overset{\ominus}{CH_2}-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

$$\underset{OH}{CH_2=\overset{|}{C}-H} \rightleftharpoons \quad H-\overset{\displaystyle O}{}-\textcircled{H} \quad CH_2=\overset{|}{C}-H \longrightarrow O^{\ominus}$$
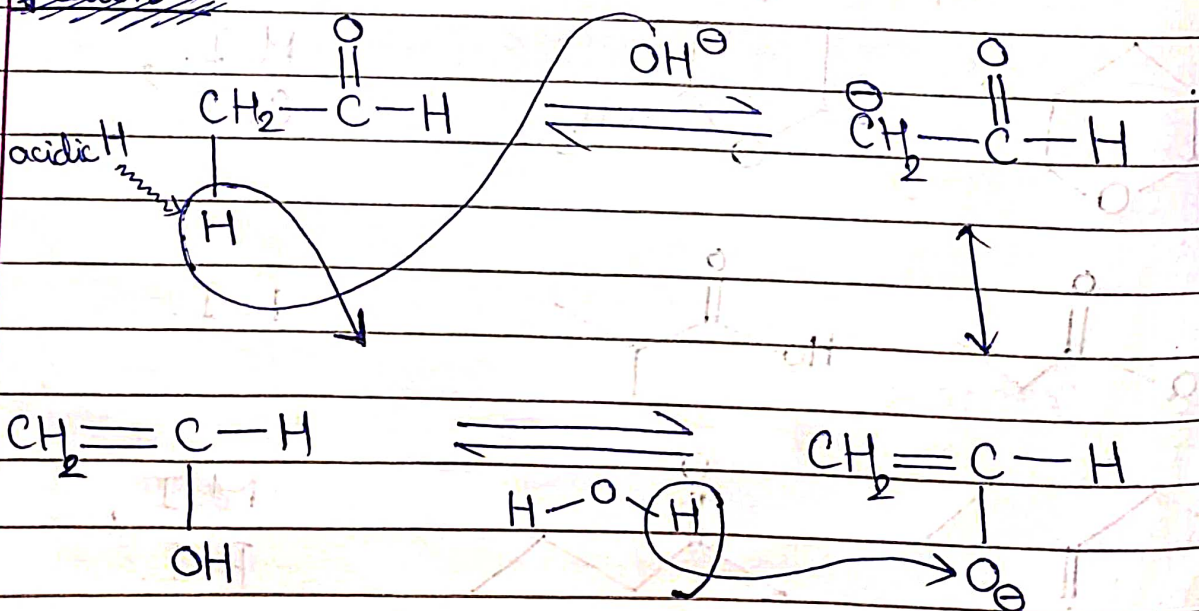
i) Tautomers are NOT resonance structures.

2) for tautomerism, molecule should have (sp³) hyb^n α C atom with (≥1) H atom.

3) Tautomers exist in Dynamic Eq.

Types —

1) Keto - enol form —

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

Keto   enol

2) Imine - enamine form —

$$R - CH_2 - CH = NH \quad \rightleftharpoons \quad R - CH = CN - NH_2$$

Imine   enamine

3) <u>Nitro – aci form</u> –

$$R-CH_2-\overset{\oplus}{N}\overset{\nearrow O}{\underset{\searrow O^{\ominus}}{}} \;\rightleftharpoons\; R-CH=\overset{\oplus}{N}\overset{\nearrow OH}{\underset{\searrow O^{\ominus}}{}}$$
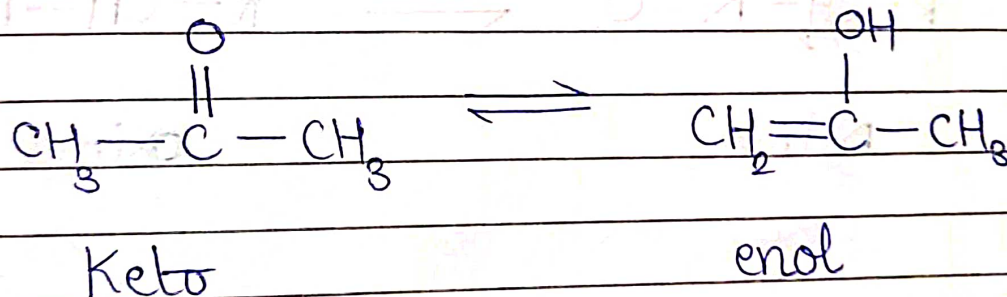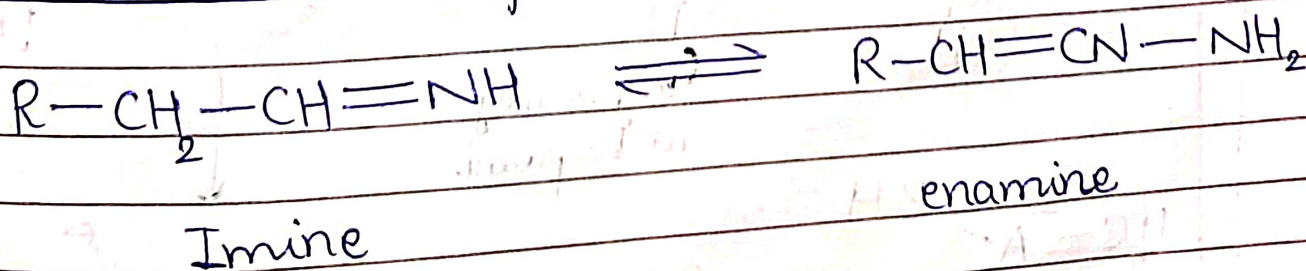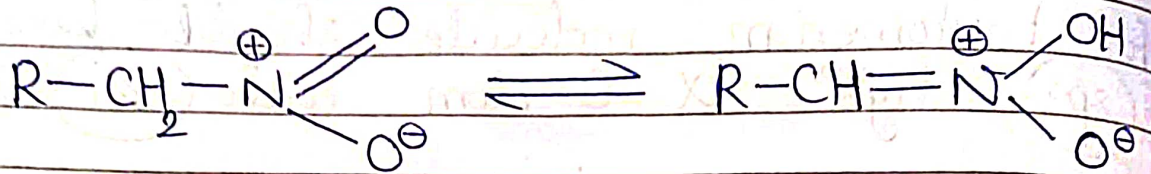
Nitro   aci

4) <u>Nitroso – oxime form</u> –

$$R-CH_2-N=O \;\rightleftharpoons\; R-CH=N-OH$$
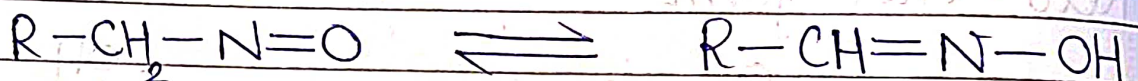
Nitroso   oxime

☆ In general,

$$H_2C-A\overset{\nearrow B}{\underset{\searrow D}{=}} \longrightarrow H_2\overset{\ominus}{C}-A\overset{\nearrow B}{\underset{\searrow D}{=}}$$

| $\underset{|}{\overset{|}{H}}$ (may or may not be present

$$H_2C=A\overset{\nearrow BH}{\underset{\searrow D}{}} \longleftarrow HC_2=A\overset{\nearrow B^{\ominus}}{\underset{\searrow D}{}}$$
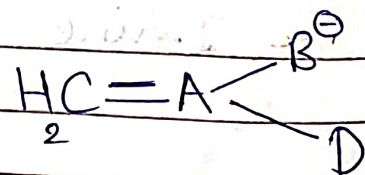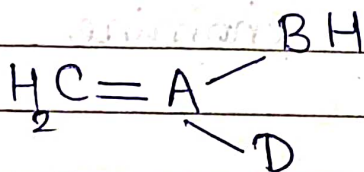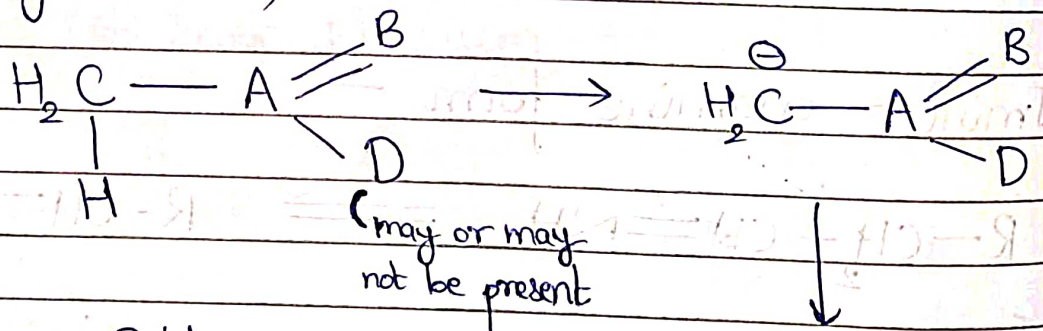
Do ~~this~~ full resonance as there may
be <u>extended</u> <u>conjugation</u>.

Q) In which of the following cases ∃ tautomerism

1)

✓ ✓ ✗

2)

✗ ✓ ✗

3)

✓ ✗

4) ★

✗

5)

$CCl_3 - CHO$ ✗

⭐ 6)
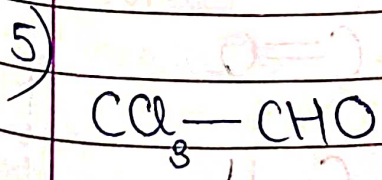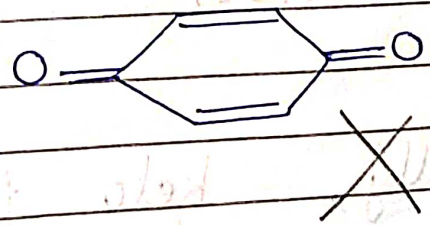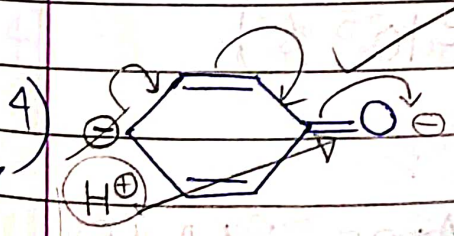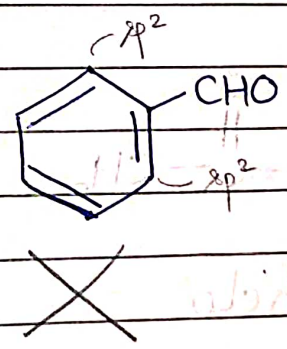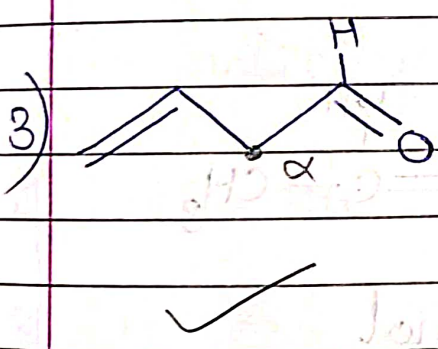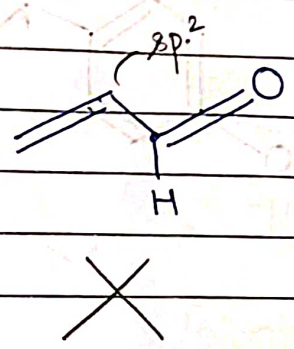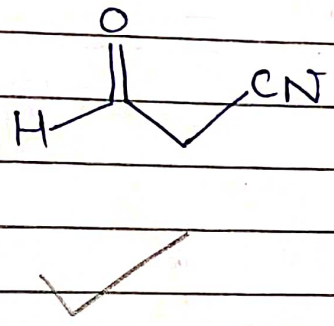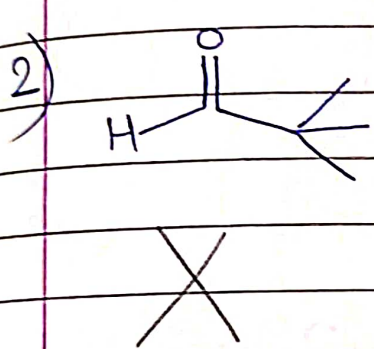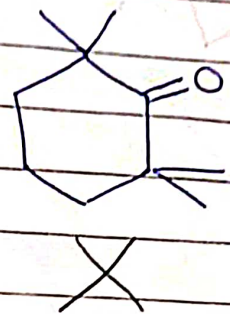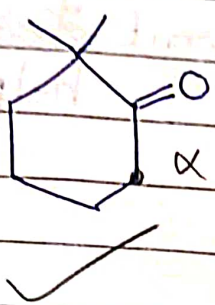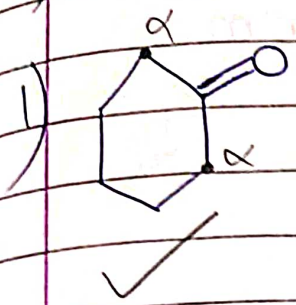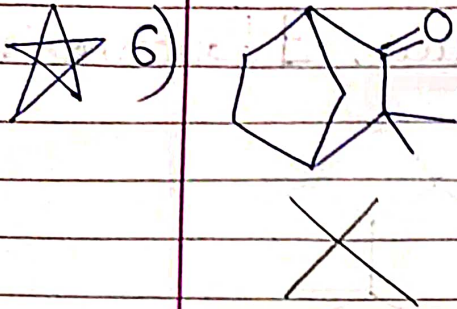
Breadt's Rule
⇒ Bridge Head C ~~# &~~ Carbon
won't ~~show~~ tautomerism
help in

✗

⭐ 7)

Generally, keto form is MORE STABLE than enol form.

⭐

$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 \rightleftharpoons CH_2 = \overset{\overset{OH}{|}}{C} - CH_3$$
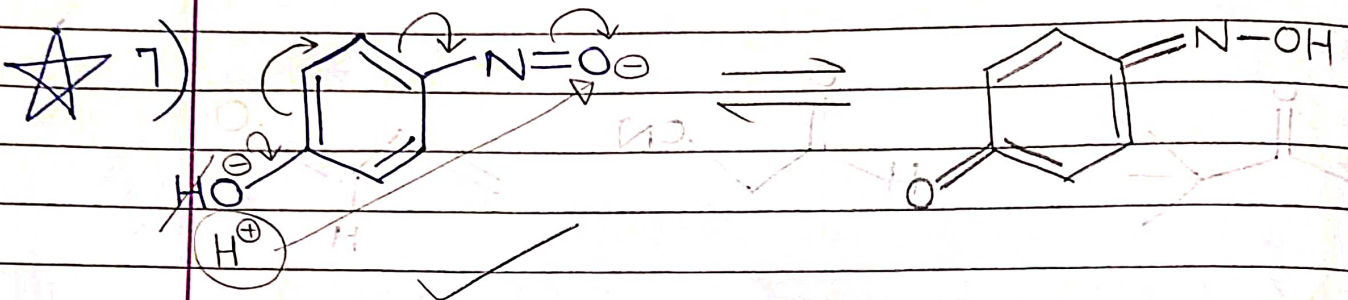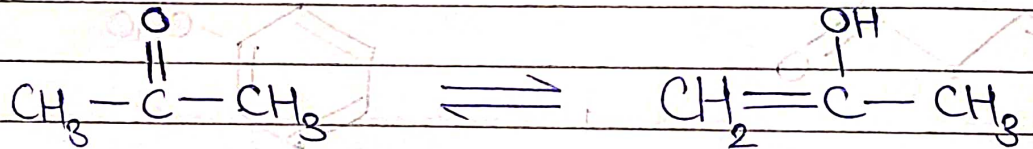
Keto   enol

Conc : $(> 99.99\%)$ $(\approx 10^{-5}\%)$

Generally, keto form MORE STABLE
than enol form.

Reason : Stength — $C=C < C=O$

Strength — $O-H < C-H$

☆ If enol form **aromatic** ⇒ It more stable
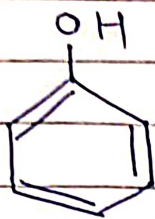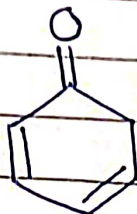
enol   Keto

Conc.: (>99.9 %)

<u>factors affecting 'enol' content</u>   { Priority Order
1 > 2 > 3 > 4 }

1) Aromaticity (↑ conc.)

3) Intramolecular H bond (↑ conc.)

2) Extended π conj. (↑ conc.)

4) Side Resonance (↓ conc.)

1) Aromaticity —

Q) Which of these keto form will result in aromatic ends ?

1) X

2) ✓

3) ✓

4) ✓

5) X

N.A.

6) X

A.A.

7)
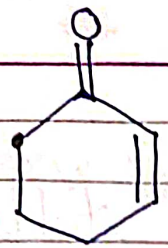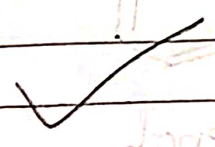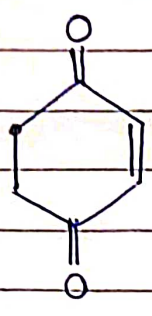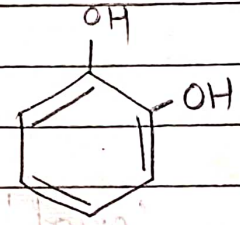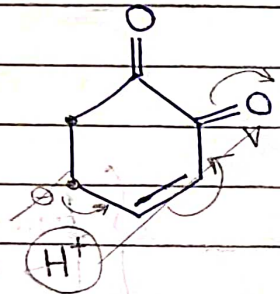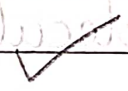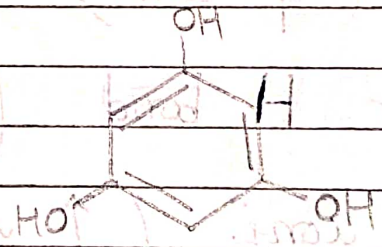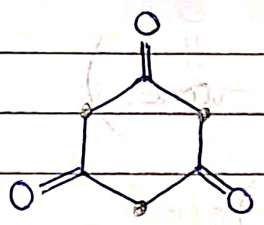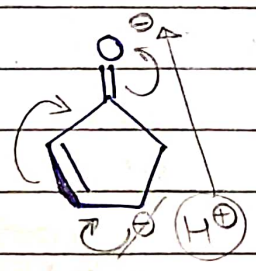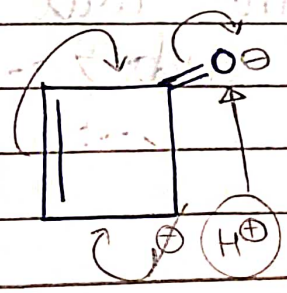
N.A.

---
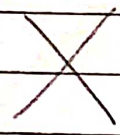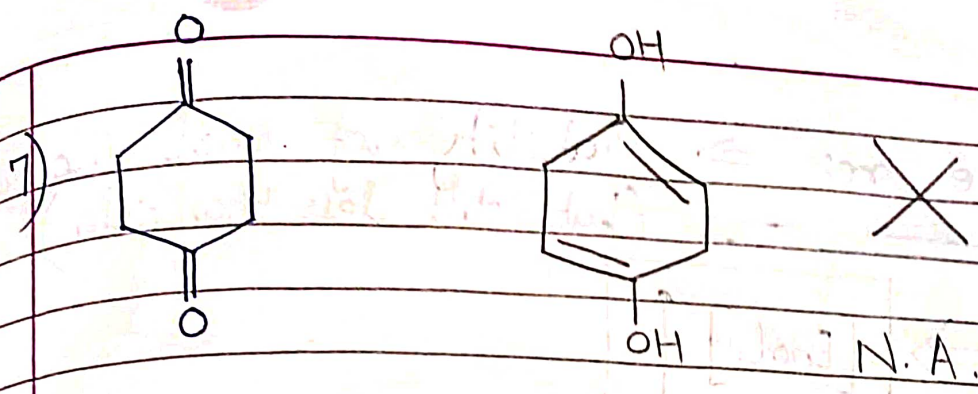
2) Intramolecular H bonding —
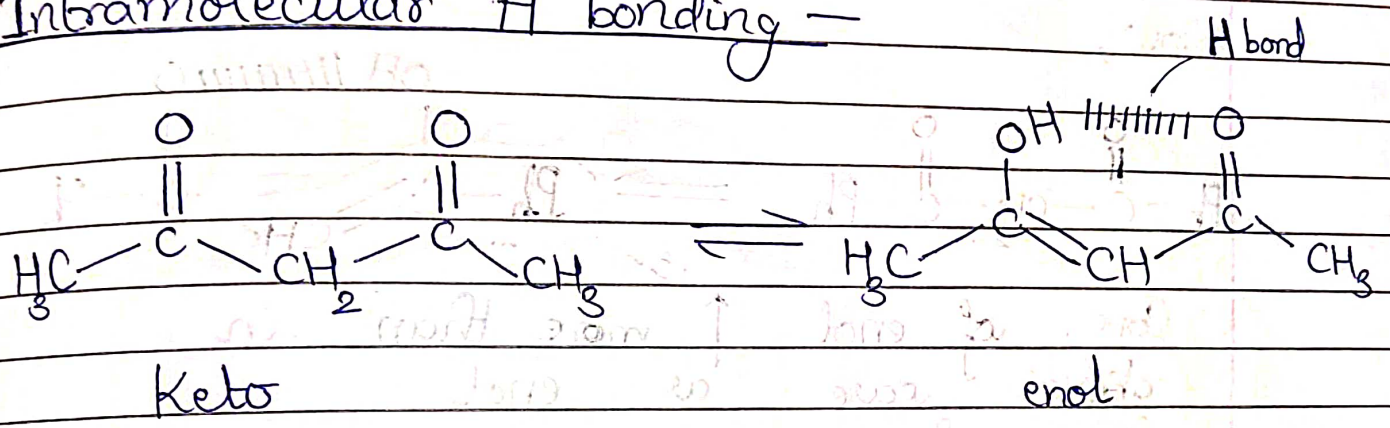
Keto

enol

Since, intra H-bonding ⇒ Stability of enol inc.
(but still less than keto)

⟶ [Enol] ↑

---
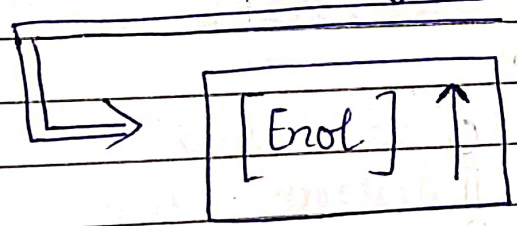
3) Extended π conj.
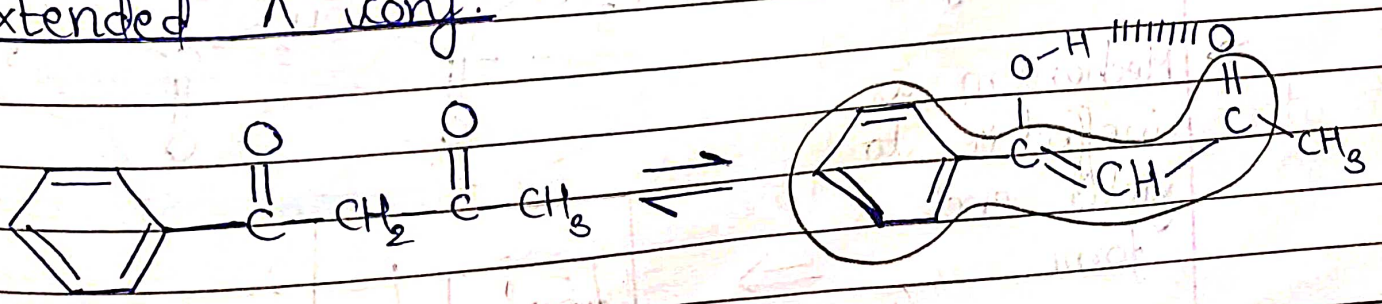
Since, more res. $\Rightarrow$ Stability of enol inc.
(but still less than keto)

$\longrightarrow$ [Enol.] $\uparrow$

Now,

$$Ph-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-Ph \rightleftharpoons Ph-\overset{OH}{\overset{|}{C}}\diagdown_{CH}\diagup\overset{O}{\overset{||}{C}}-Ph$$
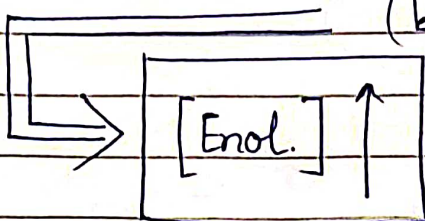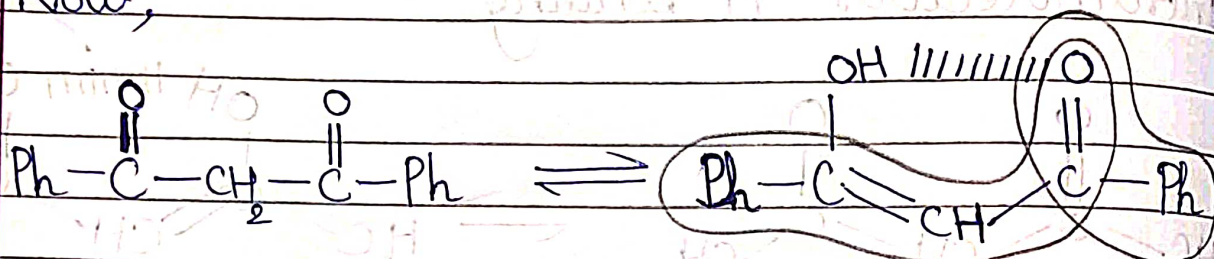
Conc. of enol $\uparrow$ more than in
above case as enol
form has more res.

4) Side Resonance —

$$CH_3O-\overset{O}{\overset{||}{C}}\diagdown_{CH_2}-\overset{O}{\overset{||}{C}}\diagdown_{OCH_3}$$
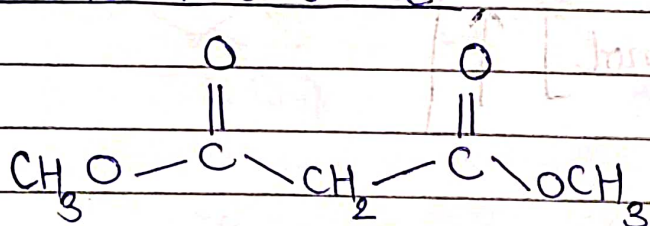
during
Mechanism

Cross conj.

$$H_3CO\diagdown\overset{}{\underset{\overset{||}{O}}{C}}-\overset{\ominus}{CH_2}\diagdown\overset{}{\underset{\overset{||}{O}}{C}}\diagup^{OCH_3}$$
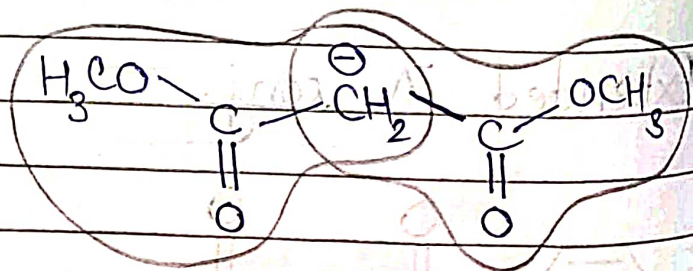
$\Rightarrow$ Mechanism is
ineffective to
yield enol
form. $\Rightarrow$ [Enol.] $\downarrow$
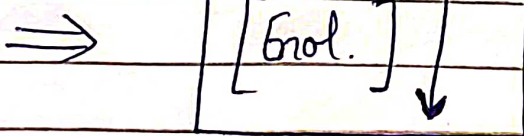
Q) Compare enol content.
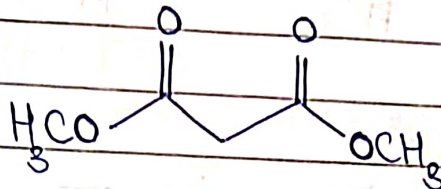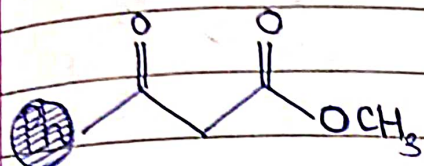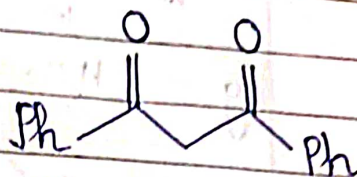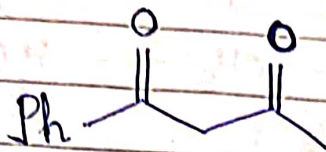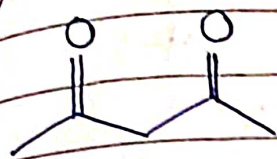
A) $\underline{c > b} > a > \underline{d > e}$

Ext^n π conj.   Side Res.

Geometrical Isomers

It arises due to diff in arrangement of grps./atoms present at restricted rotation / system.

• Cond^{n}s —

1) Restriction in Rotation.

2) Restricted ~~act~~ atoms must have 2 diff. substitu-ents

3) Diff. aerial dist. $(l_1 \neq l_2)$

Eg —
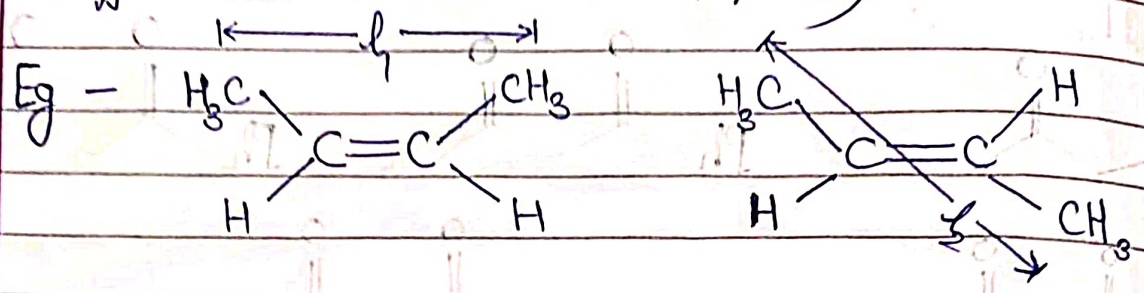
- G.I. arise in —

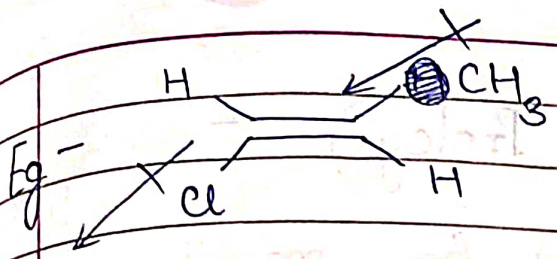1) Double bonded system

2) Substituted cycloalkane

3) Cycloalkene.

Double Bonded System —

☆ Q related to μ, M.P., B.P., stability

| $B.P. \propto \mu$ | $M.P. \propto$ stability |

Generally, | Stability : Trans > Cis |

for | Alkenes | as less steanic crowding in Trans. form

Eg –
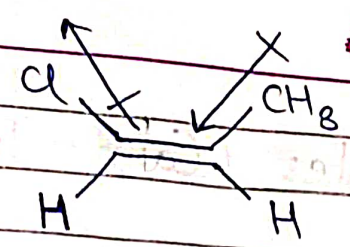
$\mu : 1 > 2 \Rightarrow$ BP : 1 > 2

Steric : 1 < 2   MP : 1 > 2
Crowd

Eg –
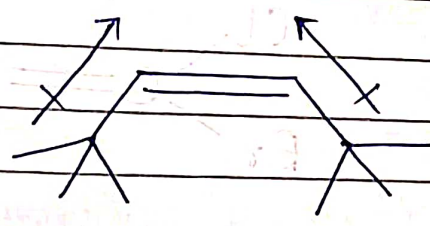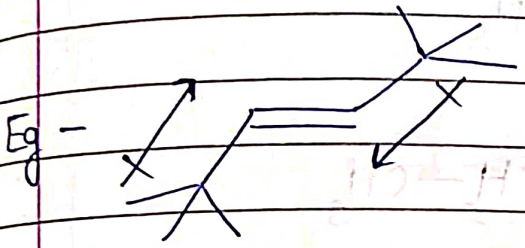
$\mu : 2 > 1 \Rightarrow$ BP : 2 > 1

Steric . 2 > 1 $\Rightarrow$ MP : 1 > 2
Crowd

opp.
same

E, Z system of Nomenclature

Z
isomer –
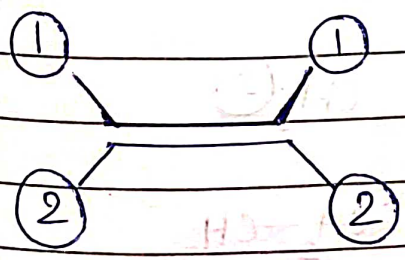
E
isomer –
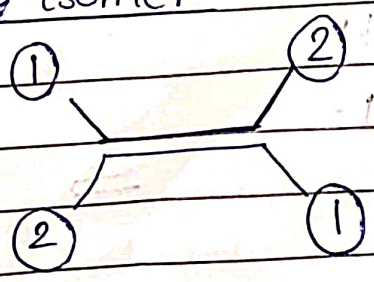
① – Top priority grp.   ② – Bottom priority grp.

CIP Rules (Cahn - Ingold Prelog) -

Two grps. are compared for priority on basis of their levelwise connectivity to (sp^2) C atom.

Eg -

$$Cl, Br \overset{C}{=} C, CH_3, CH_2-CH_3$$

first C -   Level 1

$\left(\begin{array}{c} Cl \\ Br \end{array}\right)$ $Br > Cl$
   ①   ②

Second C -   Level 1   Level 2   Level 3

Lvl 1

Lvl 2

| Same | $\left(\begin{array}{c} C \\ C \end{array}\right)$ | $\left(\begin{array}{ccc} H & H & H \\ C & H & H \end{array}\right)$ | H H H |

$C > H \Rightarrow$ $-CH_2 CH_3$ CH_3
   ①   ②

Lvl 1

Lvl 3

Lvl 2

$\Rightarrow$

② Cl, Br ① $\overset{C}{=} C$, CH_3 ②, CH_2-CH_3 ①

(Z)

Rule 1 —

1) Lvl wise priority : L1, L2, L3, ...

2) Within lvl., arrange in dec. mol. mass.

3) Comparison b/w 2 CIP set of 2 diff. grps is done by identifying <u>heavier element</u> at <u>first pt. of diff.</u>

4) Grp. with heavier element atom will have higher priority ⇒ Grp ①.

Eg -

E   Z

① C, CC(H), ...
② C, C(H)H, ...

② C, CC(H), ...
① C, C(C)C, ...
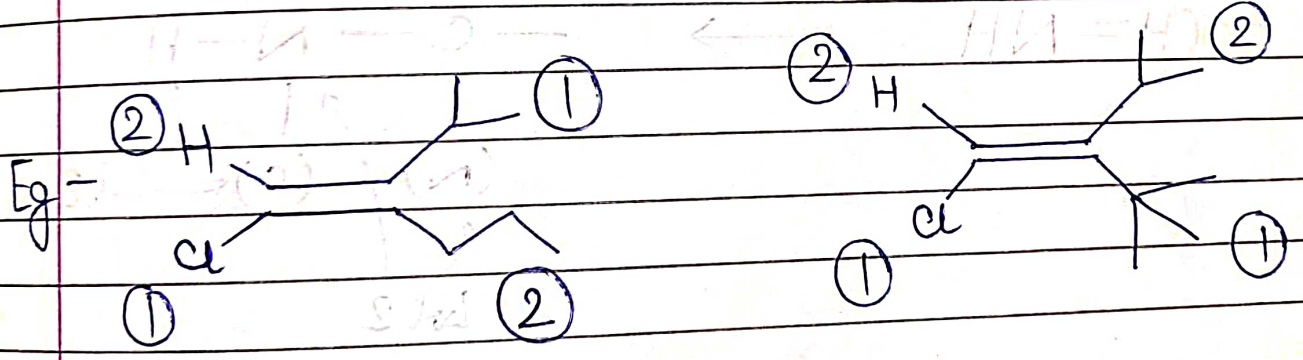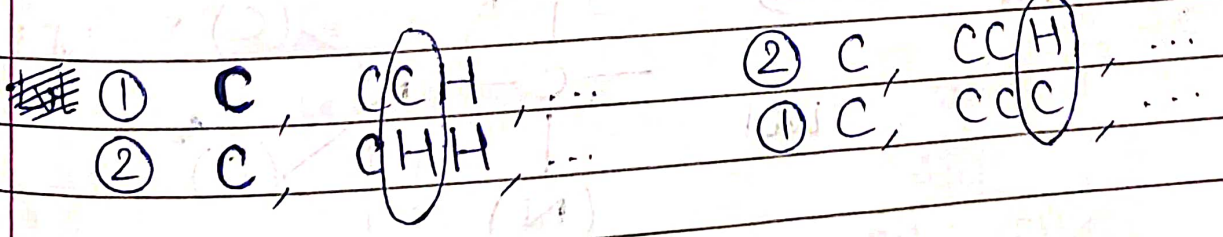
Rule 2 —

In case of unsaturated grps. or grps. containing π bond, slight modification is r

Eg —

② H
① Cl
C = C
CH = NH
C ≡ N
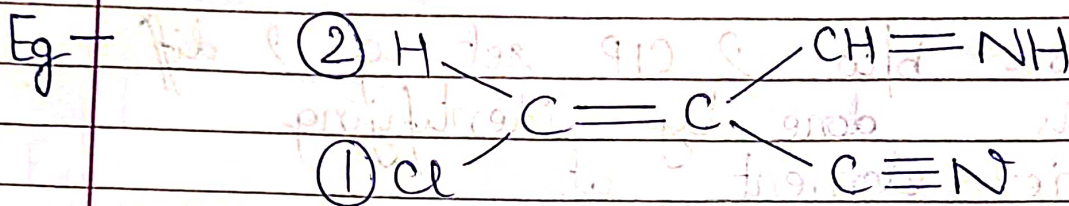
Remove 1 π bond (in substituent), add 2 pseudo atoms.

— CH = NH $\longrightarrow$ — C — N — H

(N) ← Lvl.2

(C) ← Lvl.3

Lvl.1

— C ≡ N $\longrightarrow$

(N)
— C — N
(N)
(C) ← Lvl 3
(C)
Lvl 1
← Lvl 2
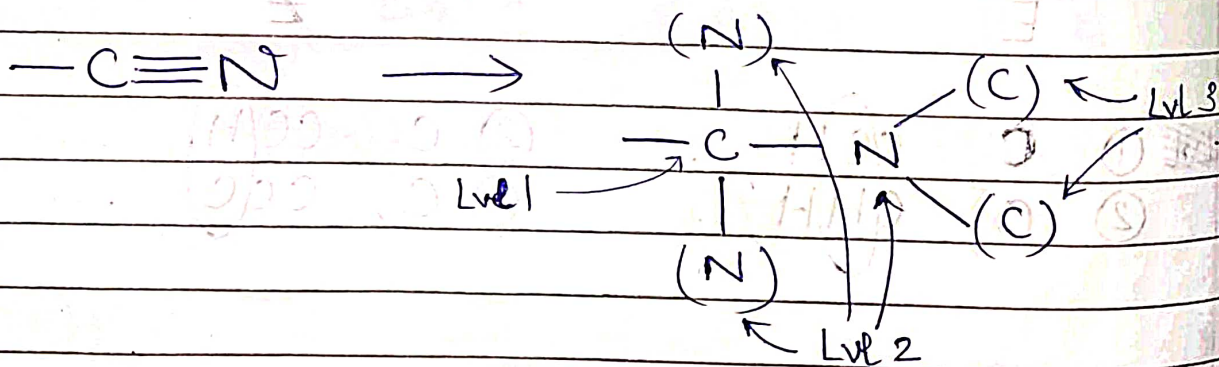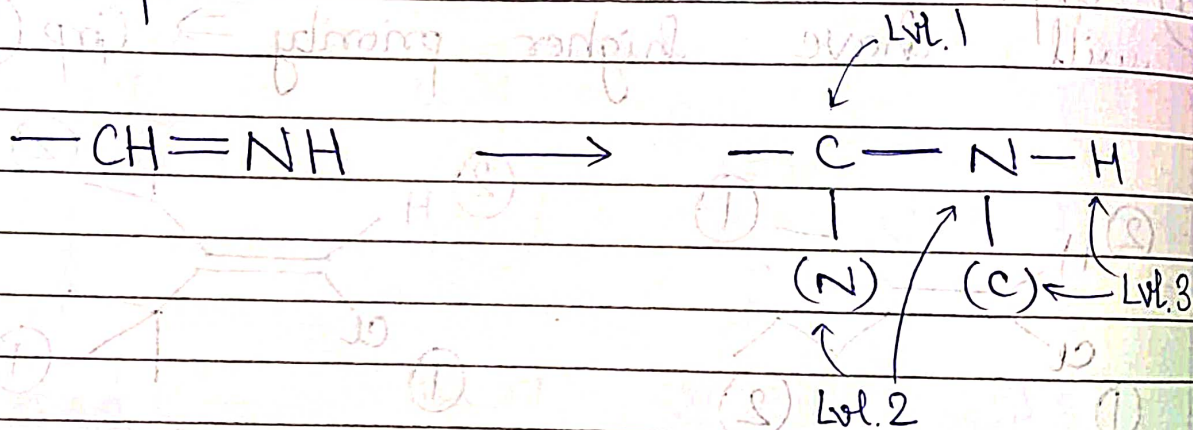
Now compare as earlier.

Q) Identify E, Z isomers —

1)
② H   COOH ②
① Cl   COCl ①

$$O-(C)$$
$$-C-O-H$$
$$(O)$$

C, /OOO, ...
C, /ClOO, ...

$$(O)^-$$
$$-C-Cl$$
$$O=(C)$$
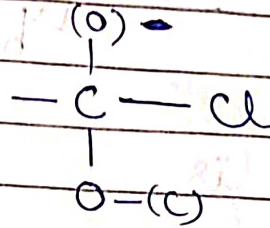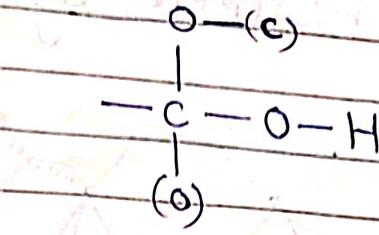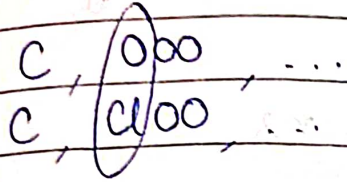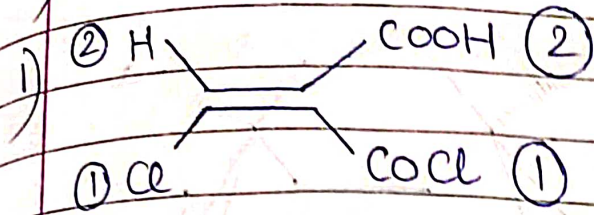
⇒ [Z]

(for cyclic substituents)

✦2) ② H
① Cl

(triangle with 1, 2, 3)

(cyclic ring with 1, 2, 3, 4, 5)

(triangle with 2, 3)

(C) ← (‖ bond wala)

A) (C₅) H H   H H
   | | | | | |
—C₁—C₂—C₃—C₄—C₅—C₁—H
   | | | | | | ↖ (add C₁)
   H H H H H (C₂)

(C₃) H H
      | | |
—C₁—C₂—C₃—C₁—H
   | | | | ↑ (add C)
   H H H (C₂)

(C) ← (‖ bond wala)

Now compare,   C   CCH   CHH, CHH, CHH
               C' CCH, CHH, CHH,
                                CCH
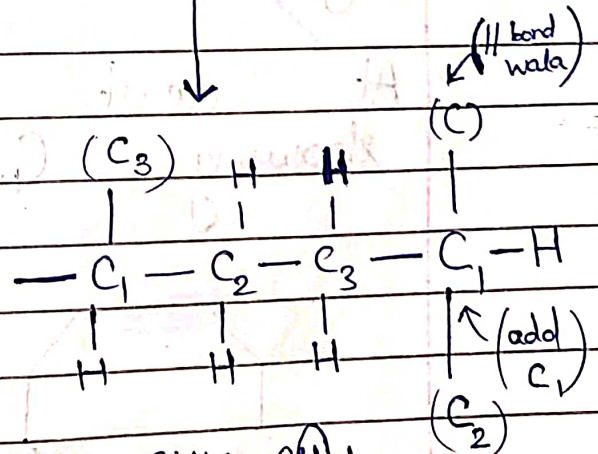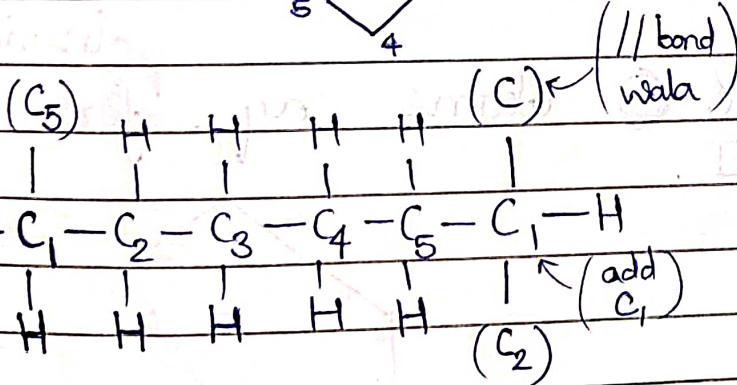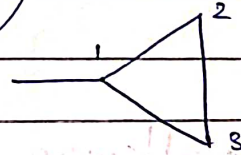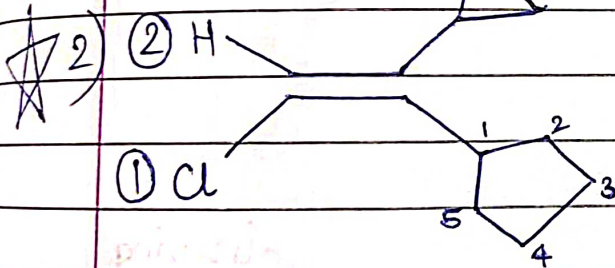
⇒ (triangle) ①   (pentagon) ② ⇒ form [E]
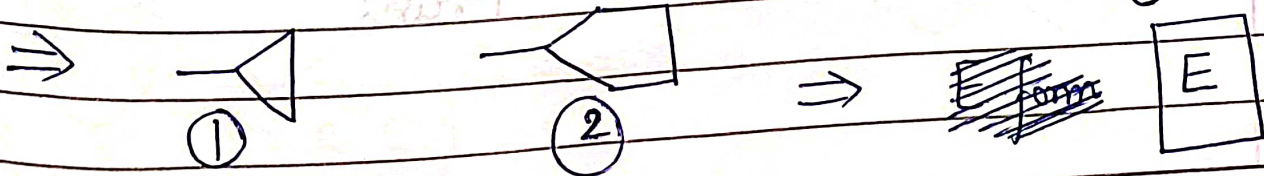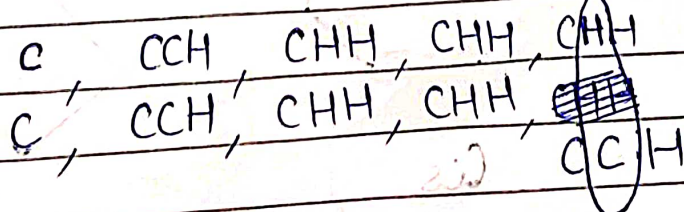
Substituted Cycloalkane
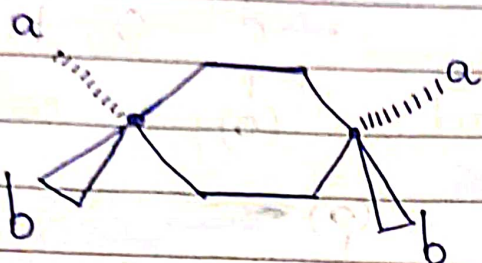
Cis
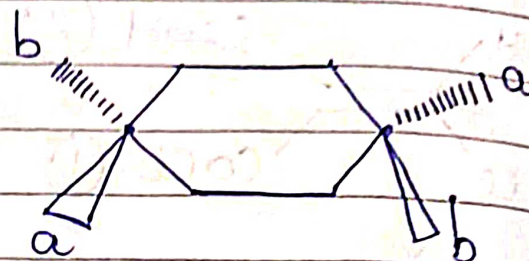
Trans

Cond^n s —

1) 2 sp^3 atom with 2 diff. substituents.

Cycloalkene

At least 8 atoms req. for in ring
showing G.I.
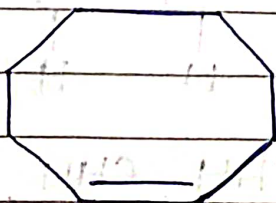
Cis
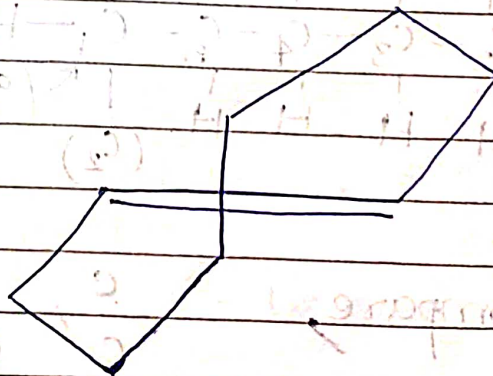
Trans

★ Cis MORE Stable : $8 \leqslant C \leqslant 12$

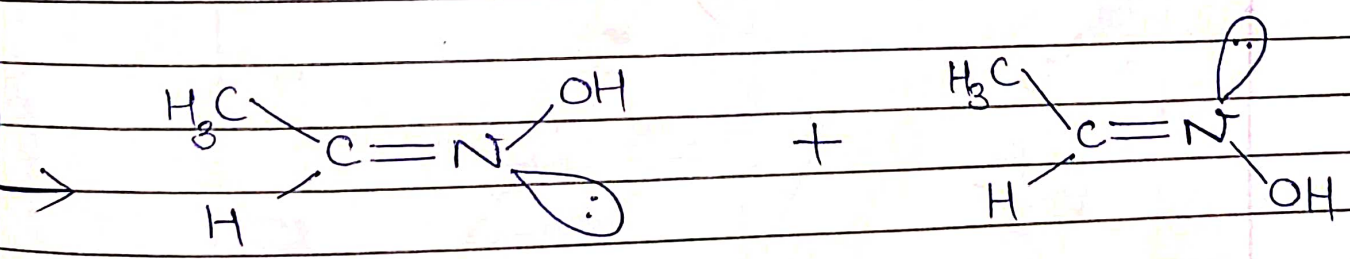Trans MORE Stable : $C \geqslant 13$

Q) Which will show G.I. ?

1)

✗

2)

✗

3)

(D.S.)
✓

4)

✗

5)

✗

6)

✗

7)

✓
(S. C.)

8)

✓
(C)

9)

✗

10)

✗

11)

✓

(D.S.)

12)

✗

13)

✓

(D.S.)

14)

✓ (D.S.)

15)

16)

✗

17) HO—N̈——⬡——N—OH

✓

18)

Oximes

$$a \,\,\, \backslash C = N \nearrow OH \\ b \,\, \diagup$$

Nomenclature :-

(C1)

$$H_3C \\ \backslash C = O \,\,+\,\, H_2N - OH \\ H \diagup$$
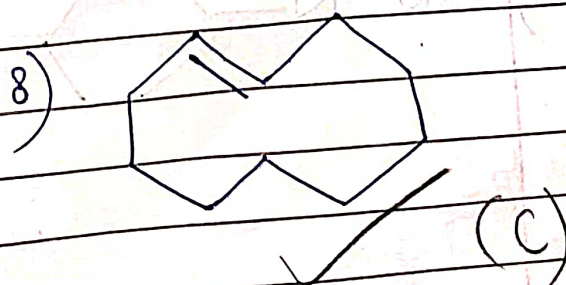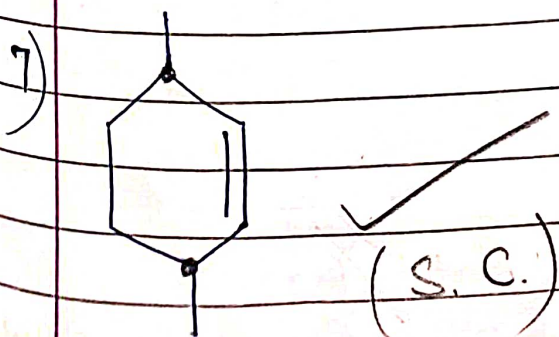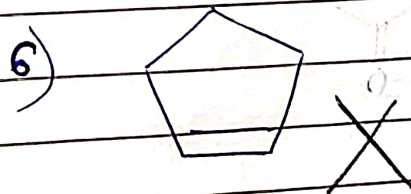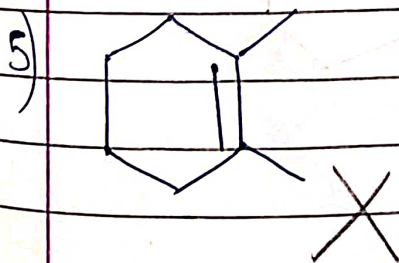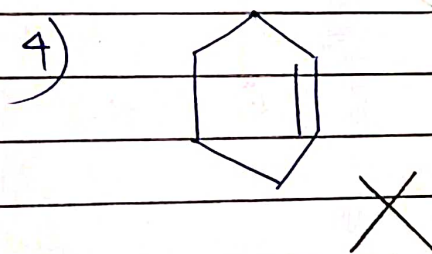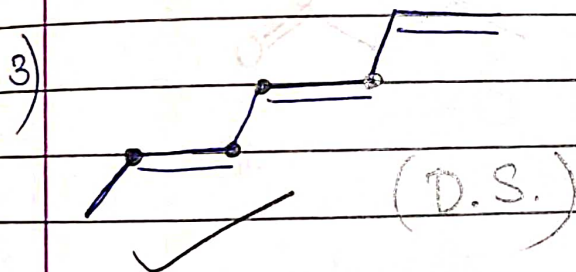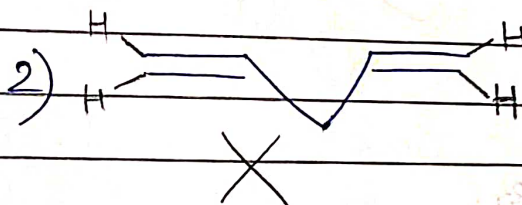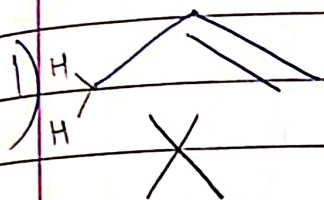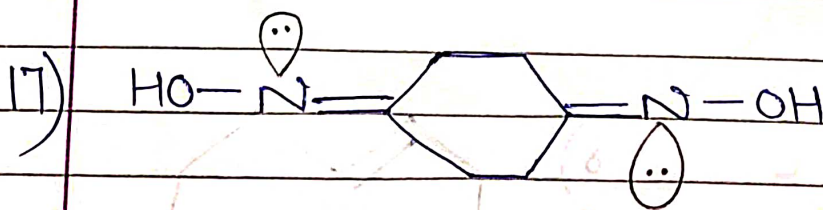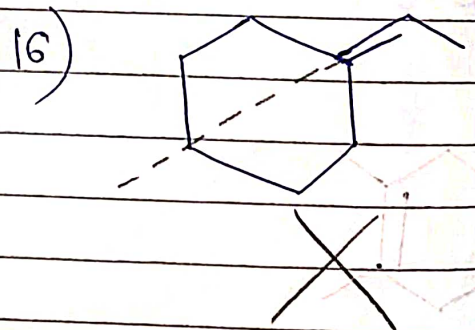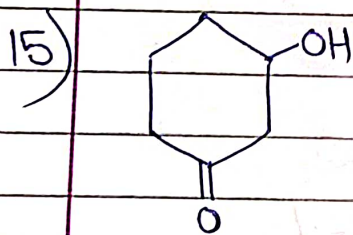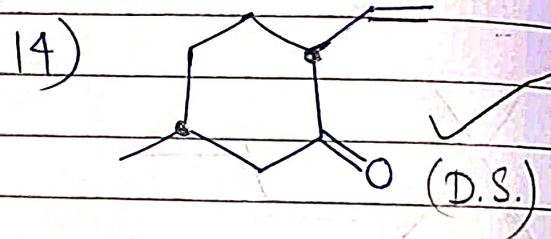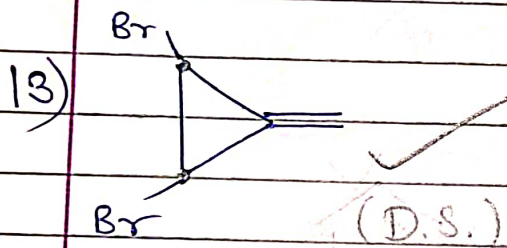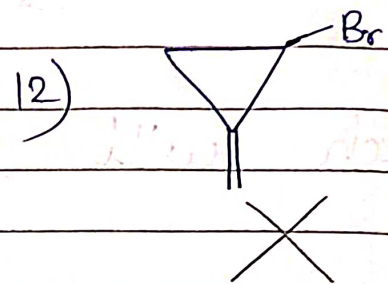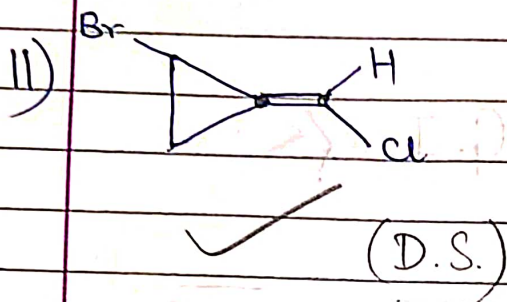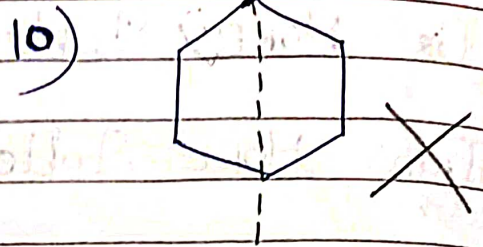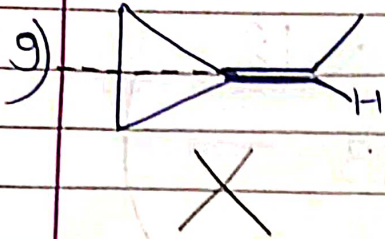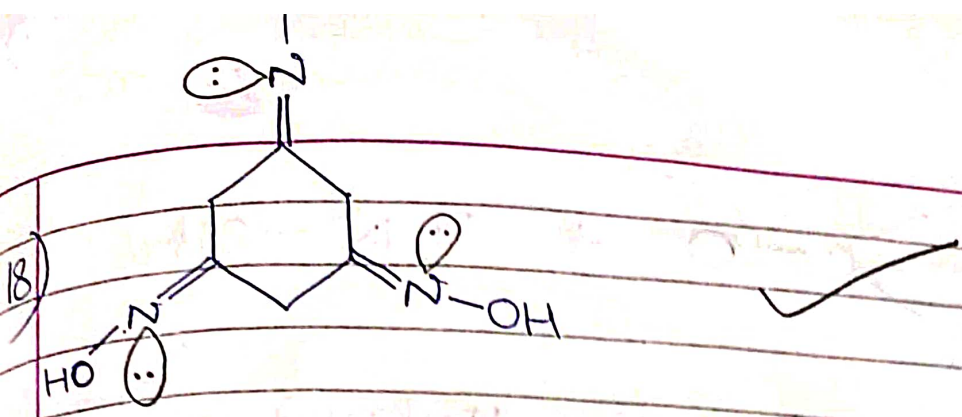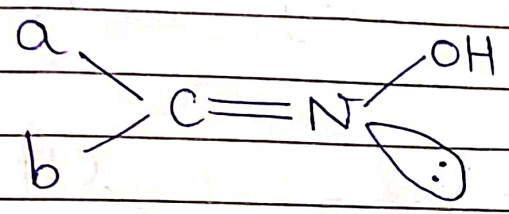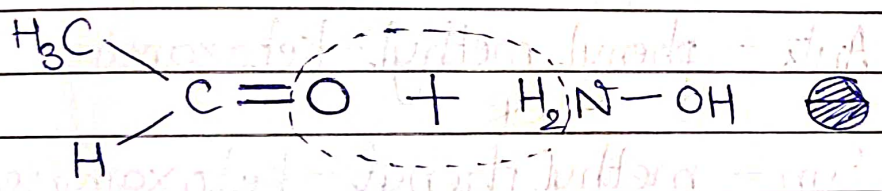
Aldehyde   Hydroxylamine

$$\xrightarrow{} H_3C \\ \backslash C = N \nearrow OH \\ H \diagup$$
   +
$$H_3C \\ \backslash C = N \\ H \diagup \searrow OH$$

Anti - Aldoxime   Syn - Aldoxime

Anti - H & OH   Syn - H & OH
opp. side   same side

(C2)

$$R_1 \diagdown C = O \quad + \quad H_2N-OH$$
$$R_2 \diagup$$

Ketone   Hydroxylamine

$$R_1 \diagdown C = N \diagup^{OH} \quad + \quad R_2 \diagdown C = N \diagup^{OH}$$
$$R_2 \diagup \qquad\qquad\qquad R_1 \diagup$$

Eg:

$$H_3C \diagdown C = N \diagup^{OH}$$
$$Ph \diagup$$
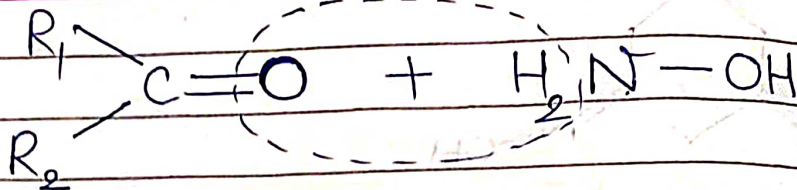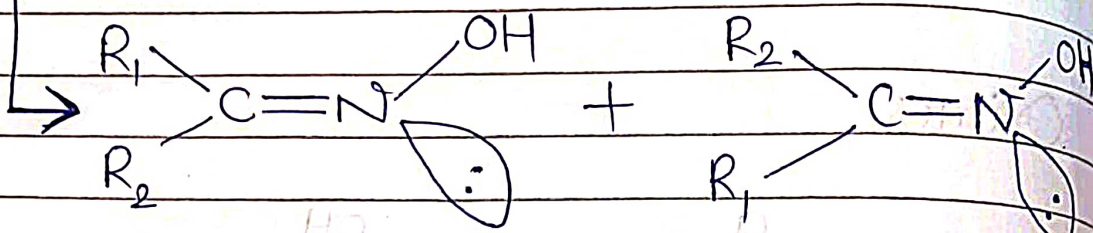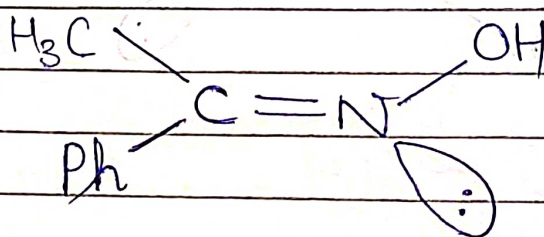
Anti – phenyl methyl–ketoxamine
                OR
Syn – methyl phenyl – ketoxamine

(See cort.   OH)

Cumelene

2 adj double bonds in compound

Eg:

Observe,

$$l_1 = l_2 \implies \underline{NOT \ G.I.!}$$

Eg:

✱ Hence,

G. I.
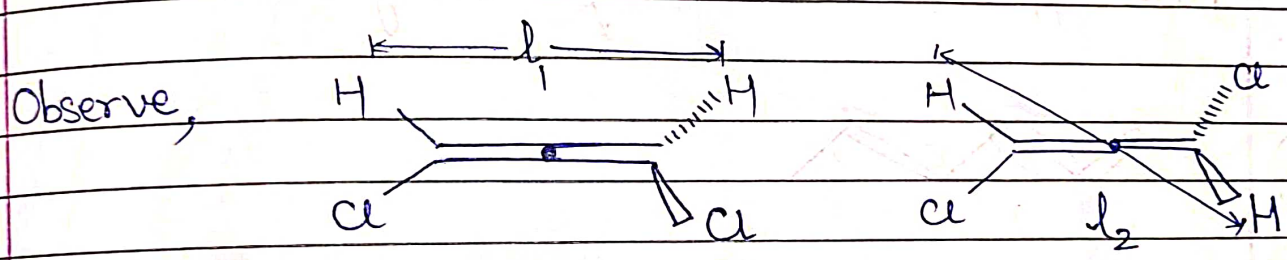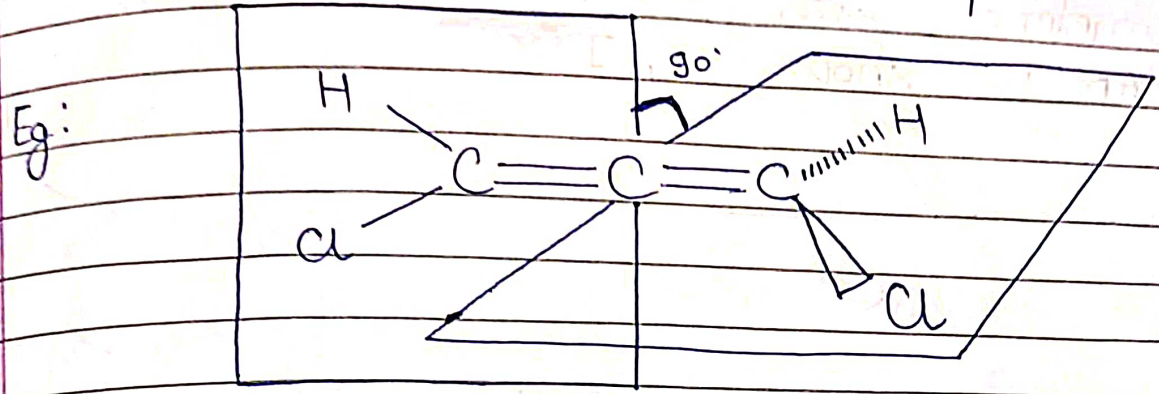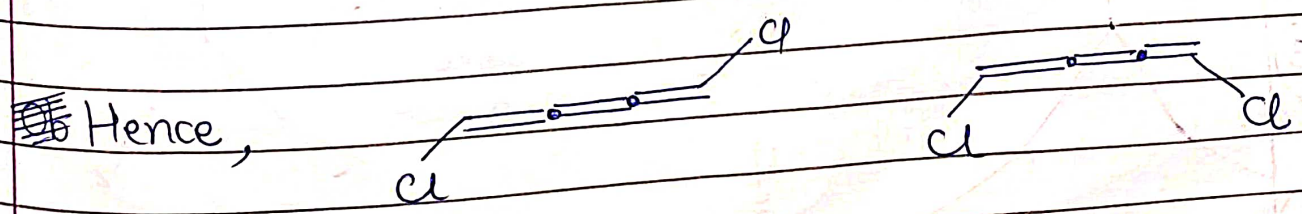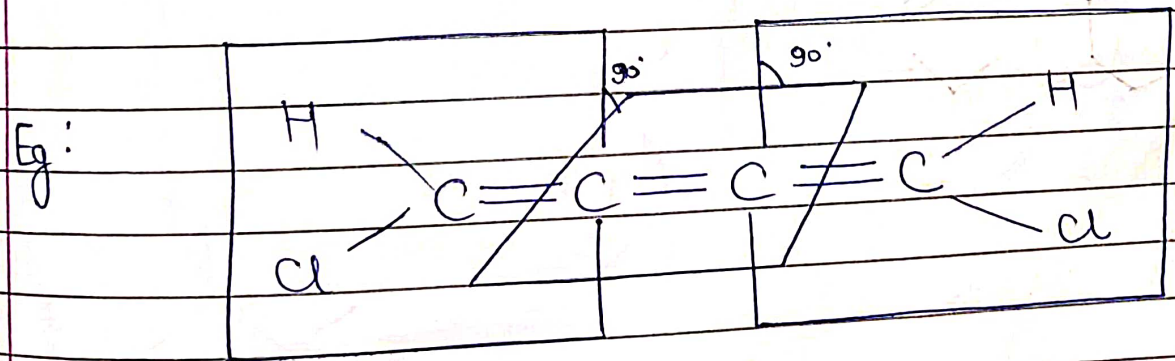
★ Cumelene with **ODD** # π bonds **CAN** show G.I.

Cumelene with **EVEN** # π bonds **CAN'T** show G.I.

Q) find # G.I. in following

1)

$$2 \times 2 = \boxed{4}$$

2)

$$2 \times 2 = \boxed{4}$$

3)

Same as

Same as

②

4)

④

5)

$$2 \times 2 = ④$$

6)

7)
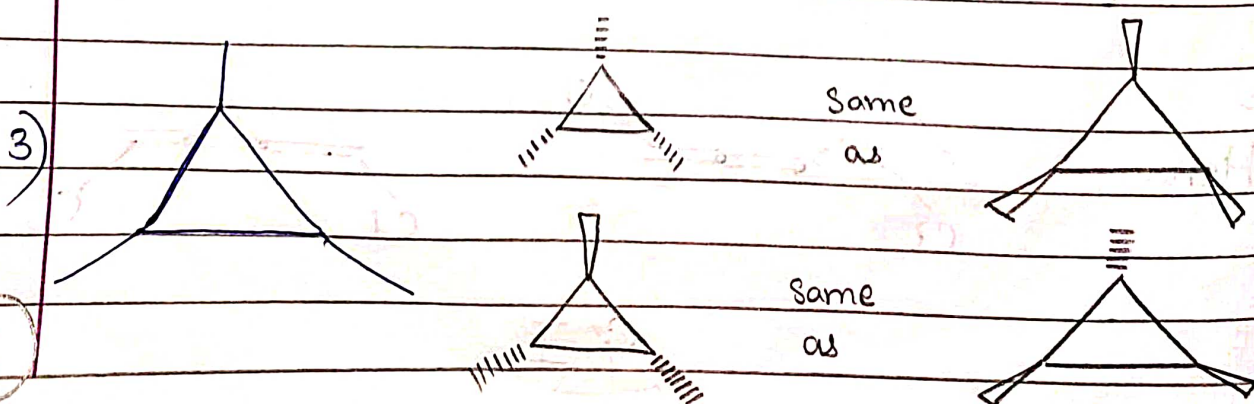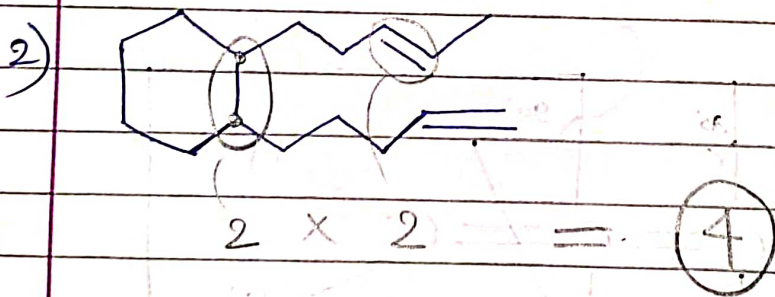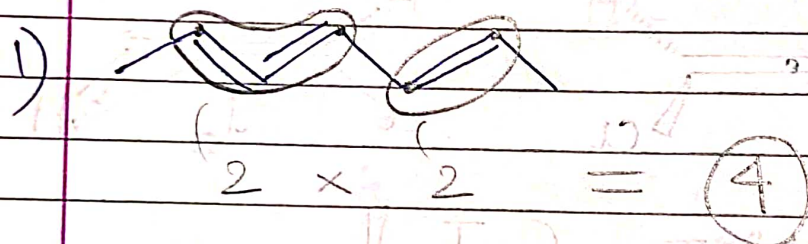
Conformational Isomers

Those isomers which are obtained due to free rotation of atoms or groups around single bond, are called confirmational isomers.

Saw horse Proj. —
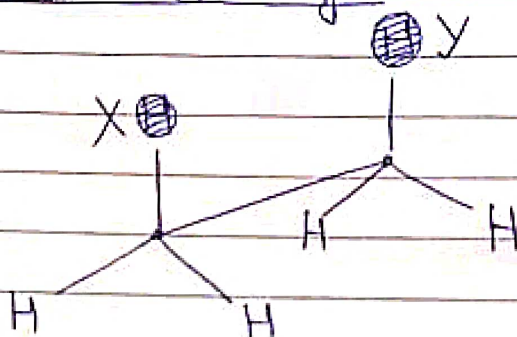
Newmann Proj. —

fully
Eclipsed
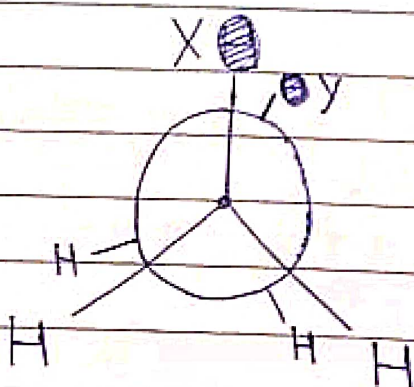
$\theta = 0°$

Gauche
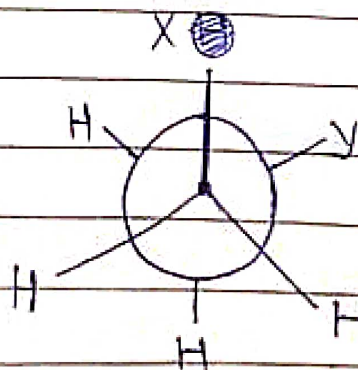
$\theta = 60°$

Partially Eclipsed
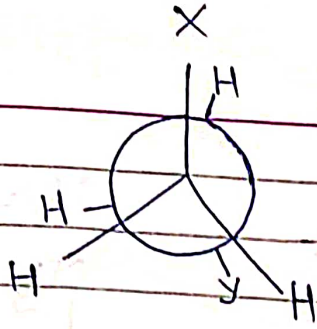
$\theta = 120°$

Anti / Staggered
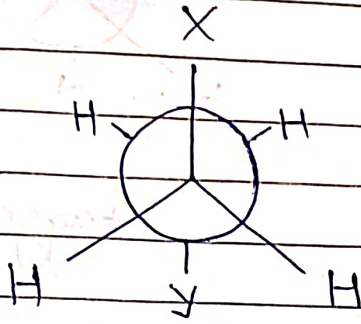
$\theta = 180°$

C-1 :   X = H ,   Y = H
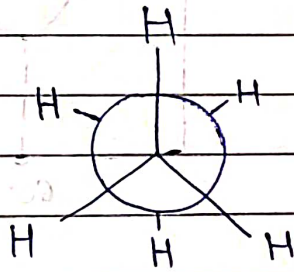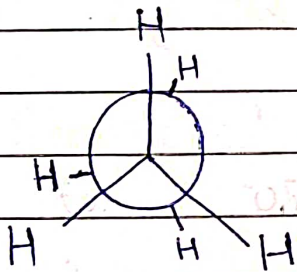
Eclipsed   Staggered

Energy

60°   120°   180° θ

C-2 :   X = CH$_3$ y = H

Eclipsed   Staggered

60°   120°   180°   θ
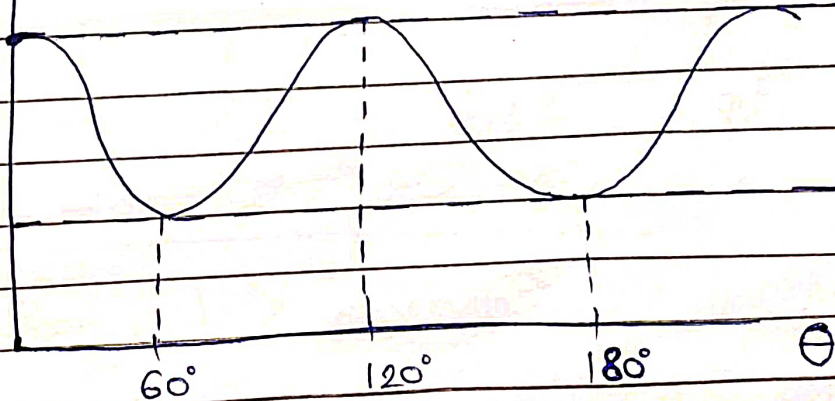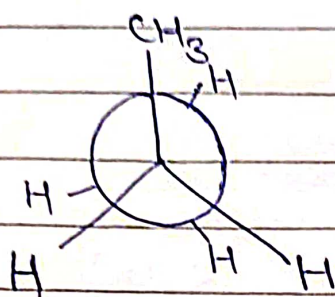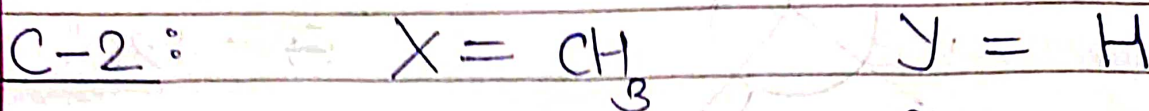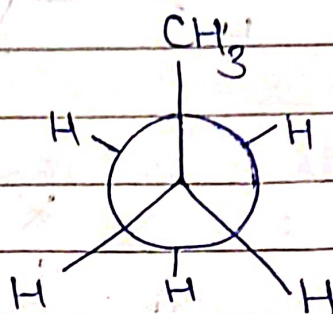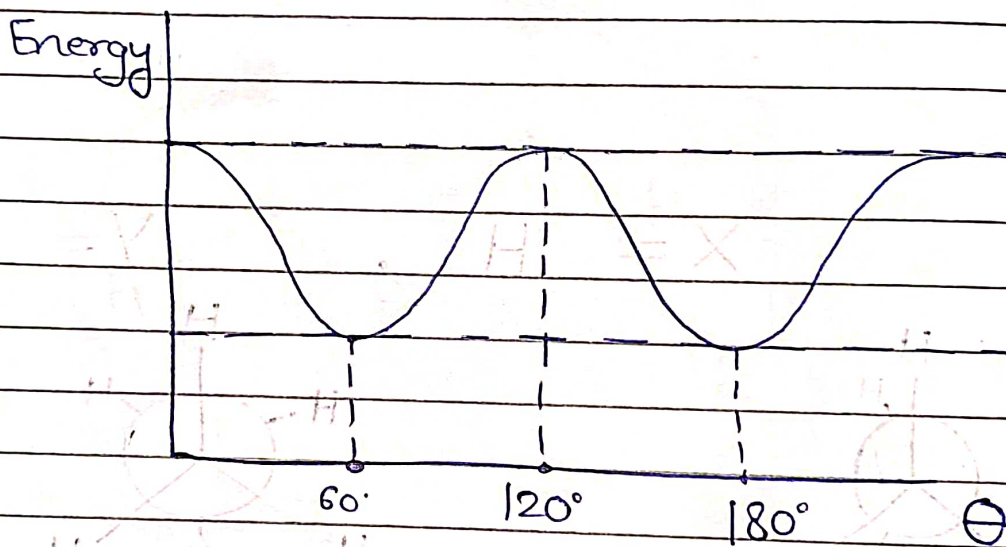
(in terms of ene

This graph is above earlier graph   as
CH$_3$ — H ⟹ Van der Wall   Strain inc.

C-3 :   X = CH₃   Y = CH₃
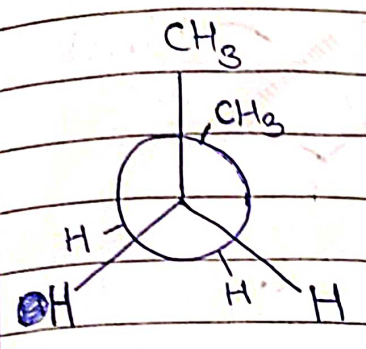
fully Eclipsed   Gauche

Staggered   Partially Eclipsed

Energy

60°   120°   180°   θ
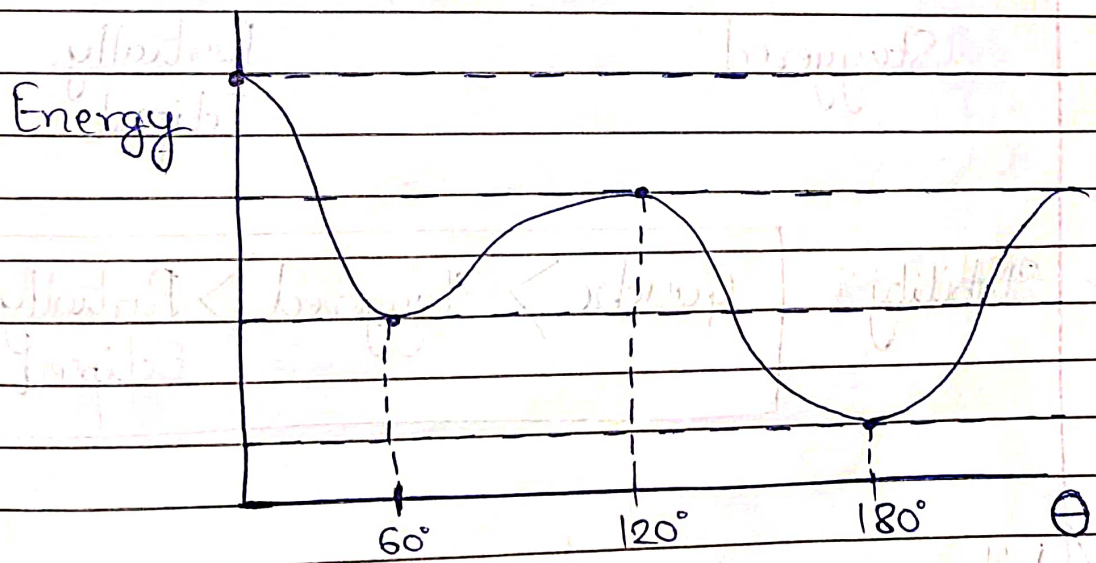
Stability : | Staggered > Gauche > Partially > fully
                               Eclipsed   Eclipsed

☆ C-4 :   X = F   Y = OH
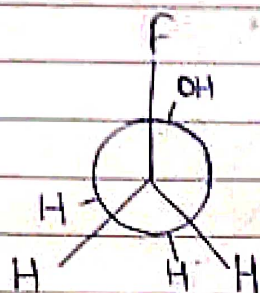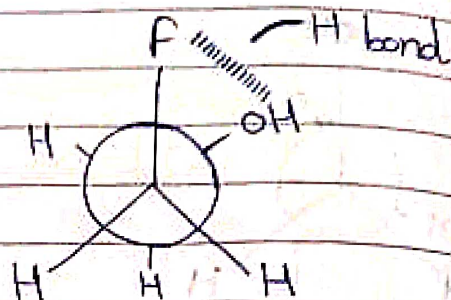
fully Eclipsed   Gauche

(Torsional Strain ⬭)
⇒ No H bond
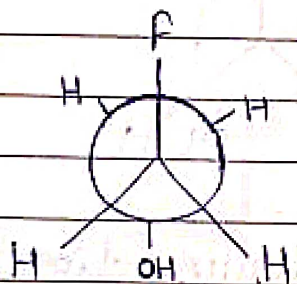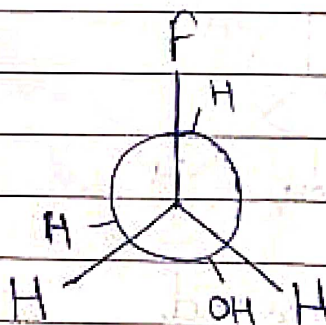
Staggered   Partially
                                 Eclipsed

☆ Stability : | Gauche > Staggered > Partially > Fully |
                                       Eclipsed   Eclipsed

☆ Whenever X = OH & Y = F, NO₂, CHO,
                              COOH, CONH₂, OH, ...

H bond in Gauche
⇒ | Gauche more stable |

Key pts —

1) Energy needed for single bond rot. is available at room temp.

2) Conformers are NOT true isomers as they can't be isolated.

3) Eclipsed form   —   Unstable

   Staggered form   —   Stable

<u>Reason</u> : In eclipsed, Van der Wall Strain
(due to bulkiness of grps.)

&t Torsional Strain (due to bp-bp repulsion).
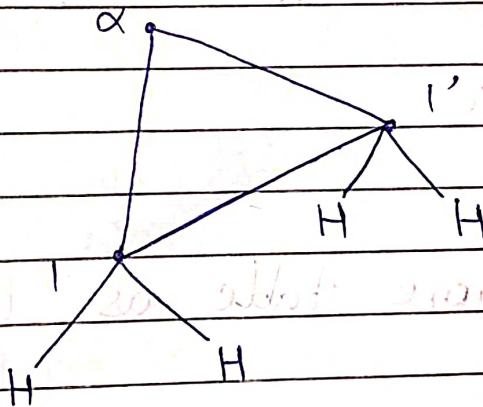
Q) Write most &t least stable conformer.

	Most	Least

α   β

1) $Ph — CH — CH_2 — Ph$
         |
         CH_3

2)

Most

Least

3)

Most

Least

4)

α   β
$CH_3 \leftarrow CH_3$

OH   OH

Most

Least
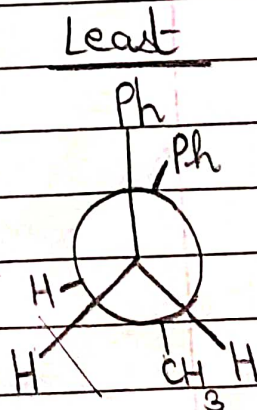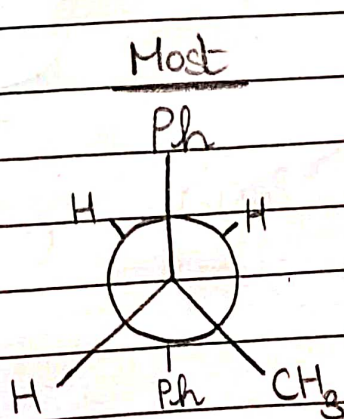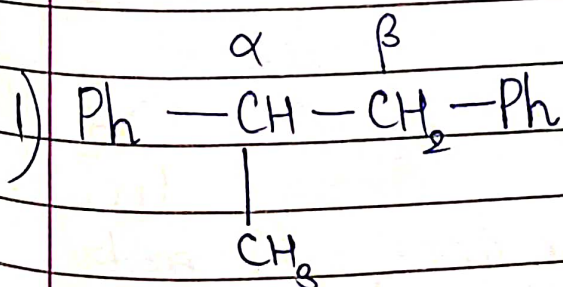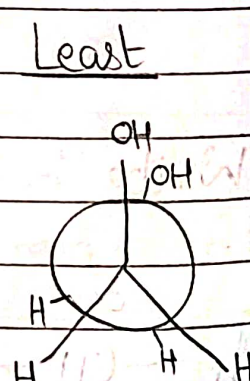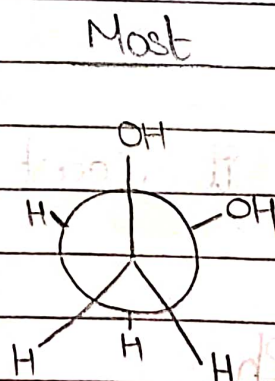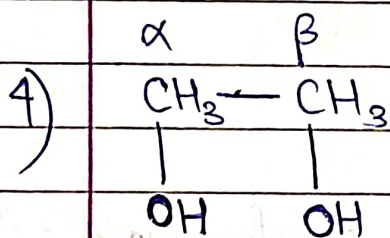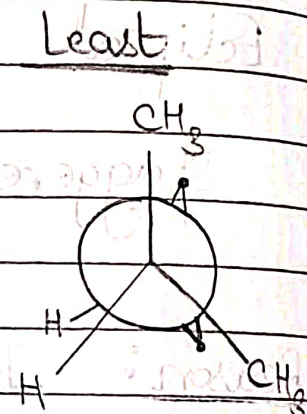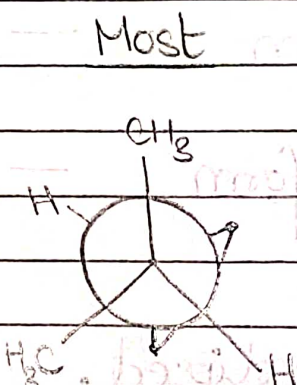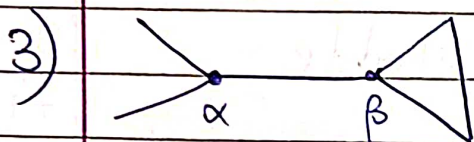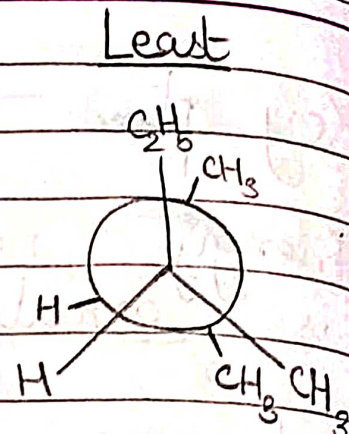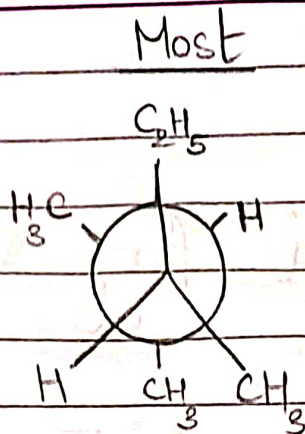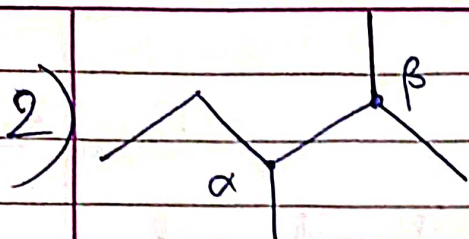
Cyclic Conformational Isomerism
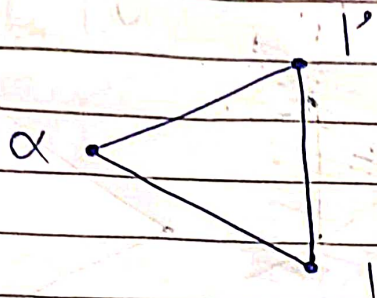
Cyclopropane

Newmann Proj.
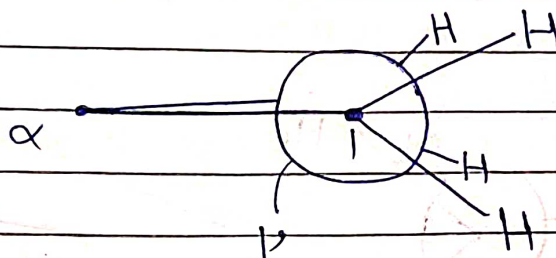
Sawhorse Proj.

Only eclipsed form possible in this case.

But with larger rings, isomers and/or substituents start appearing.

Q) Compare stability of Cis & Trans form of 1,2- dimethylpropane.

A) 1,2-dimethyl propane

CH₃ ̇CH₃

H

H

Cis

H CH₃

CH₃

H
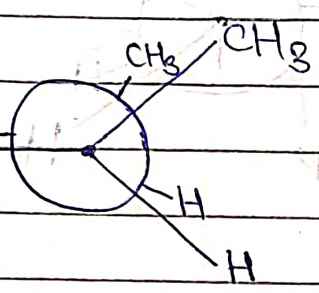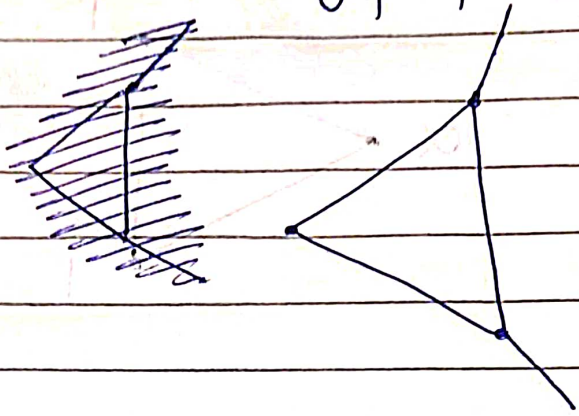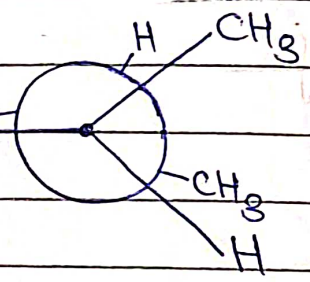
Trans

Trans more stable as less Van der Wall strain.

Conformers in Cyclohexane

Cyclohexane
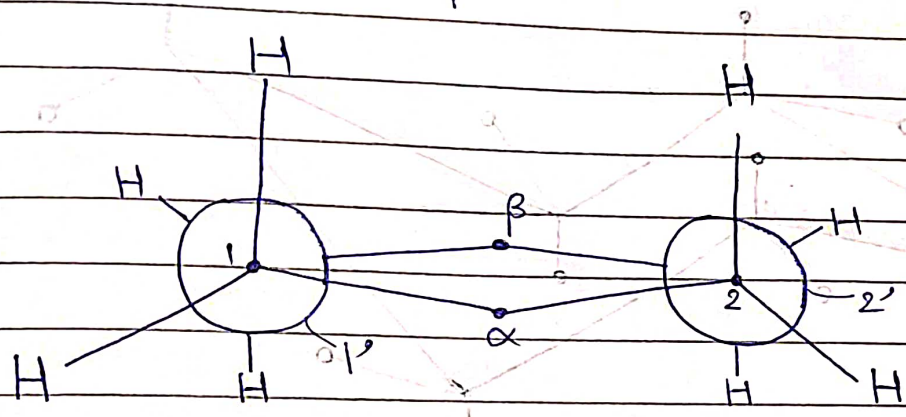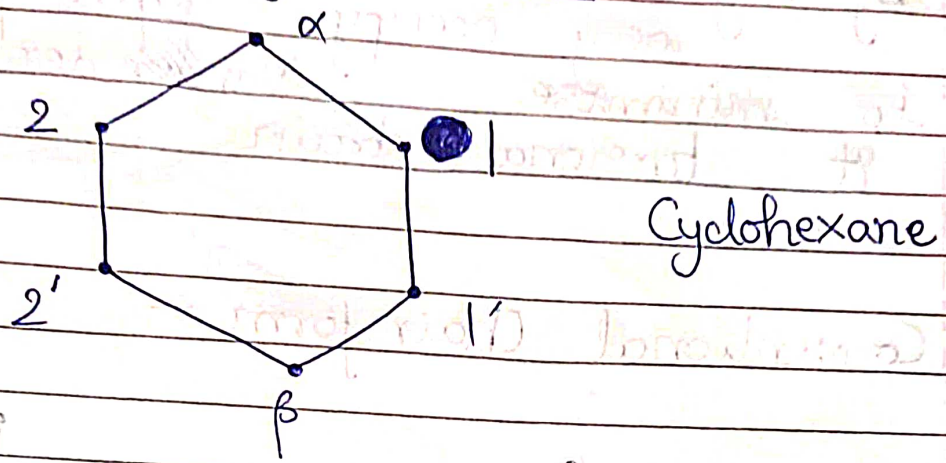
This is **NOT** as shown above as all C atoms **NOT** in one plane.

Actual, (axial post i.e. _Gauche_)
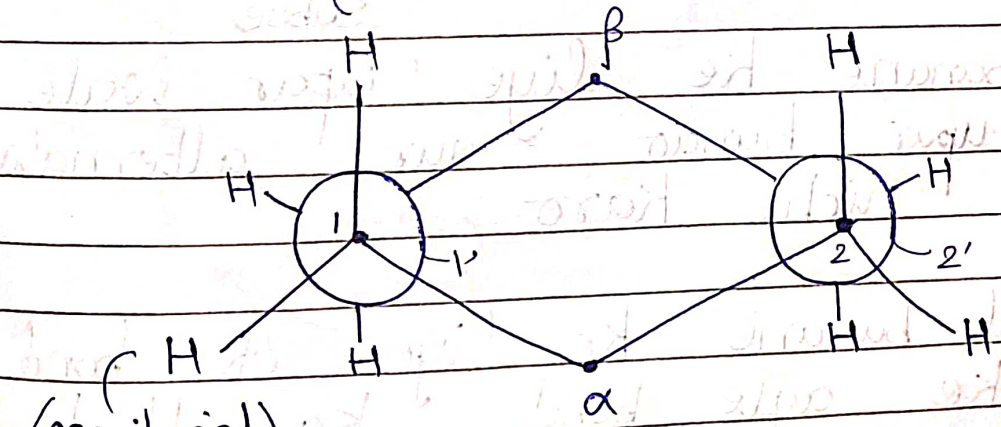
(equitorial post i.e. _Staggered_)   Chair form

& Any substituent would like to occupy equi post. to minimise Van der wall Strain & torsional strain

<u>Conventional Chair form</u> —
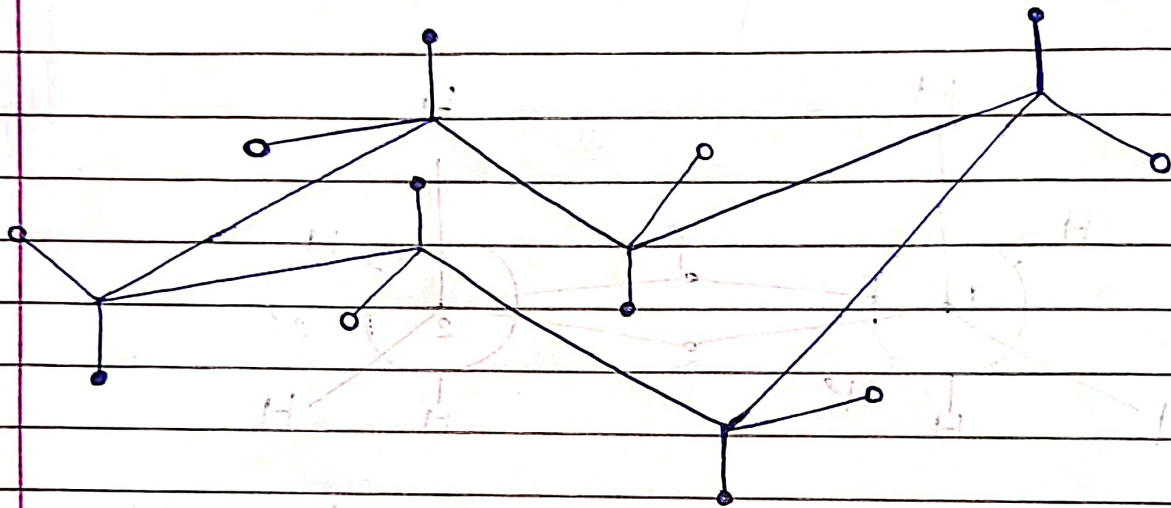
• — ⟶ Axial post.   **○** — ⟶ Equi post.

Axial banane ke liye ^{sabse} upar wale C pe upar banao aur alternatively upar niche karo.

Equitorial banane ke liye ek bond chhod chhod ke agle bond ke || banao.
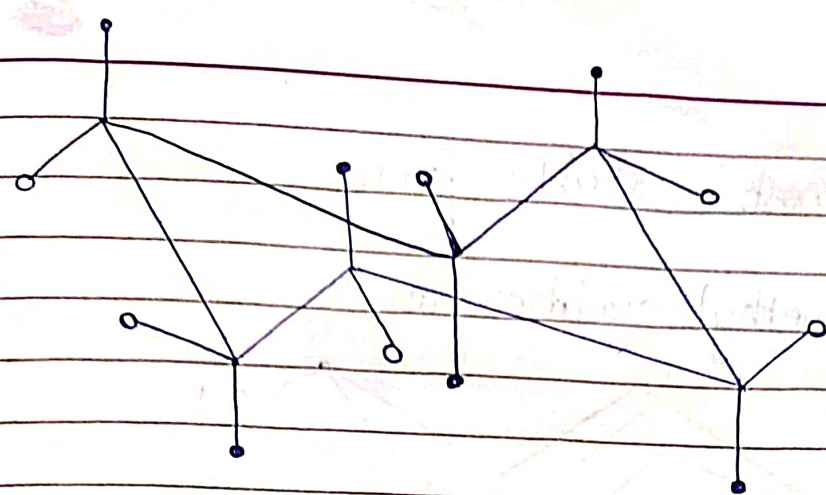
• — Axial post.   ○ — Equi. post.

Imp. Pts. —

1) Every C atom in cyclohexane chair form is associated with 2 types of bonds — axial & equi.

2) Adj. C atoms have axial post. in opp. dirxⁿ.

3) Any substituent will try to occupy equi. post. as it is 'anti' form. Axial post. is 'gauche' form.

Q) Draw most stable form.

1) 1,2 - dimethyl cyclohexane

CH₃

CH₃
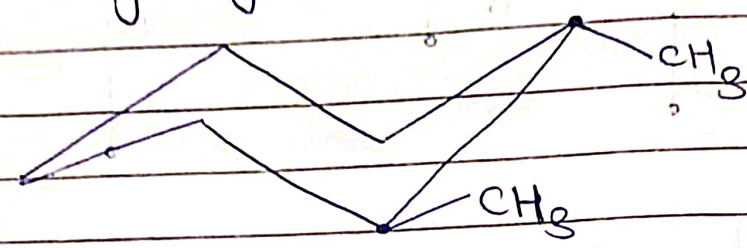
2) 1,3 - dimethyl cyclohexane

CH₃

CH₃
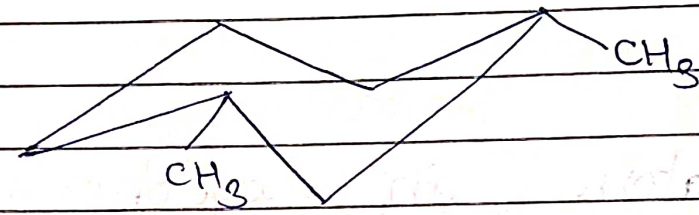
3) 1,4 - dimethyl cyclohexane

H₃C

CH₃
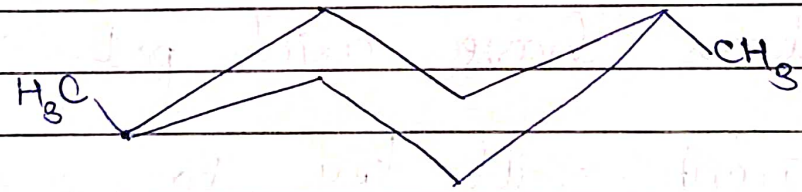
4) 1,2,3,4,56 - hexacyclopropyl cyclohexane
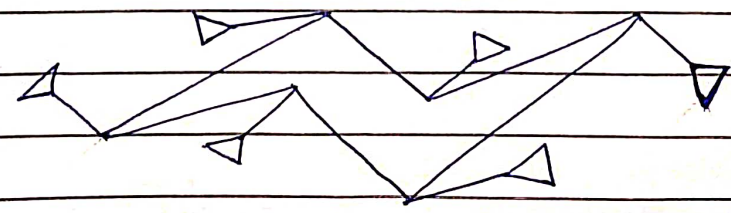
Q) Draw the following

1) 1,3,5 - trimethylcyclohexane all CH₃ in axial post.
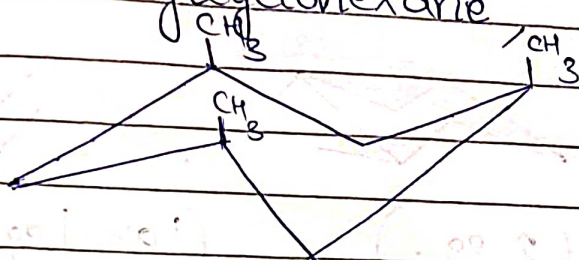
2) 1,2,3,4,5,6 - hexachlorocyclohexane, all Cl at axial post.

Q) Compare stabilities.

1)

(eq.)   (ax.)

2)

(2 eq.)   (2 ax.)

3)

(1eq., 1ax.)　　　　　　　　　(2 eq.)

4)

(2 ax.)　　　　(2 eq.)　　　(1 ax. 1 eq)　　　(1 ax. 1eq)
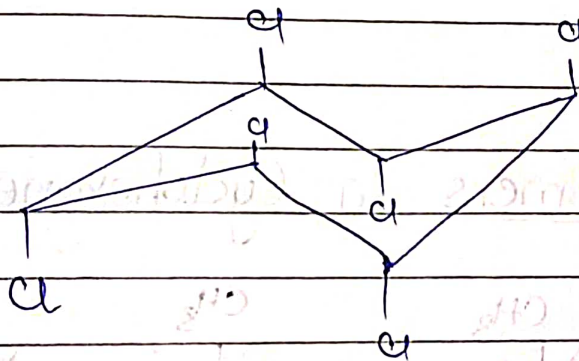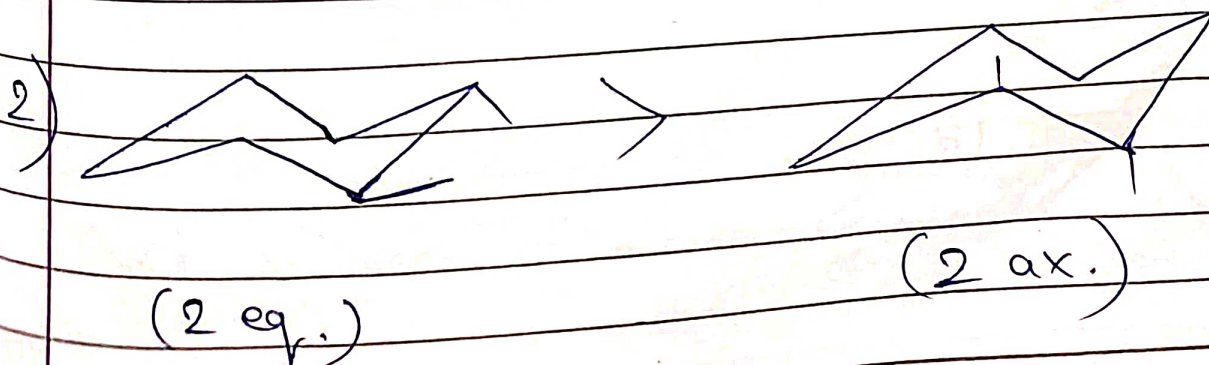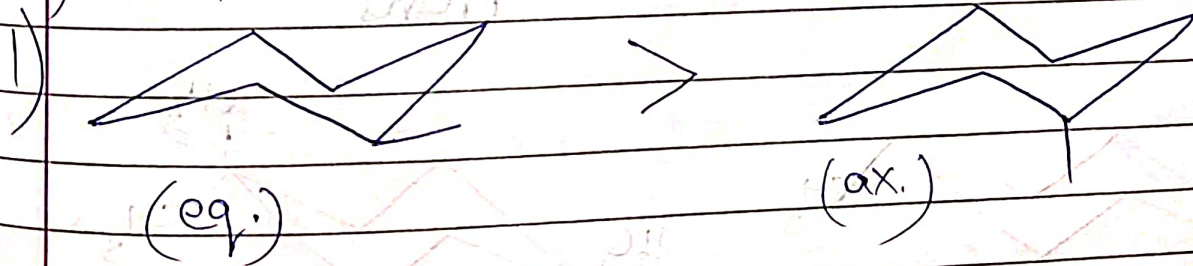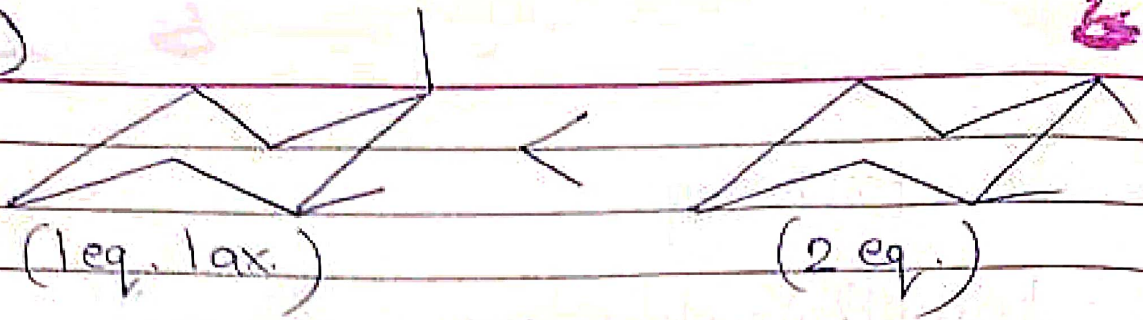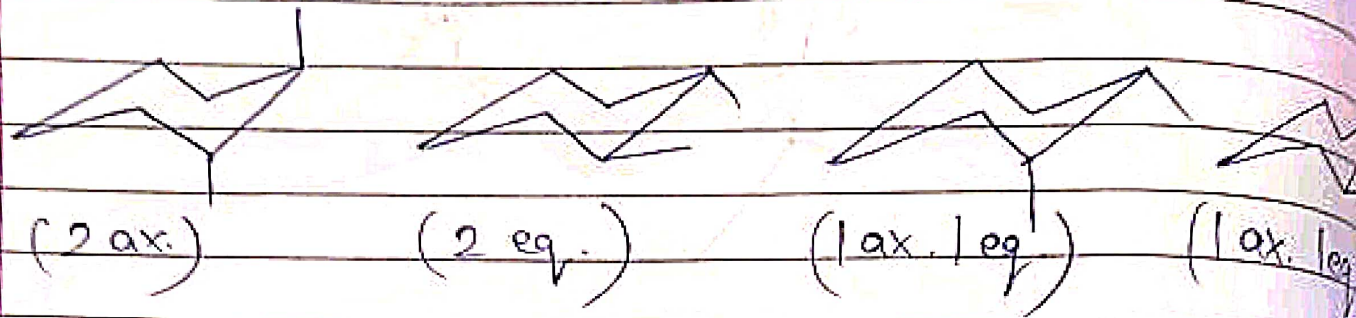
$$\boxed{b > c = d > a}$$

Geometrical Isomers in Cyclohexane

CH_3　　　　CH_3　　　　CH_3　　　　H

H　　　　H　　　　H　　　　CH_3

Cis　　　　　　　　Trans

CH_3 　　　　 CH_3

H_3C 　　　 CH_3

CH_3
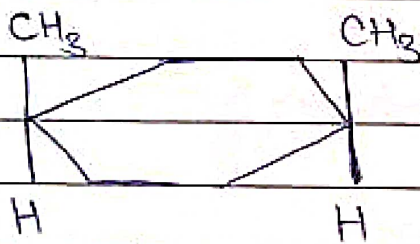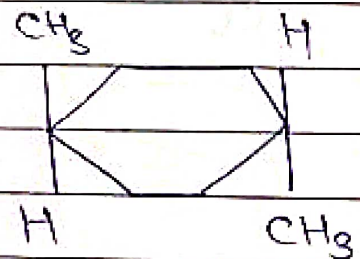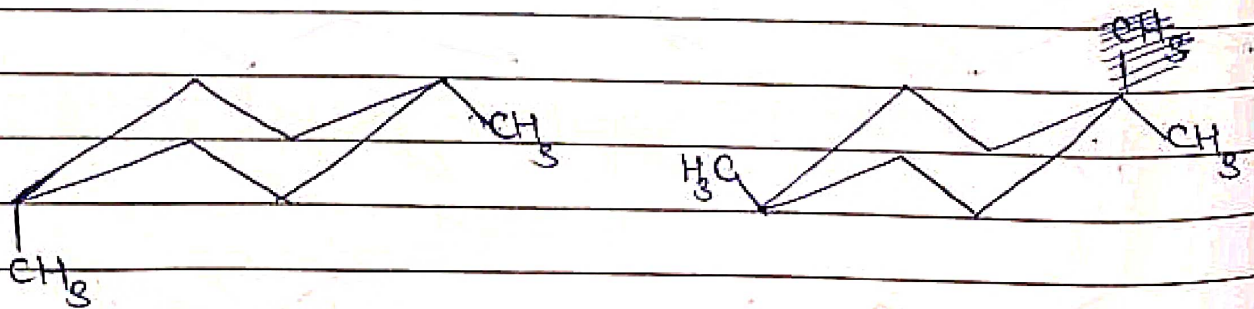
To identify Cis or Trans, we use following method.

(I)

(II)

If bonds belong to.
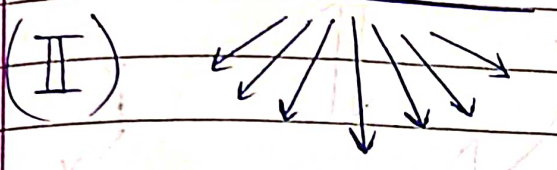
(I) (I) ⟺ Cis
(II) (II) ⟺ Cis

(I) (II) ⟺ Trans

Q) Identify Cis or trans.

1)

Trans

2)

Cis

3)

Cis

4)

Cis

5)

Trans

6)
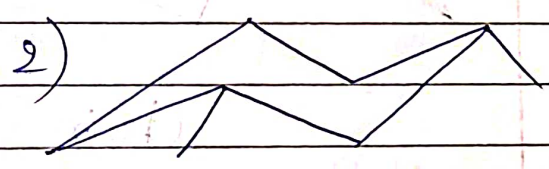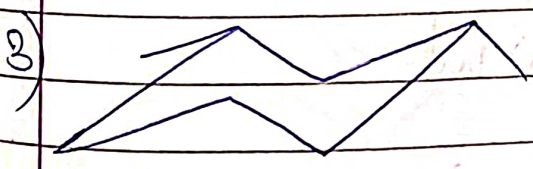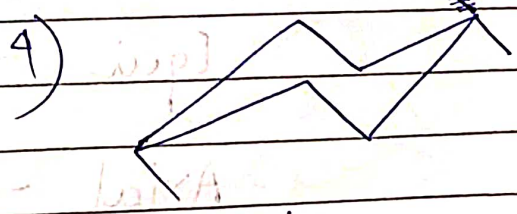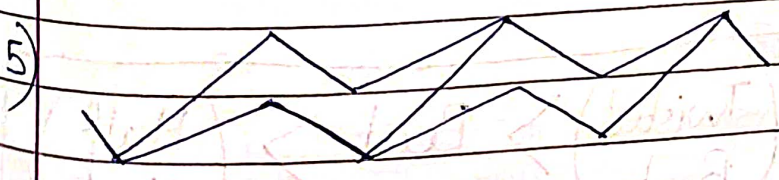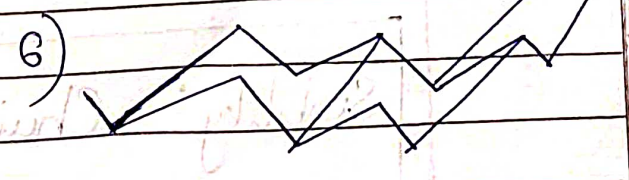
Trans

Ring flipping in Cyclohexane

Chair

Half Chair

Twisted
Boat

Half Chair

Boat

Chair

☆ Twisted Boat is Optically Active.
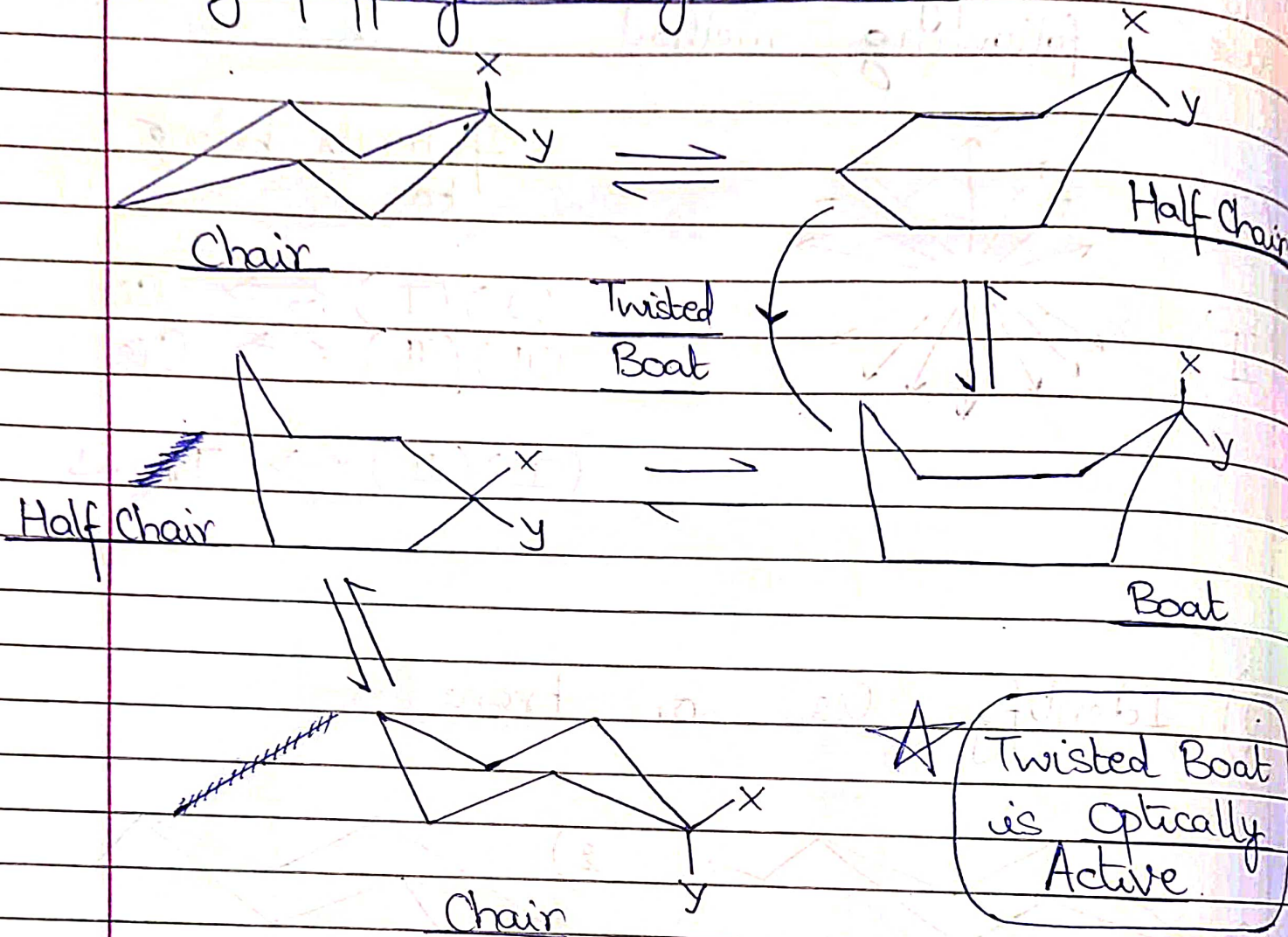
After flipping of ring,

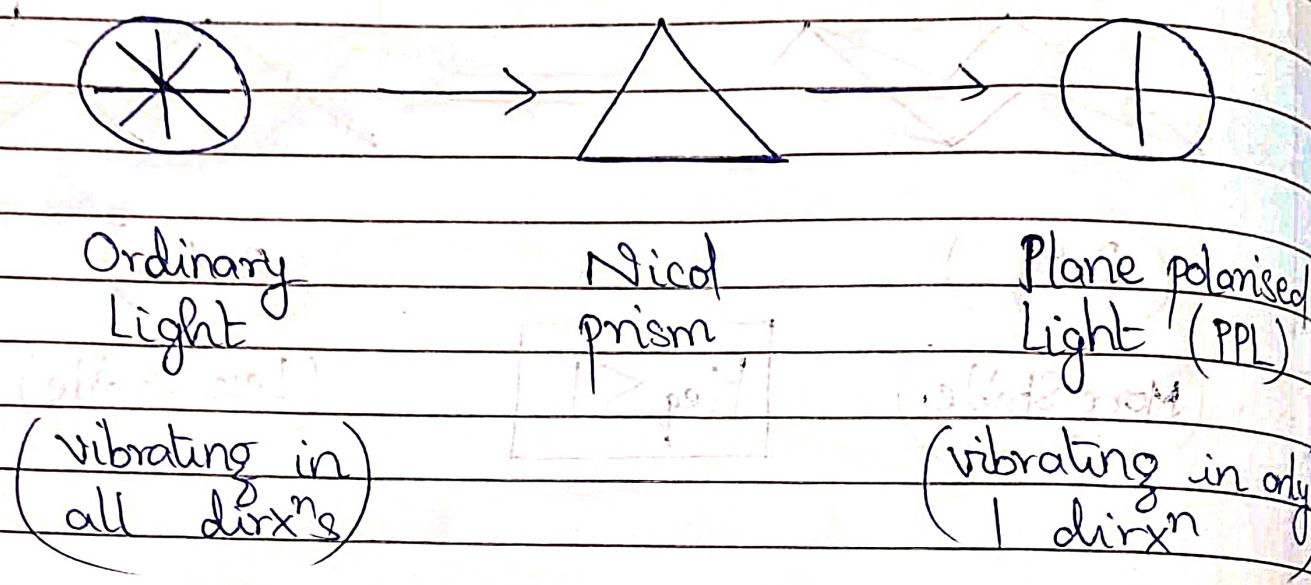Equi. $\longrightarrow$ Axial

Axial $\longrightarrow$ Equi.

Stability: Chair > (Twisted Boat) > Boat > (Half Chair)

Q) Compare K_{eq}.

1)

(2 Eq.)

(More Stable) $\boxed{K_{eq} < 1}$ (2 Ax.)

(Less Stable)

2)

(2 Eq.)   (2 Ax.)

(More Stable) $\boxed{K_{eq} < 1}$ (Less Stable)

Q)

	R		K_{eq}
A)	H	P)	4
B)	CH_3	Q)	1
C)	$-CH_2-CH_3$	R)	16
D)		S)	6400

D) $-C\begin{smallmatrix}CH_3\\|\\-CH_3\\|\\CH_3\end{smallmatrix}$

$\boxed{\begin{array}{l} A \to Q \\ B \to P \\ C \to R \\ D \to S \end{array}}$

Optical Isomerism

Ordinary Light	Nicol prism	Plane polarised Light (PPL)
(vibrating in all dirx^n s)		(vibrating in only 1 dirx^n)

Dextro (d or +)

Leavo (l or −)

Polarimeter tube

(Organic Comp. sol^n)

Comps. which show diff. behavior towards PPL are called Optical Isomers.

Optically Active	Optically Inactive
Deviate on PPL	Do NOT deviate on PPL
Eg: Dextrorotatory, Leavorotatory	

Theoretically, Assymmetric $\longrightarrow$ Optically Active

Symmetric $\longrightarrow$ Optically Inactive

Basics of Optical Isomerism

Chiral Centre —

sp^3 hyb^n atom connected to 4 <u>diff. grps.</u>

(l.p. included)

If chiral centre is C, it is called chiral C.

Q) Calc. no. of chiral centres in following

1)

2)

OH

3)

Cl

2

4)

Cl

O

5)

1

6)

Me   Me

2

7)

Cl

O

8) H₃C

OH   CH₃

Br   Cl

Br

7

9)

Cl

H₃C

N

5

10)

Me   Cl

HO

CH₃

N

7

deloc. $\Rightarrow$ sp^2 N

11) OH

1

12)

2 H

2

13)

2

14)
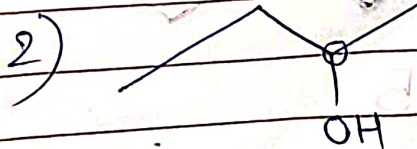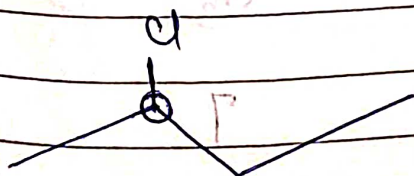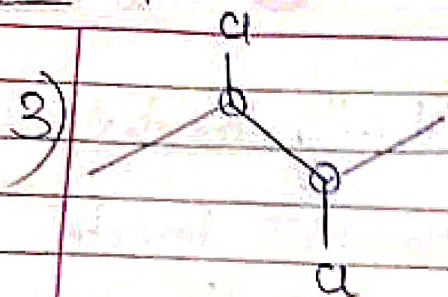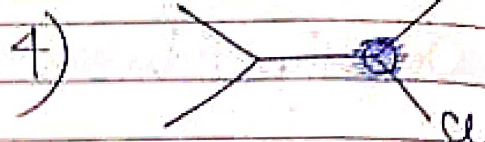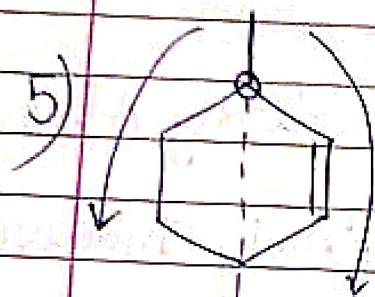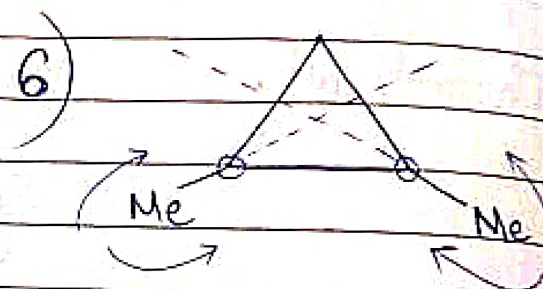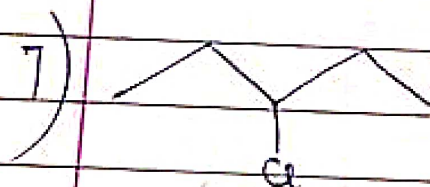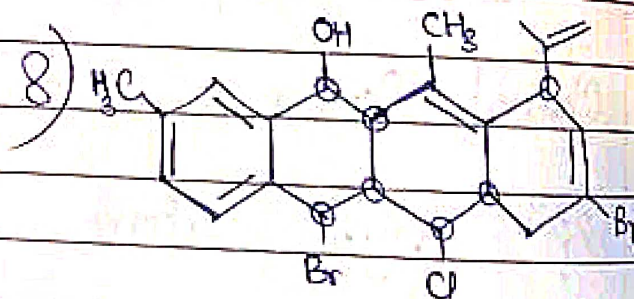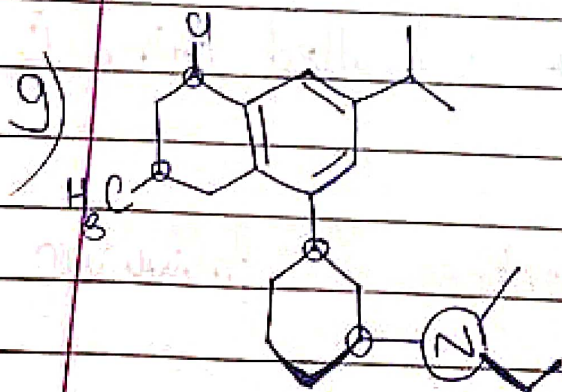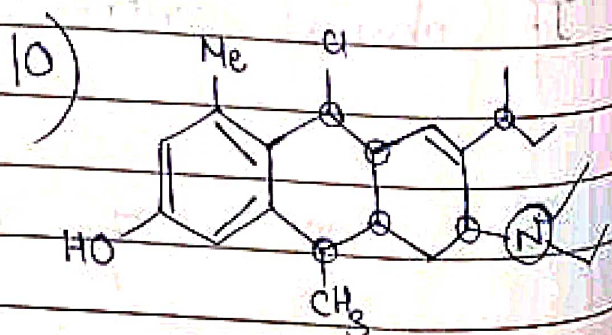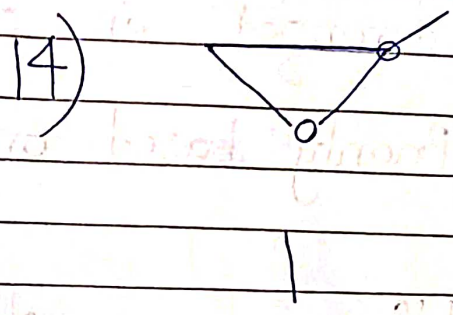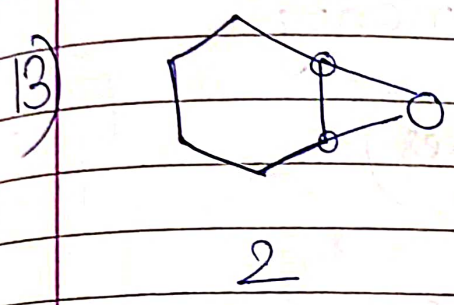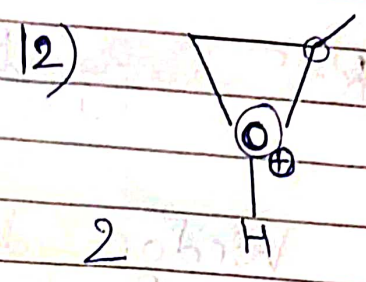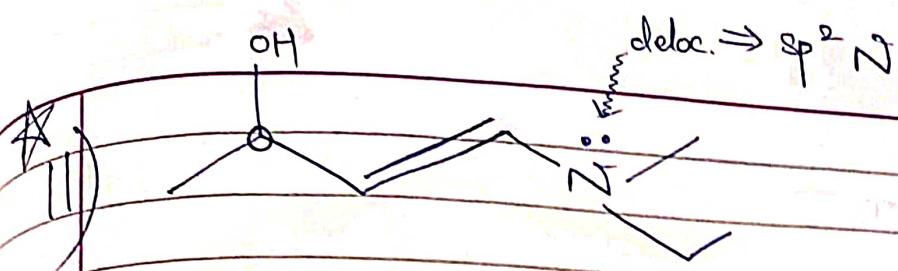
★ If # Chiral Centres in a molecule is ① , then it MUST be Optically Active.

Except: Amines

R$_1$

Chiral Centre

N

R$_2$

R$_3$

Here N is Chiral centre but amine is optically inactive.
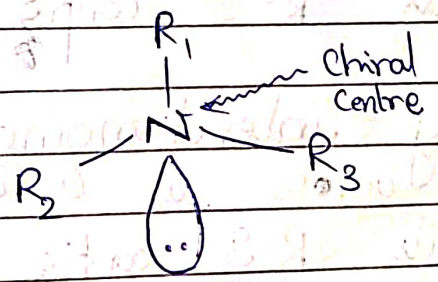
R-S Configuration -

C1: Wedge dash formula

1) Grps. around chiral centre are arranged in order of priority.
(Priority based on CIP Rules)

2) 4th grp. must be away from viewer (if not, we will interchange posi.)

3) By interchanging EVEN pairs of grps. across a chiral centre, its R-S config. remains Same.

4) By interchanging ODD pairs of grps. across a chiral centre, its R-S config changes.

5)

R   S

Eg:

HOOC — ④
HO ⑪ H
① CH₃
⑤
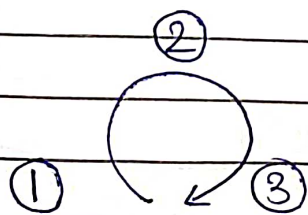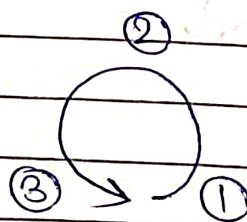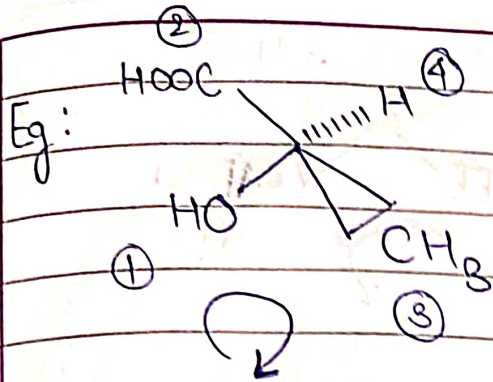
Appears : R
Interchange : 0
Actual : (R)

Eg: ②
HOOC — H④
HO — CH₃
① ③
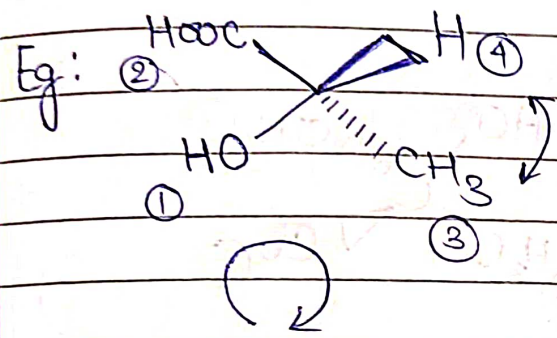
Appears : R
Interchange : 1
Actual : (S)

Eg: ②
HOOC — OH ①
H — CH₃
④ ③
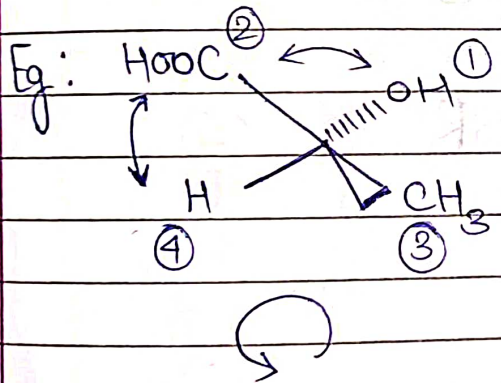
Appears : S
Interchanges: 2
Actual : (S)

Eg: ② COOH
② COOH ③ H ④
④ H — ⑧ OH
OH ①
①

R — S

Eg:
② COOH
HOOC ② ⑧ OH ①
⑨ H ④
H — OH
④ ① OH
①

R — R

Eg:

③ H₃C ⟍ ||||| OH ①
         C
② Et ⟋   ⟍ H
              ④

(↺)

S

⑧ H₃C ⟍ ||||| H ④
         C
② Et ⟋   ⟍ OH
              ①

(↻)

R

Eg:

④ H₃C ⟍ ||||| Cl ①
         C
HO ⟋   ⟍ CHO
②   ③

(↺) G

R

② HO ⟍ ||||| CHO ③
         C
④ H₃C ⟋   ⟍ Cl ①

(↻)

R
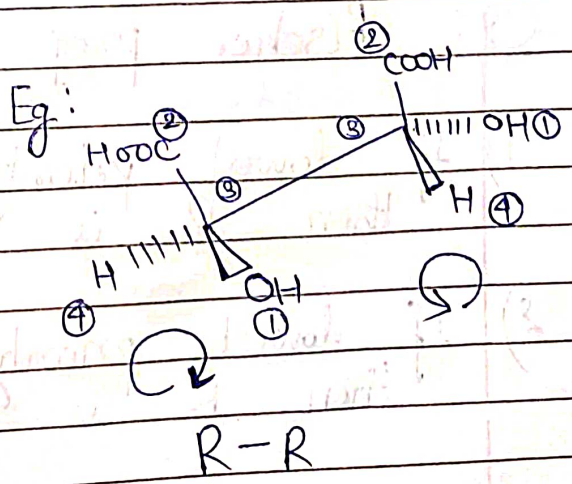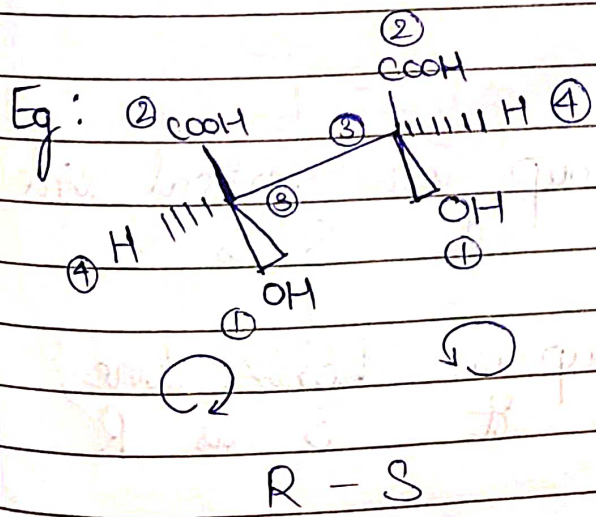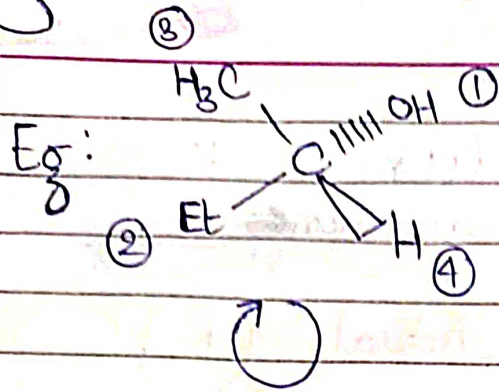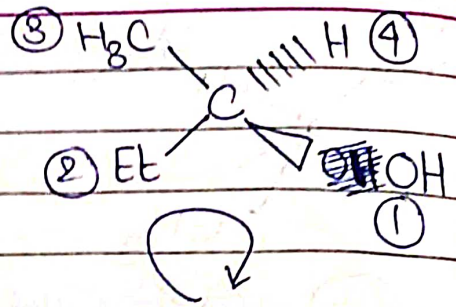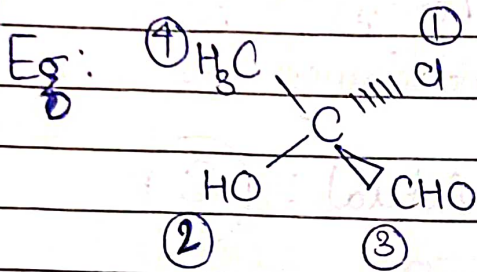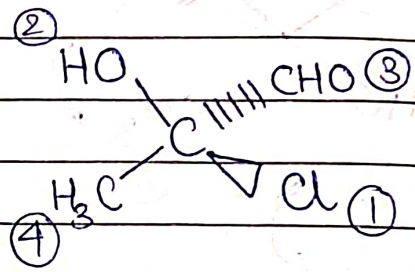
C2: Fischer proj.

1) If lowest priority group on vertical line, then R is R & S is S

2) If lowest priority group on horiz. line, then R is S & S is R.

Eg :

$$\underset{S}{Cl} \overset{F \; ④}{\underset{Br \; ②}{|}} I \; ①$$

Appears : R

Actual : R

Eg :

$$\underset{③ Cl}{\overset{≡I \; ①}{\underset{Br \; ②}{|}}} F \; ④$$

Appears : R

Actual : S

Eg :

$$\underset{④}{\underset{H}{\overset{③ CH_3}{\underset{H}{|}}}} \overset{Br \; ①}{\underset{Cl \; ①}{\underset{②}{|}}} \quad ⟳ \Rightarrow S$$

$$CH_3 \;③ \qquad ⟲ \Rightarrow R$$

Eg : ① Br $\overset{③ CH_3}{\underset{CH_2}{\underset{②}{|}}}$ (H) ④ $\quad ⟳ \Rightarrow R$

① Br $\overset{②}{\underset{③ CH_3}{|}}$ (H) ④ $\quad ⟲ \Rightarrow R$

①

1) Eg : ④H ——②COOH, ③ OH ①, ⇒ R

④H —— ② OH ① ⇒ S

②COOH

2) Eg : ④H ——②COOH, ③ OH ① ⇒ R

① HO —— ② (H)④ ⇒ R

②COOH

3) Eg : HO ——COOH—— (H) S

(H) —— OH S

COOH

4) Eg : HO ——COOH—— (H) S

HO —— (H) R

COOH
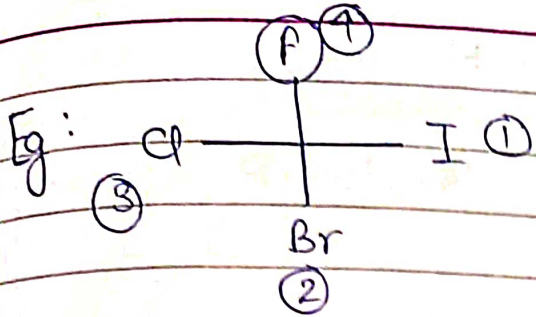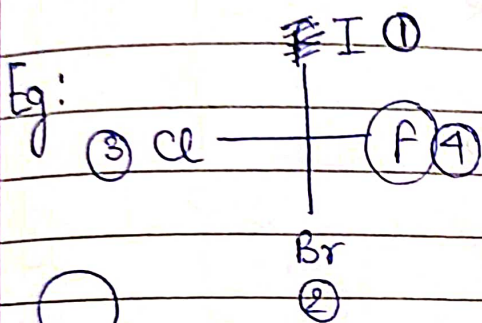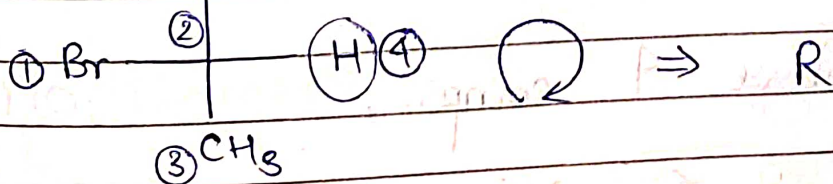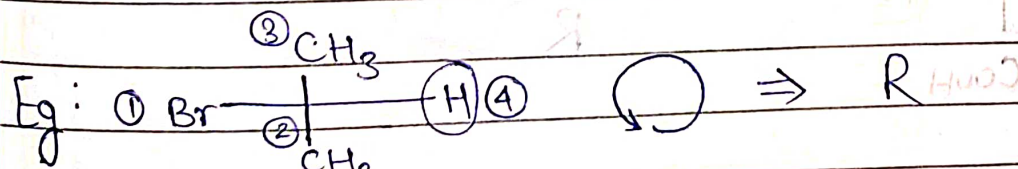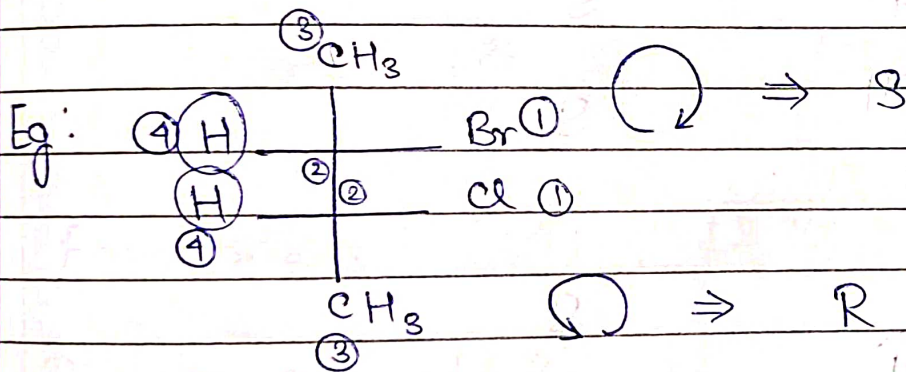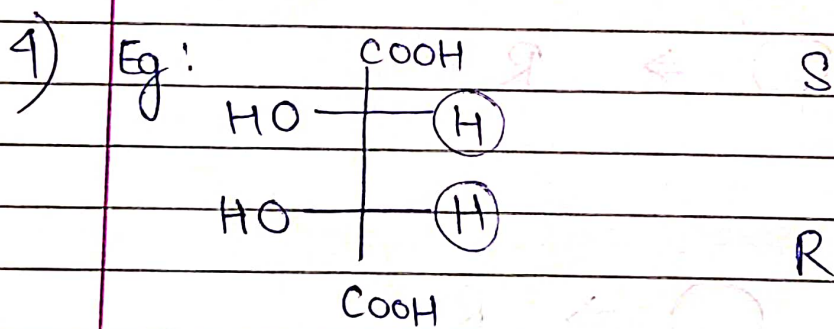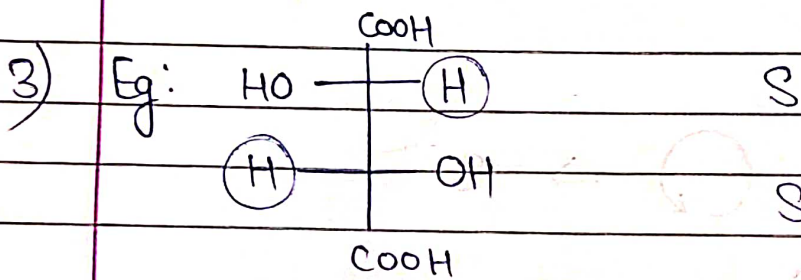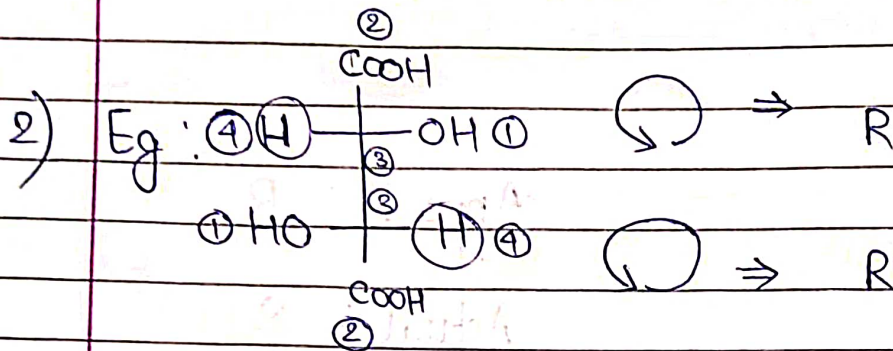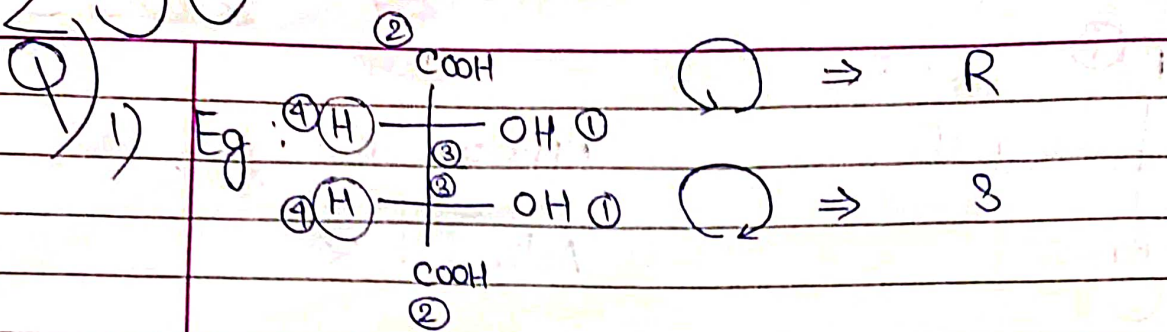
Out of above 4 comps.,

Enantiomers : (2, 3)

If we name comps. 1 & 4 in IUPAC,
we get

(2R, 3S) OR (2S, 3R) for both.

⇒ Identical : (1,4)

Now, Diastereomers : (1, 2) ; (1, 3)

Q)

COOH
(H)——OH
(H)——OH
CH₃
①

R, R

COOH
(H)——OH
HO——(H)
CH₃
②

R, S

COOH
HO——(H)
(H)——OH
CH₃
③

S, R

COOH
HO——(H)
HO——(H)
CH₃
④

S, S
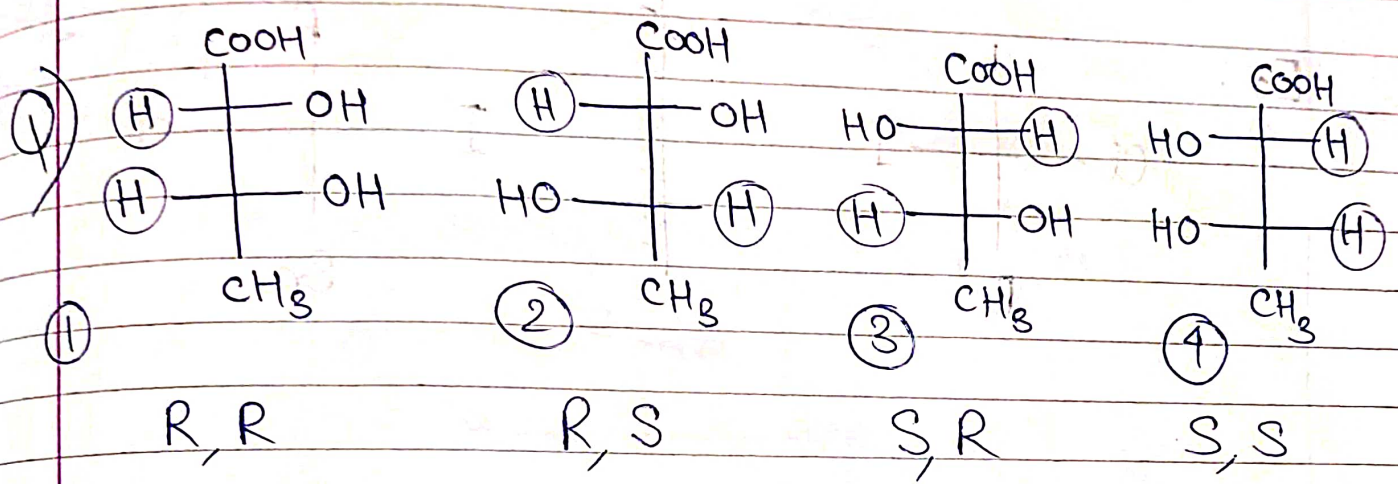
Name : (2R, 3S)   (2S, 3R)

Enantiomers : (1,4) ; (2, 3)

Diastereomers : (1,2) ; (1,3) ; (4,2) ; (4,3)

Enantiomers

Stereoisomers which are non superimposable mirror images are known as enantiomers

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★ Enantiomers have same physical prop^ts such as b.p., m.p., solubility, ...

Eg:

```
        F                    F
 Cl ──┼── I      |     I ──┼── Cl
        |                    |
        Br                   Br
```
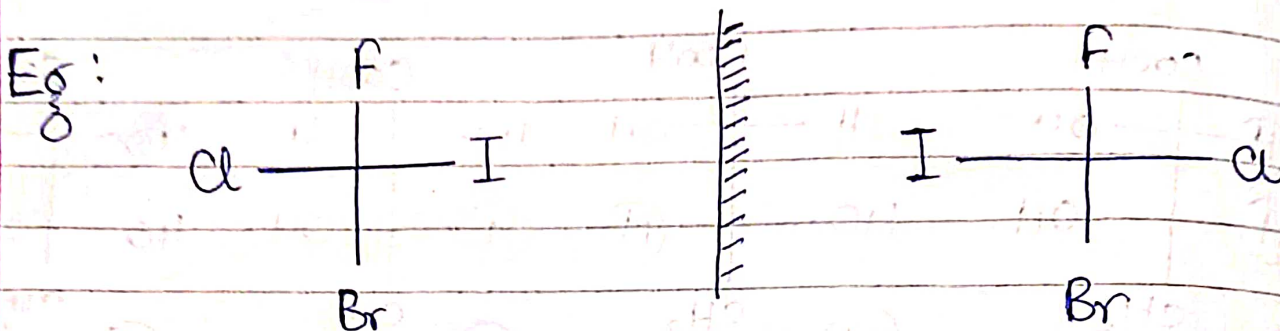
Diastereomers

Stereoisomers which are NOT mirror images of each other are known as diastereomers.

They have diff. physical prop^ts such as b.p., m.p., solubility, ...

Fisher Proj.

Only Eclipsed conformer will convert into fisher proj.

In fisher proj., mostly max. carbons must be on vertical line & carbon containing fx^nal grp. must be on top of vertical line.

Eg:

Eclipsed

$$COOH$$
$$H \longrightarrow OH$$
$$H \longrightarrow OH$$

fischer Proj.

$$COOH$$

Eg:

$$CH_3$$
$$H \longrightarrow Br$$
$$Cl \longrightarrow H$$
$$CH_3$$

Eg:

$$CH_3$$
$$H \longrightarrow Br$$
$$Br \longrightarrow H$$
$$CH_3$$

DATE
PAGE

Q) Draw fischer proj.

1)

Br—H   Br—H   CH₃
  | | Br—┼—H
 CH₃   CH₃   Br—┼—H
                    CH₃

2)

H—Br   H—Br   COOH
  | | H—┼—Br
 COOH   COOH   H—┼—Br
                    COOH

3)

H—OH   CH₃   CH₃
  | | H—┼—OH
 CH₃   H—OH   HO—┼—H
                    CH₃

4)

 CH₃   HO—H   CH₃
  | | HO—┼—H
H—OH   CH₃   HO—┼—H
                    CH₃

5)

Br—H   H₃C—H   CH₃
  | | Br—┼—H
 CH₃   Br   H—┼—Br
                    CH₃

Q) 1)


```
    COOH          COOH          COOH
H ──┼── OH     H ──┼── OH    HO ──┼── H
H ──┼── OH    HO ──┼── H     HO ──┼── H
    COOH          COOH          COOH
    (a)           (b)           (c)
```
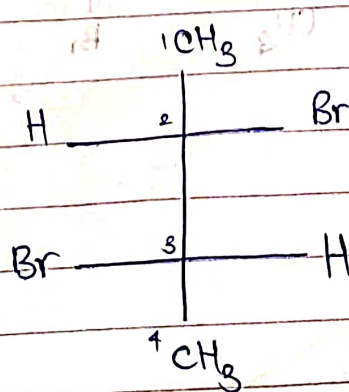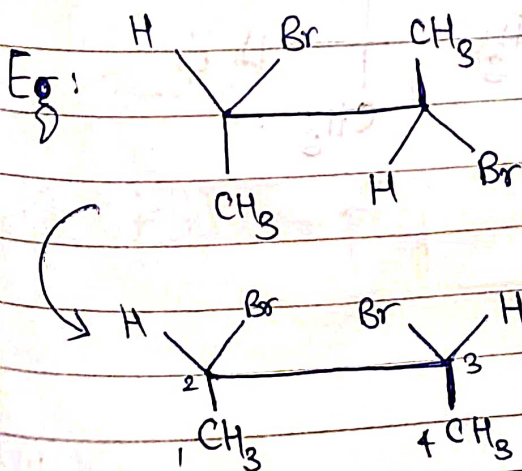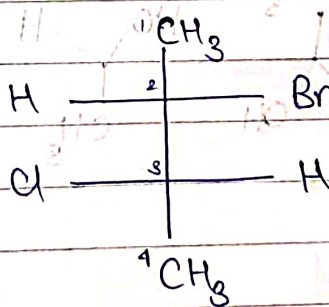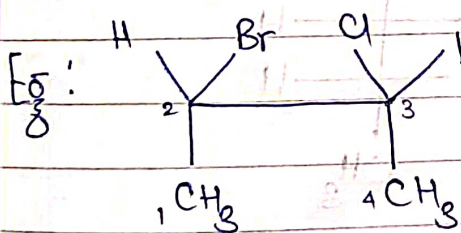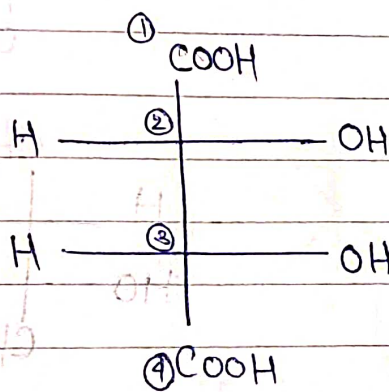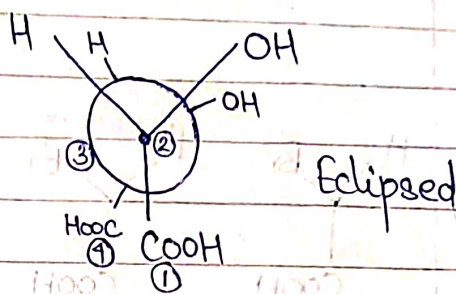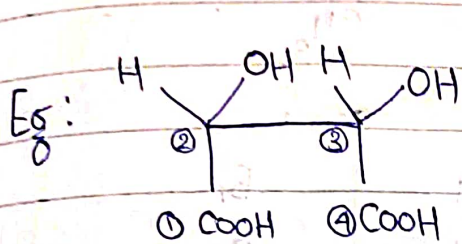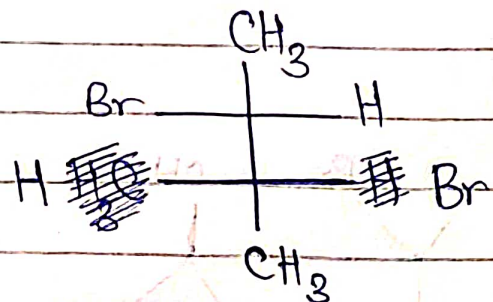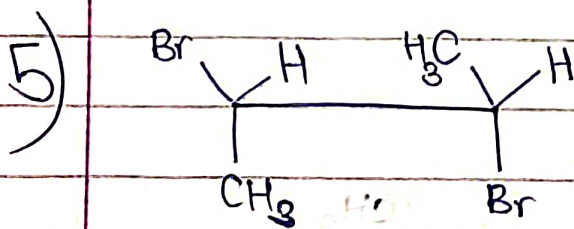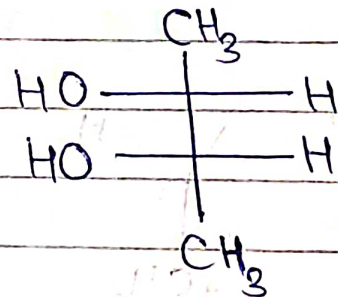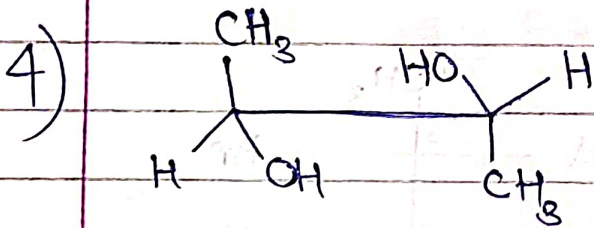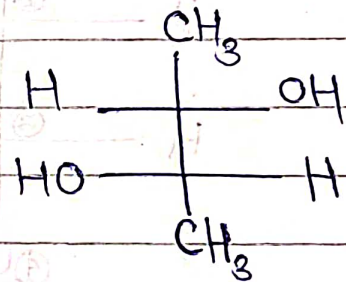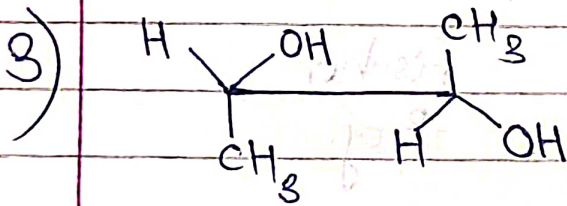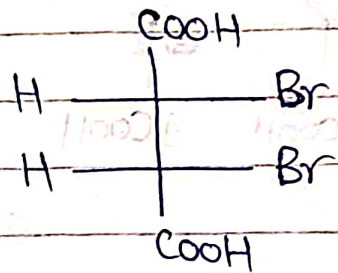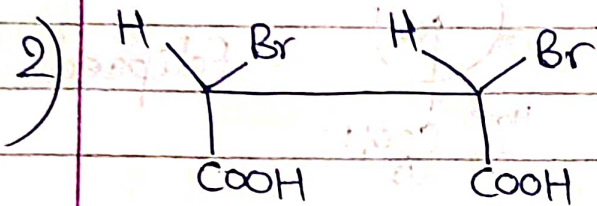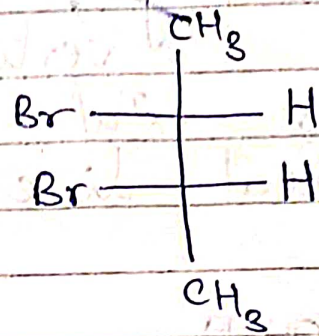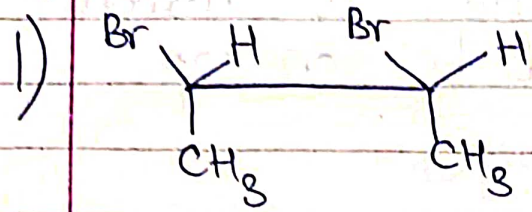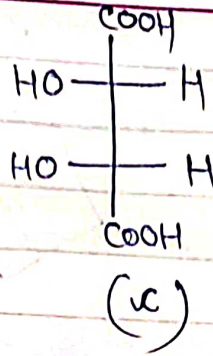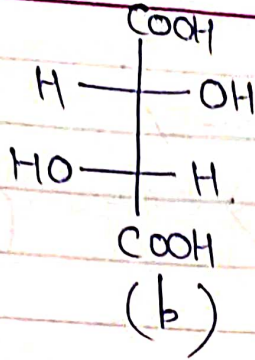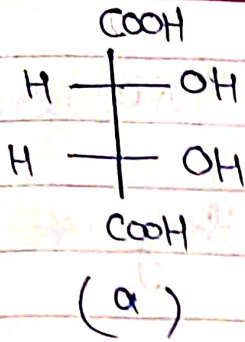
En: ─   Dia: (a,b); (b,c)

(a) & (c) identical as 180° ↻ gives other.

2)


```
   (a)            (b)            (c)
```
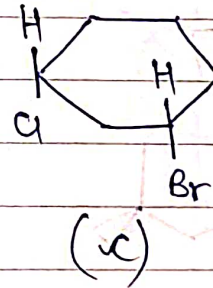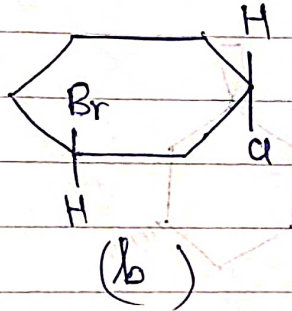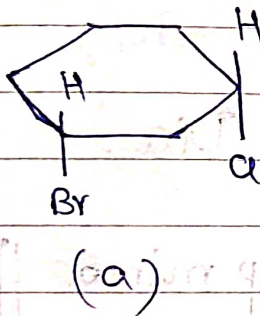
En: (a, c)   Dia: (a,b); (b,c)

for finding R-S in cyclic, take

below plane (ıllı)

above plane (▬)

Eg:

↻ ⇒ R

↺ ⇒ S
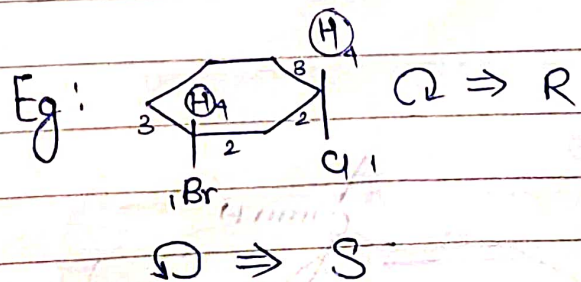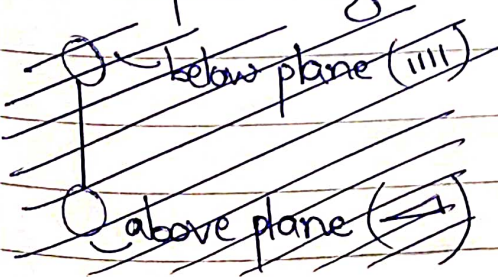
as fischer proj.

3)
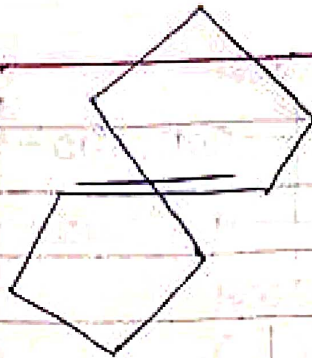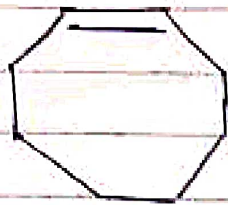
Diastereomers

(as they are Geo. iso)

4)
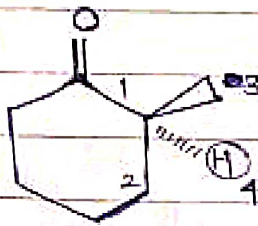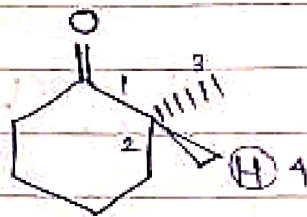
S   R

En.

5)

Dia.

(Keep mirror || to page)

6)
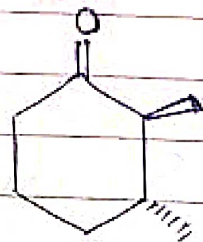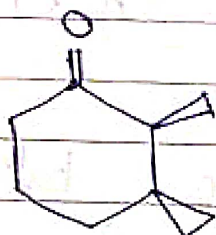
Dia.

7)
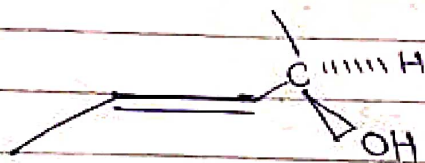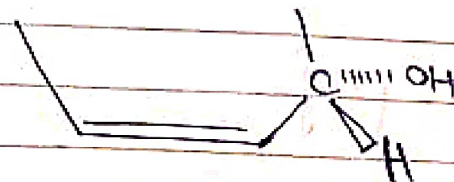
Trans   Cis

Dia.
(They are Geo. iso.)

9)

Dia.

10)

Dia.

11)

(a)

(b)

(c)
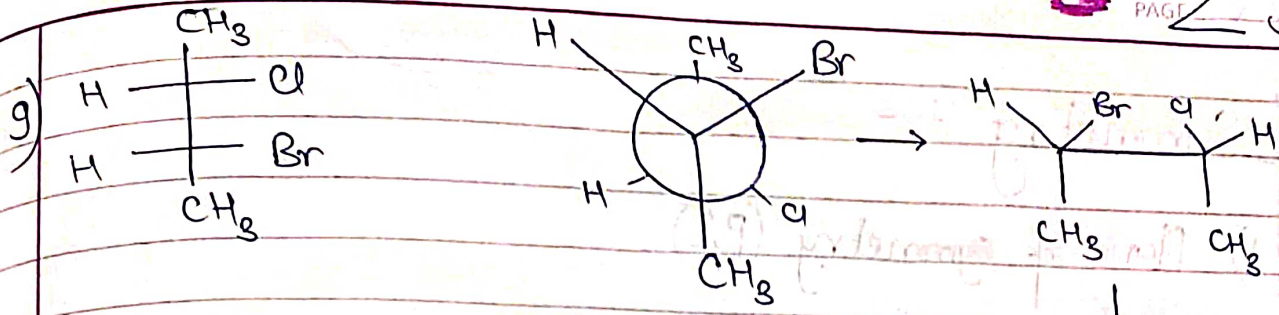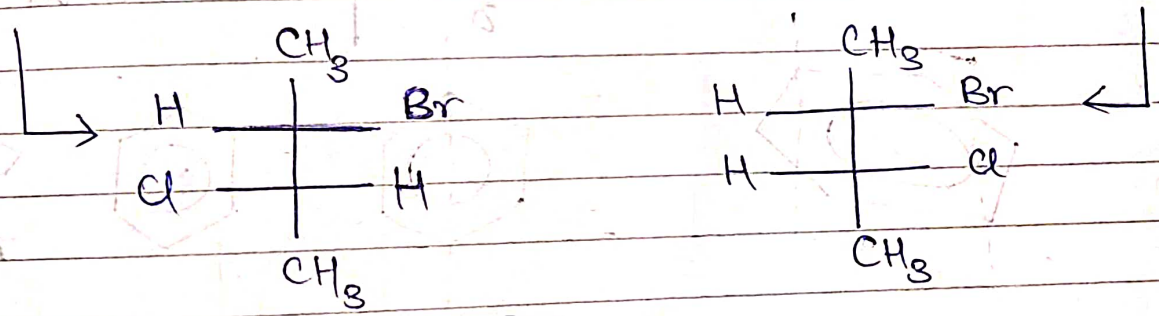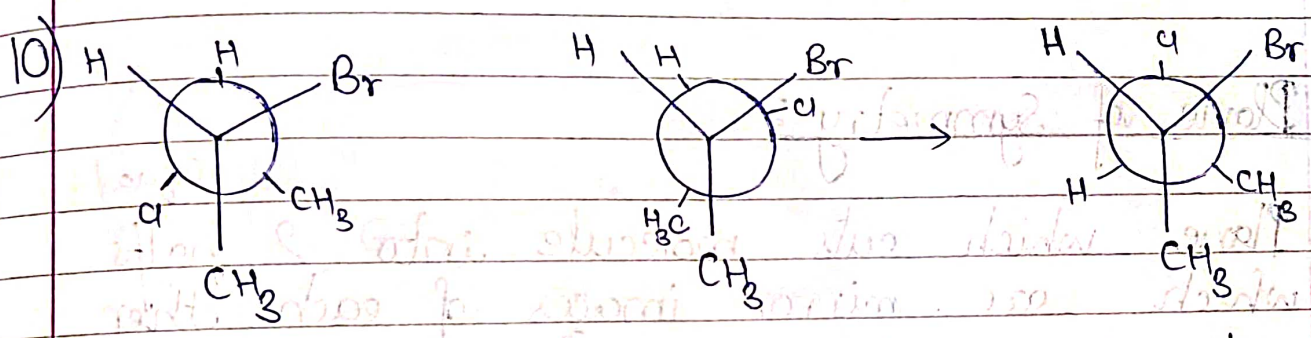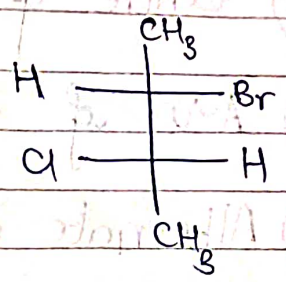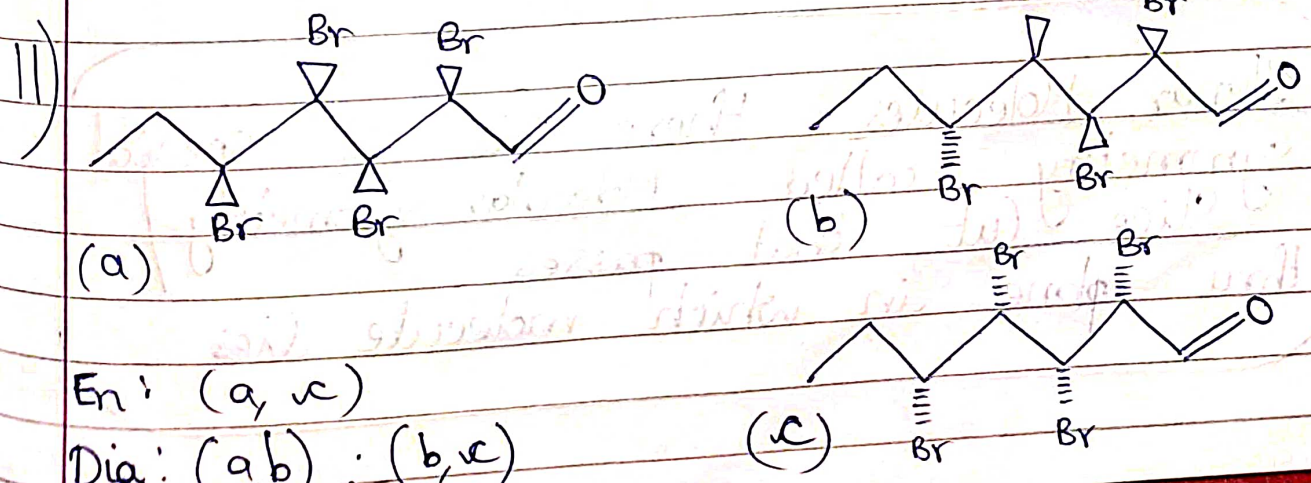
En : (a, c)
Dia : (a,b) ; (b,c)

Symmetry —

1) Plane of symmetry (PoS)

2) Centre of symmetry (CoS)

3) Axis of symmetry (AoS)

4) Alternate axis of symmetry (AAoS)

Plane of Symmetry :

Plane which cuts molecule into 2 equal halfs which are mirror images of each other

Eg:

3 + 3 + 1
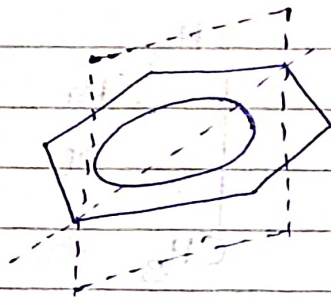
7 PoS
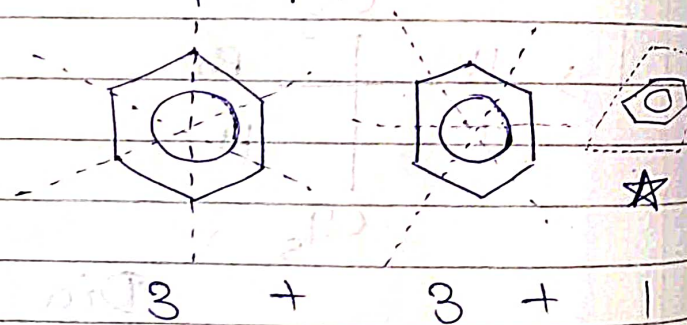
★ Planar Molecules there is a special symmetry called Molecular Symmetry Slice / Cut that passes thru plane in which molecule lies

Eg:
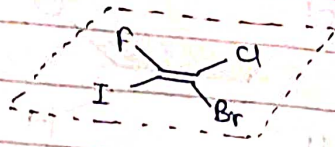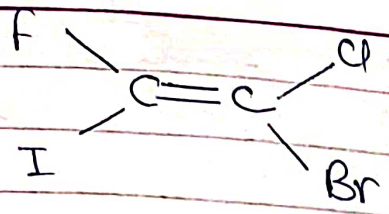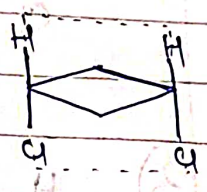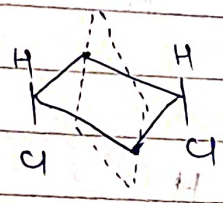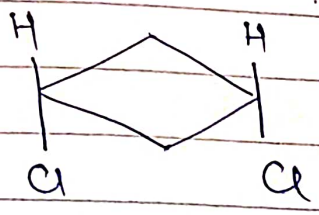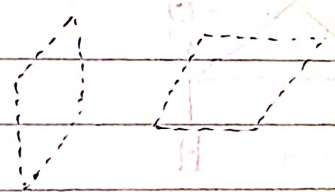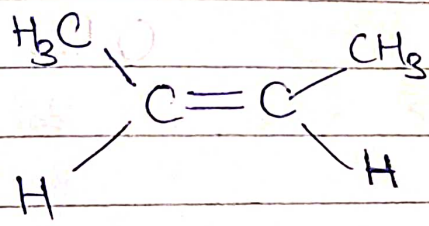
I PoS

Eg:

2 PoS

Eg:

2 PoS

Eg:

2 PoS

Q) 1)

2 PoS

2)

2 PoS

3)

1 PoS

4)

0 PoS

5)

1 PoS

6)

0 PoS

7)

1 PoS

8)

0 PoS

9)

Thru Cl s

PoS
4

Thru H s

Thru CH₃ s

10)

2 PoS

11)
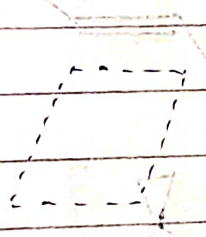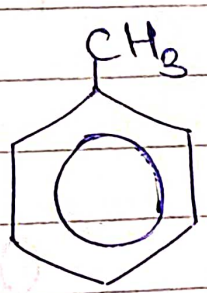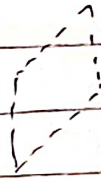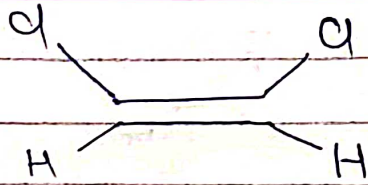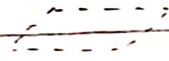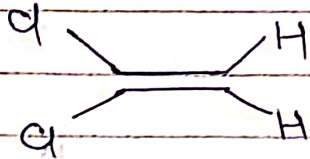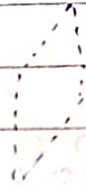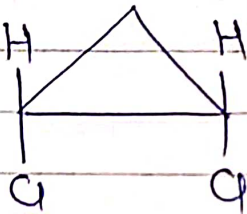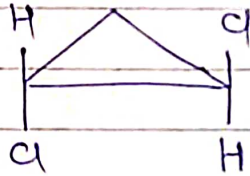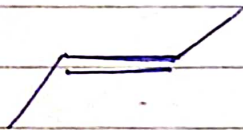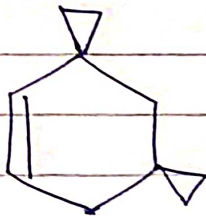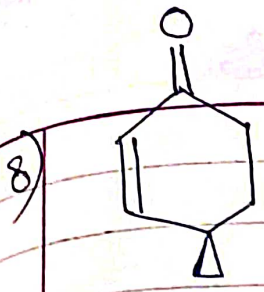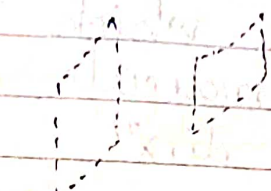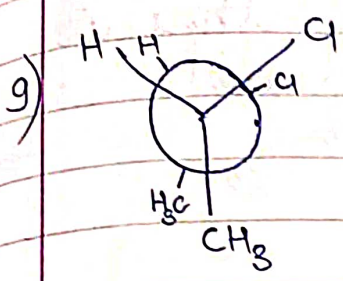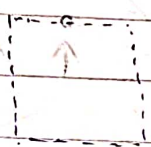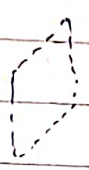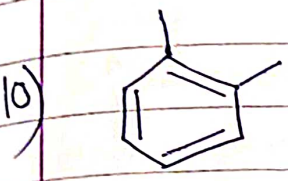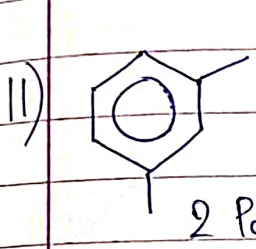
2 PoS   3 PoS   4 PoS   3 PoS

12)

   ⟹   2 PoS

⭐13) CH₄
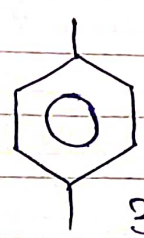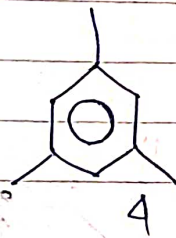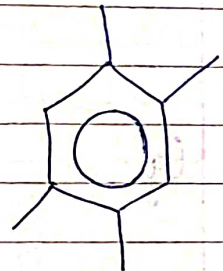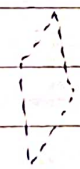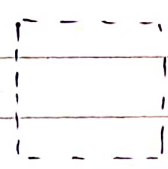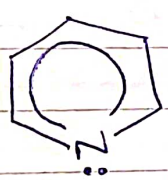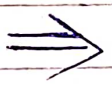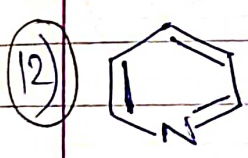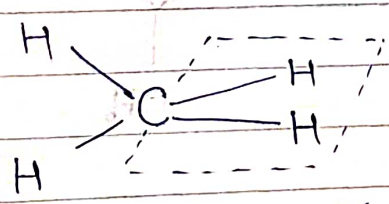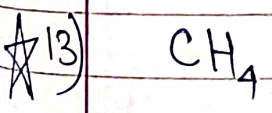
Pick any 2 H &
1 C to give
a PoS

⟹ $^4C_2$ PoS ⟹ 6 PoS

⭐14)

4 PoS

(Connecting midpts
of AB, A'B', A"B")

(A'oo'B' , Aoo'B , A"oo'B")

⭐15)
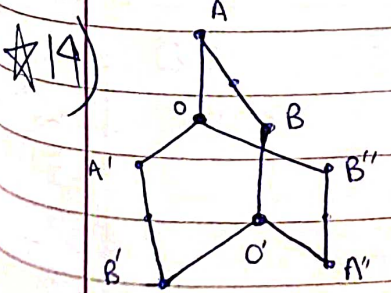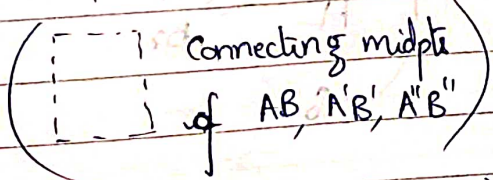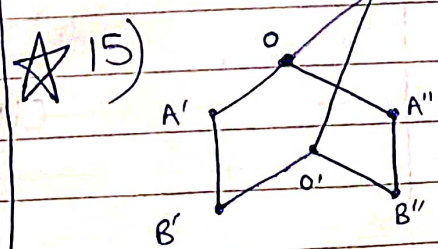
2 PoS

(Aoo' , Connect midpts of A'B, A"B & A)

Centre of symmetry:

Pt. thru which any line drawn thru it
∩ the molecule at equal dist.
in opp. dirxⁿ.
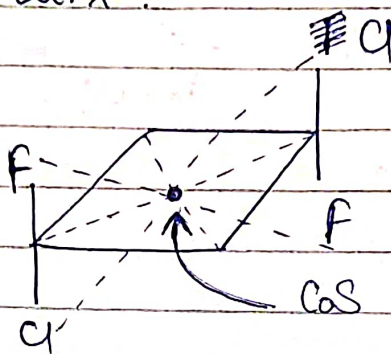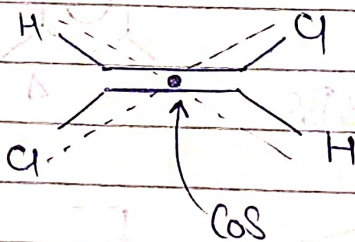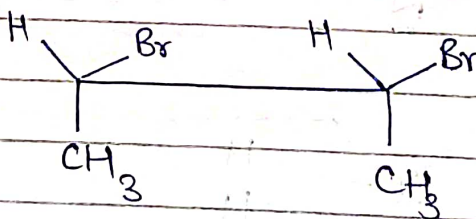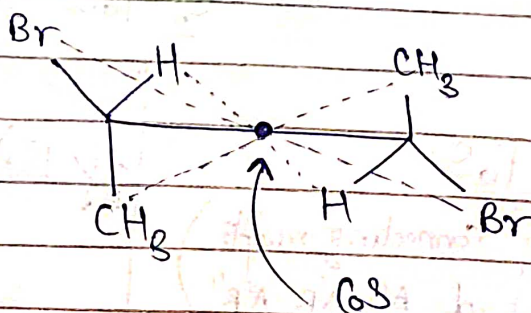
Eg:

CoS

Eg:

CoS

Eg:

CoS ✗

Eg:

CoS

Eg: CoS X   CoS X

Eg: CoS

Eg':

$$CH_3$$
$$H —— Cl$$
$$Cl —— H$$
$$CH_3$$

As fischer proj.

$\Rightarrow$ Eclipse form

$\Rightarrow$ CoS X
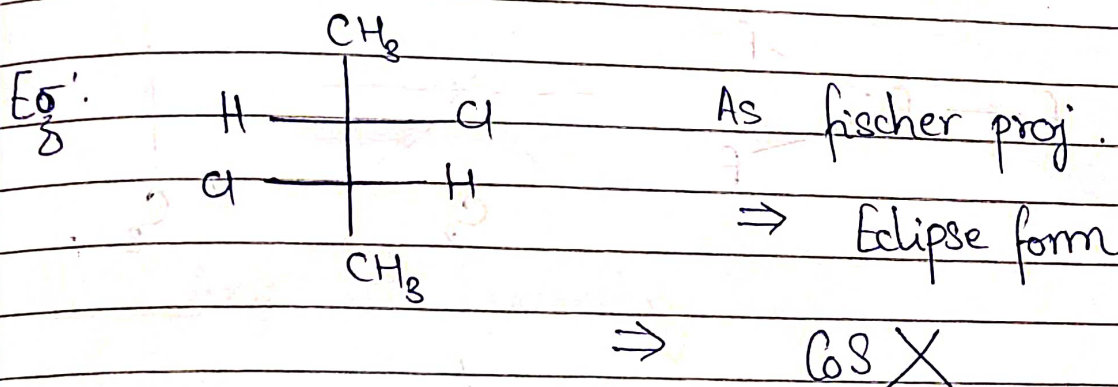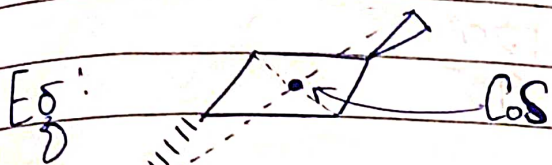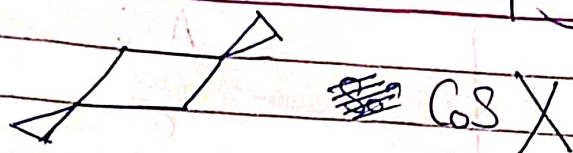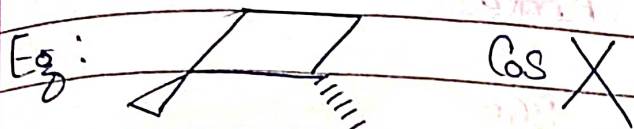
☆ Both CoS & Molecular Symmetry/Slice Cut are ABSENT in fischer proj.

Axis of symmetry:

If a molecule is rotated by $360°/n$ & we get indistinguishable comps., then it is known as axis of symmetry.

Axis	Angle
C_1	$360°$
C_2	$180°$
C_3	$120°$
C_4	$90°$

Eg:

C_2 C_3

Eg:

C_2

Eg:

C_3 C_2

Eg:

C_2, C_3, C_6

Eg:

C_2

Eg:

C_2 $\odot$

Eg:

C_2
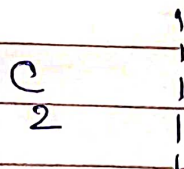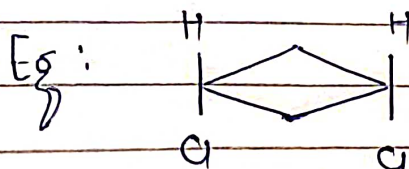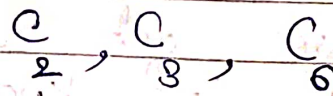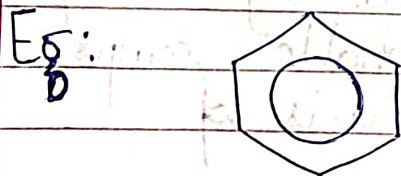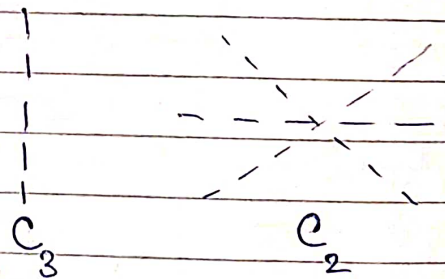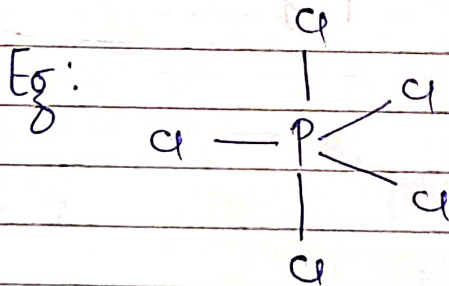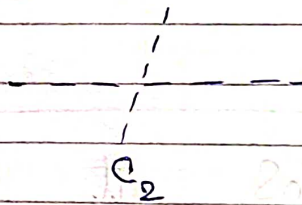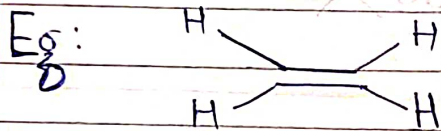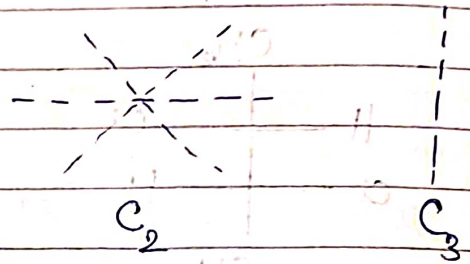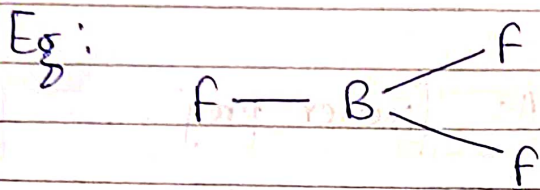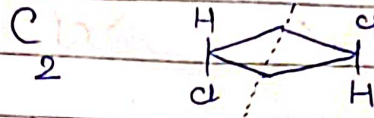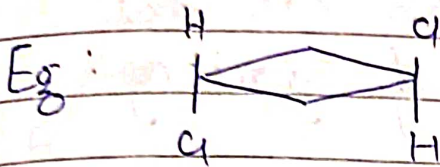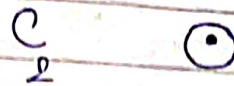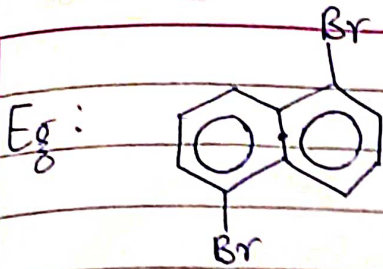
Alt. Axis of Symmetry :

If a comp. is rotated by $360/n$ &
then on drawing mirror image,
we get indistinguishable comp.
then there is presence of alt. axis
of symmetry

Eg: $\xrightarrow[180°]{S_2}$

Same
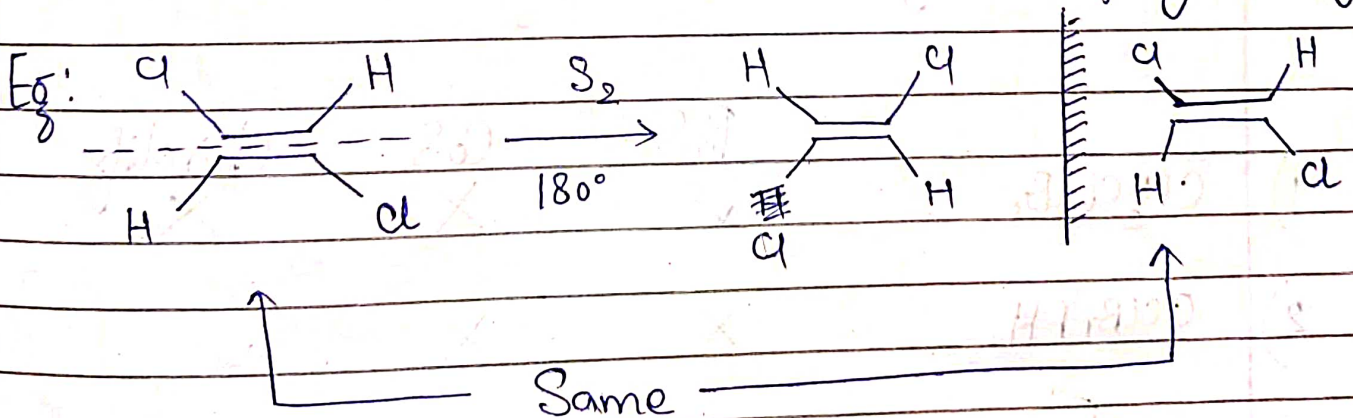
✷ (Mirror & Axis should be Normal
to each other.)

Eg:

Eg:
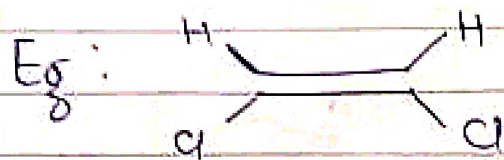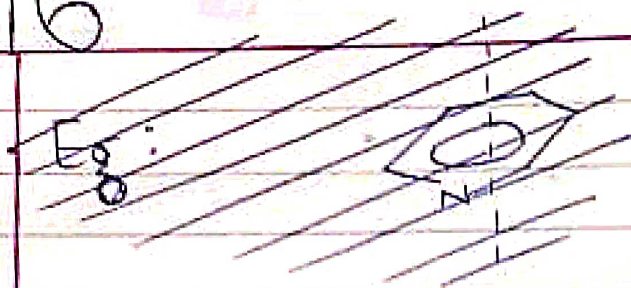
No alt. axis
of symmetry

Chirality & Optical Activity

Chirality is mandatory for molecule
to be optically active.

Cond^n's for : POS $\times$, CoS $\times$, AAoS $\times$
Optical Activity :

		PoS	CoS	Chirality	OA
1)	CH_2ClBr	✓	✗	✗	✗
2)	$CClBrFH$	✗	✗	✓	✓
3)		✓	✗	✗	✗
4)		✗	✗	✓	✓

5)   ✓ ✗ ✗ ✗

6)   ✓ ✗ ✗ ✗

7)   ✓ ✗ ✗ ✗

8)   ✓ ✗ ✗ ✗

9)   ✓ ✗ ✗ ✗

10)   ✓ ✗ ✗ ✗

11)   ✓ ✗ ✗ ✗

12)

13)

14)

15)   ✓   ✓   ✗   ✗

16)   ✗   ✗   ✓   ✓

17)   ✗   ✗   ✓   ✓

☆ 18) $CH_3 - CH_2 - N$ with CH_3 and H substituents

Chiral centre

   ✗   ✗   ✓   ✗
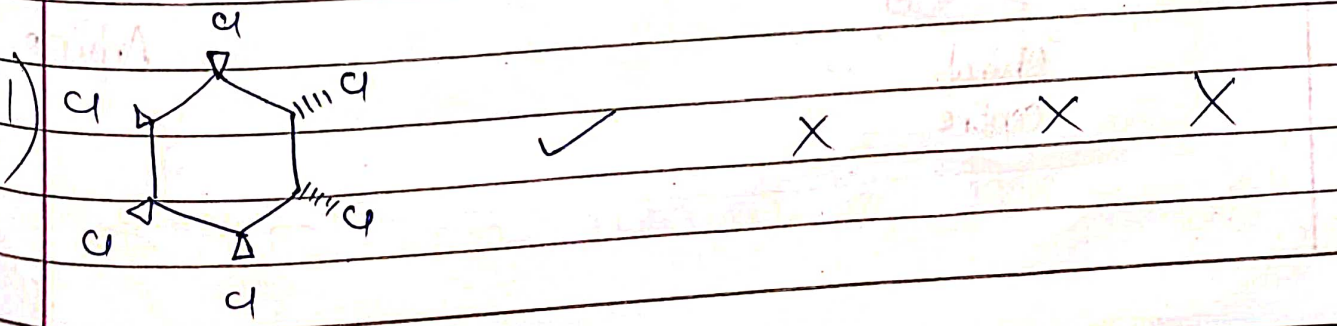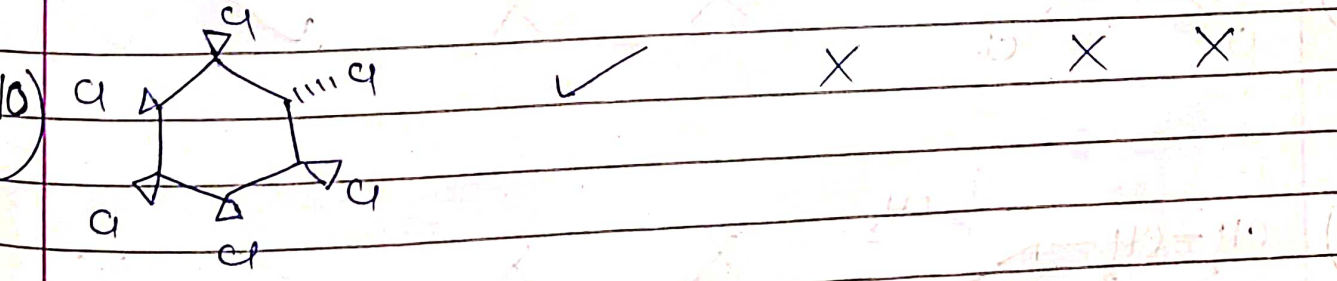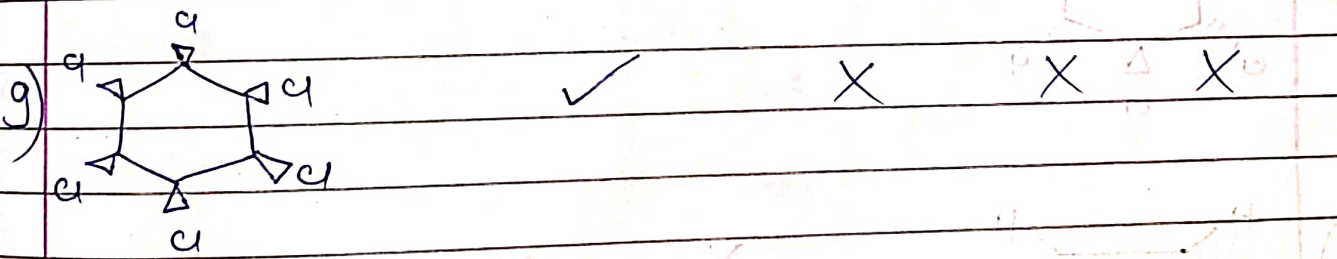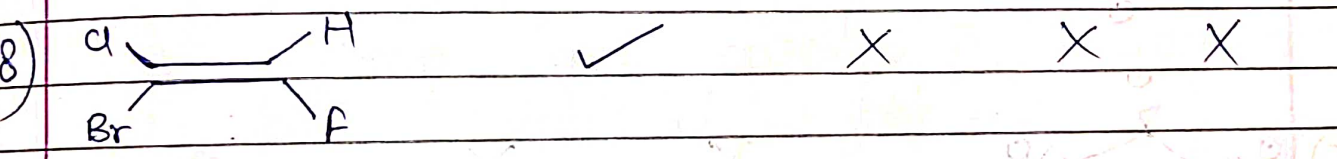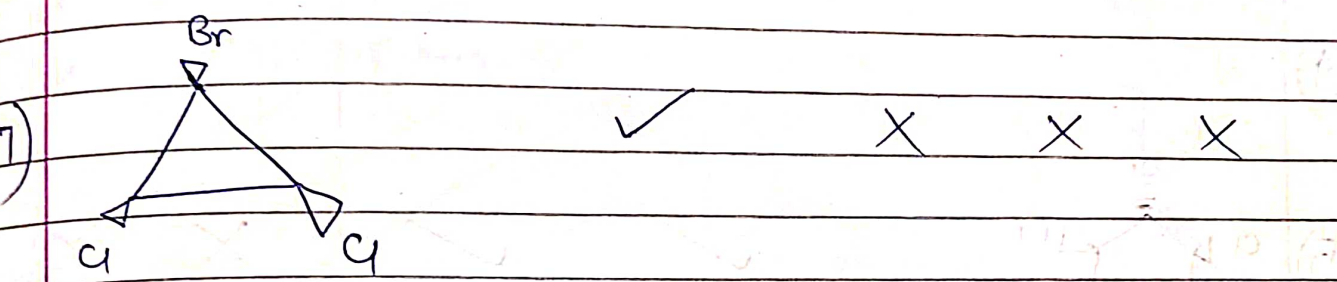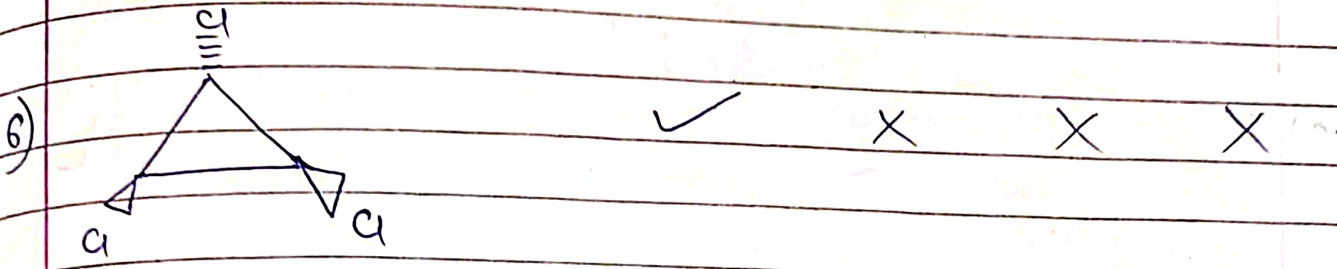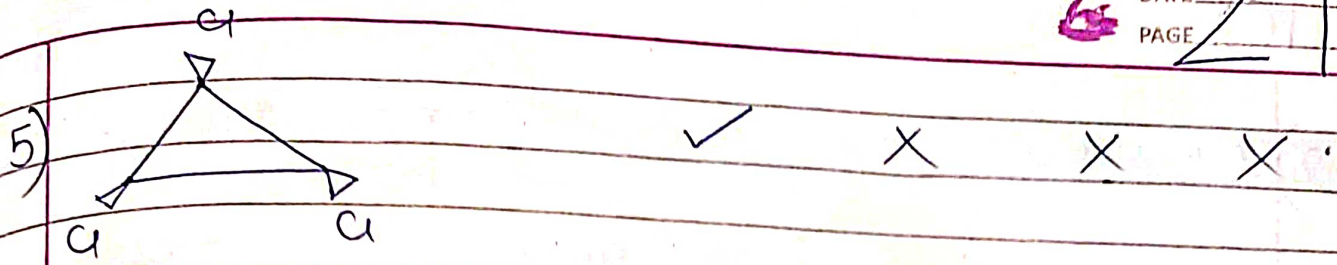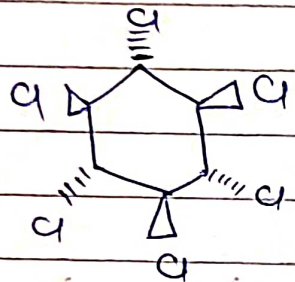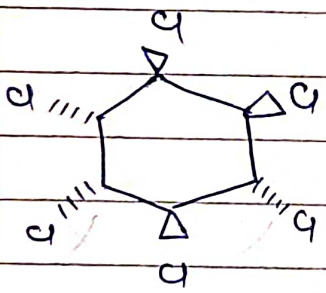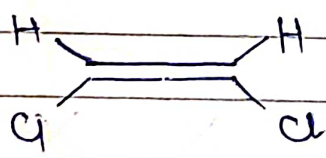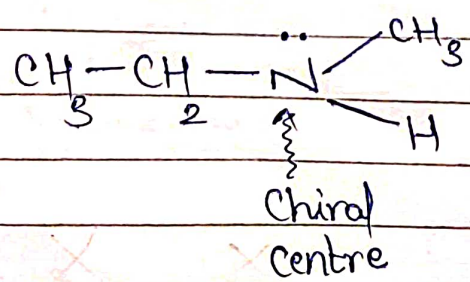
Amine

Meso. comp. & Racemic Mixture

Meso — Any comp. with $\cancel{2}$ chiral centre & at least 1 PoS or CoS.
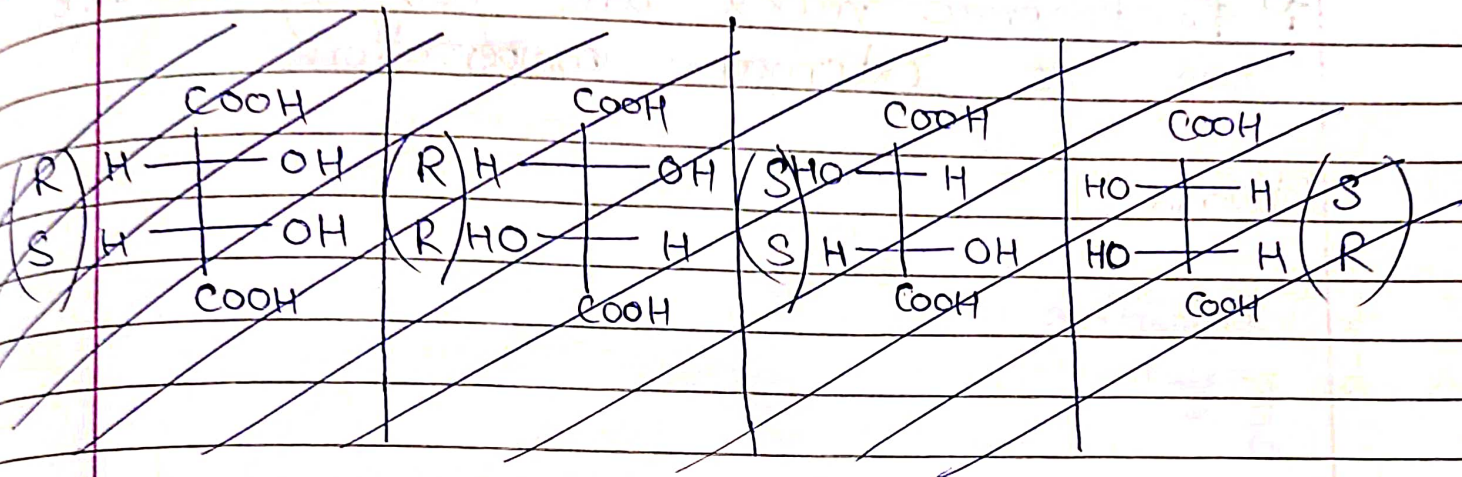
Meso. comp. are optically Inactive due to internal compensation.

Observe,
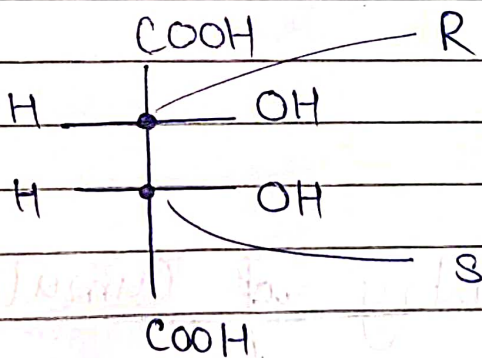
✱ Chiral centres are symmetric about PoS.

If one tries to rotate $\circlearrowright$, other compensates by $\circlearrowleft$.

→ No net rotation on PPL.
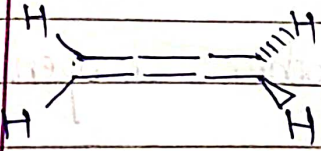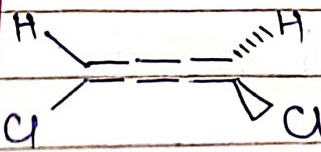
Racemic Mix. — Equimolar mix. of 2 enantiomers is known as racemisc mix.

Racemic mix.s are optically Inactive due to external compensation

Observe,

Stereochemistry of Cumulene

	PoS	CoS	Chirality	Chiral Centre	G.I
1)	✓	✗	✗	✗	✗
2)	✗	✗	✓	✗	✗

3) ✓ ✗ ✗ ✗ ✓
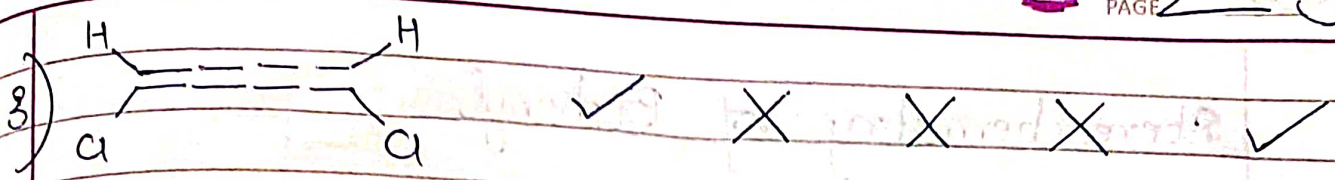
★ If π bonds replaced by ring, basic geometry remains same. (even no.)

(and connect C at diametrically opp. ends in ring)

	PoS	CoS	Chirality	Chiral Centre	G.I.
1)	✗	✗	✓	✗	✗
2)	✗	✗	✓	✓	✓
3)	✗	✗	✓	✓	✓
4)	✗	✗	✓	✓	✗
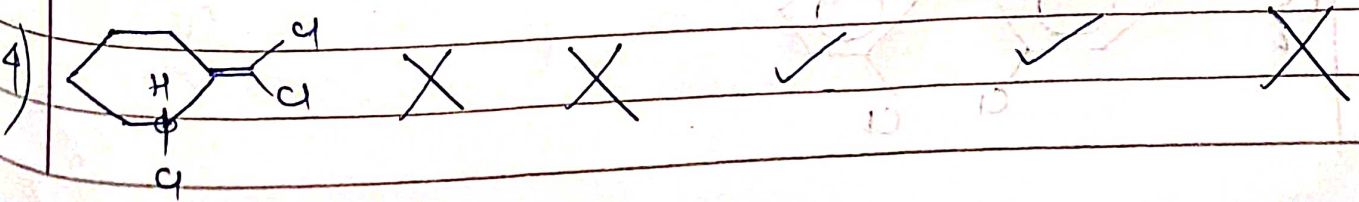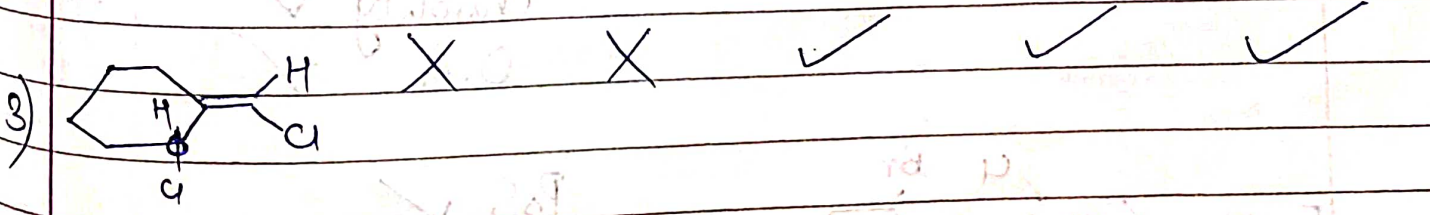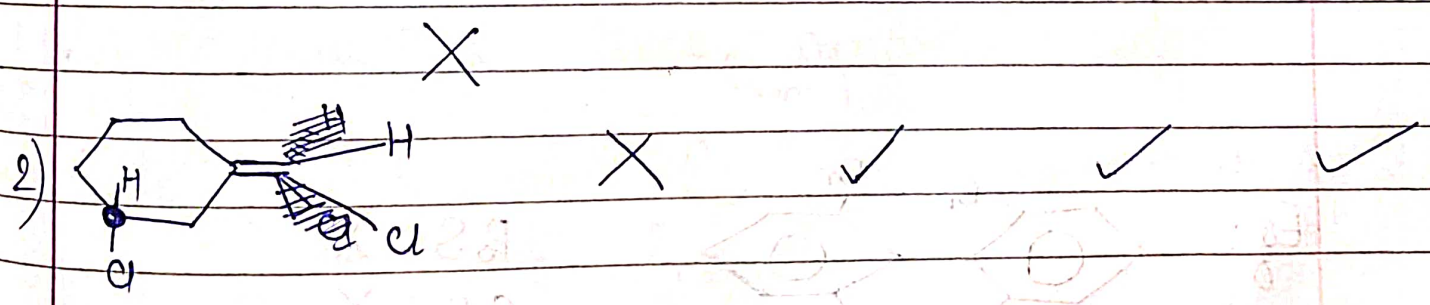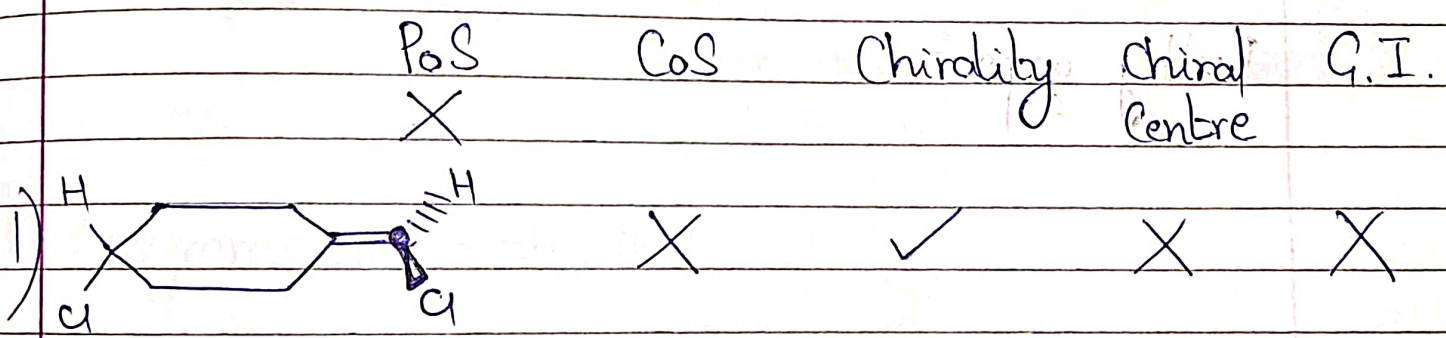
Stereochemistry of Biphenyl
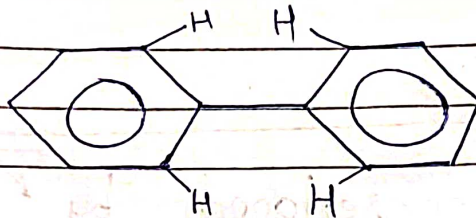
✷ As of now rings are in same plane.

If atleast 3 H at ortho post. substituted with bulky grps, then rings become ⊥.

Bulky grps :

Eg:

PoS X
CoS X
Chirality ✓
O.A. ✓

Eg:

PoS ✓

Calc. of no. of Stereoisomers

```
          ┌─────────────────────────┐
          │    Stereogenic region   │
          └─────────────────────────┘
         ┌──────────────┴──────────────┐
┌───────────────────────┐      ┌──────────────────┐
│  Geometrical Centres  │      │  Chiral centre.  │
└───────────────────────┘      └──────────────────┘
```

(double bonds around
 which G.I. possible)
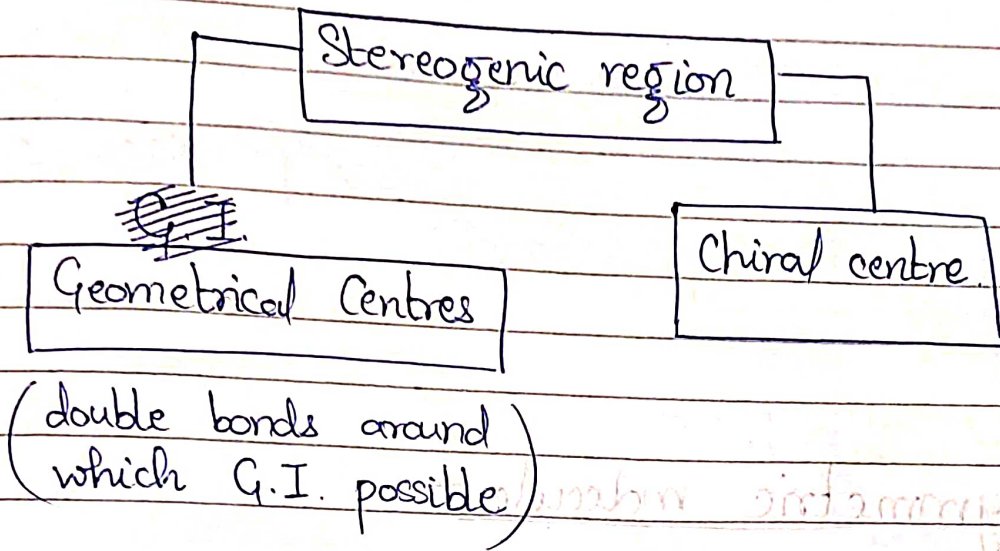
Stereogenic region — Around which ~~GT o~~ stereoisomers are possible.

1) Assymmetric molecule —
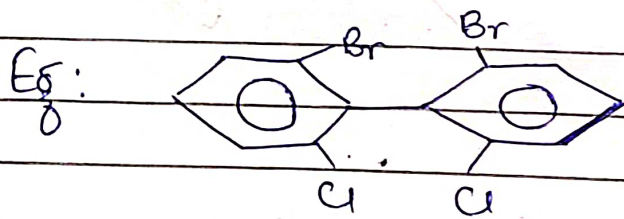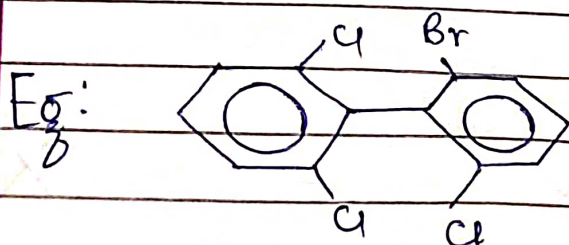
Chain: Pick terminal C, move one C at a time, comparing ends.
(from both ends)

Cycle: Pick one C, move around it (one at a time) comparing 2 at a time.

$$\boxed{\# \text{ Stereoisomers} = 2^n}$$

n = No. of stereogenic regions.

2) <u>Symmetric molecule</u> —

Cl: n = even

(if chiral centres there)

$$\left(\# \text{ Optically Active isomers}\right) = 2^{(n-1)}$$

$$\left(\# \text{ Optically Inactive isomers}\right) = 2^{\left(\frac{n}{2}-1\right)} \text{ (Meso.)}$$

$$\left(\begin{array}{c}\text{Total} \\ \text{stereoisomers}\end{array}\right) = \begin{array}{c} 2^{(n-1)} \\ + \\ 2^{\left(\frac{n}{2}-1\right)} \end{array}$$

for <u>ANY</u> case

Eg:

C2: $n = odd$

Middle Carbon

Geometrical Centre

Chiral centre
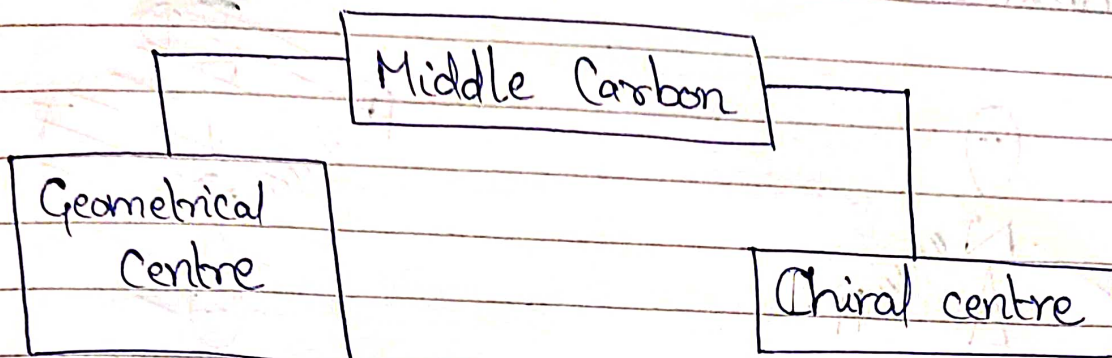
$$Total = 2^n - 2^{\left(\frac{n-1}{2}\right)}$$

$$Total = 2^{(n-1)}$$

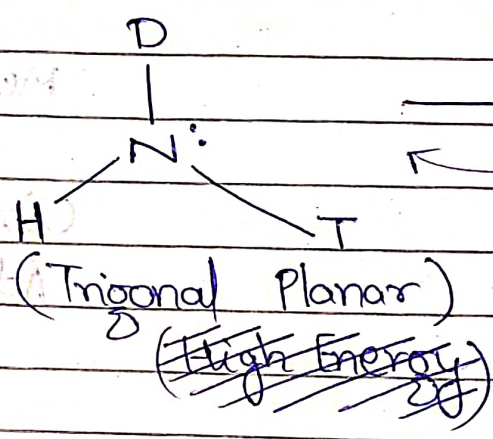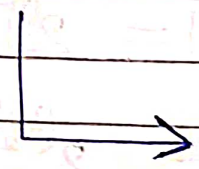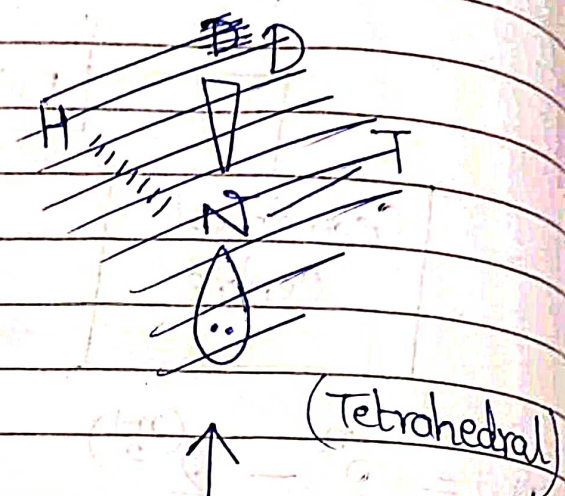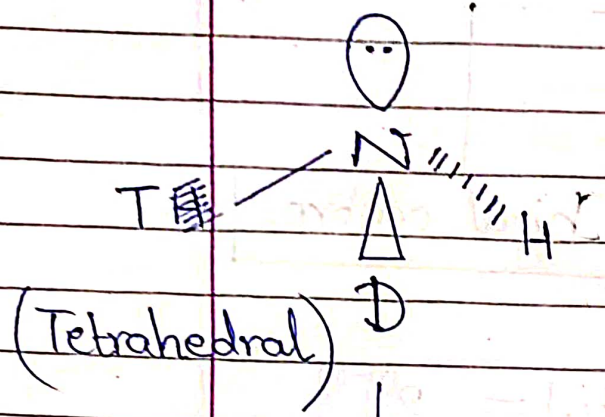$$Meso. = 2^{\left(\frac{n-1}{2}\right)}$$

$$Optically\ Active = 2^{(n-1)} - 2^{\left(\frac{n-1}{2}\right)}$$

Amine Inversion

(Tetrahedral)

(Trigonal Planar)

~~(High Energy)~~

← High Energy!

(Tetrahedral)
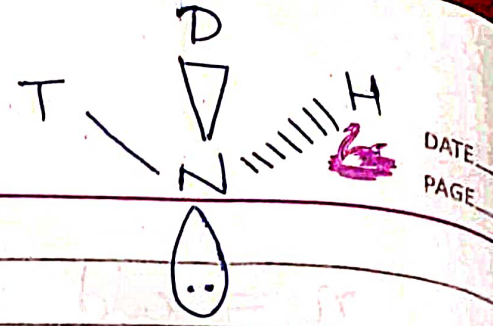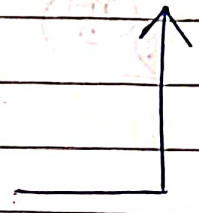
Observe 1st comp. is 'R' & 2nd comp. is 'S'. Still these are NOT enantiomers as these can interconvert into each other

This happens regardless of whether comp. is chiral or not.

i.e. inversion happens in $\ddot{N}H_3$ as well.