

06/06/17

{H.W: Page 14
E-2 full E.D.E}

Isomerism:

*

Isomerism:

SBG STUDY

Isomer

Iso

mer

⇓

⇓

Same

Part. (M.F)

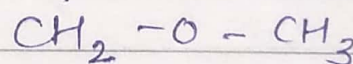
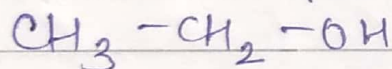
Compounds having same molecular formula but different properties are known as ~~Isomerism~~ Isomers. And the topic in which we study about Isomers is known as Isomerism.

Ex 1

C_2H_6O

gas

Liquid



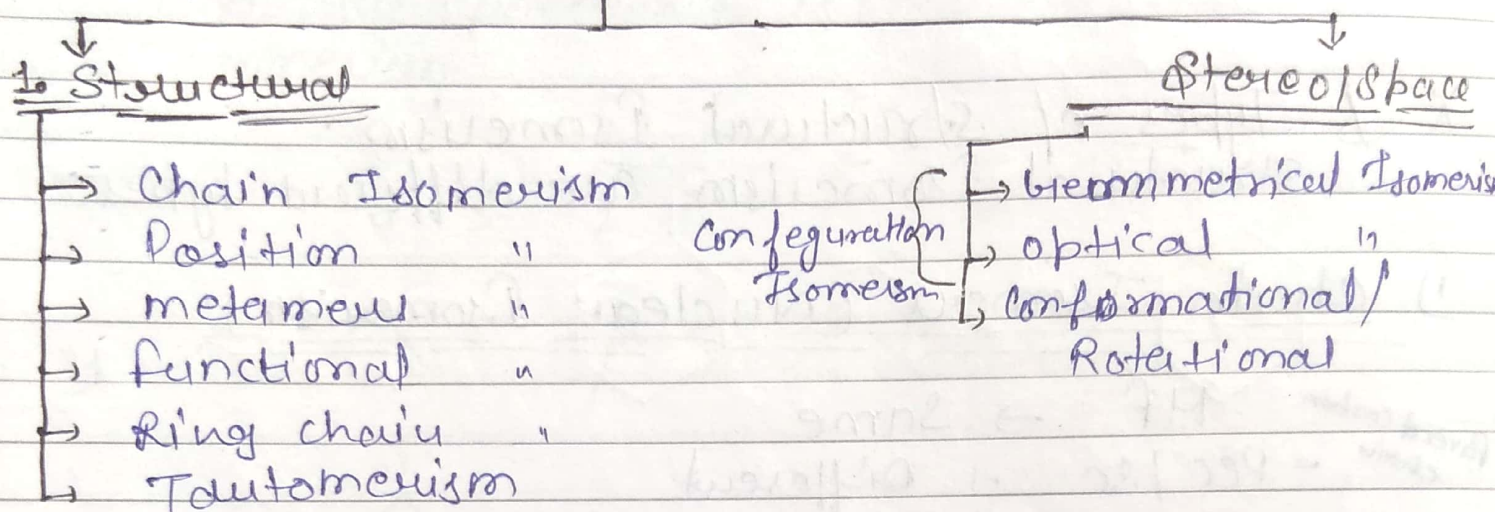
- Ethanol (Ethyl alcohol)
- Alcohol
- N.P
- When treated with Na-metal evolve H_2

- methoxymethane (Dimethyl ether)
- Ether
- P
- Naki

* Characteristic / Properties of Isomers!

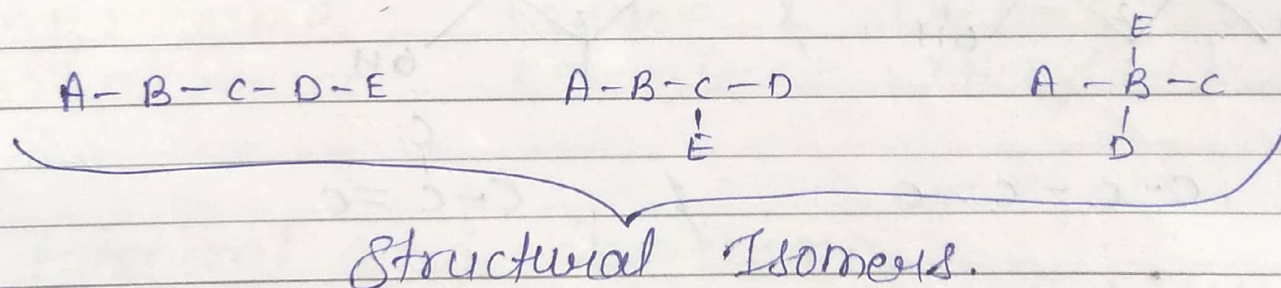
- They have same molecular formula
- They have same molecular weight.
- They have different physical or chemical or both properties
- They have same general formula.
- They have different name

* Types of Isomerism:

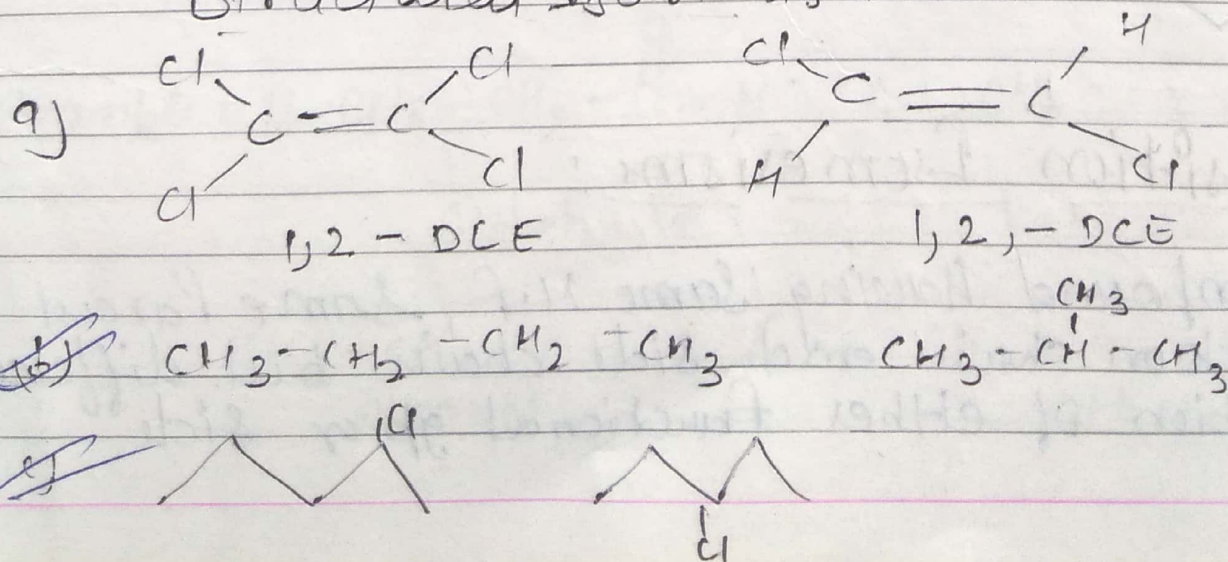


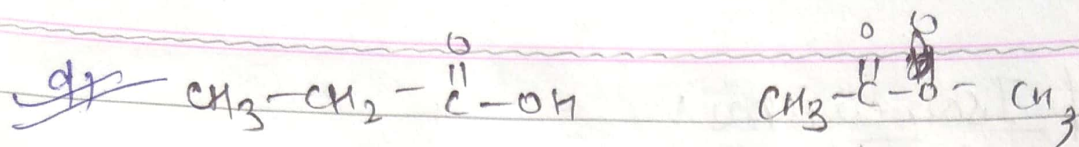
* Structural Isomerism: Constitutional Isomerism

Compounds having same m.f but different structure are known as structural isomerism and the phenomena as structural isomerism.



Ques: Which among following pair are/is structural isomerism.



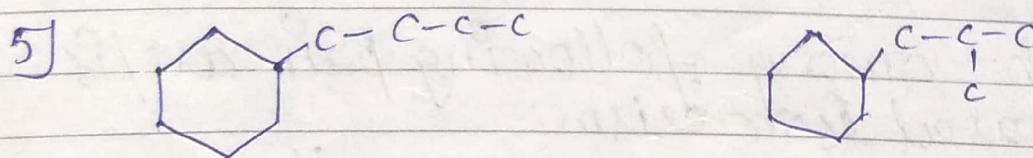
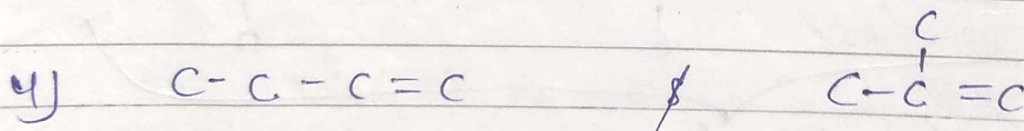
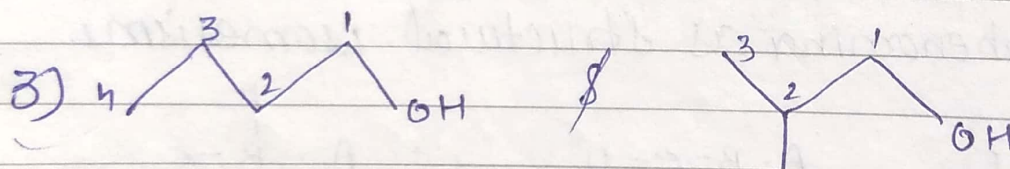
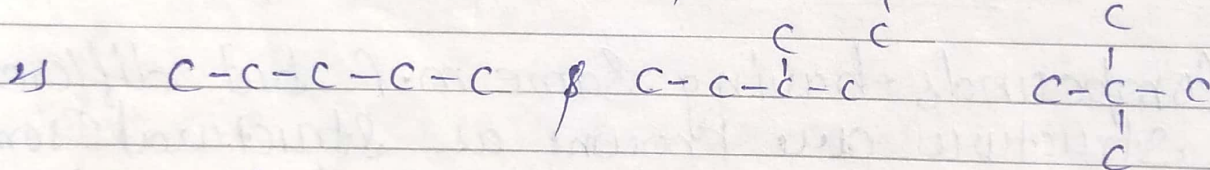


* § Types of Structural Isomerism:
structural isomerism are different types

1) Chain Isomers (Nuclear Isomerism):

Parent carbon chain $\rightarrow$ PCC / SC $\rightarrow$ Same
MF $\rightarrow$ Different

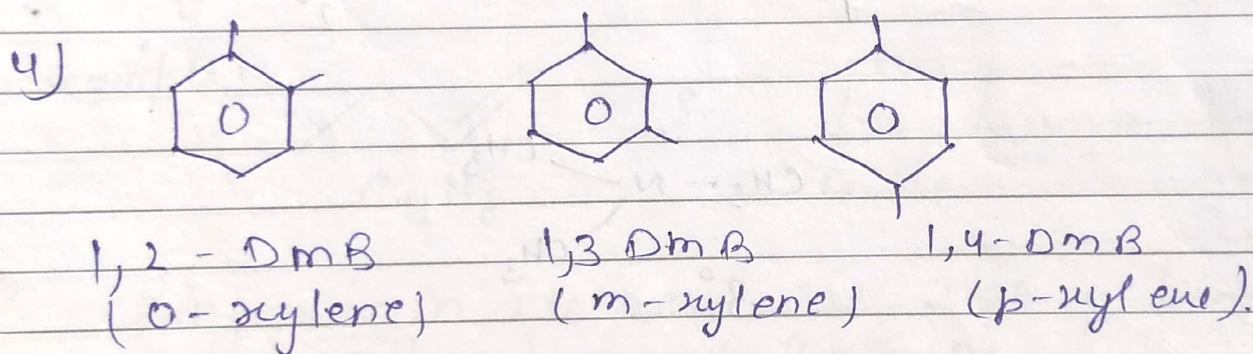
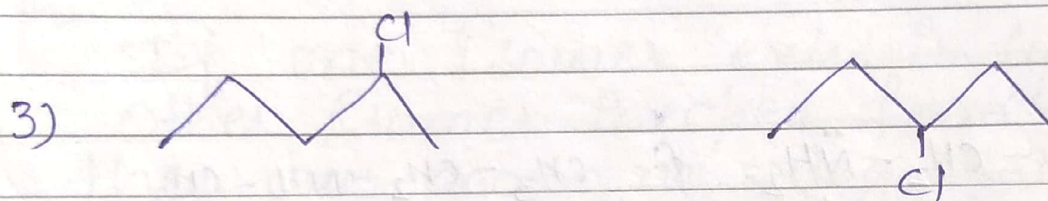
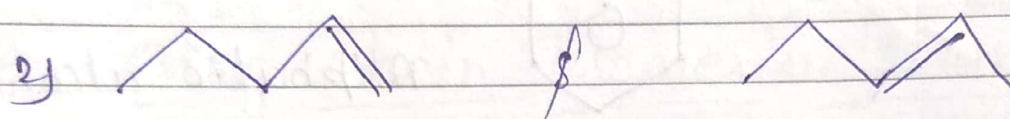
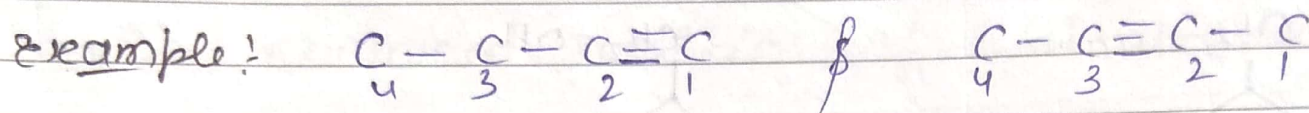
Example: $\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$ $\neq$ $\text{C}-\text{C}-\text{C}$



2) Position Isomerisms:

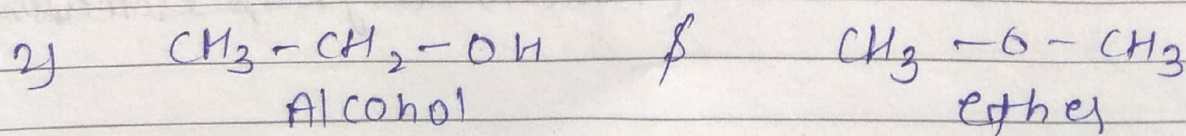
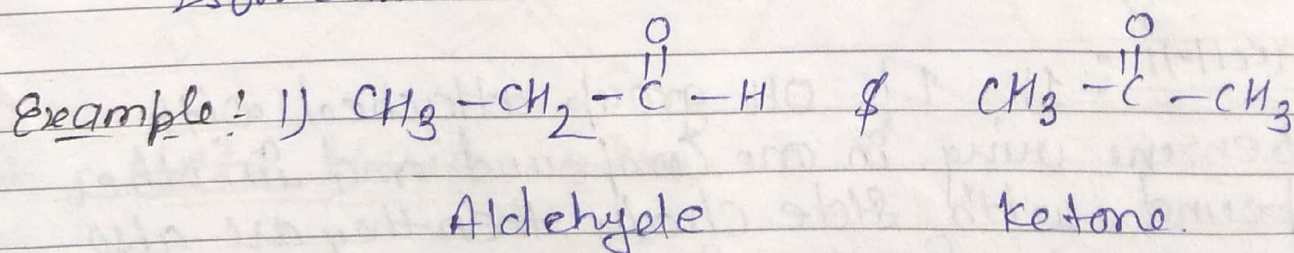
Compound having same M.f, same Parent carbon chain and side chain but different position of either functional gp or side

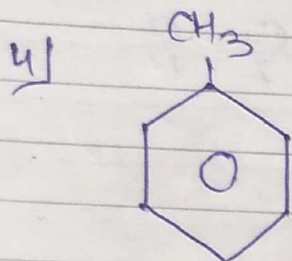
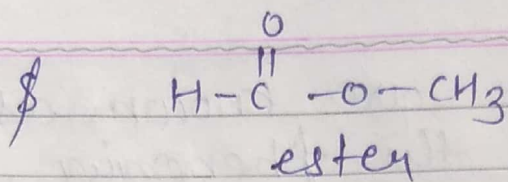
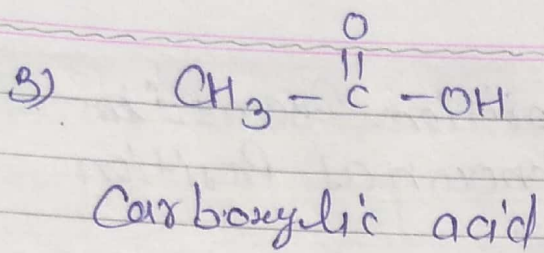
group are known as Position Isomerism and the phenomena is known as Position Isomerism.



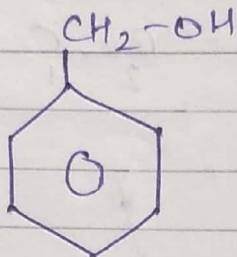
* Functional group Isomerism

The comp. having same M.f But different functional group are known as functional Isomerism.

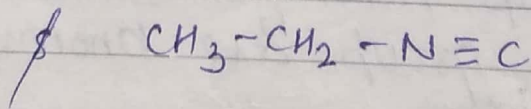
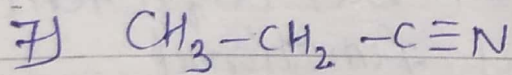
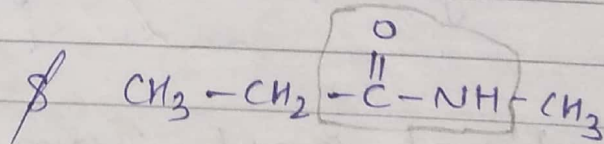
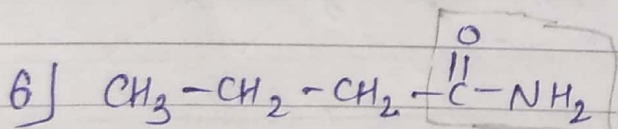
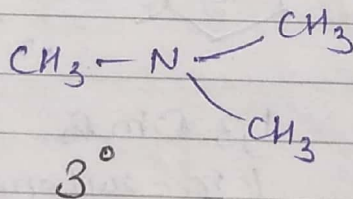
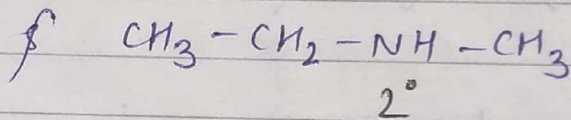
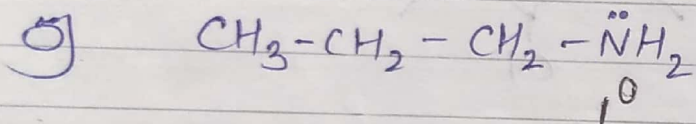




Phenol



Aliphatic alcohol.



सादृश्यता :- 1) If OH group attached with benzene ring in one compound and in other compound with side chain then they are also known as FGI (functional group isomerism)

2) 1° , 2° , 3° amines and amide are also functional isomerism to each other. If their m.f are same.

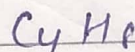
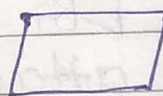
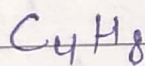
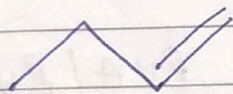
3) The chemical reactions of FGI are different

* Ring-Chain Isomerism / Isomers. ^(Functional)

If one Isomer exist in cyclic form and other Isomer in open form chain then they are known as ring chain Isomers.

Example!

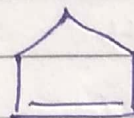
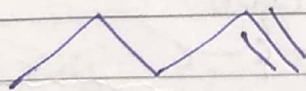
1)



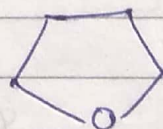
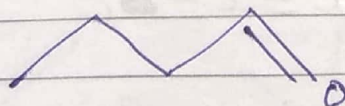
Ring-chain Isomers are also a kind of functional group Isomers.

Example!

2)



3)



* Meta Metisims! ~~Met~~

* Meta merism:

* Monovalent atom: $-\overset{\overset{O}{\parallel}}{C}-$, $-O-$, $-\overset{\overset{O}{\parallel}}{C}-O-$

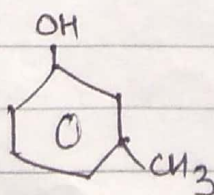
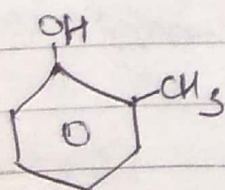
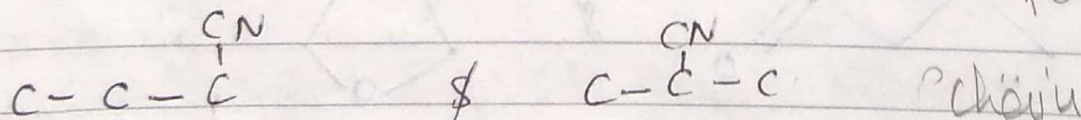
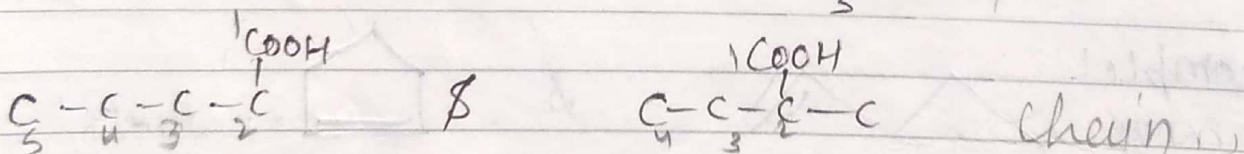
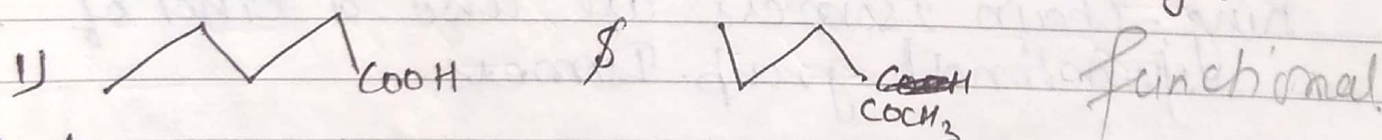
* Poly valent group: $\swarrow -\overset{\overset{O}{\parallel}}{S}(=O)_2-O-$, $-\overset{\overset{O}{\parallel}}{C}(=O)-O-\overset{\overset{O}{\parallel}}{C}(=O)-$ 

Compound having same mf, same structural formula But Different nature of group / both group attached with poly valent atom or Polyvalent group are known as metamers and the phenomena is called meta merism.

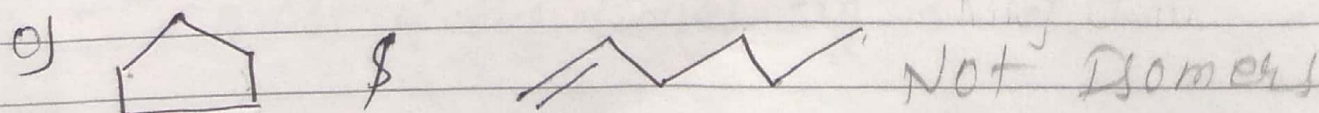
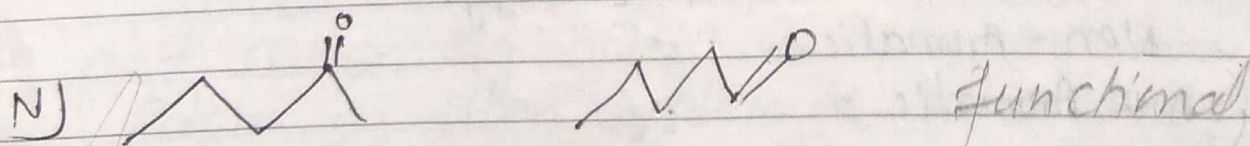
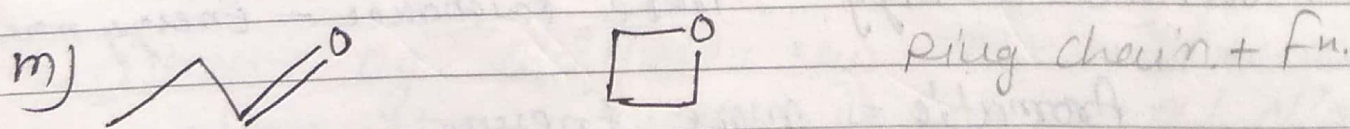
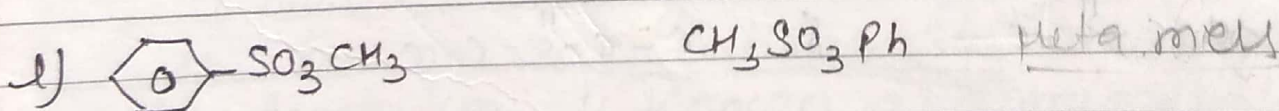
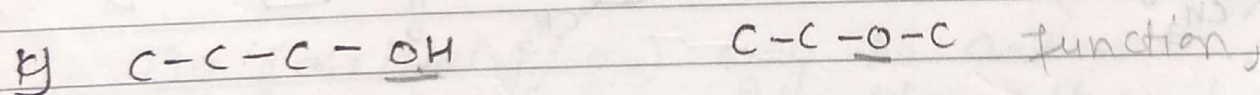
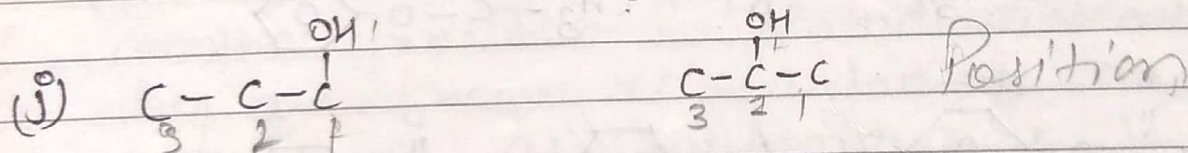
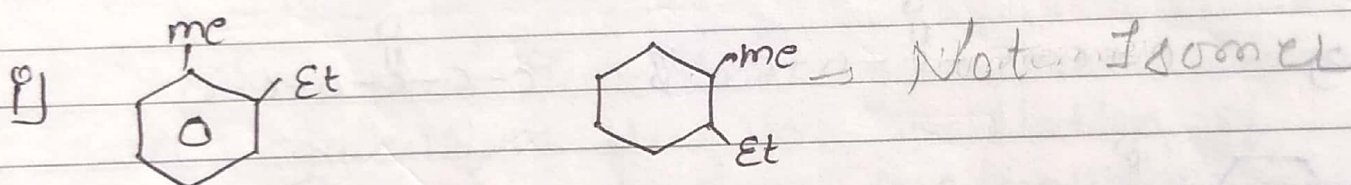
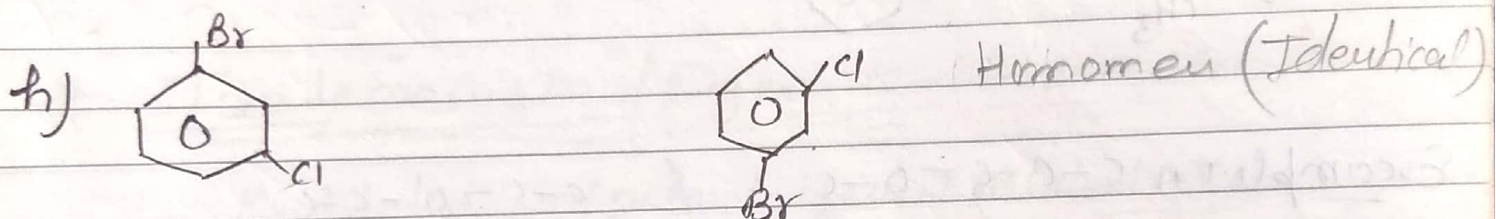
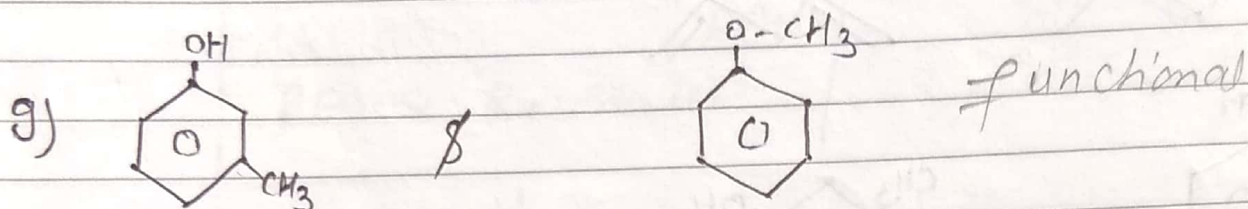
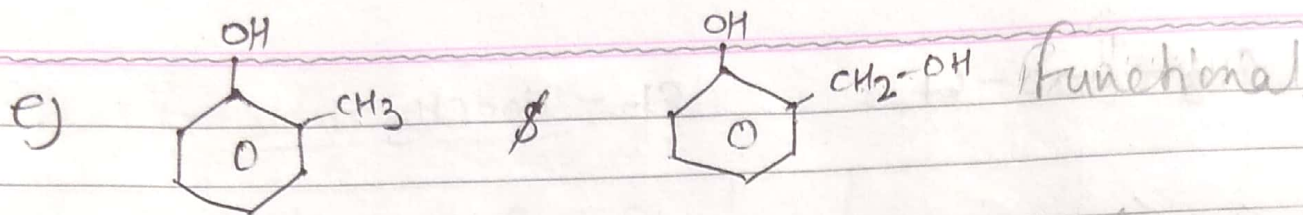
mf $\rightarrow$ Same
flr $\rightarrow$ Same.

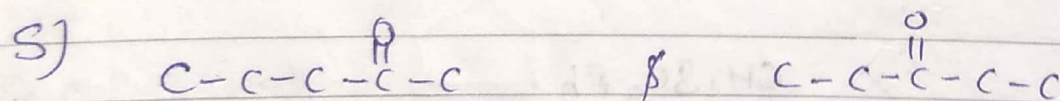
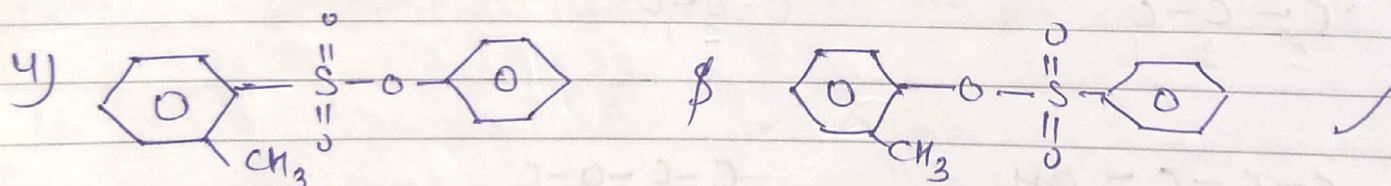
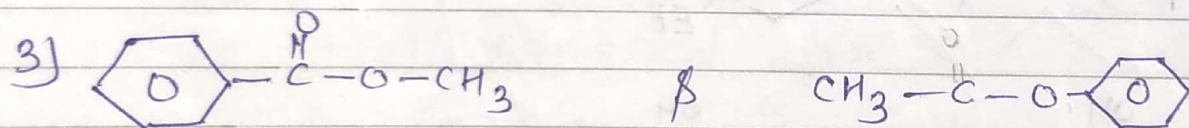
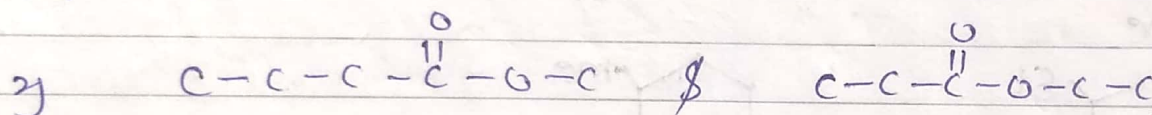
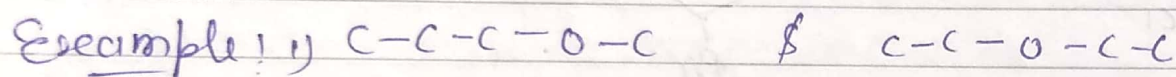
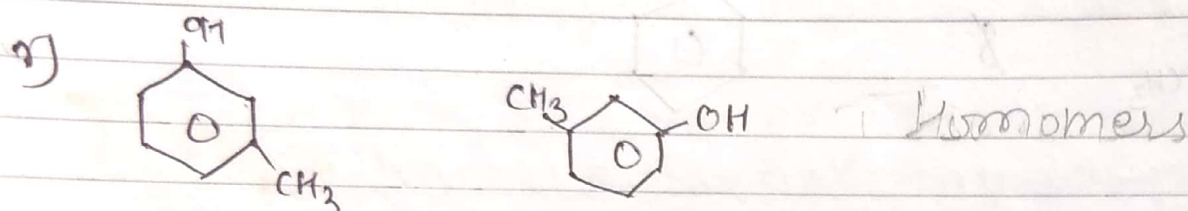
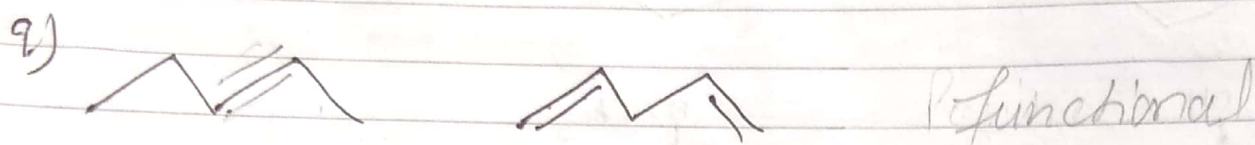
Both group attached with PVA / PVB $\Rightarrow$ Diff.

Ques! Identify Isomerism in following pairs.



Position





* Resonance energy! more Resonance - Energy more

Aromatic $\Rightarrow$ more Energy.

Non-Aromatic $\Rightarrow$

Anti Aromatic $\Rightarrow$

* Resonance Energy:

$RE \propto A \cdot N \propto \frac{1}{A \cdot N}$
$RE \propto \text{Resonance}$

* Tautomerism / Dynamic - Isomerism

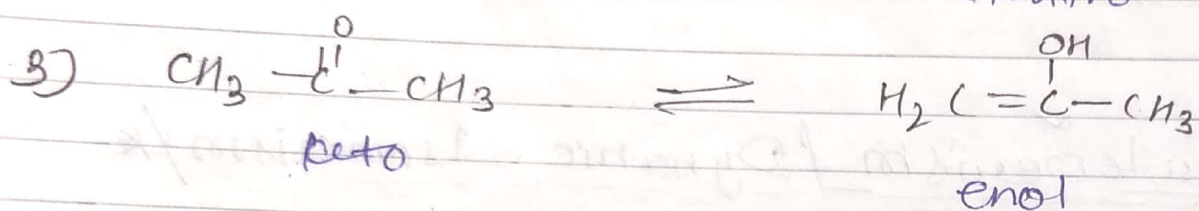
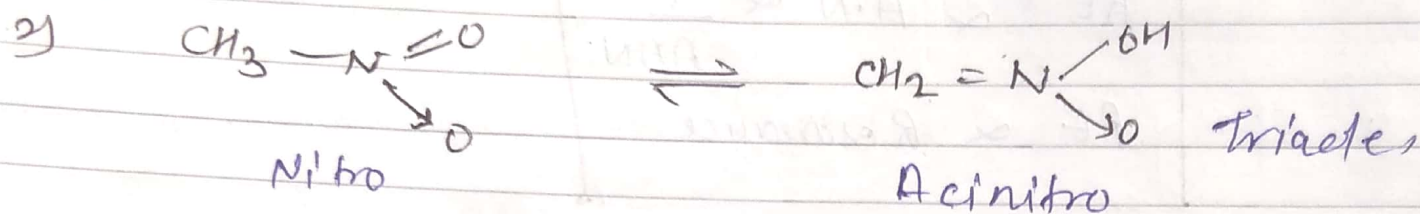
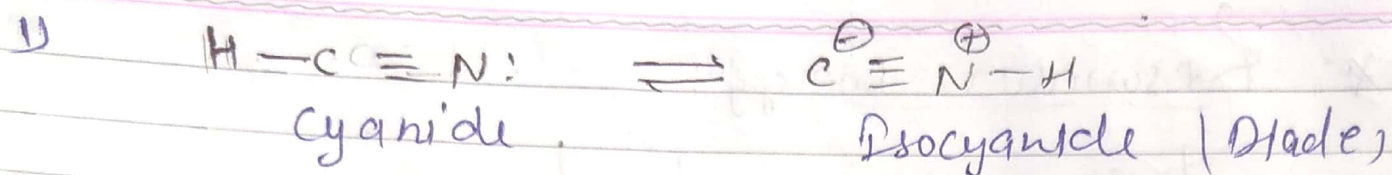
Kryptotropism / Desmotropism / Allelotropism

When two functional gp isomers becomes in equilibrium due to oscillation of an atom or group from one position to another position in same molecules then they are known as tautomers and the phenomena as tautomerism.

* Og (oscillating / gp) may be cation or may be anion. When og is cation then tautomerism is known as cationtropy and when og is anion tautomerism is known as aniontropy.

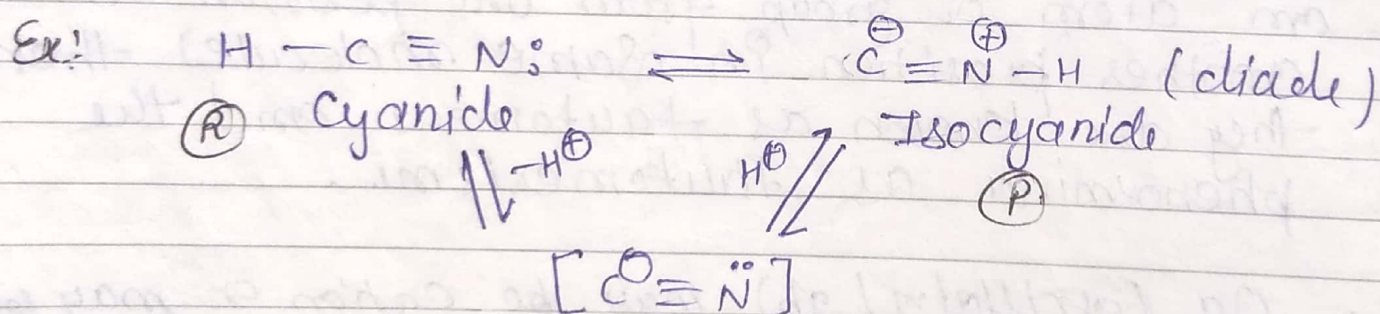
When og oscillate b/w one and two atom then system is known as diade. and when og oscillate b/w one and three atom then system is known as triade.

In most of the cases og is H^+



* Tautomerism is of following type:

(i) Cyanide & Isocyanide Tautomerism:



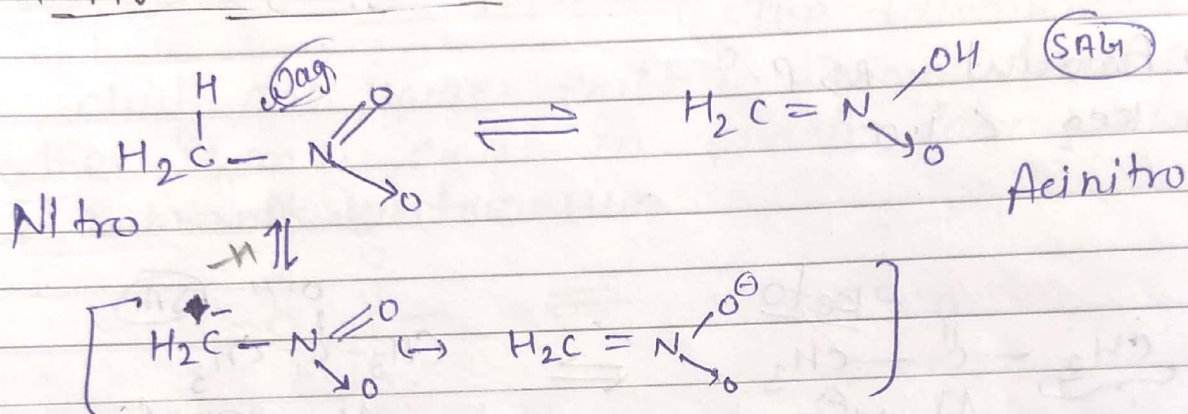
• Amount of $\text{H}-\text{C}\equiv\text{N:} > \text{C}^{\ominus}\equiv\text{N}^{\oplus}-\text{H}$

• $\text{K}_{\text{eq}} = \frac{[\text{P}]}{[\text{R}]} = \frac{[\text{C}^{\ominus}\equiv\text{N}^{\oplus}-\text{H}]}{[\text{H}-\text{C}\equiv\text{N}]}$

• $\text{K}_{\text{eq}} < 1.0$

Note! Tautomerism is a Intramolecular ABR in this process that tautomer is major which have less Acidic and Basic group.

2) Nitro - acinitro!

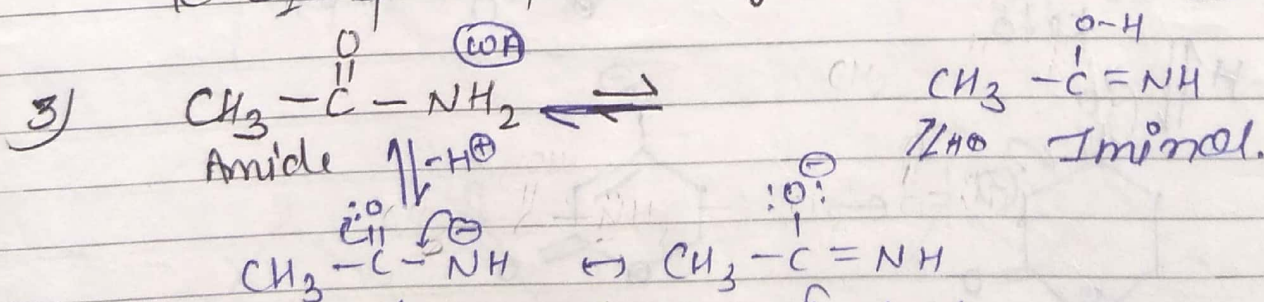


* Method to make Tautomer!



- Amount order Nitro > Acinitro
- Keq < 1.0

Ques! Make Tautomer, decide major, minor and Keq for following compound. (SA)

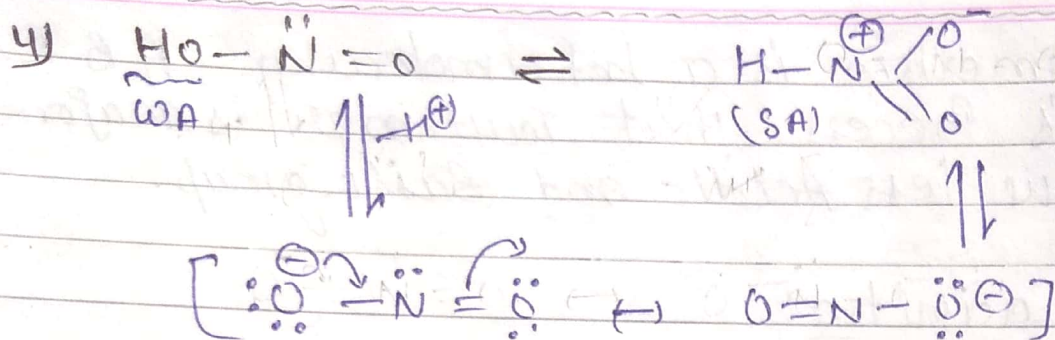


- Amount order = Amide > Iminol.
- Keq: $\frac{[\text{Iminol}]}{[\text{Amide}]} =$
- Keq < 1

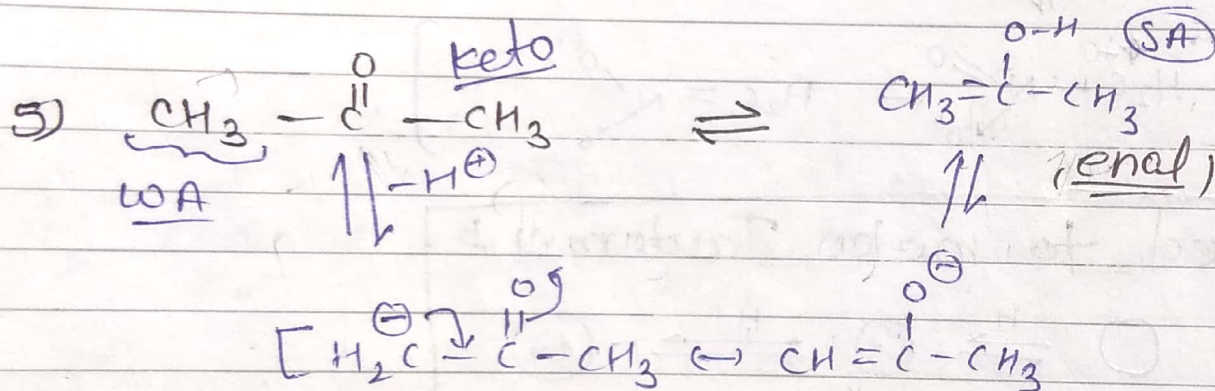
Neutron $\Rightarrow$ WA

(+) E.N $\uparrow$

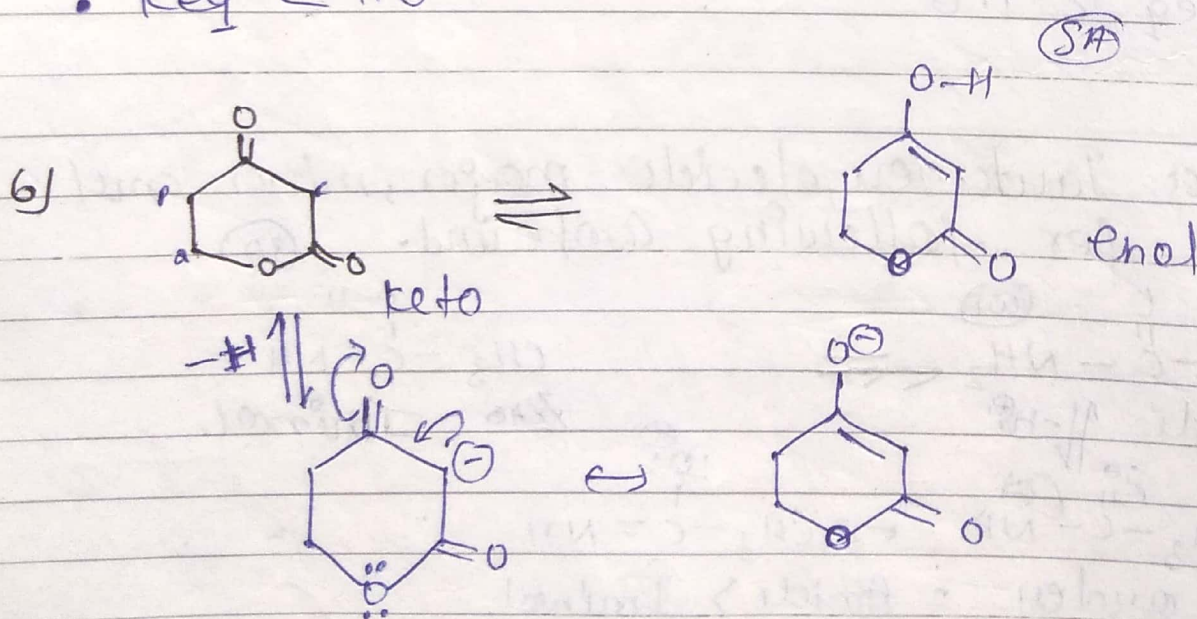
(+) Acid Strong



- Amount $R > P$
- $K_{eq} < 1.0$

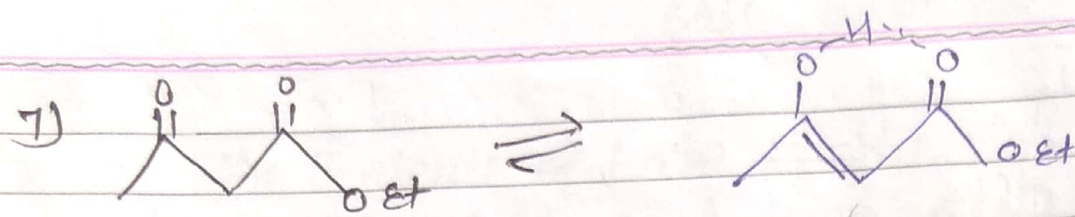


- Amount $\neq$ order: keto $>$ enol.
- $K_{eq} < 1.0$



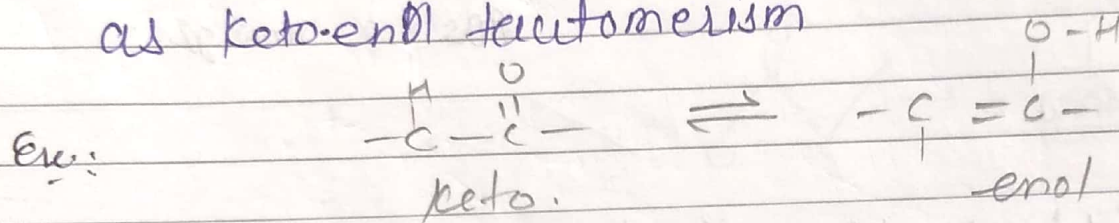
* If enol aromatic, more stable Acid

H-bonding



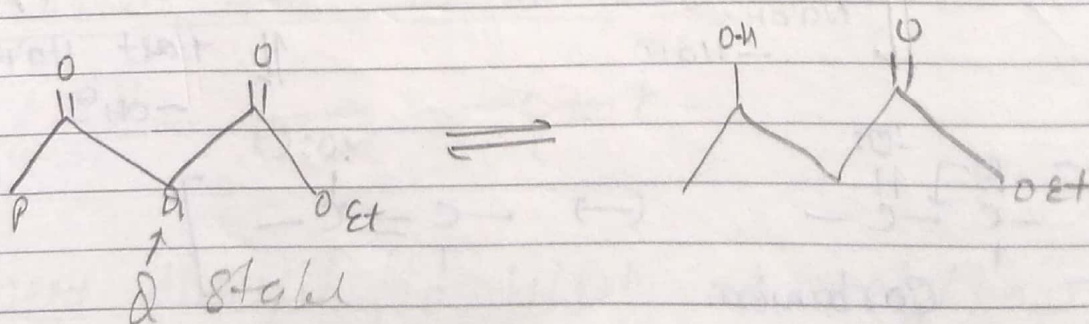
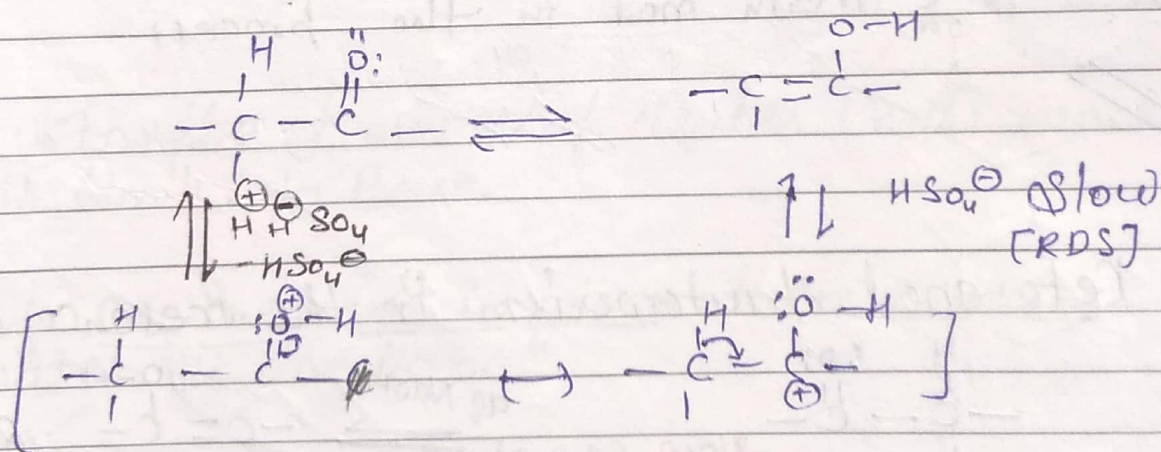
* Keto-enol tautomerism:

The tautomerism in which one isomer exists in ketonic form and another isomer exists in enolic form is known as keto-enol tautomerism.

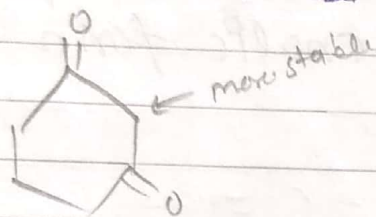
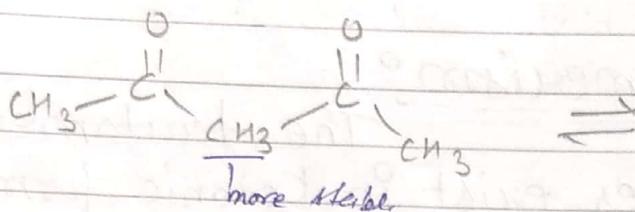
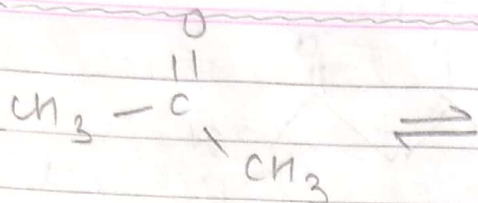


Acid or base or H_2O

* Mech.ⁿ in the Presence of Acid



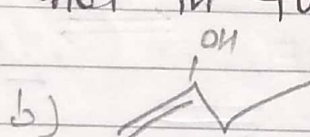
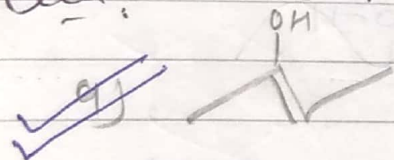
Base + acid $\rightarrow$ acid
 NaOH Base.



RDS $\rightarrow$ slow step.

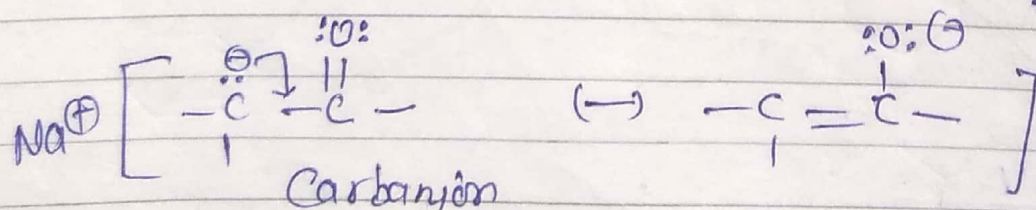
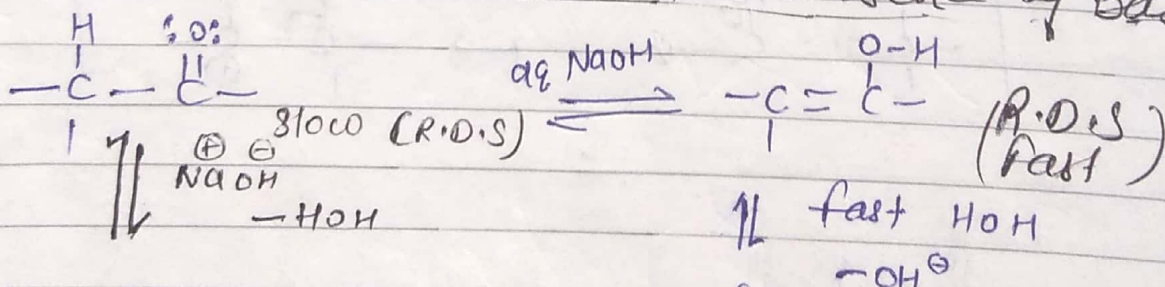
* In acidic medium that enol form ~~nam~~ mainly which is more stable (if there is change of more than one enol in same compound).

Ques! The main ~~not~~ in the process



c) Both d) None

* Keto enol tautomerism In the Presence of Base:

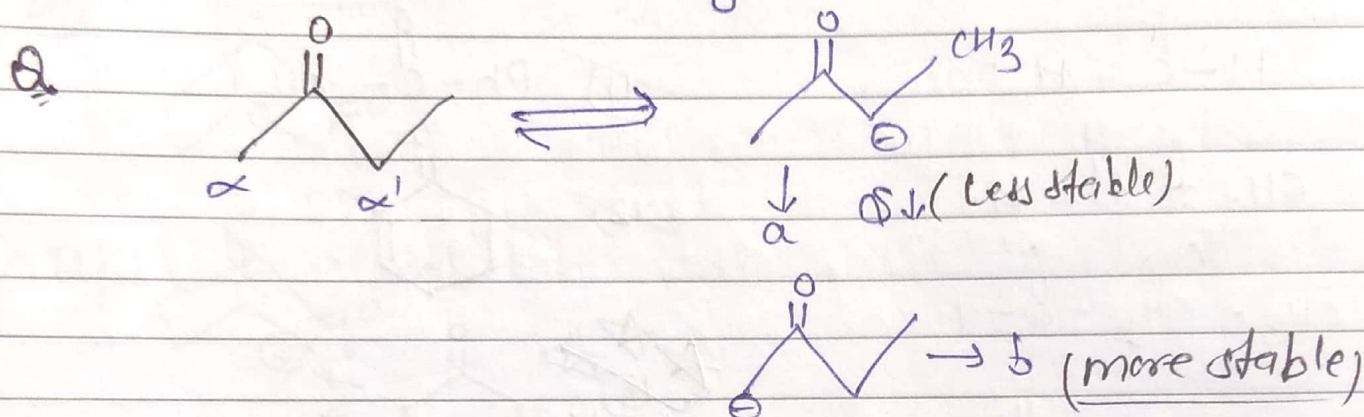


water $\Rightarrow$ semi Base

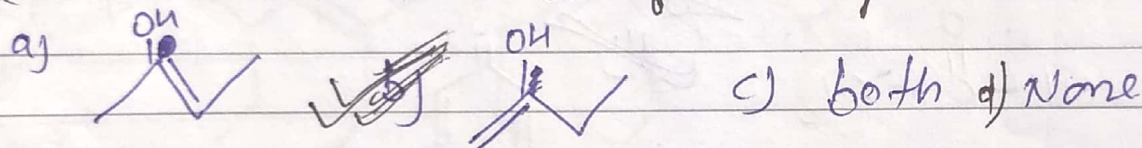
Acid - S. enol

Base = anion stability

* In the presence of base if there is a choice of formation of 2 enol then make that enol which comes strong most stable



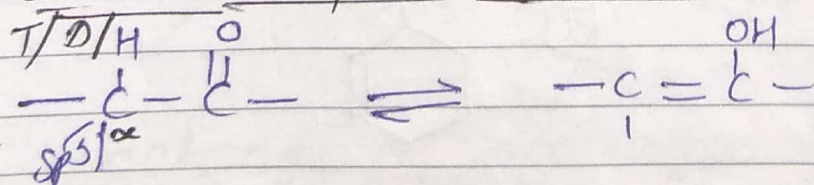
Q the main enol of above process



Note: In the Presence of Water (H_2O) mechⁿ is similar to Base.

* If no medium is given then consider water as medium.

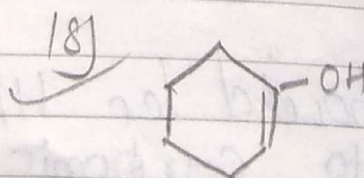
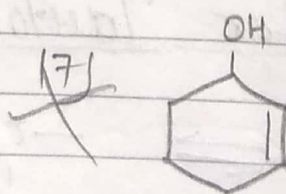
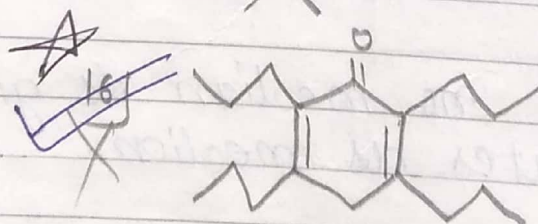
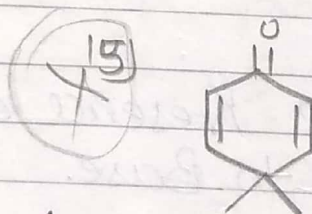
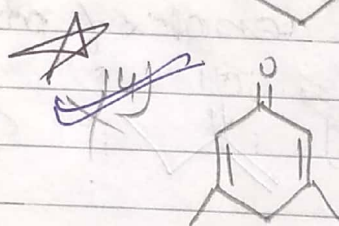
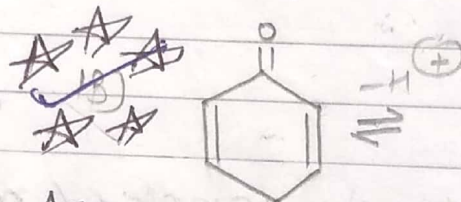
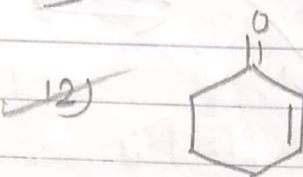
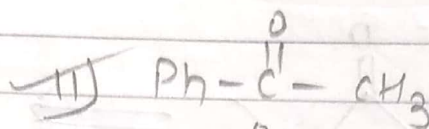
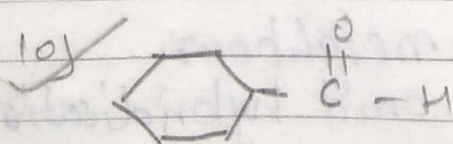
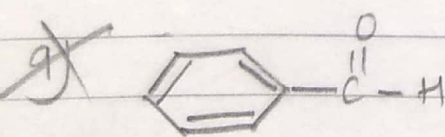
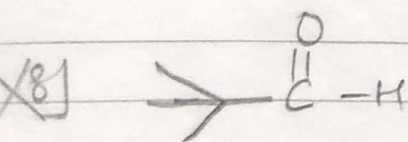
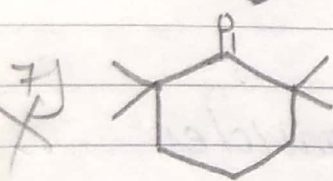
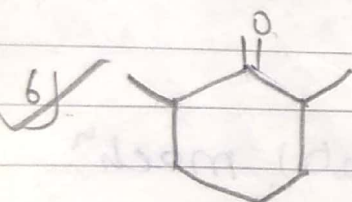
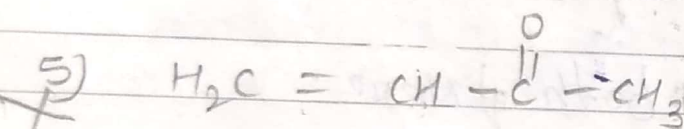
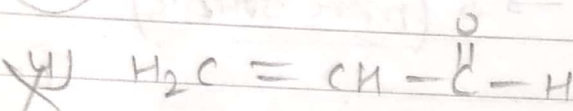
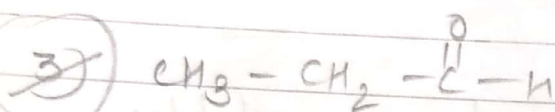
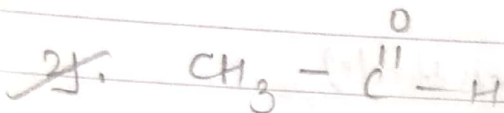
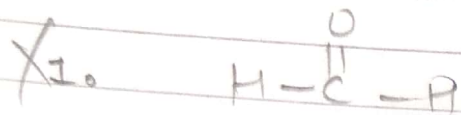
* Condition for Tautomerism:

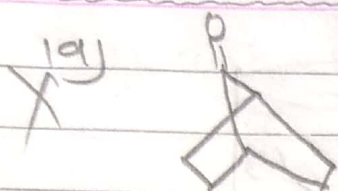


1) There should be H/D/T at neighbour Carbon to carbonyl group. and hybridisation of α Carbon should be sp^3 .

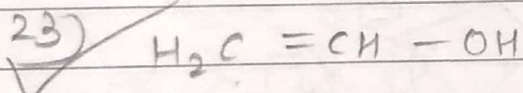
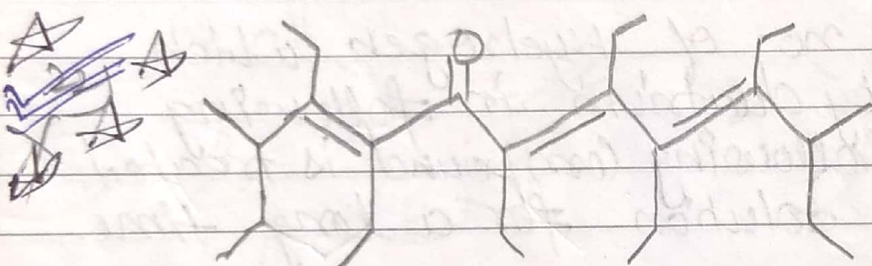
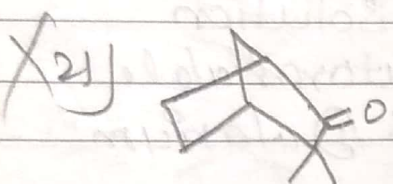
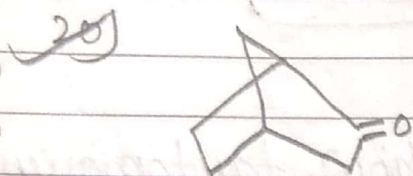
2) There should be ^{OR} OH group on double bond.

Que.^o Identify the comp. among following which will keto enol tautomerism.

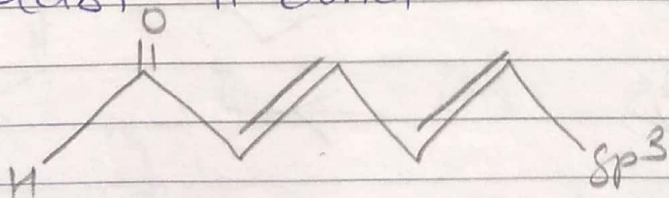




*

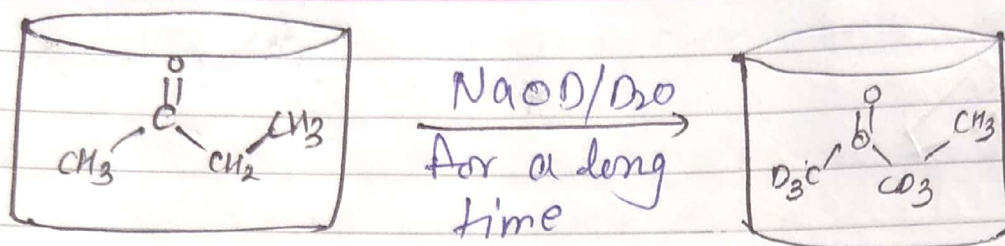


Note: When Carbonyl Comp. is Conjugative then see the same condition at α carbon to last π bond



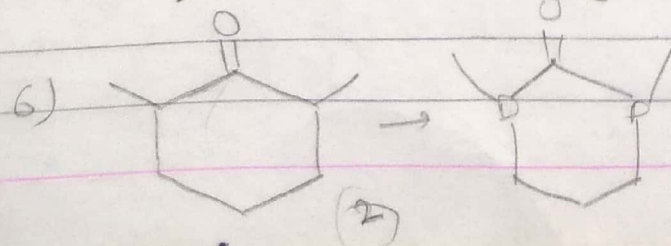
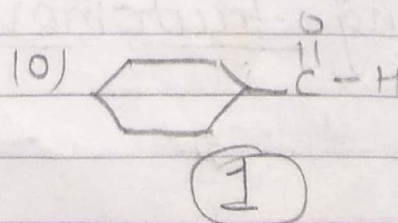
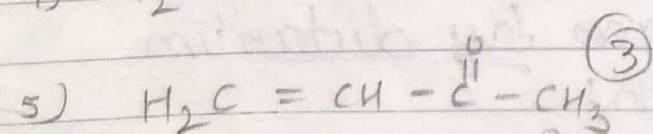
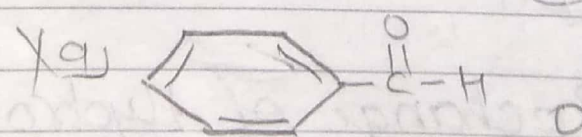
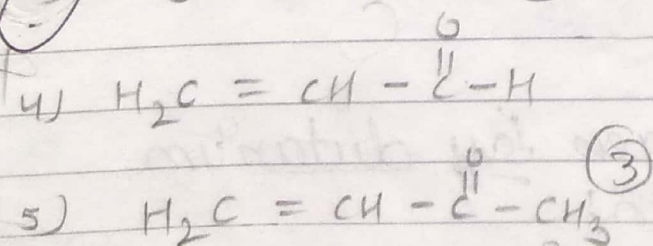
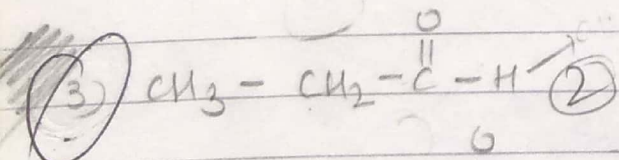
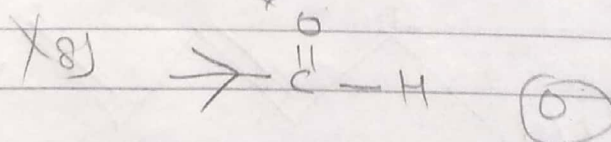
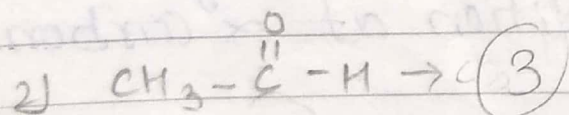
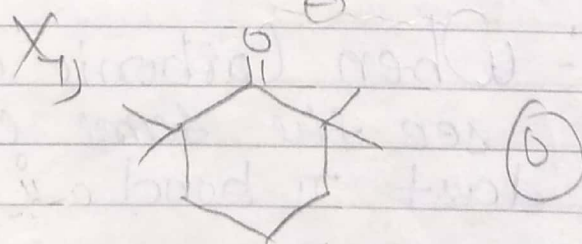
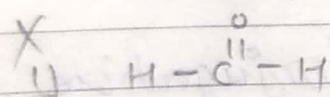
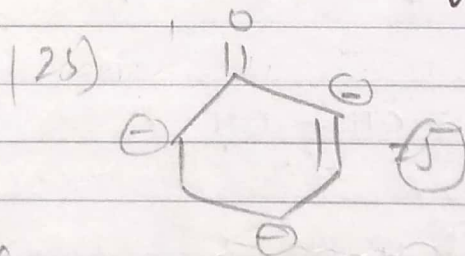
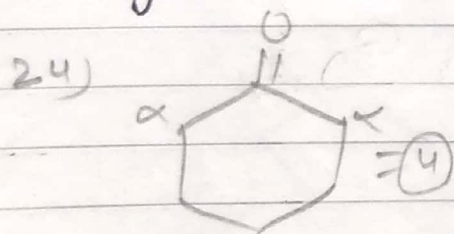
* Exchange of Hydrogen by deuterium during tautomerism!

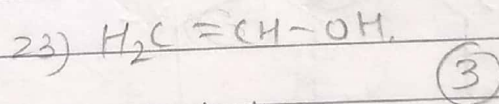
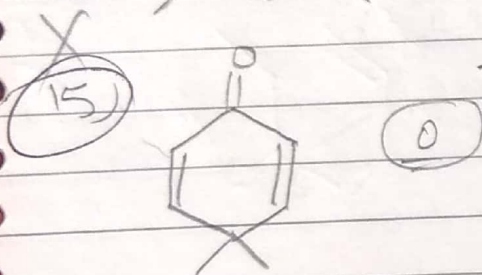
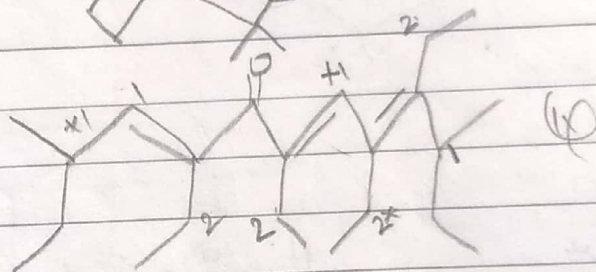
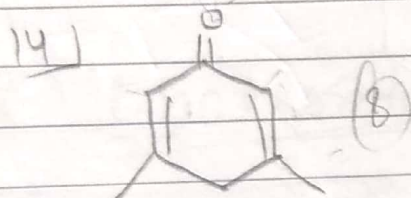
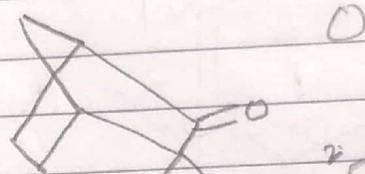
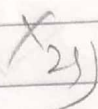
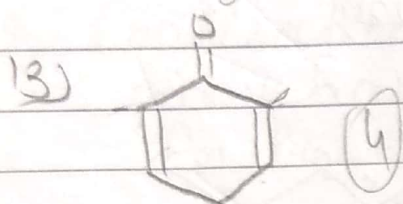
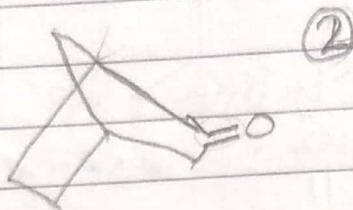
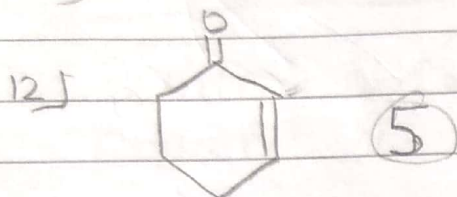
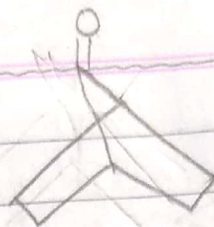
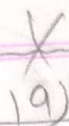
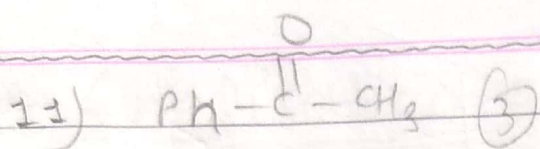
② Resonance with H_2O or D_2O



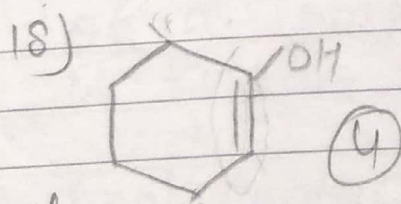
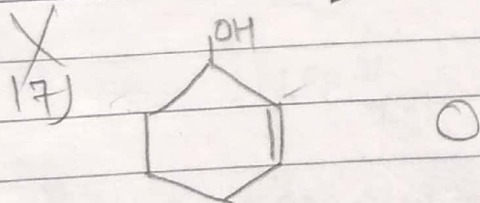
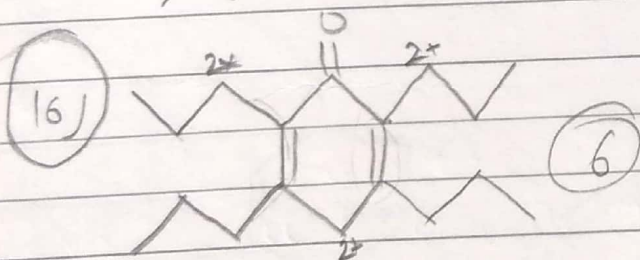
* A compound which is able to show tautomerism when treated with $NaOD/D_2O$ solution for a long time then all tauteronizable hydrogen get exchange by D (Deuterium).

Ques! Decide Total no. of hydrogen which are exchange by deuterium in following comp., when following compound is treated by $NaOD/D_2O$ solution for a long time.





malice keto,
amal de a'de



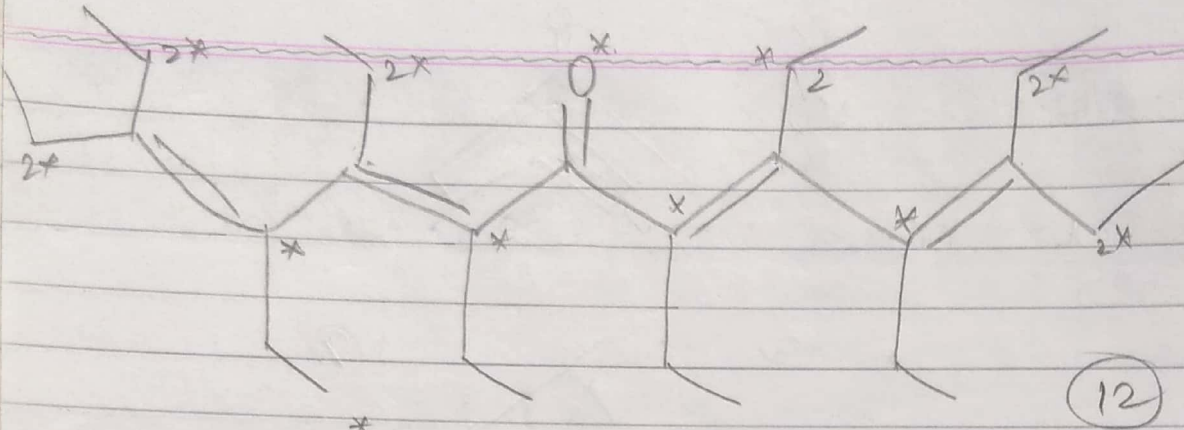
enol

make keto

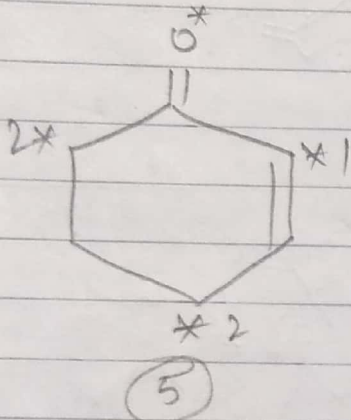
and Count Hydrogen.

1 = 12 - then 12

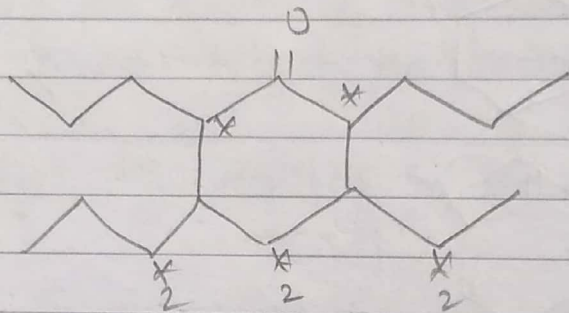
Ques



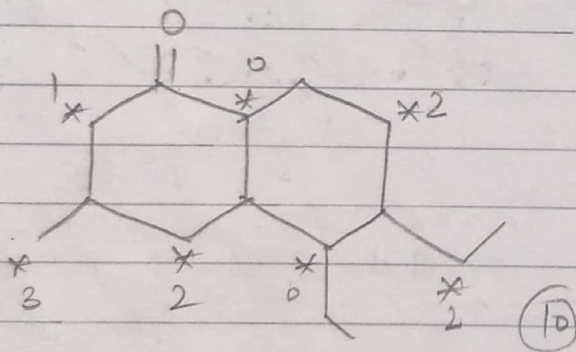
Ques



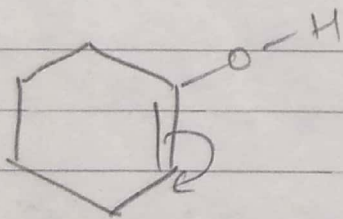
Ques



Ques



Ques!

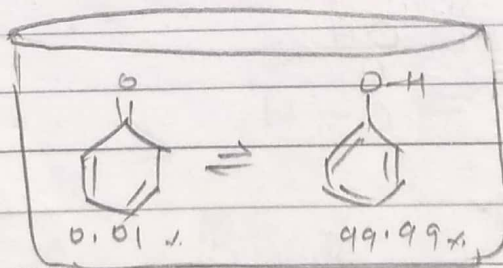
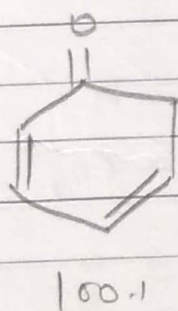
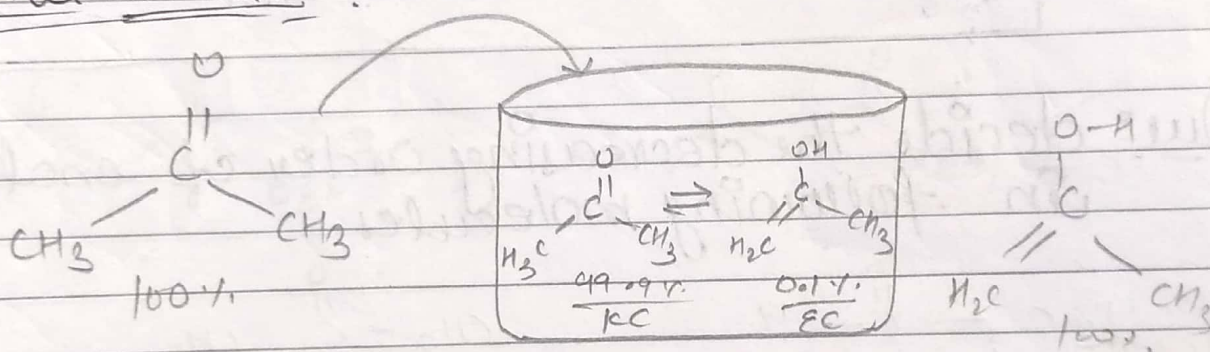


* Enolisation :

The Process by which keto isomer is converted to enol isomer is known as enolisation.

* Enolisation can be done in aq. acidic and basic in all medium.
for Page no -

* Enol Content :



* The Percentage of enol isomers in solution of a compound showing keto enol tautomerism is known as enol content.

Enol Content vary from compound to compound

Enol Content:

firstly use (1st)

Stability: $EC \propto \text{stability of enol} \propto AN \propto \frac{1}{AAN}$

$EC \propto \text{Resonance}$

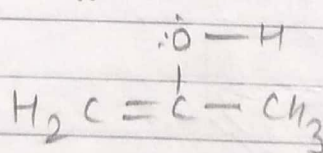
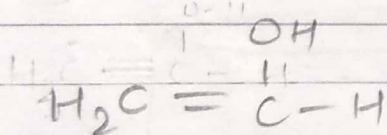
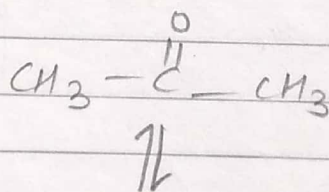
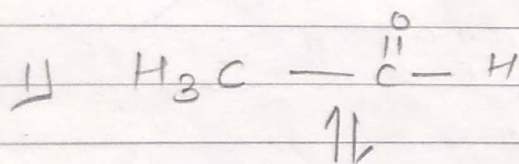
$EC \propto H.C$

$EC \propto \frac{1}{\text{Steric Hindrance / strain}}$

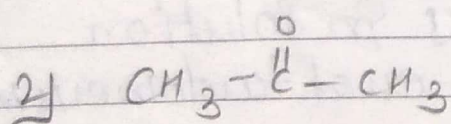
2.

$EC \propto \text{Acidity Nature of Hydrogen in keto isomer} \propto -H/H/\# \text{ effect}$

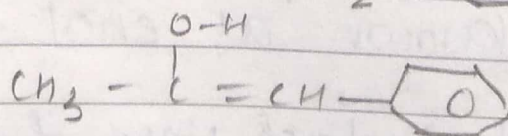
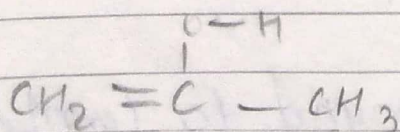
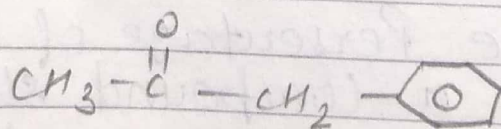
Ques: decide the decreasing order of enol content in following molecules.



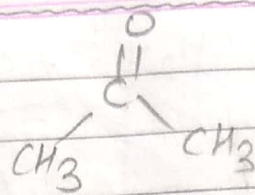
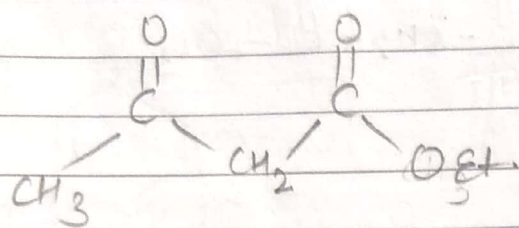
$\alpha = 3$



<



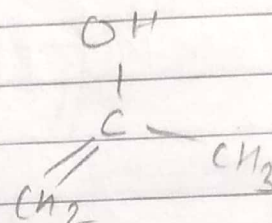
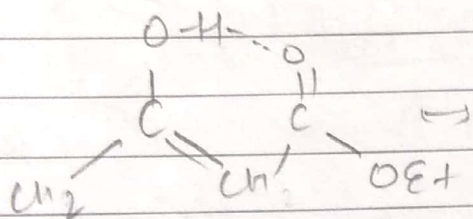
3)



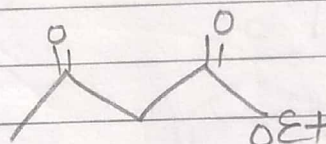
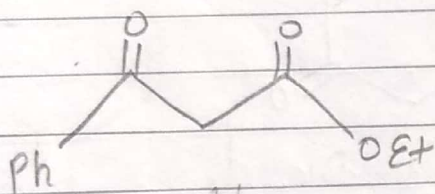
Simple ketone

β -ketoester

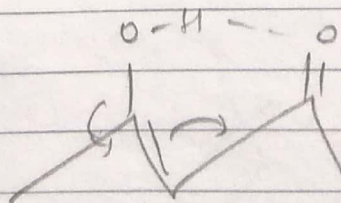
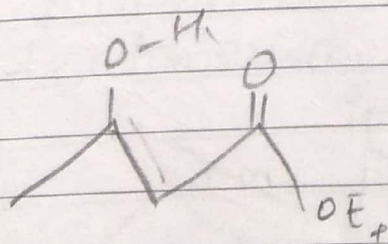
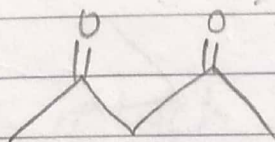
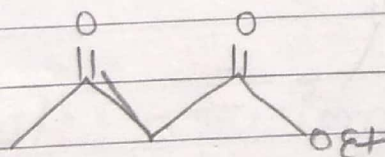
β -ketoester



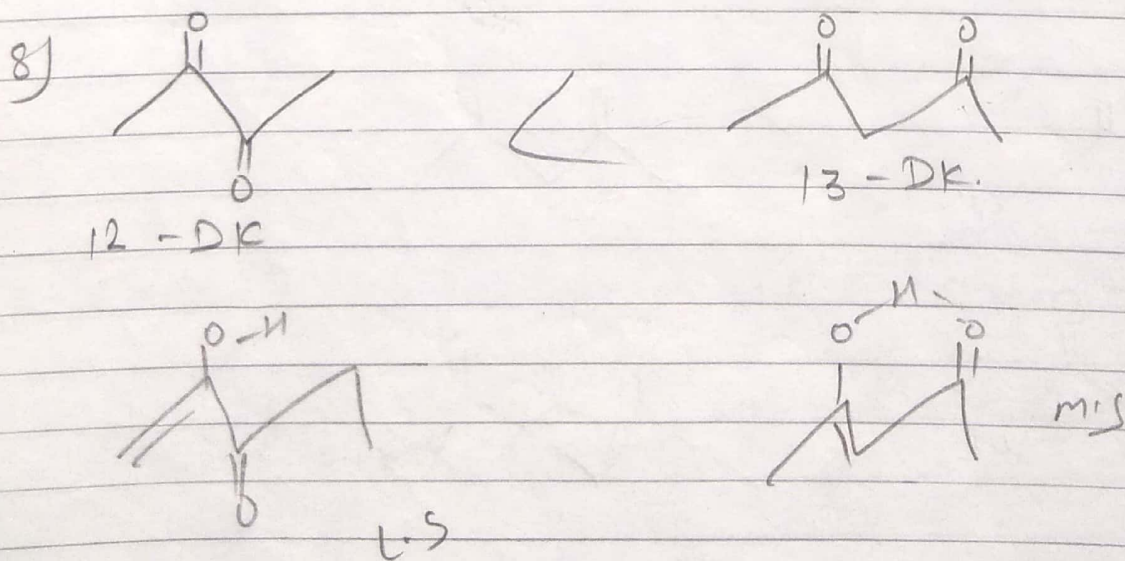
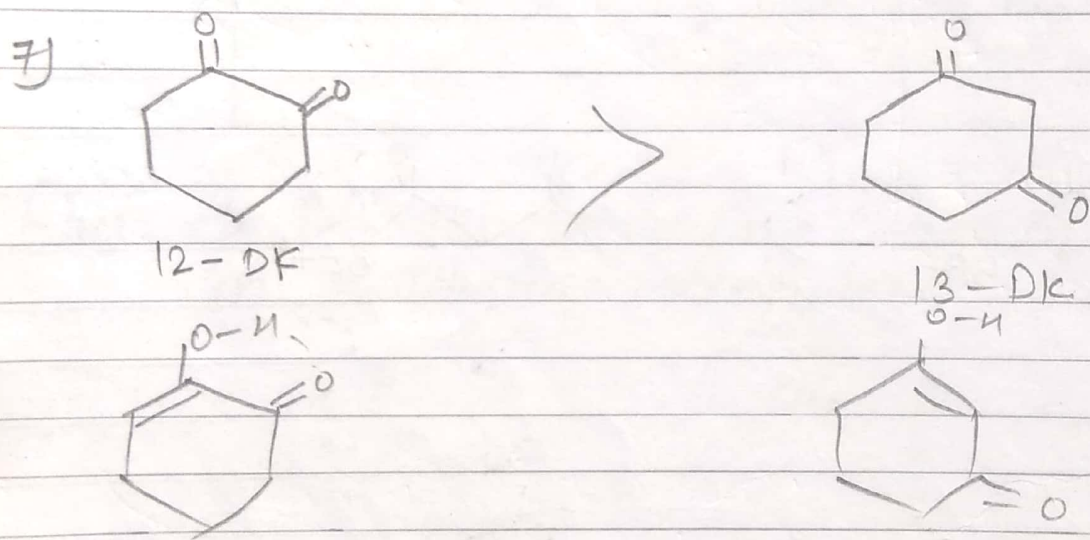
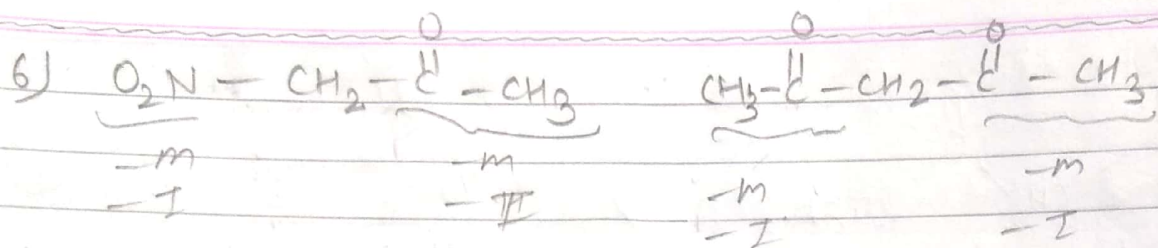
4)



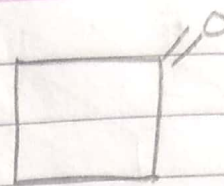
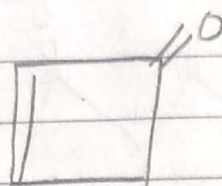
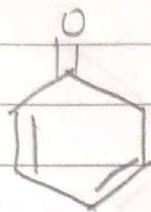
5)



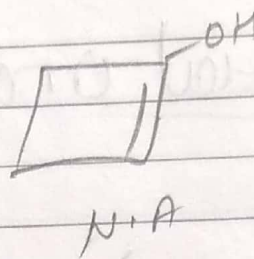
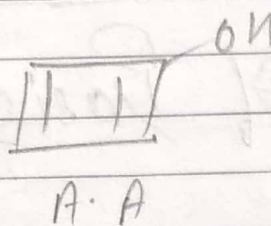
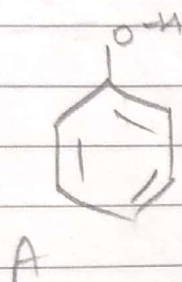
It is much better



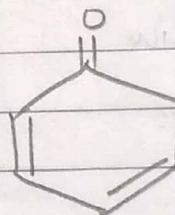
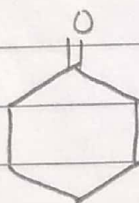
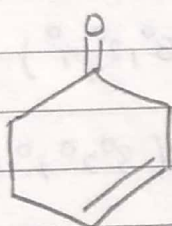
9)



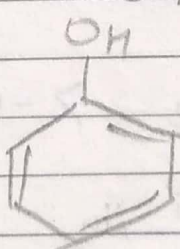
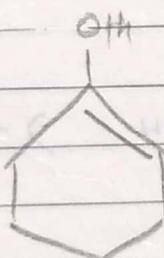
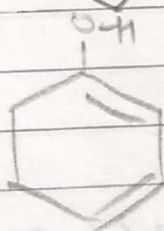
17372



10)

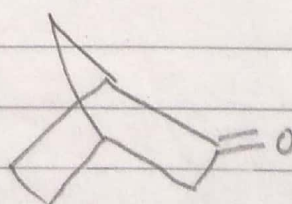
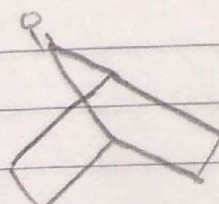


37172



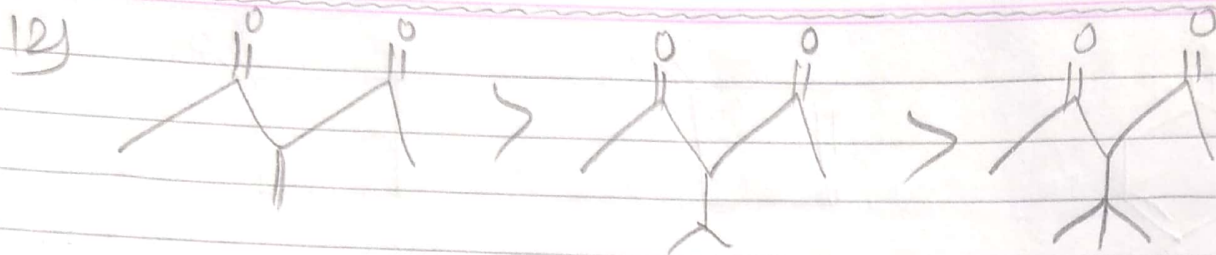
Note! — The compound of which enol is Anti-Aromatic do not show keto enol tautomerism.

(11)

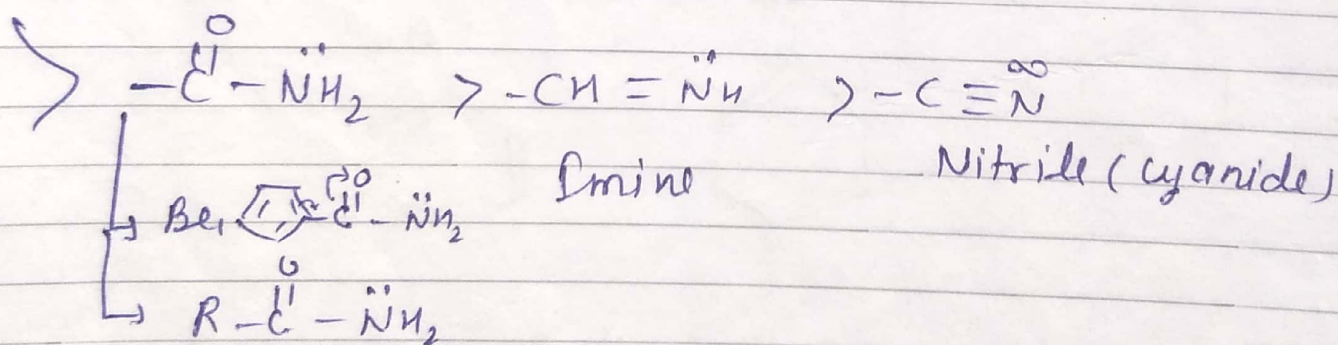
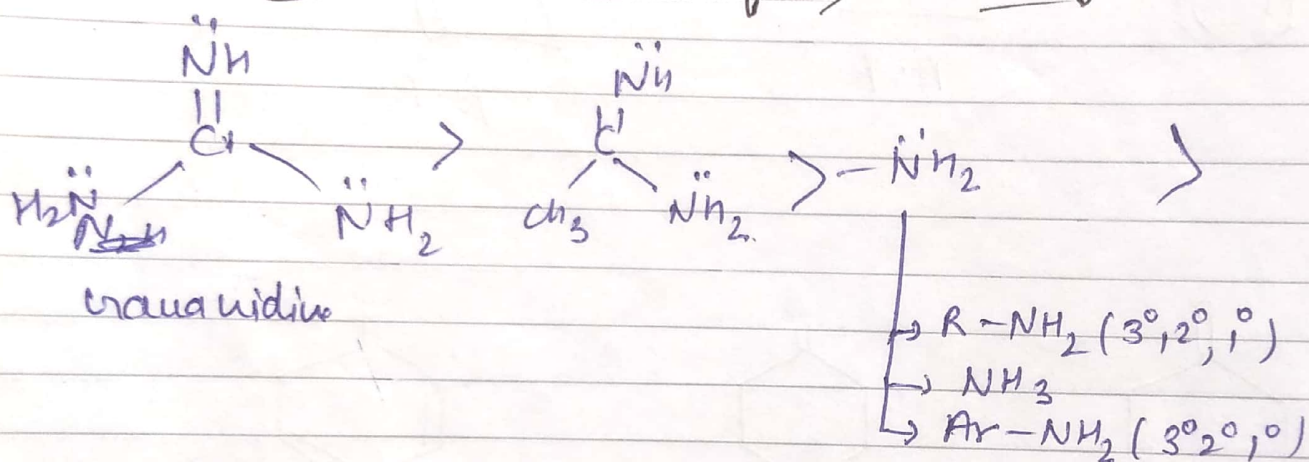


DNSKIT

Dr. enol



General order of Basicity

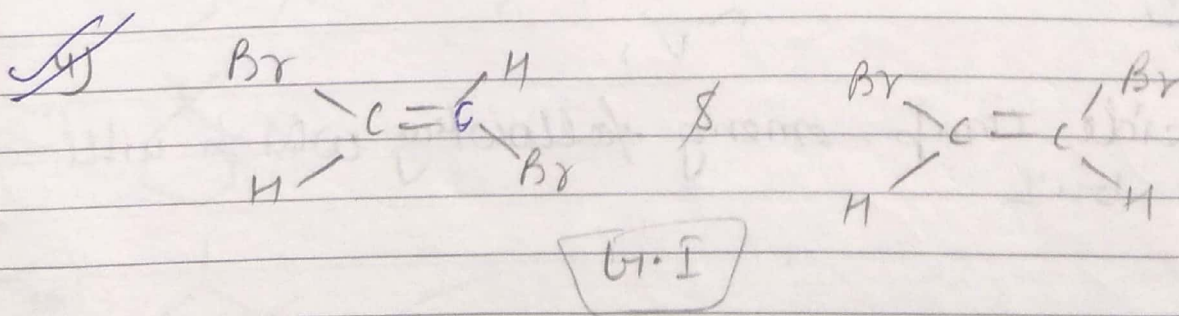
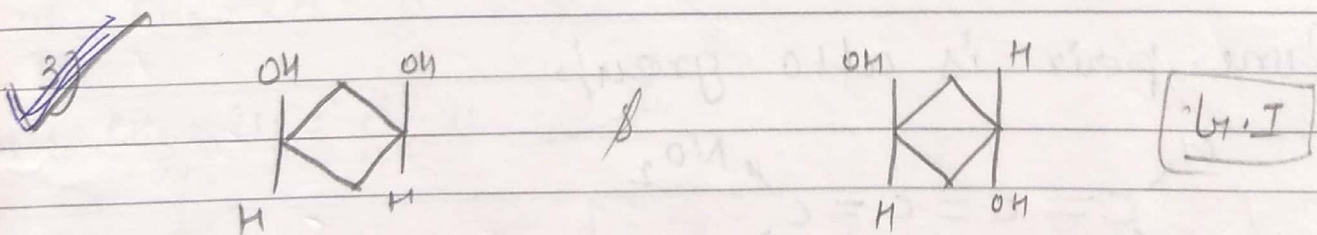
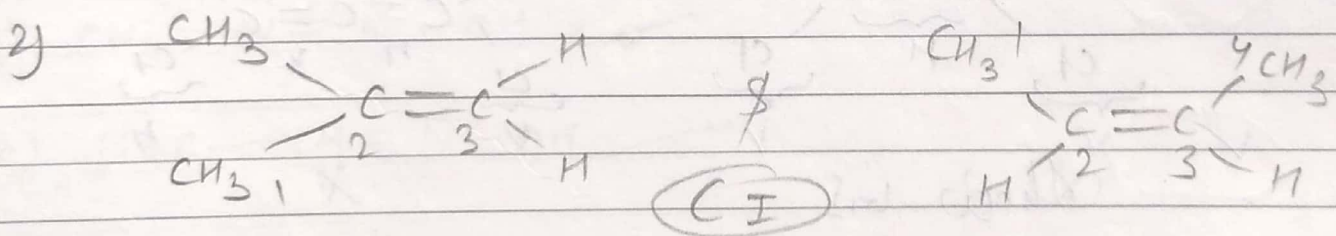
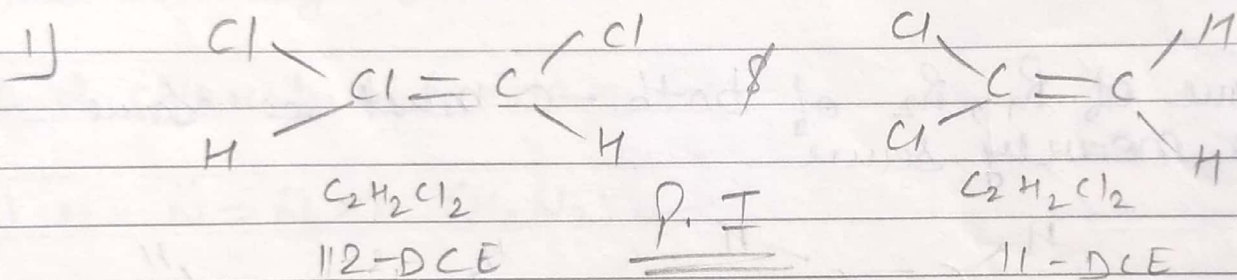


Stereo / Space

Geometrical Isomerism

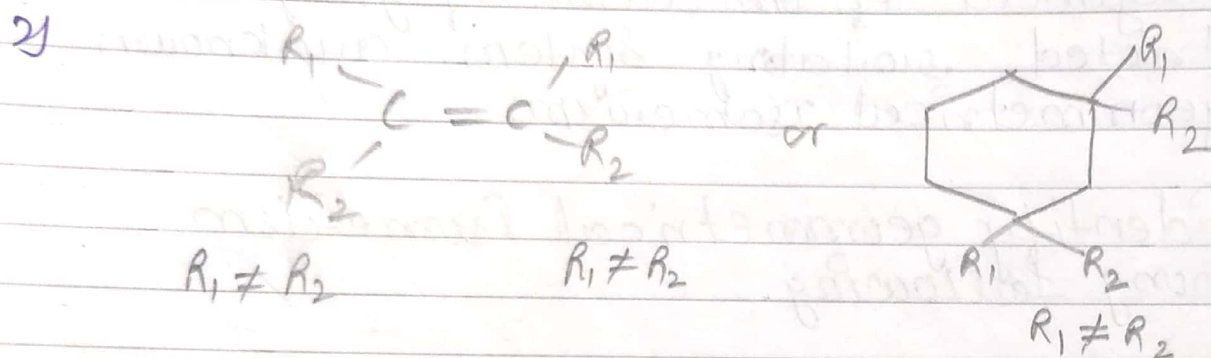
The molecules having same m.f, same structural formula but different arrangement of ~~an~~ atoms or group around restricted rotatory system. are known as geometrical isomerism.

Ques! Identify geometrical isomerism among following.

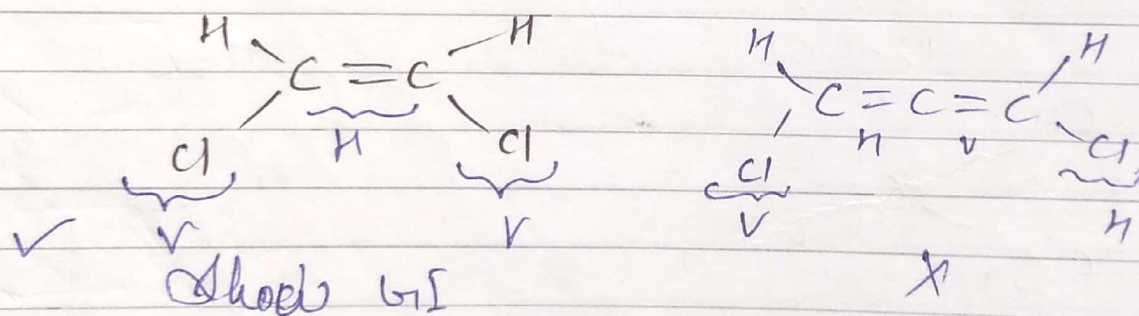


* Condition for Geometrical Isomerism:

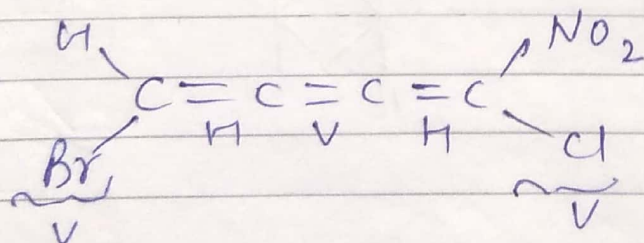
1) There should be restricted rotatory system in compound (double bond or cycle)



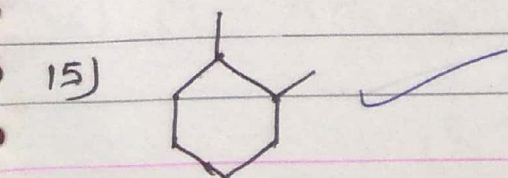
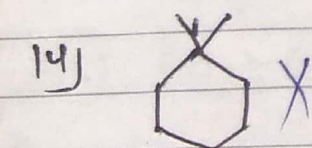
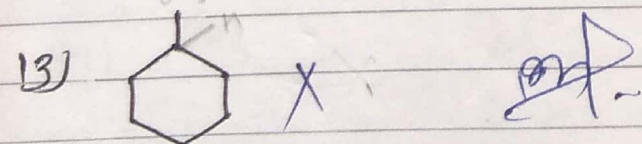
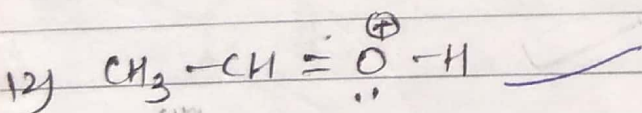
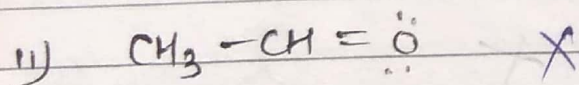
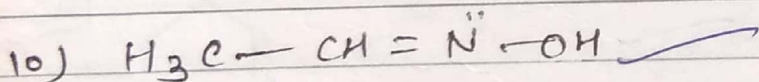
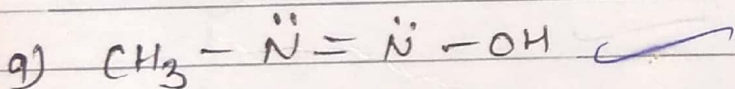
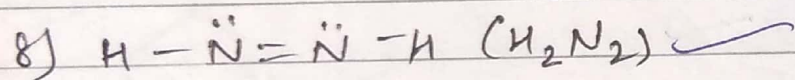
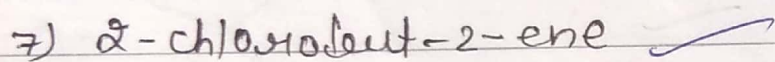
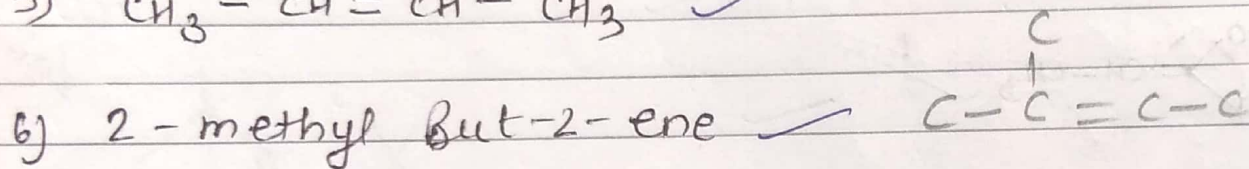
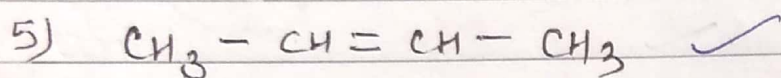
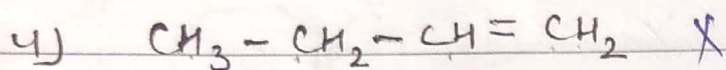
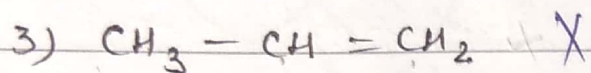
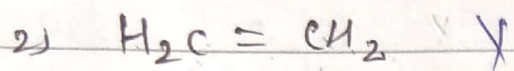
3) Plane of R_1, R_2 of both $-C$ must be same or nearly same

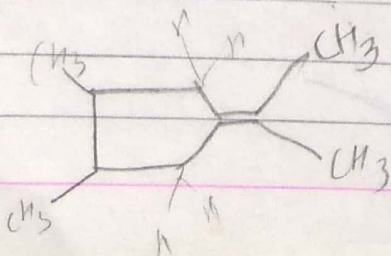
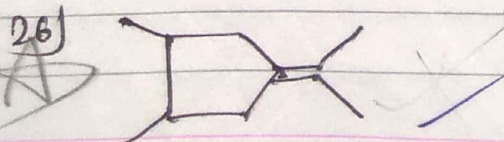
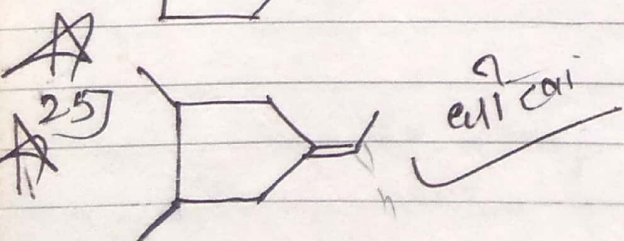
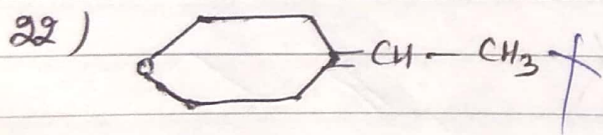
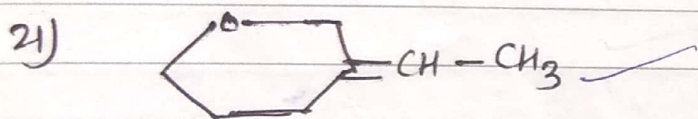
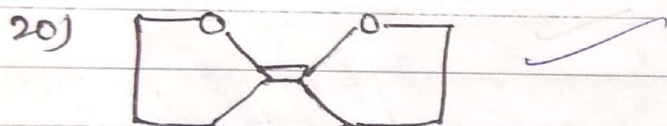
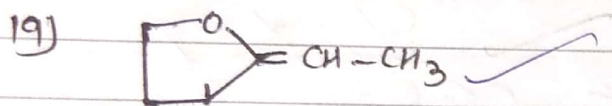
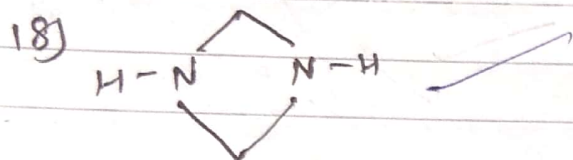
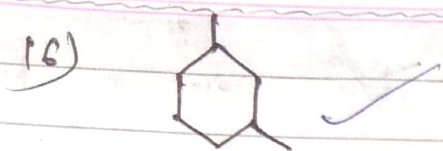


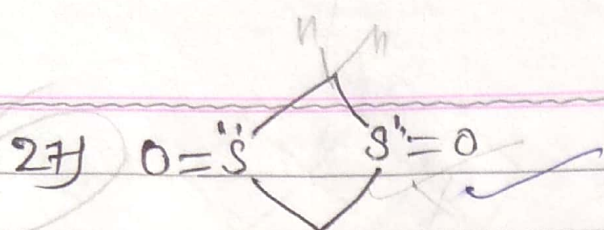
4) lone pair is also group



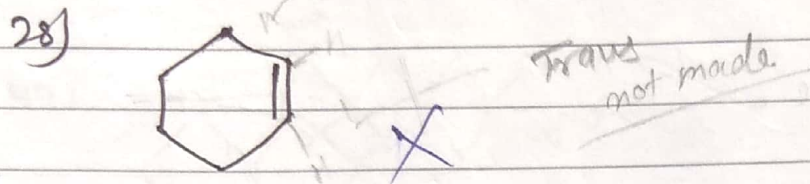
Ques: Decide comp. among following which will show G.I.





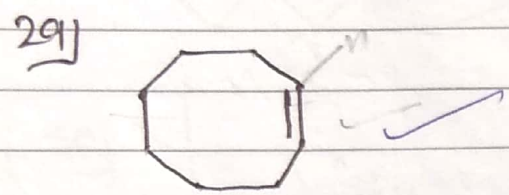


6 carbons not made.
 Trans ✓

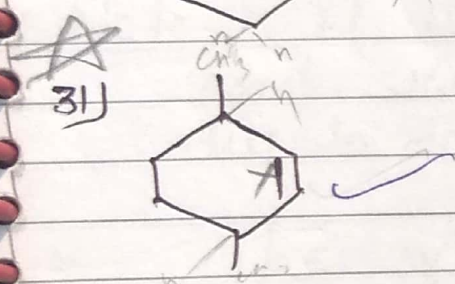
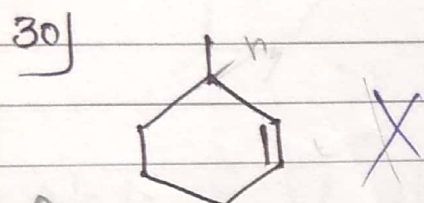


Small not made Trans

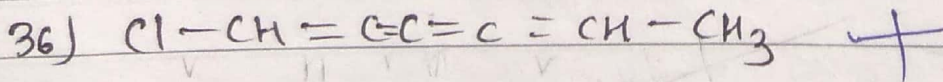
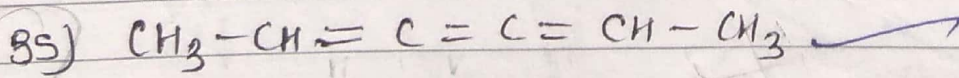
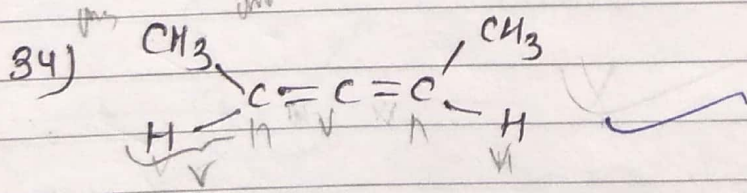
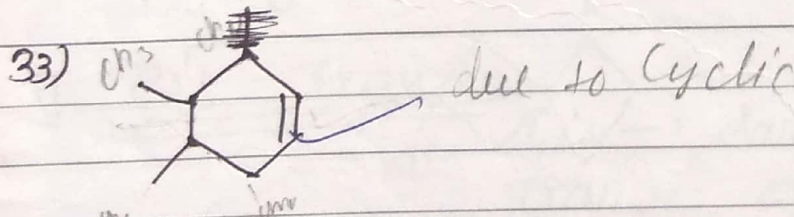
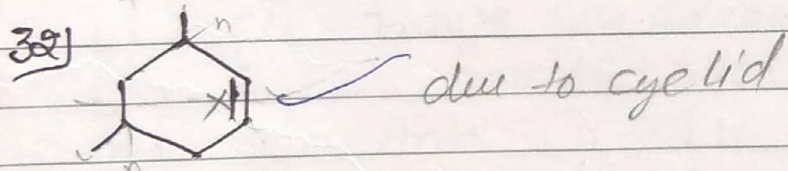
Big not show G.I

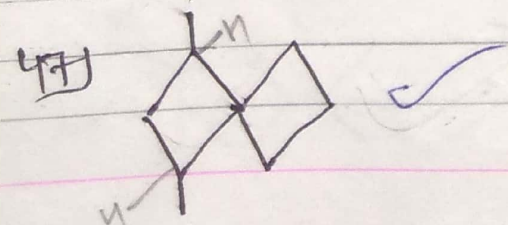
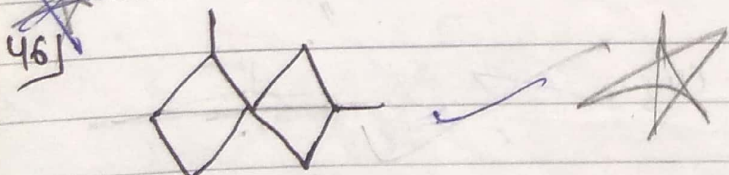
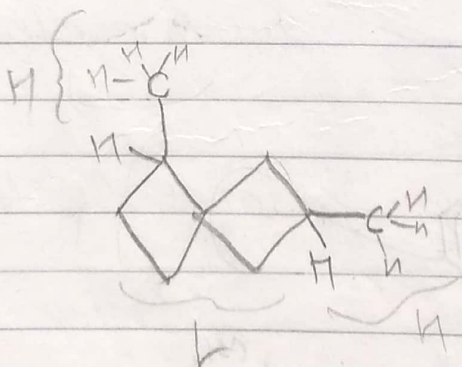
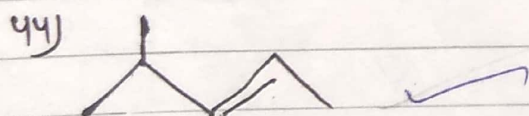
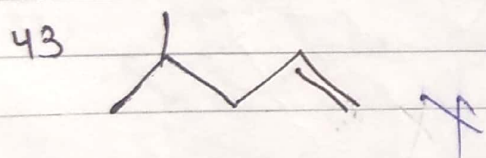
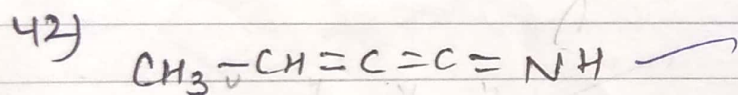
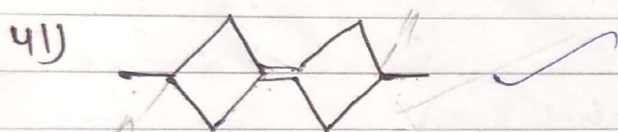
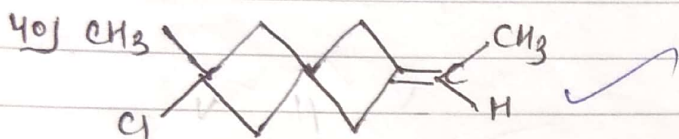
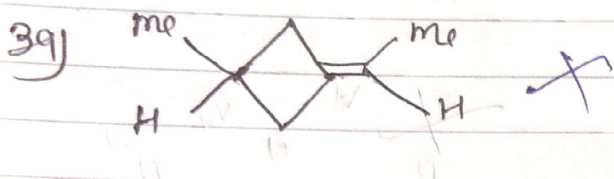
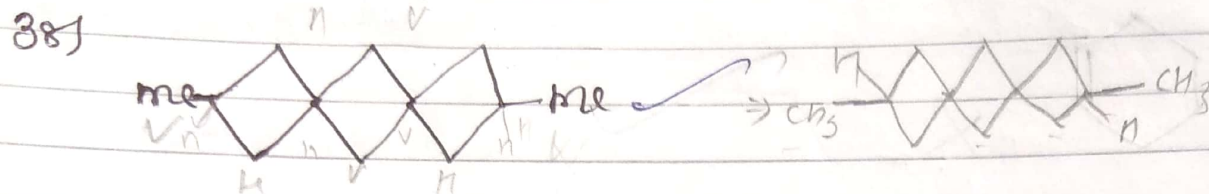
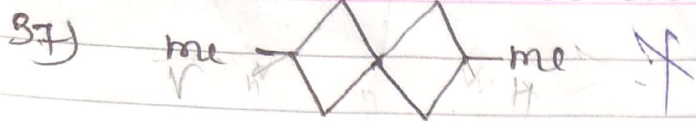


in Trans give Ck and E
 GE G.I Show both



with cyclic show G.I

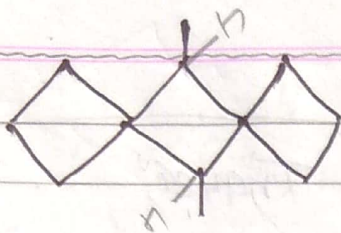




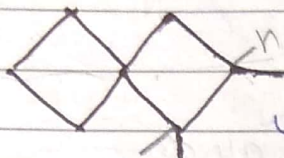
hick.

Trans ✓

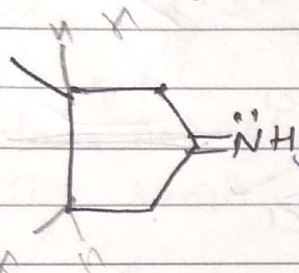
48)



49)



50)



Note: If double bond is Present in cyclic comp. then upto 6 carbon G.I not occur due to double bond

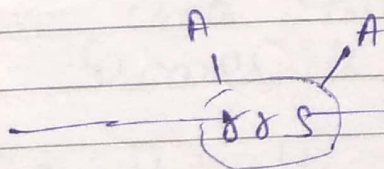
* Types of G.I : (Geometrical Isomerism)

- 1) $\rightarrow$ Cis - Trans less Advance.
- 2) $\rightarrow$ E - Z more Advance.
- 3) $\rightarrow$ Syn - Anti

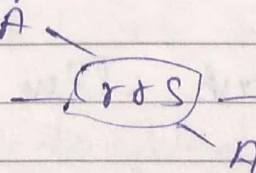
1) Cis - Trans

Cis $\rightarrow$ same side

Trans - opposite side. (Across sys)

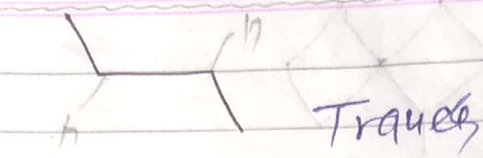
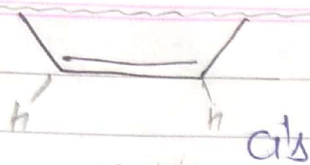


Cis

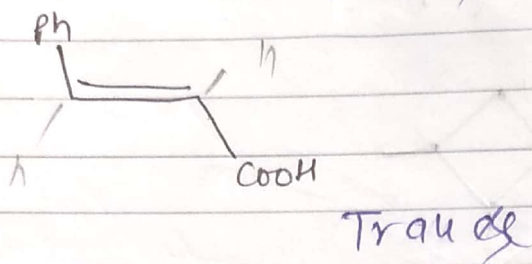
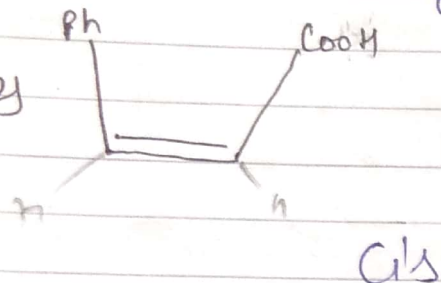


Trans

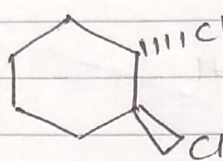
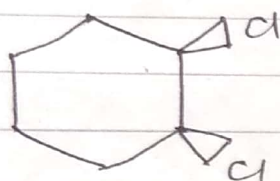
Eg 1 11



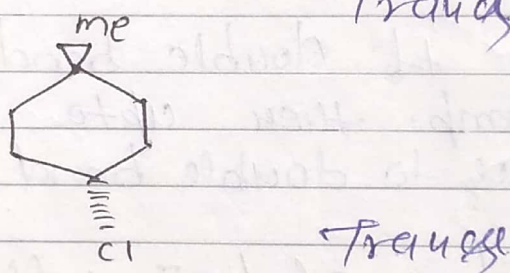
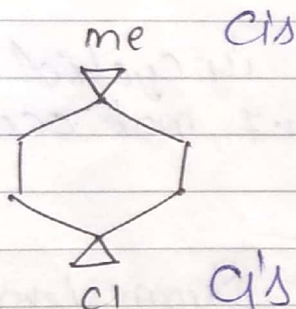
2)



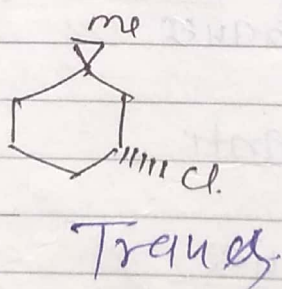
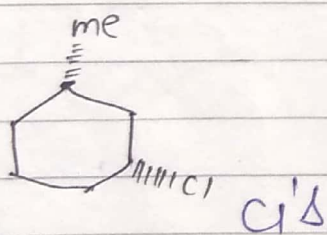
3)



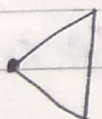
4)



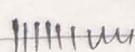
5)



*



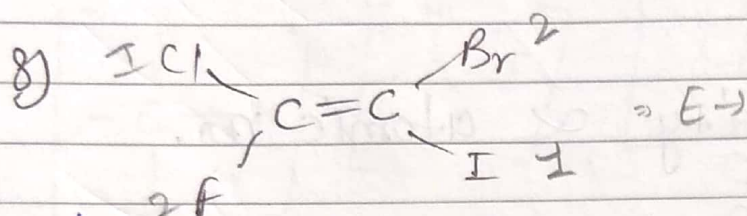
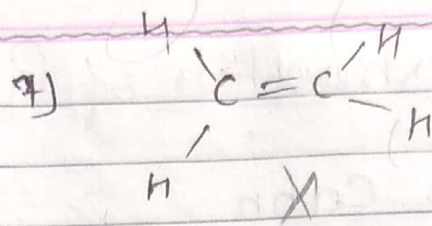
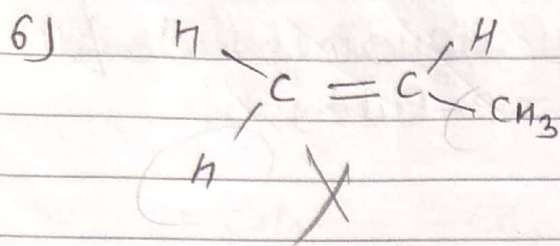
wedge line (GTO)



Dash line (GAFO)



Normal line -> group is in plane of paper

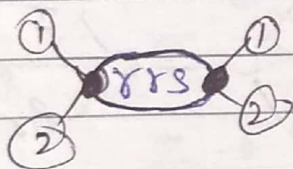


does not show cis trans

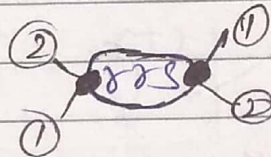
* It show E2 only. GI only.

* E/Z (GI) $\frac{0}{0}$

- 'E' $\Rightarrow$ Entgegen $\Rightarrow$ Across/O.S.
- 'Z' $\Rightarrow$ Zusammen $\Rightarrow$ Same side



Z $\rightarrow$



E $\rightarrow$

* If Higher priority gp around rrs are towards same side then isomer will 'Z'.

* and they are across to each other the isomer is known as 'E'.

* Priority of group is decided by sequence rule or CIP-Rule.

* Determination of Priority:- by Sequence-Rule / (CIP-Rule).

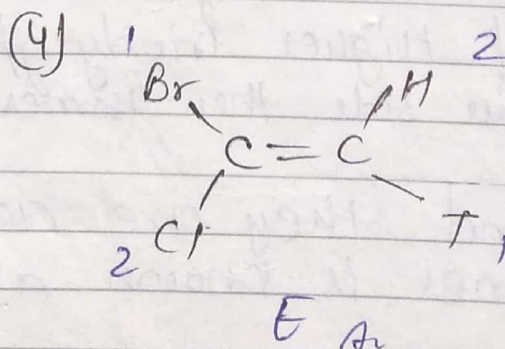
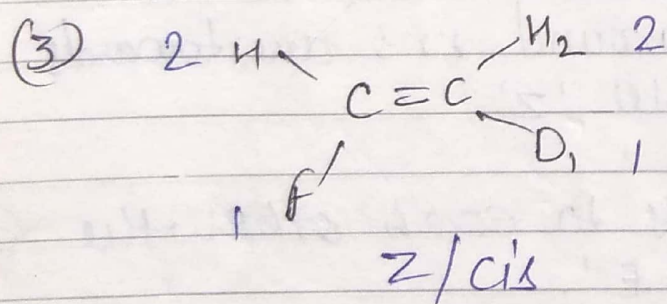
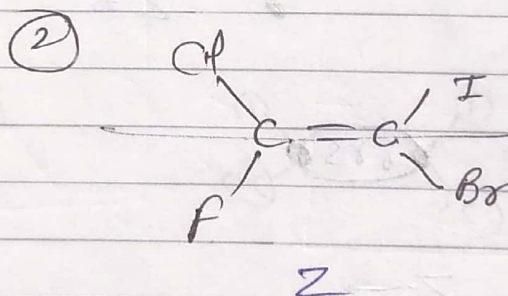
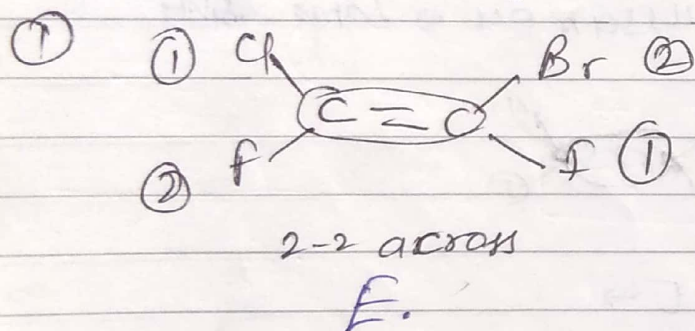
- C $\Rightarrow$ Cahn
I $\Rightarrow$ Ingold
P $\Rightarrow$ Prelog } CIP

1) for atom Priority $\propto$ atomic no.

Br I Cl F
Ans $I > Br > Cl > F$

2) For Isotopes:

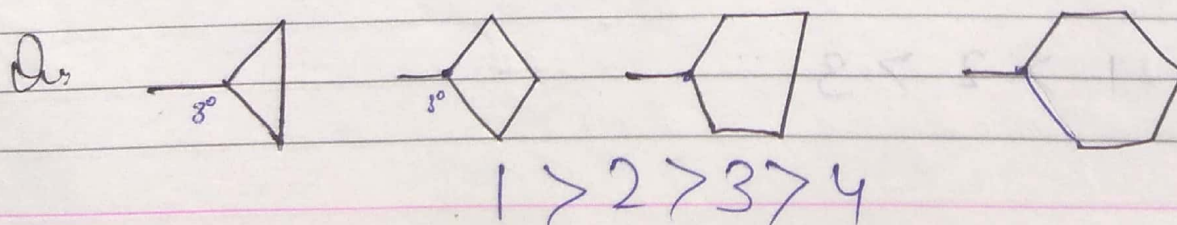
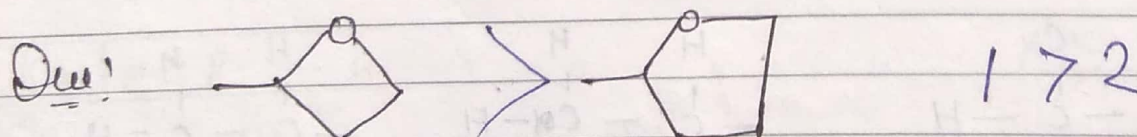
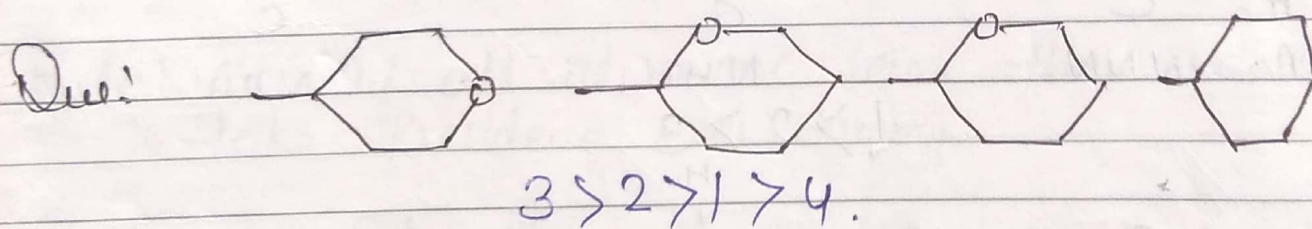
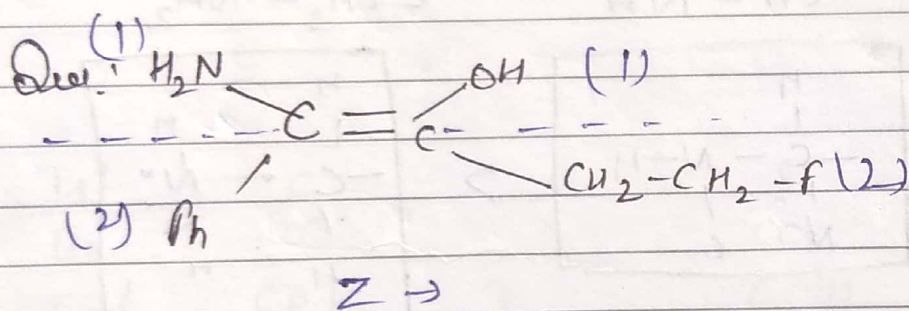
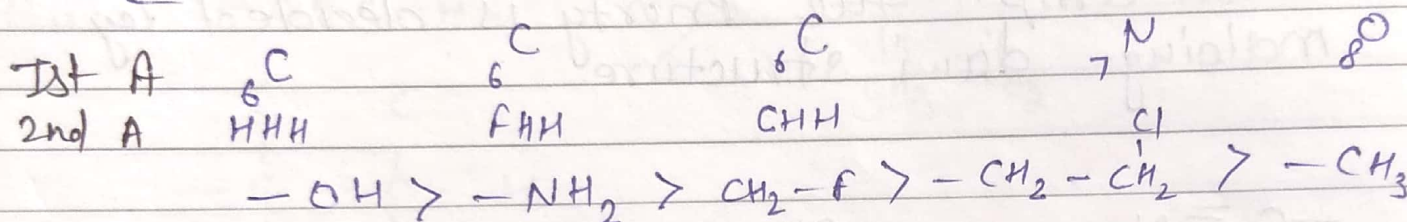
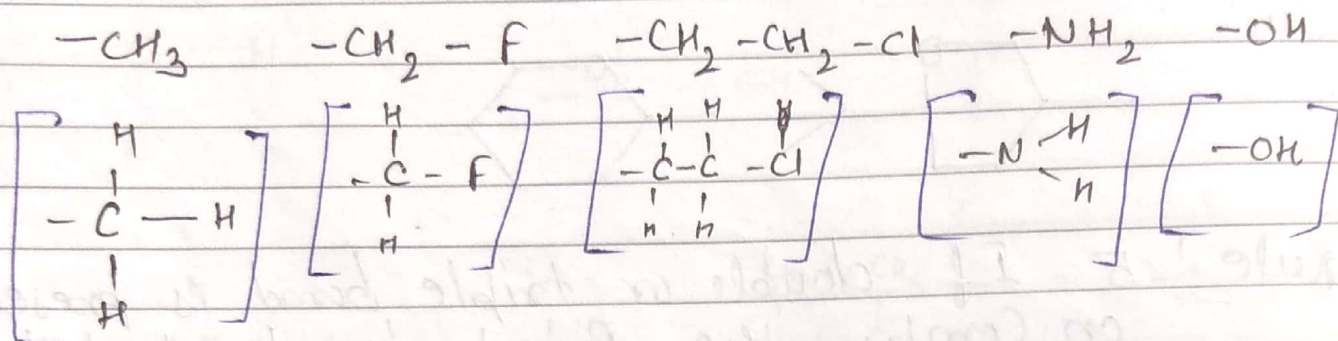
Priority $\propto$ Atomic mass



Rule: 3 For group:- Priority is decided by 1st atom

of the gp. if first atom is common then we take help from 2nd atom. if 2nd is common then

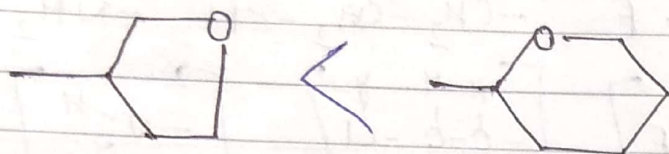
we take left half 3rd atom.
So, m.



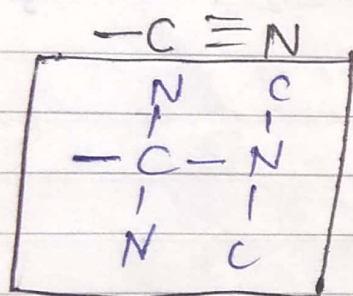
Rule 4

* If no other gp present then Priority of Small ring is greater than Large ring.

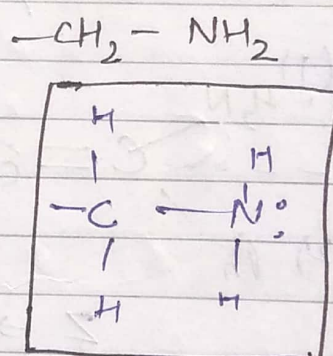
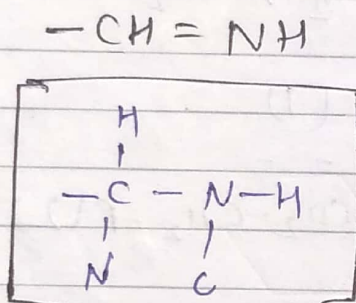
Que!



Rule 5 If double or triple bond is present on Comp. the Priority is decided by making dupli structure.



dupli st.



1st A: C

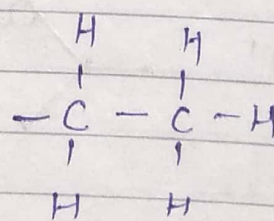
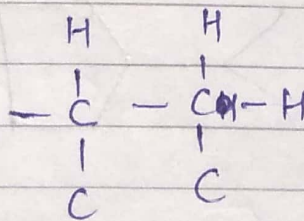
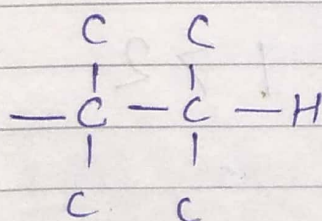
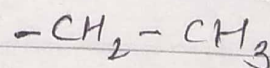
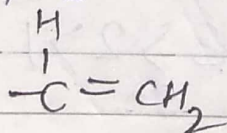
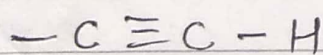
2nd A: NNN

C
NHH

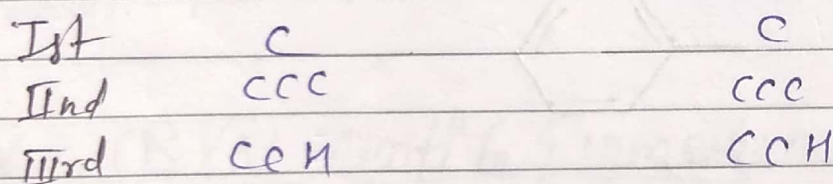
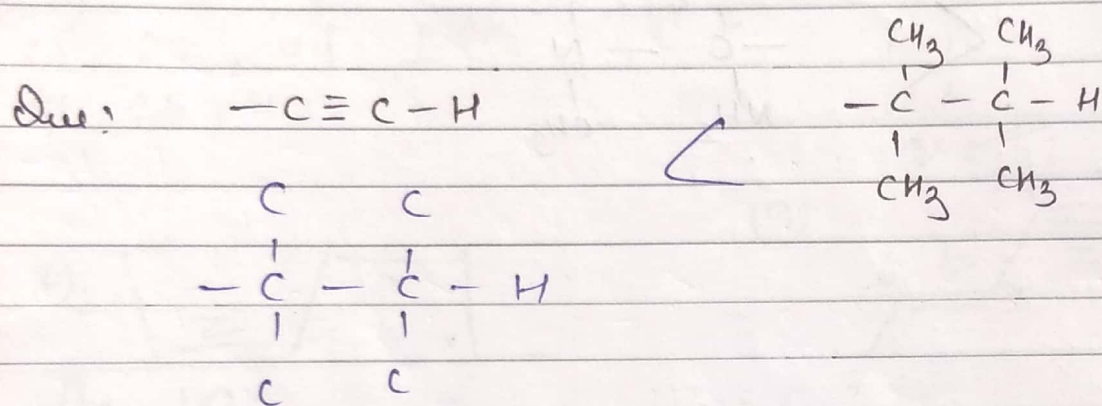
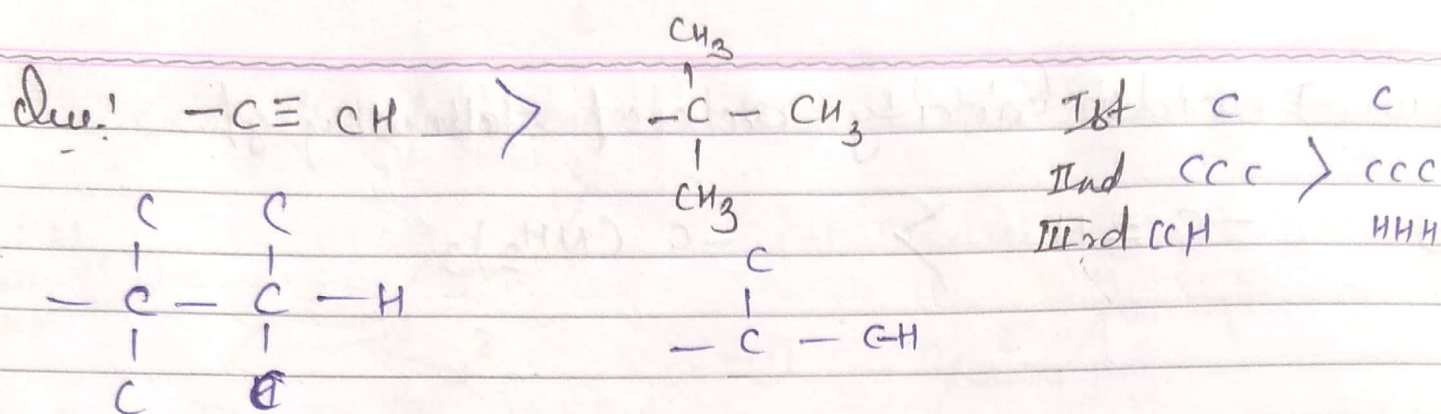
C
NHH

1 > 2 > 3

Que!



1 > 2 > 3



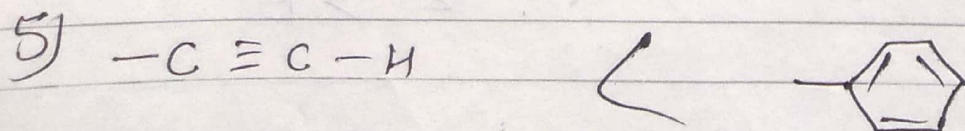
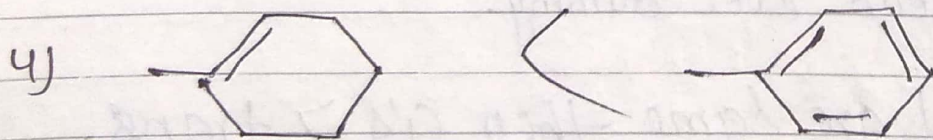
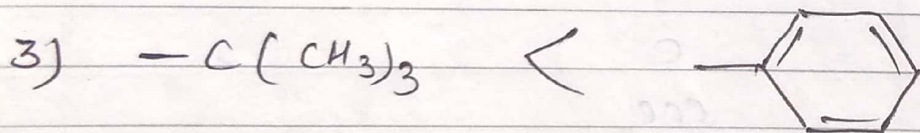
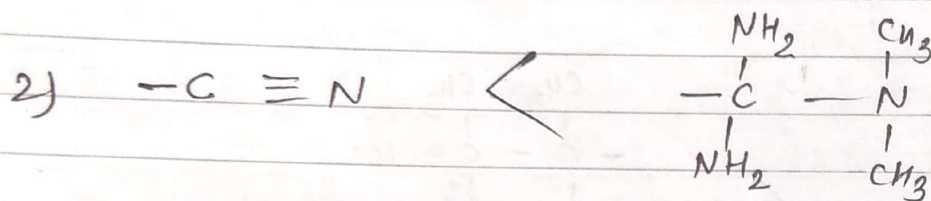
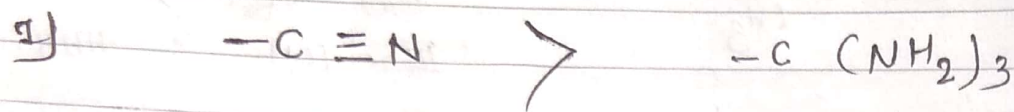
Rule! 6 If all atom are same then real take precedence over dummy.

Rule: 7 If all are same then cis > trans.

Rule: 8 " " " " " " $R > S$

Rule: 9 " " " " " " $Z > E$

Ques: Decide Priority order of following gr.



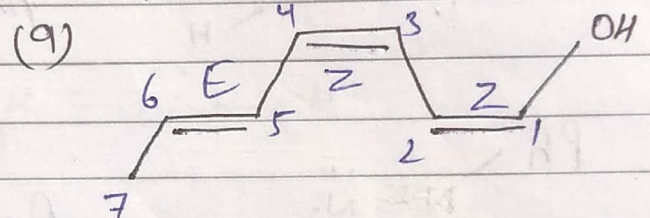
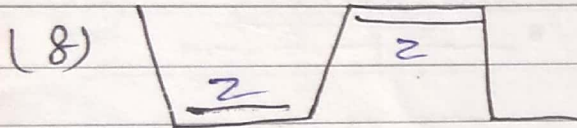
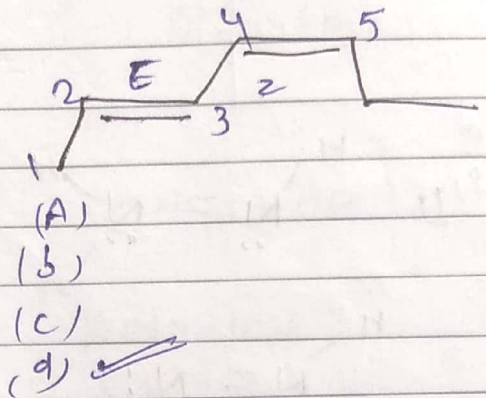
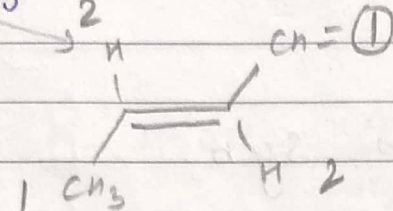
Z-cis
E-trans

Q. See the following photo and decide correct option

(6) (2E)(4E) Hepta 2,4-diene

(7) (2E)(4Z) Hepta 2,4-diene

- a) 2Z, 4Z
b) 2E, 4E
c) 2Z, 4E
d) 2E, 4Z

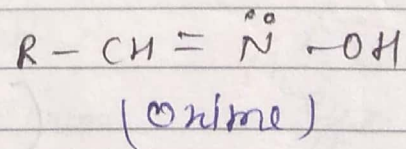
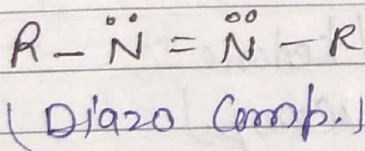


(2Z)(4Z) Hepta-2,4-diene

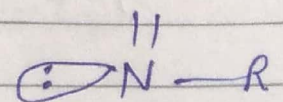
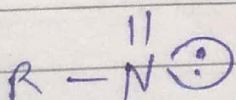
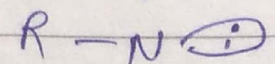
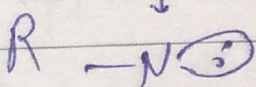
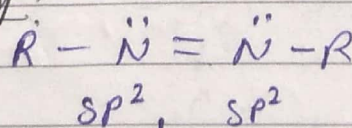
(1Z)(3Z)(5E) Hepta-1,3,5-trien-ol

X SN anti G. Isomerism :-

Where lone pair present on any / both terminal atom.



1) Diazo Compound :-

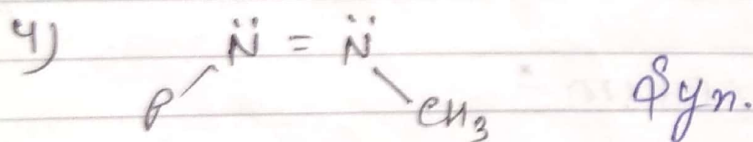
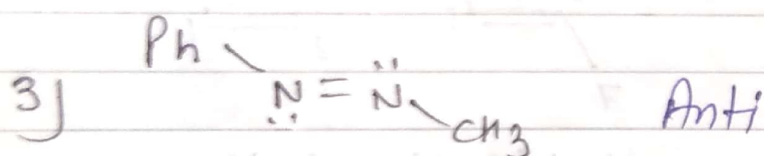
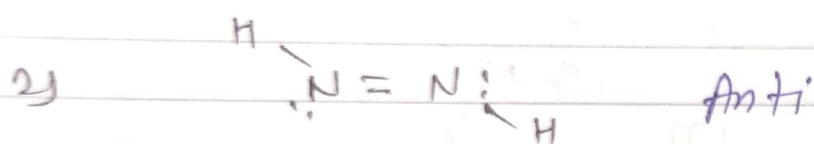
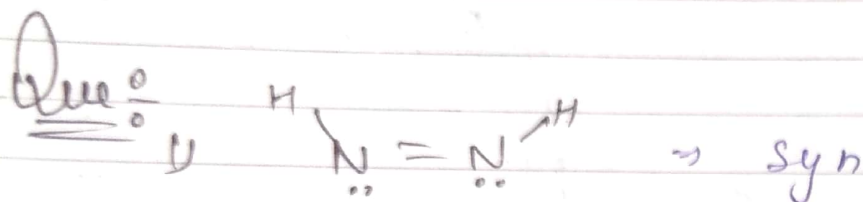
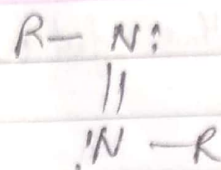
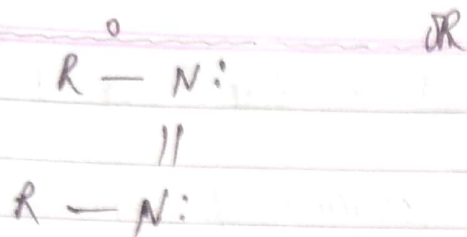


Syn

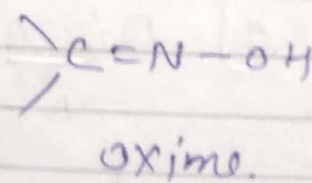
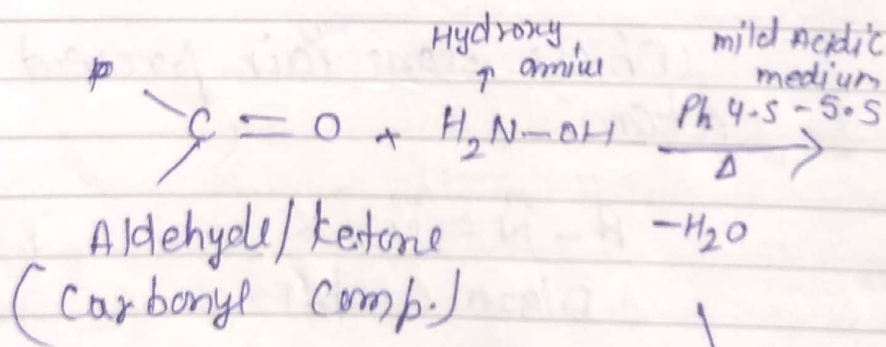
Anti.

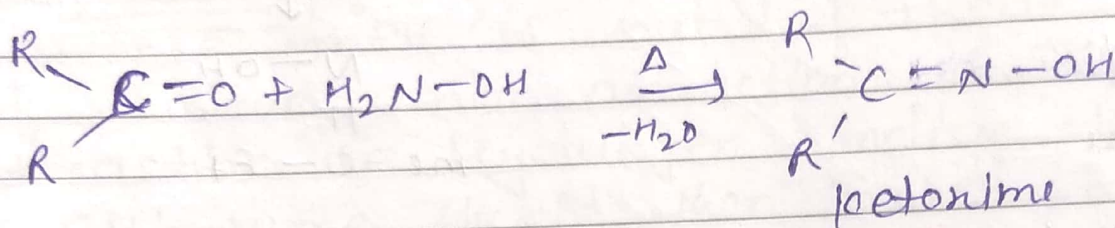
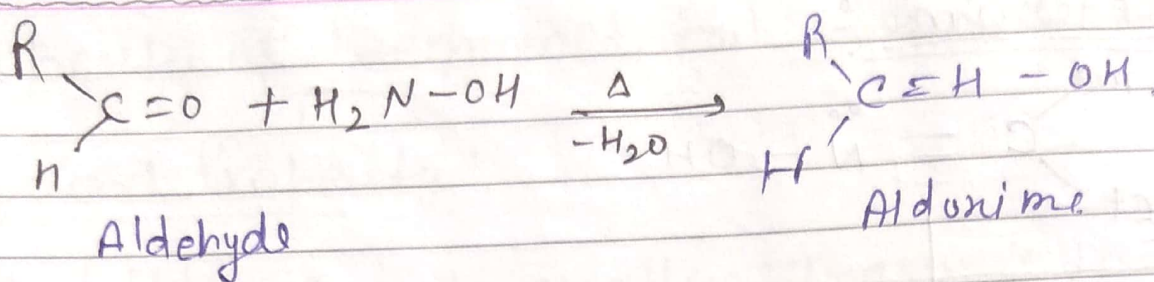
C-C = ally

C-

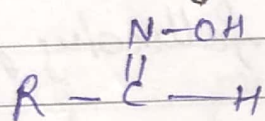
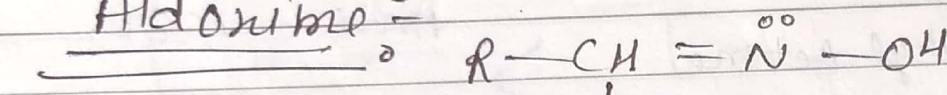


* Oxime :

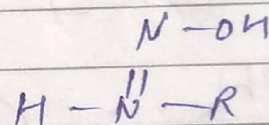




(I) Aldoxime

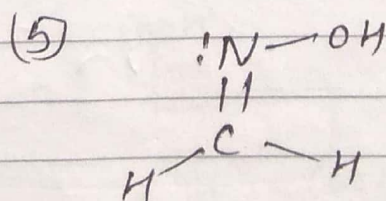
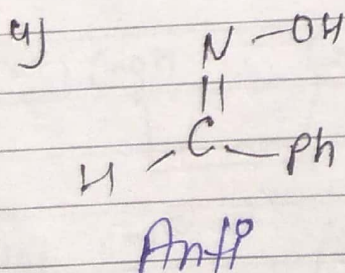
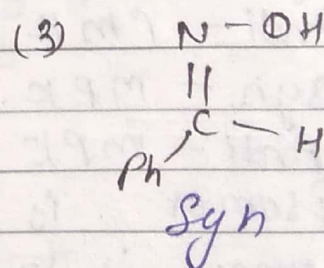
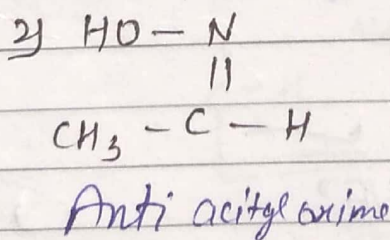
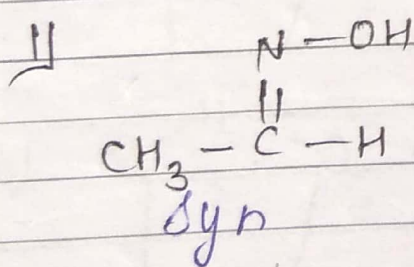


Syn-Aldoxime



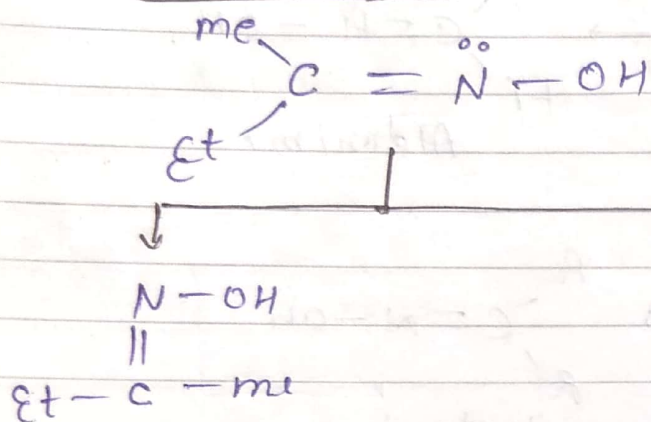
Anti-Aldoxime

Ques: Identify Syn and Anti Oxime. 😊



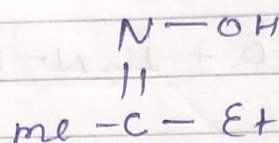
Both ^{CH} Not given G.T
(DNSGII)

2) keto oxime:



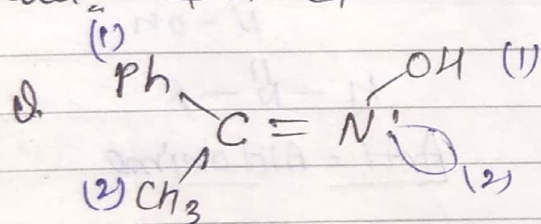
Syn - methyl ethyl ketone
CR

Anti - Ethyl methyl ketone



Syn - EMP
Anti - MER.

Que: Select the correct option for following photo.



1) Name of keto oxime is

1) Syn - phenyl methyl ketoxime ✓

2) Anti - PMK

3) Syn - MPK.

4) Anti - MPK ✓

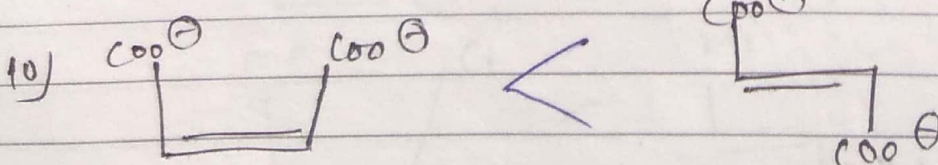
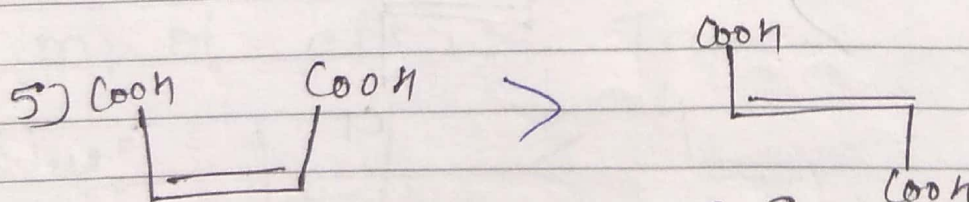
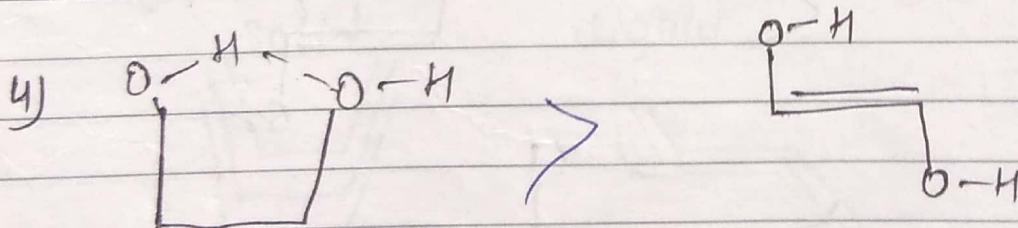
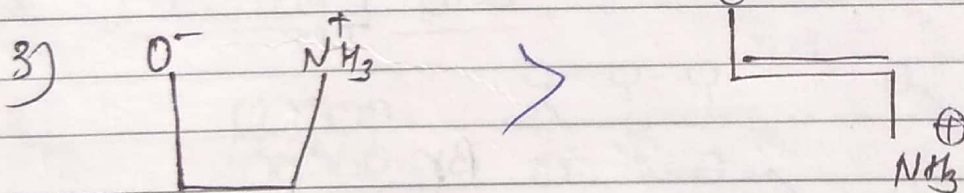
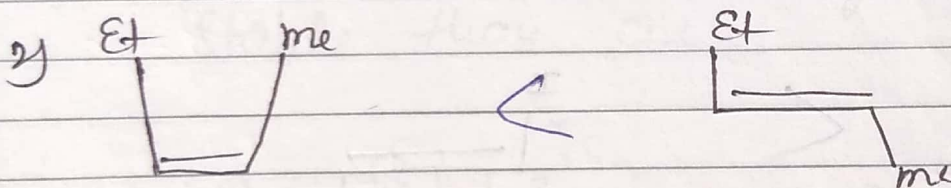
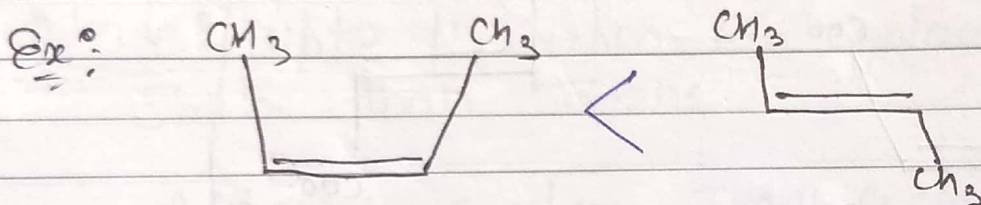
5) Isomer is 'E'

6) Isomer is 'Z' ✓

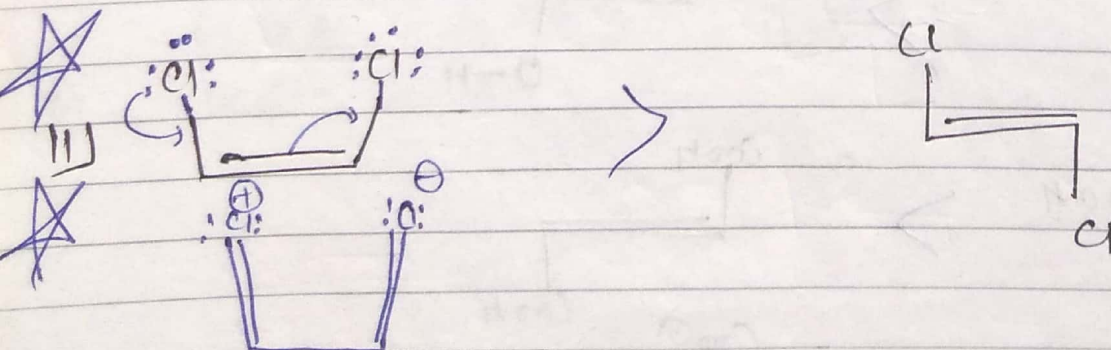
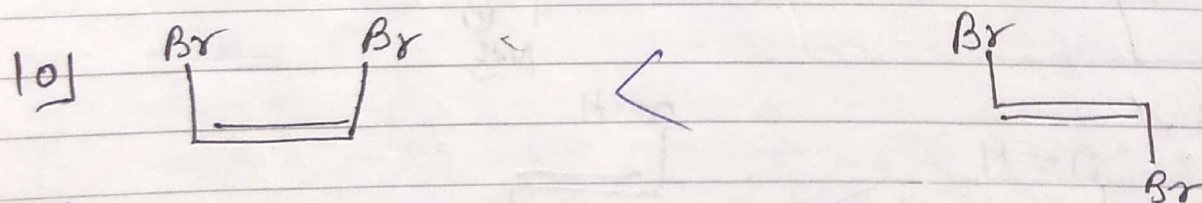
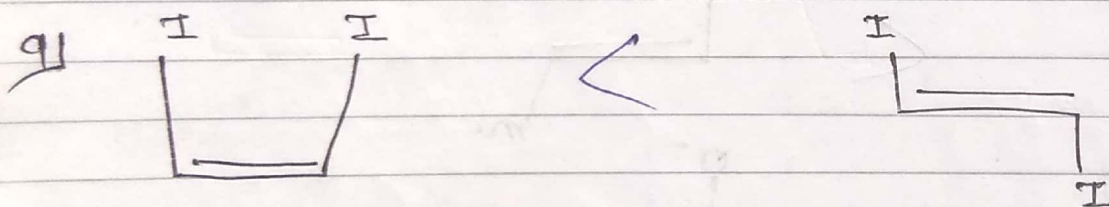
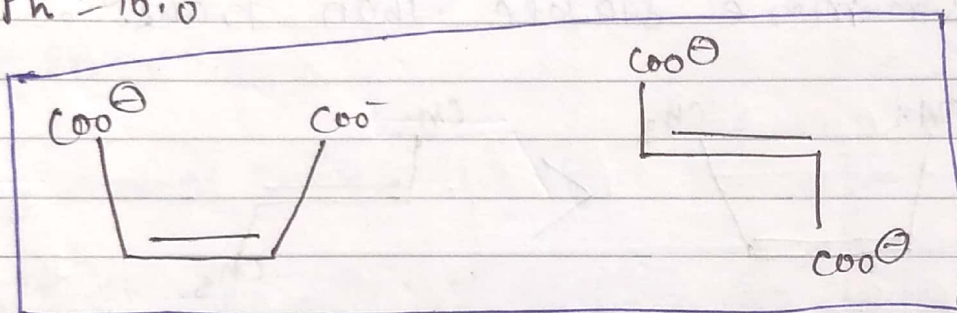
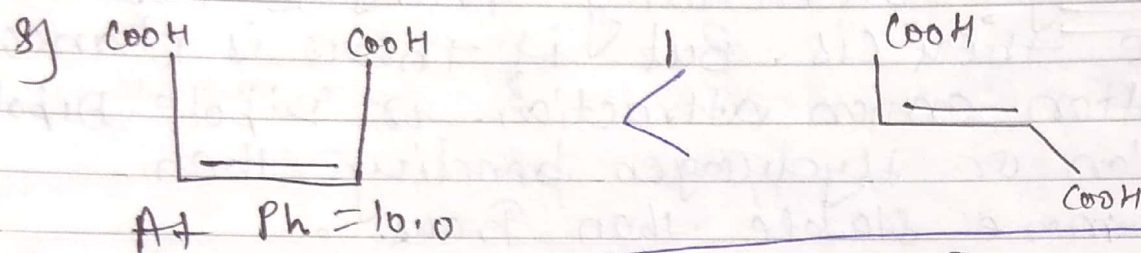
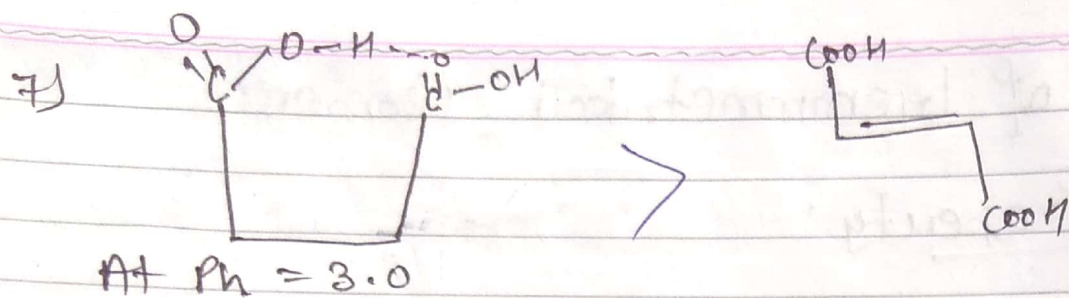
* Property of Geometrical Isomers:

1) Physical Property:

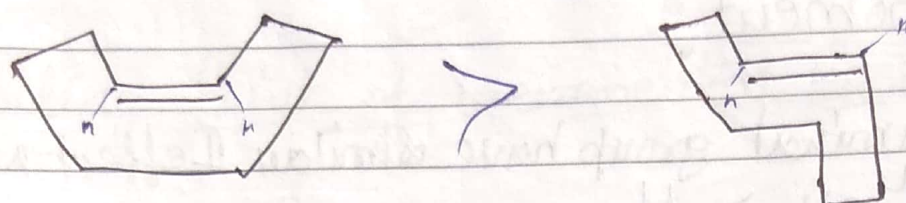
i) Stability : Generally Trans is more stable than cis. But if there is chance of Cation-anion attraction, or Dipole-Dipole attraction or hydrogen bonding then cis is more stable than Trans.



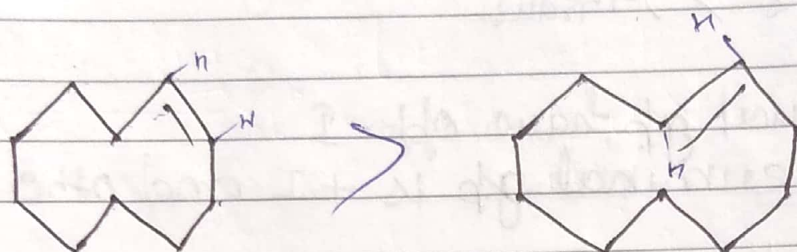
Back Bonding Power $\Rightarrow$ cl more



12)



13)



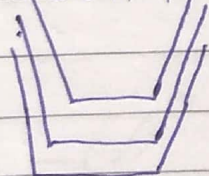
Note: upto 11 carbon cis cycloalkene is more stable than Trans

After 11 carbon Trans cycloalkene is more stable than cis.

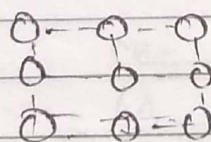
* Melting Point:



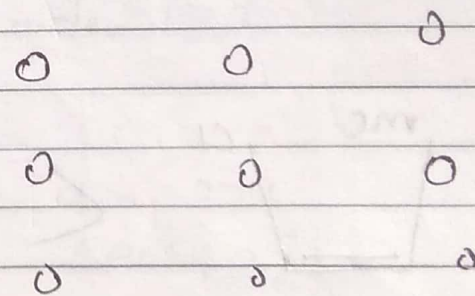
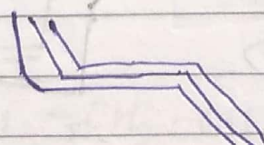
Solid



mp of cis < Trans

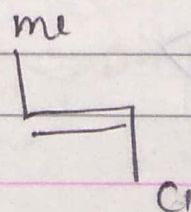
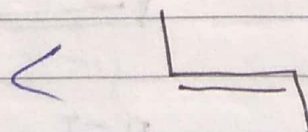
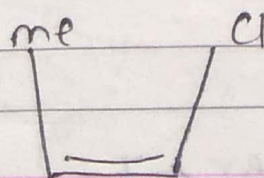
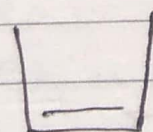


liquid



gas.

Ex:

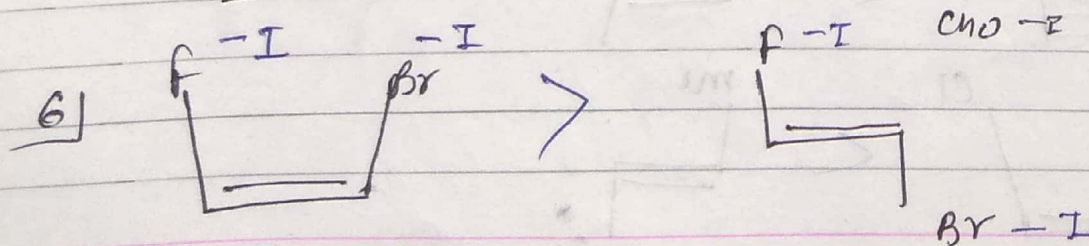
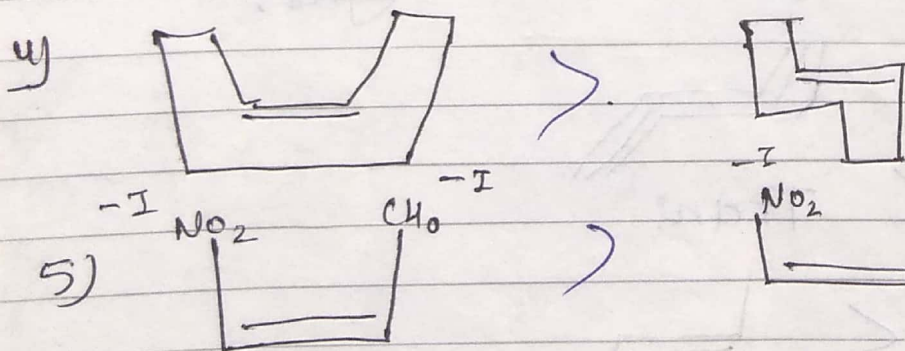
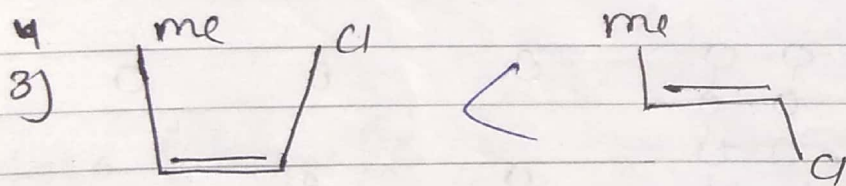
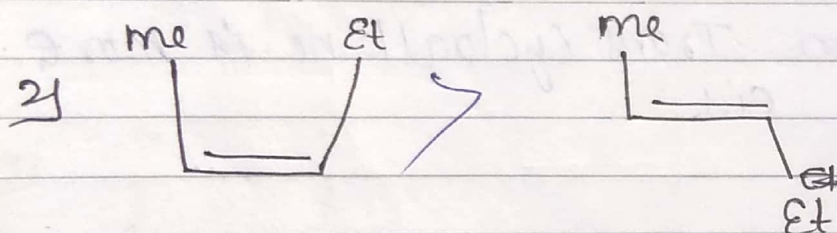
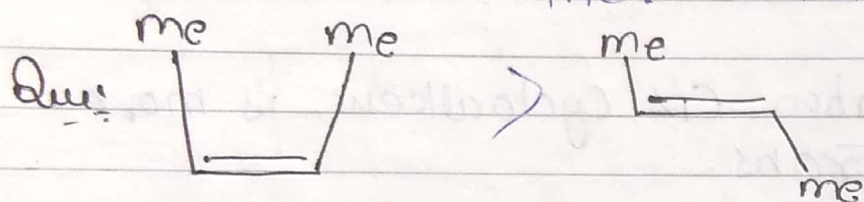


* Dipole moment :

1) when terminal group have similar Effect Nature.
then $\mu_{cis} > \mu_{trans}$.

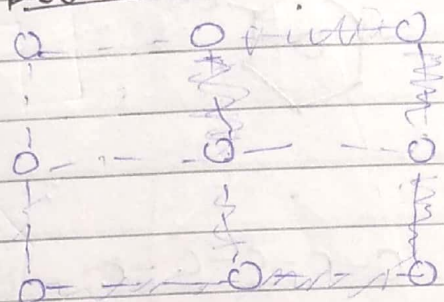
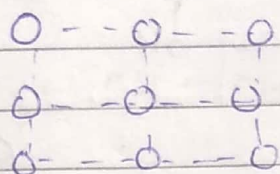
2) When ^{me} terminal gp have opp. I
when one terminal gp is +I and other is
-I gp

then $\mu_{trans} > \mu_{cis}$.



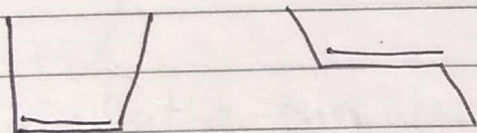
15/06/17

* Boiling point of Unsymmetrical Isomerism:



$B.P \propto$ Inter molecular H.B $\propto$ ~~Intramolecular H.B~~
 $\propto$ Dipole-Dipole Attraction
 $\propto$ Dipole moment
 $\propto$ $\mu \propto$ Polarity
 $\propto$ ~~m.wt~~ $\propto$ m.wt $\propto$ Surface Area $\propto \frac{1}{\text{Branching}}$

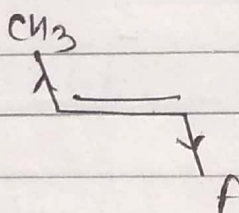
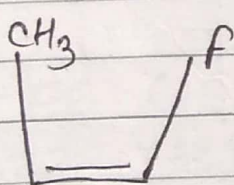
Q: 1)



$M = 1 > 2$

B Point order 1 > 2

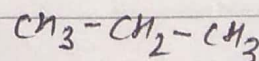
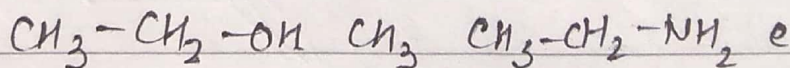
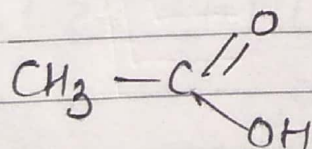
Q: 2)



$M = 2 > 1$

BPO = 2 > 1

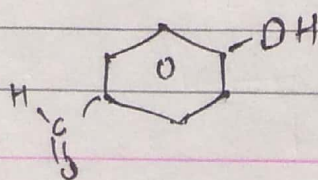
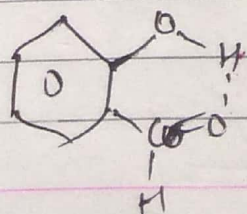
3]



H.B.O = 1 > 2 > 3 > 4

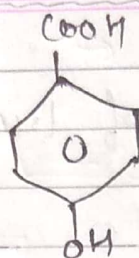
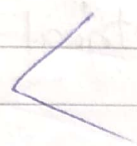
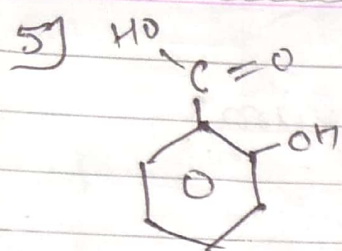
B.P.O = 1 > 2 > 3 > 4

(4)

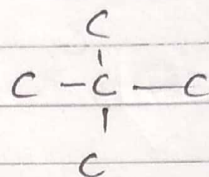
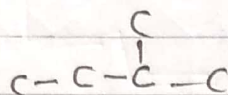
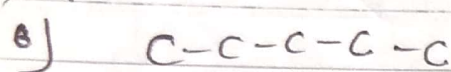


2 > 1

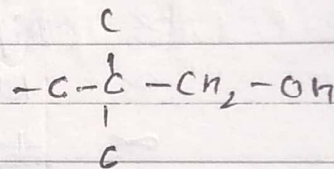
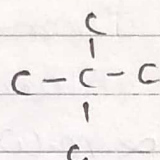
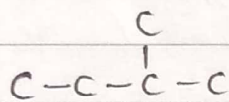
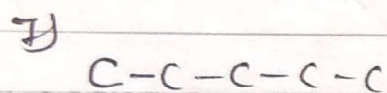
Solubility $\div$ Polarity



★



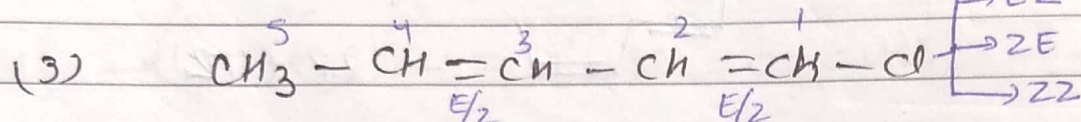
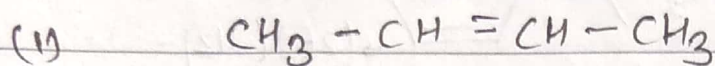
1 > 2 > 3



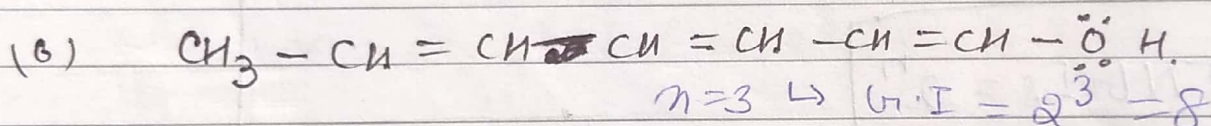
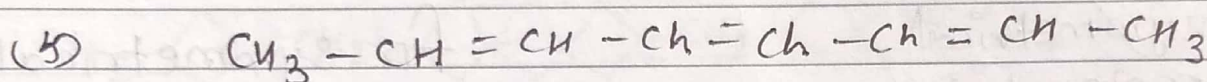
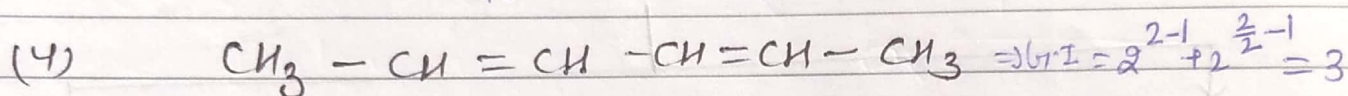
4 > 1 > 2 > 3

Imp:

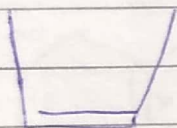
* Calculation of G.I



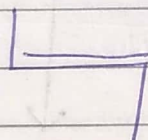
→ EE
 → EZ
 → ZE
 → ZZ



Ans
 (1)

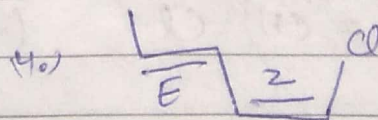
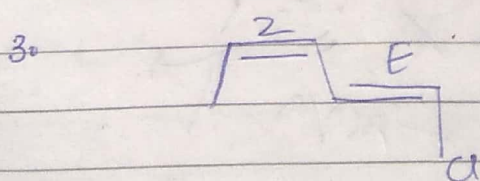
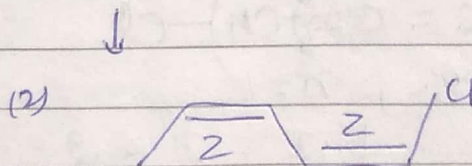
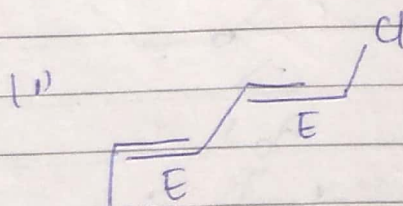


(ZZ) - But-2-ene
 Cis-But-2-ene



(ZE) - But-2-ene
 Trans-But-2-ene

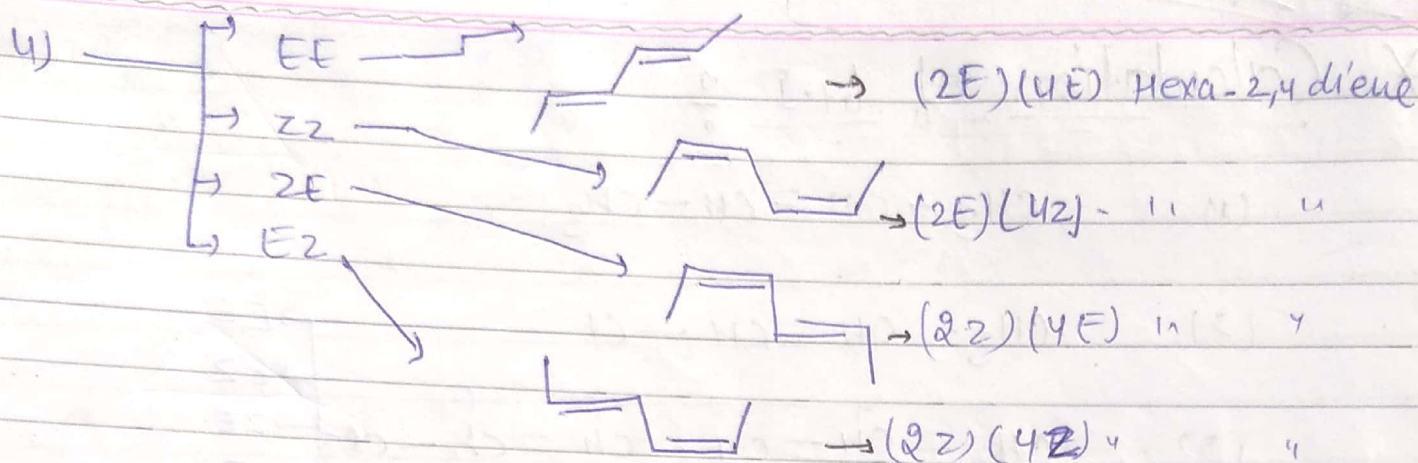
- (3) 1. EE (1E) (3E) - 1-chloropenta-1,3-diene
 2. ZZ (1Z) (3Z) " " " " "
 3. EZ (1E) (3Z) " " " " "
 4. ZE (1Z) (3E) " " " " "



G.I

= even = X

Z > E
cis > Trans



For unsymmetrical molecules

for symmetrical

$$TN_{G.I} = 2^n$$

n = NO of rrs which can show G.I

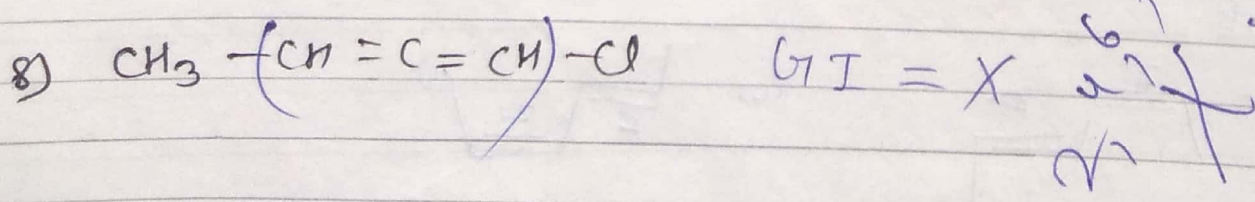
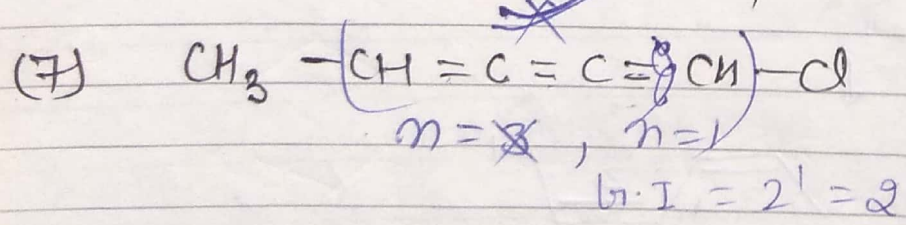
When n = even no.

$$TN_{G.I} = 2^{n-1} + 2^{\frac{n}{2}-1}$$

when n = odd no.

$$TN_{G.I} = 2^{n-1} + 2^{\frac{n-1}{2}}$$

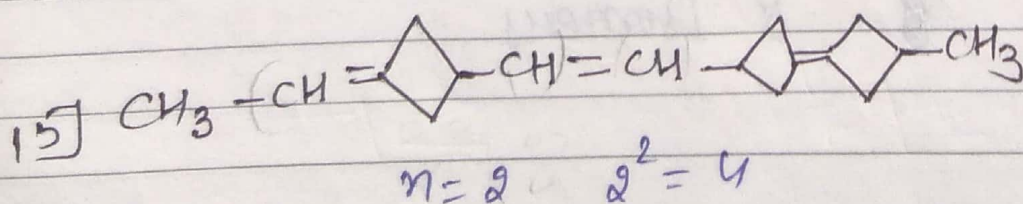
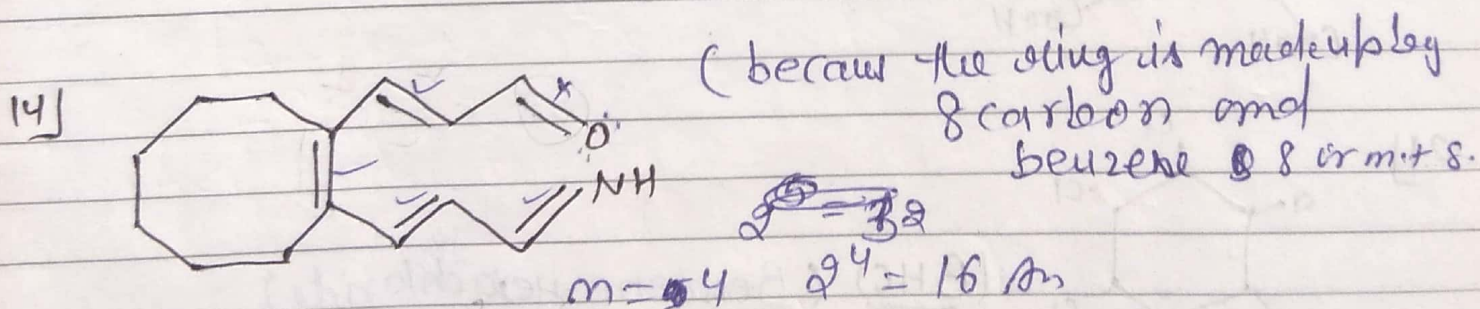
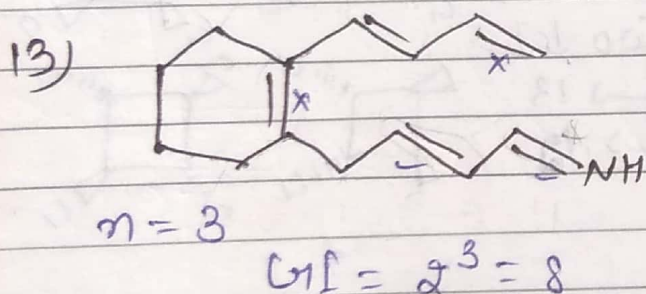
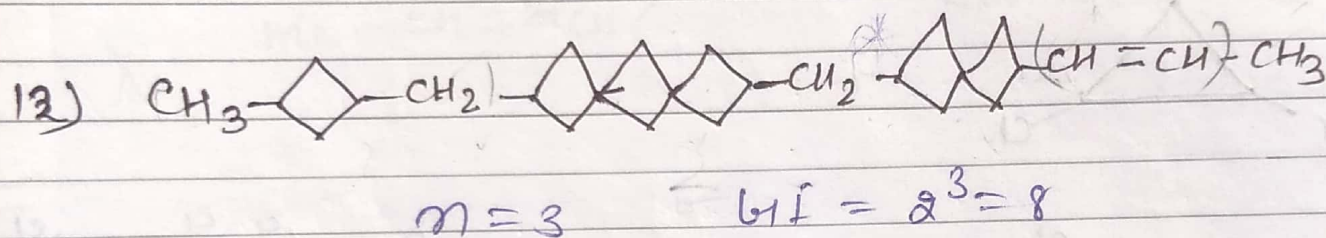
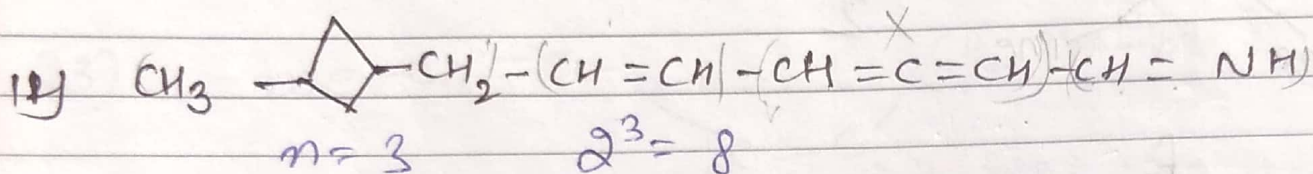
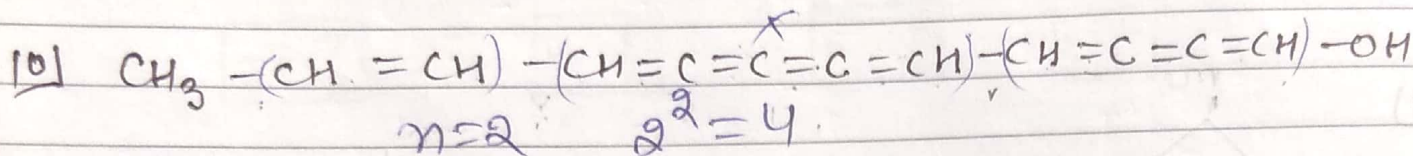
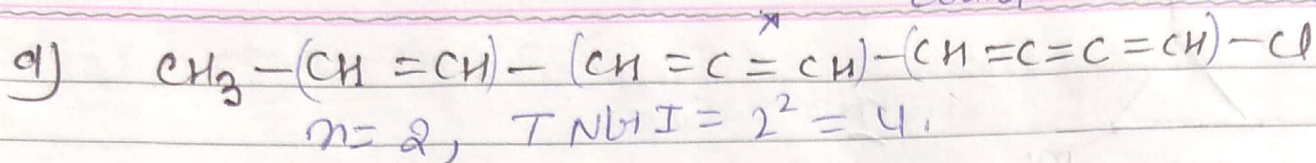
* Calculate TN_{G.I} in following molecules; w

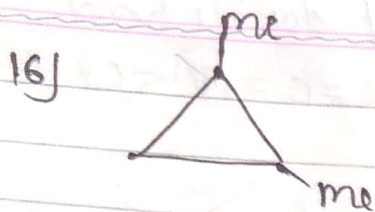


Cycle with 8 carbon

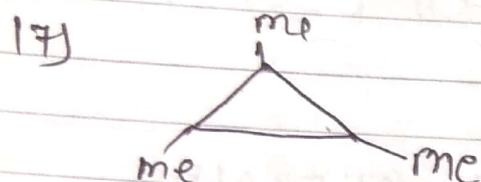
Cycle = n or $n+1$

6 or 7 or more than 7
Count double bond.

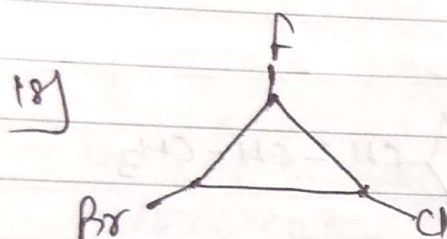




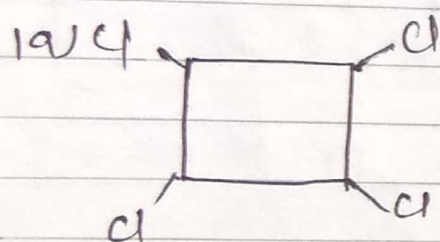
2



2

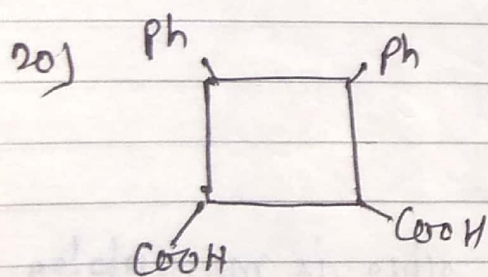
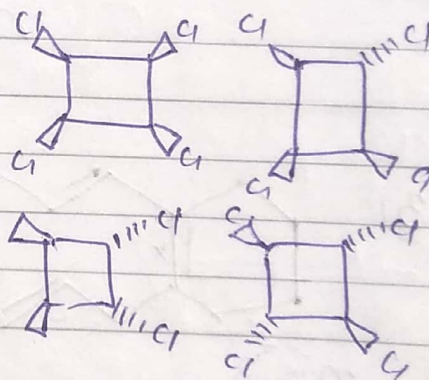


4

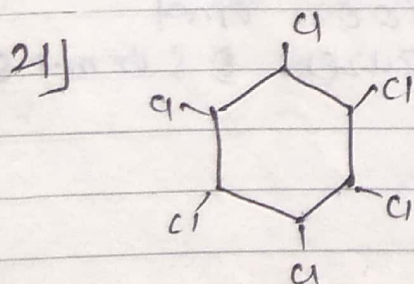


4 →

all ↑
all ↓
Two ↓↓
↳ 13
↳ 12

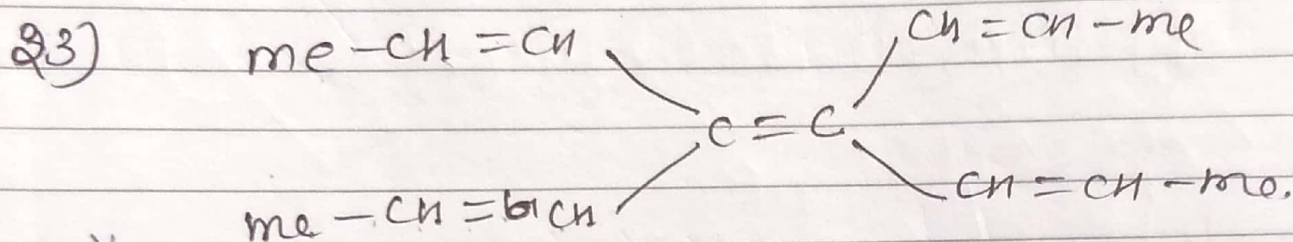
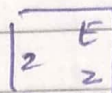
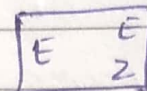
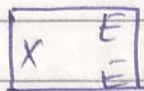
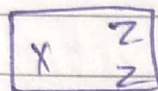
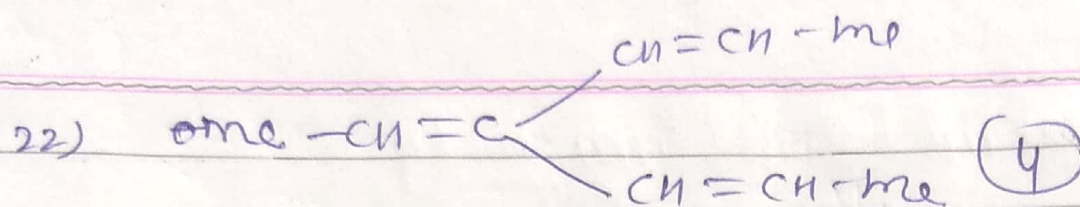


6



(BHC) (Benzene hexachloride)

8 Isomers



X

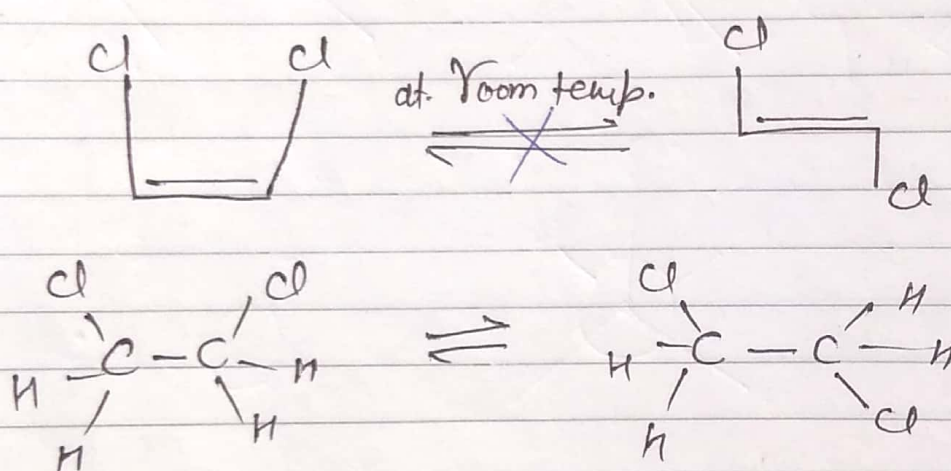
* Conformational Isomerism

OR

Conformational Isomer Analysis

OR

Rotational Isomerism:



- * Rotation ^{along} in $C \equiv C$ is not possible
- * Rotation along $C-C$ is possible.
- * The different isomers (forms) of a compound which are created due to rotation along $C-C$ of a compound. Rotation of single bond is called rotational isomerism, Rotamers, Conformational Isomers, Conformation and the topic in which we study about these isomers is known as Rot Conformational Analysis

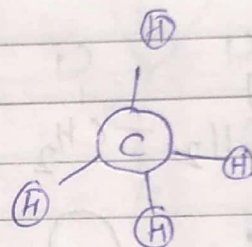
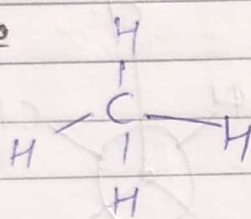
Note: Conformational Isomers can be inter converted to each other at room temp.

* Some Important terms used in Conformational Analysis:

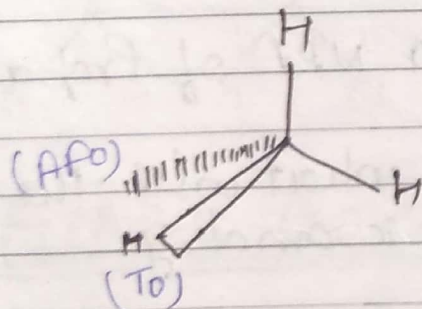
1) Method of representation of Molecules/Isomers:

- Ball - Stick
- Wedge - dash
- Saw-horse Projection formula
- Neomann " "
- Fisher " "

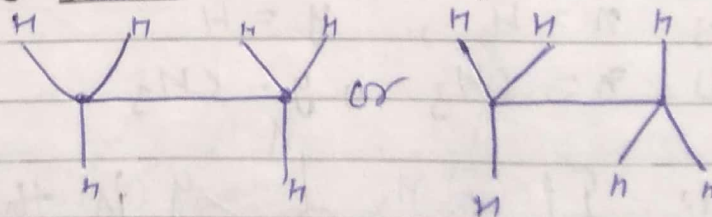
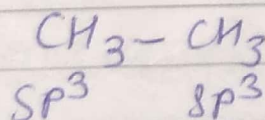
* 1) Ball - Stick:



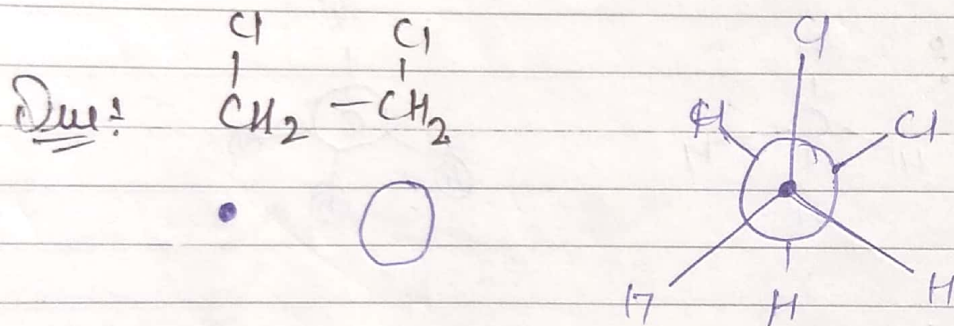
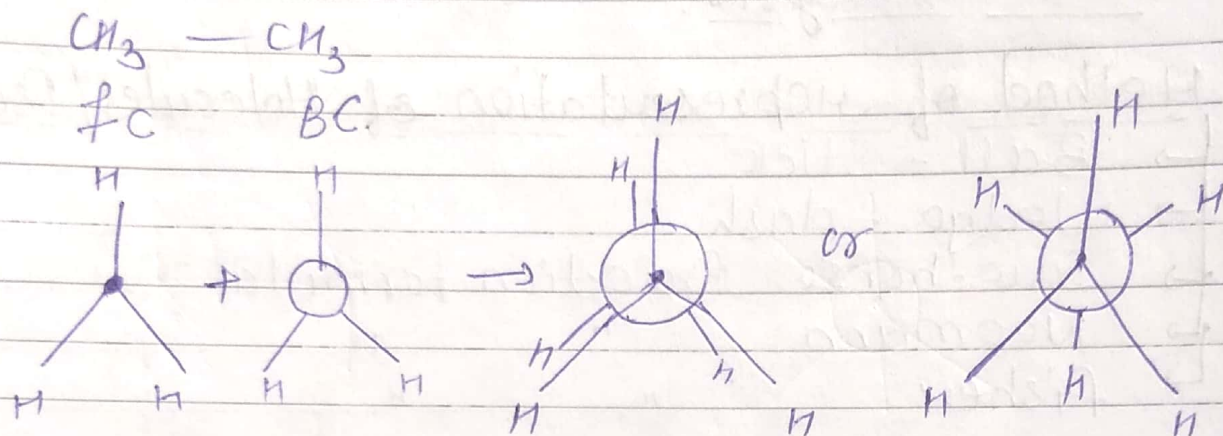
2) Wedge - Dash:

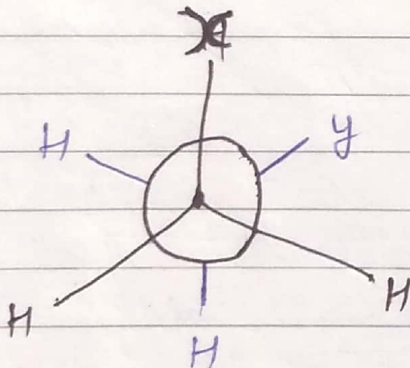


3) Saw-horse Projection formula:

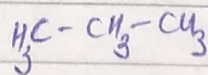


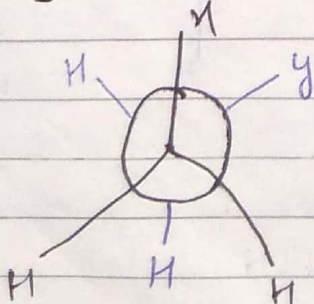
Q4) Neomann Projection formula :



Que: If  is a NPF of Propane then what will the value of x and y.

- Options:
- $x = \text{H}$, $y = \text{CH}_3$
 - $x = \text{CH}_3$, $y = \text{H}$
 - $x = \text{H}$, $y = \text{H}$
 - $x = \text{CH}_3$, $y = \text{CH}_3$



Que: If  is the NPF for butane then what value of x and y:

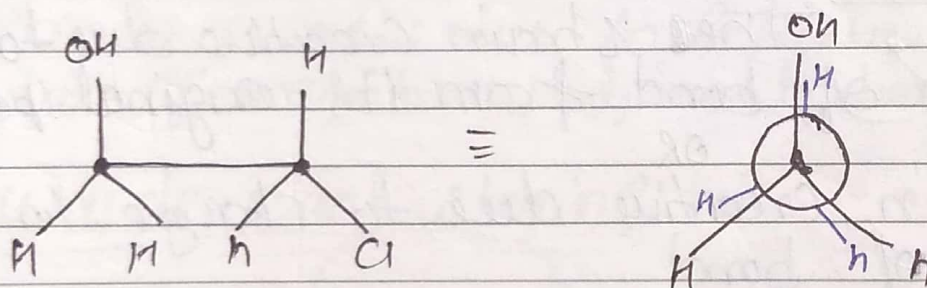
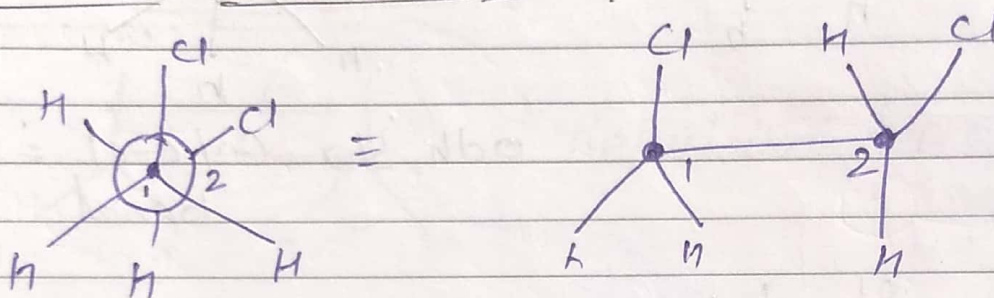
Imp.

Sat. 2nd F
Mon: 10:00 AM

PPT (2012)

- a) H , C_2H_5
b) C_2H_5 , H
c) CH_3 , CH_3
d) C_2H_5 , C_2H_5
e) H , H

* Inter Conversion of Newman to sawhorse and sawhorse to Newman:

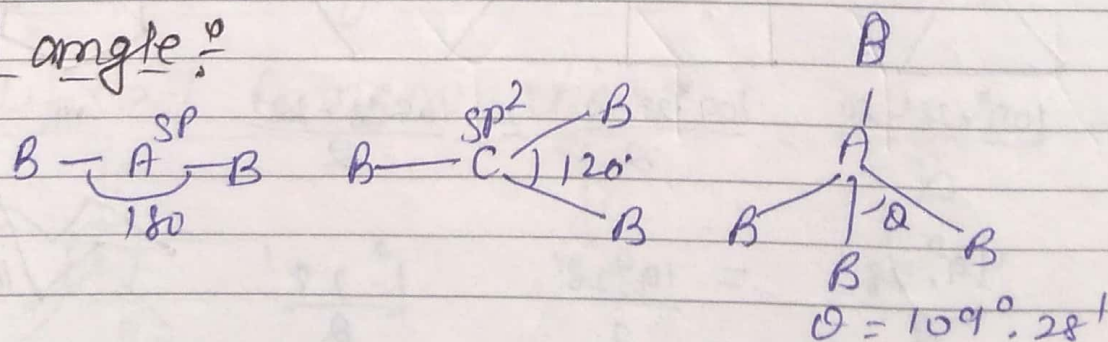


angle = 120°

* Fisher Projection formula (In optical isomerism)

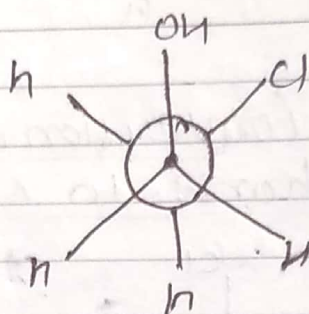
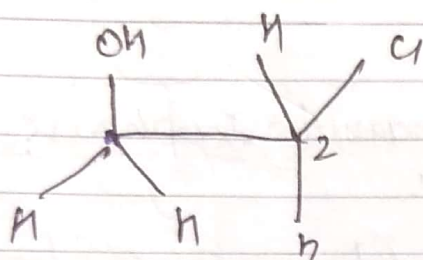
* Different terms used

1) Bond angle



2) Dihedral Angle!

The Angle b/w Plane of bonds of two neighbour atom / Adjacent atom is known as Dihedral Angle.



odh b/w C-O / C-Cl = 60° bond.

* Angle Strain!

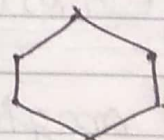
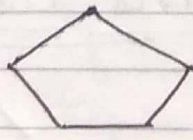
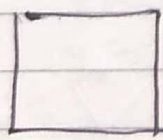
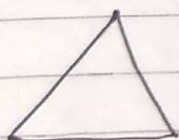
The strain created due to deviation of bond from its original position

OR

The strain created due to change in angle of bond.

$$A.S = \frac{\theta_{\text{expected}} - \theta_{\text{real}}}{2}$$

Q.

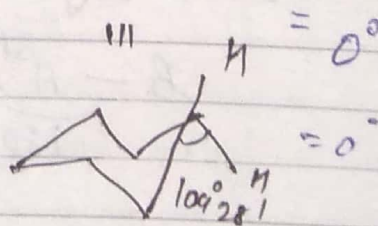


$$= \frac{109^\circ.28' - 109^\circ.28'}{2}$$

$$AS = \frac{109^\circ.28' - 60}{2} = \frac{109^\circ.28' - 90^\circ}{2} = \frac{109^\circ.28' - 108^\circ}{2}$$

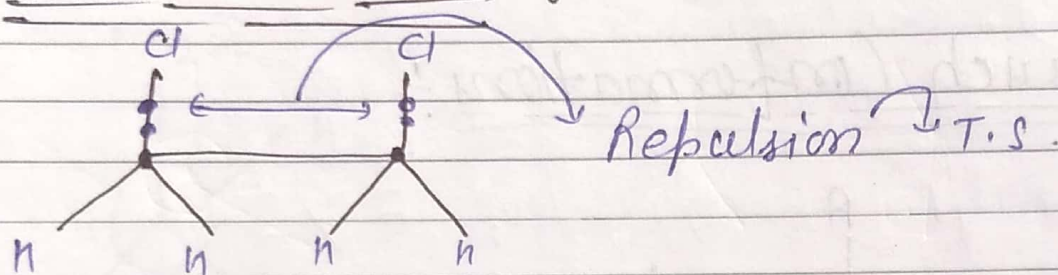
$$= \frac{49^\circ.28'}{2} = \frac{19^\circ.28'}{2} = \frac{1^\circ.28'}{2}$$

$$= 29^\circ.44' = 9^\circ.44' = 0^\circ.44'$$



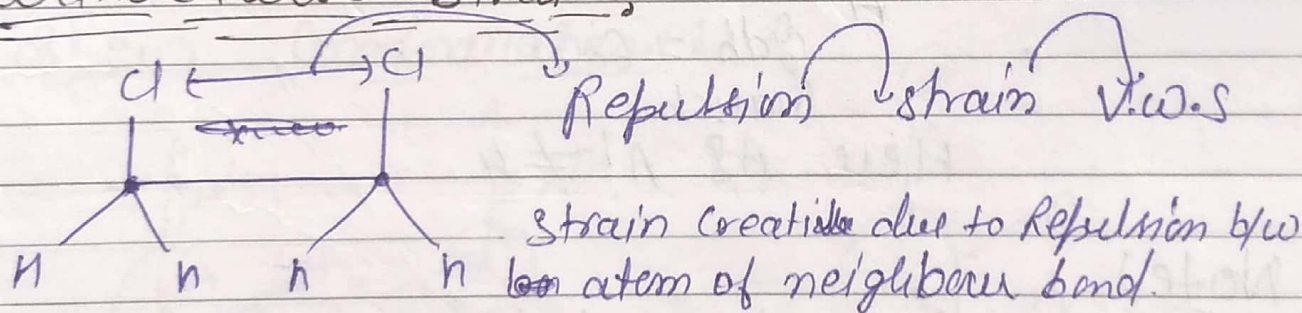
Angle strain order = $1 > 2 > 3 > 4$
 Stability order = $4 > 3 > 2 > 1$
 Reactive order = $1 > 2 > 3 > 4$

* Torsional strain :



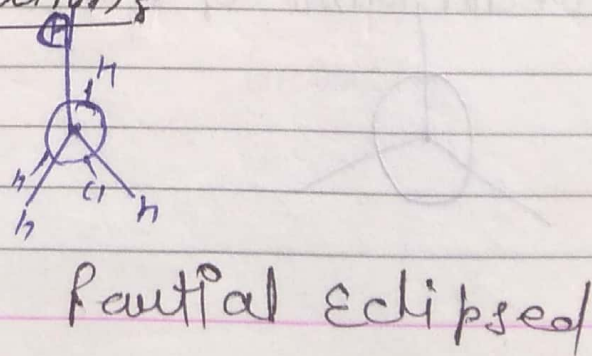
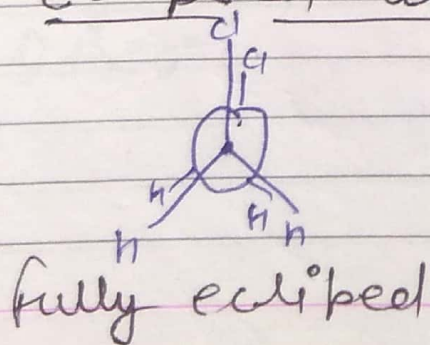
* Strain created due to Repulsion b/w bond pair of neighbour / adjacent bond.

* Wanderwaal strain :

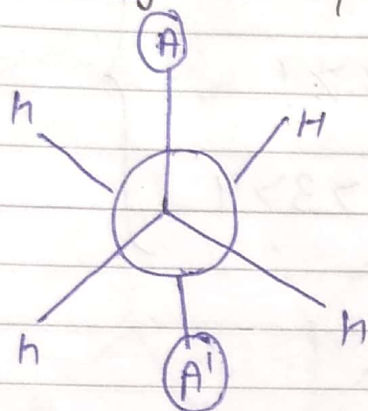


* Types of Conformations :

1) Eclipsed Conformation :



2) Staggered / Anti Conformations:

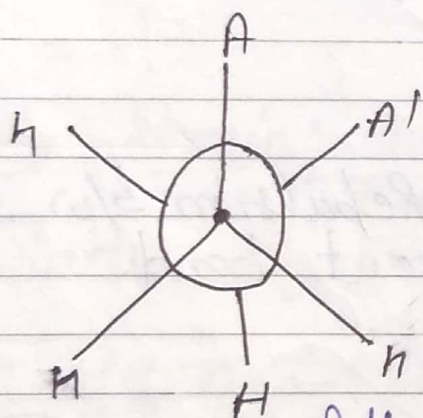


$$A = A'$$

or

$$A \neq A'$$

3) Gauche Conformations:



$$\angle H-A-H = 60^\circ$$

Gauche

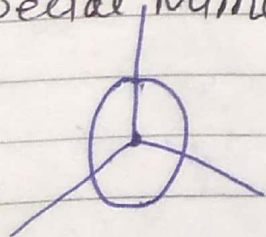
Here $A \neq A' \neq H$

Note:

• for Gauche $A \neq A' \neq H$

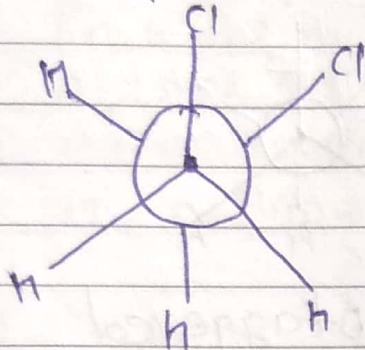
* If either A or A' or Both = H then conformation is staggered.

Q. Decide Name of Conformation,



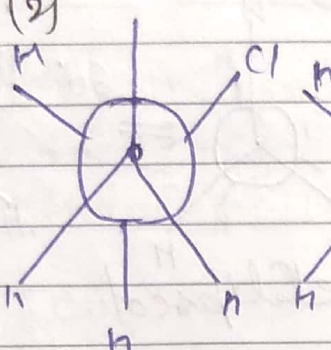
Ques: Decide Name of Conformation

(1)



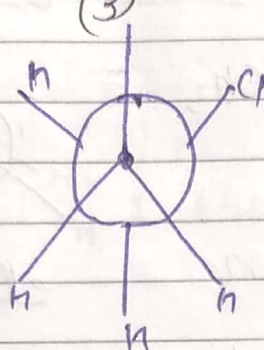
gauche

(2)



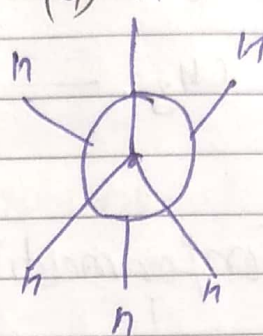
gauche

(3)



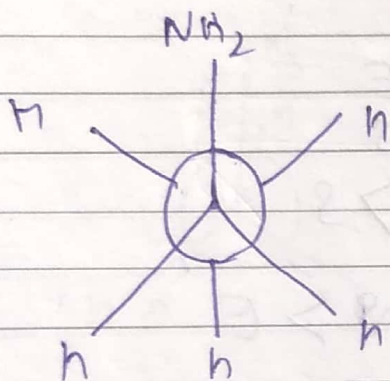
staggered

(4)



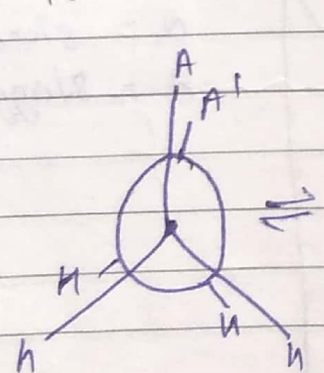
staggered

(5)

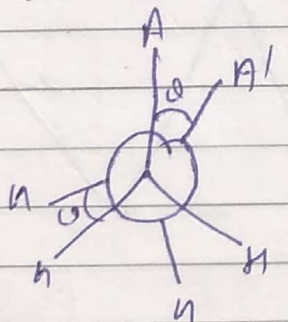


'staggered'

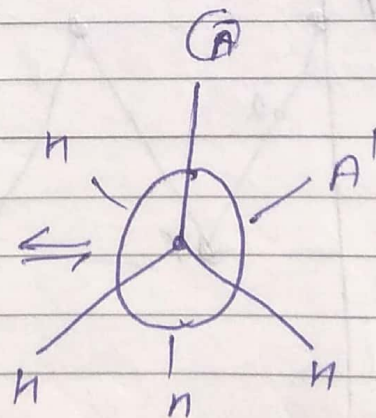
* Skew Conformations!



Fully Eclipsed
 $\Delta\phi = 0^\circ$

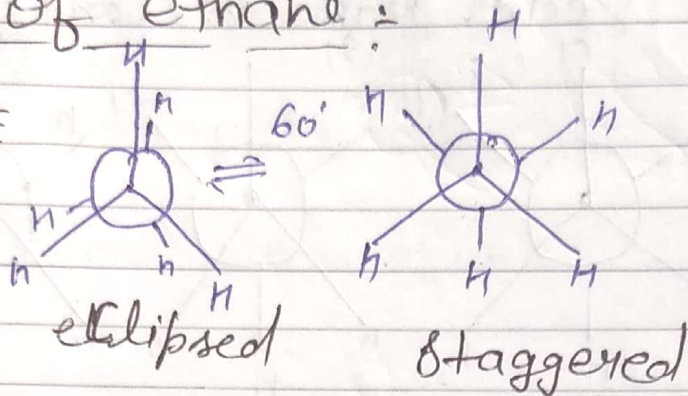
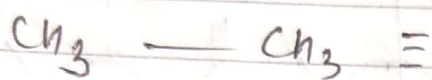


$\Delta\phi \neq 0$
Skew



$\Delta\phi = 60^\circ$
gauche

* Conformations of ethane :



Conformation

→ total no = ∞

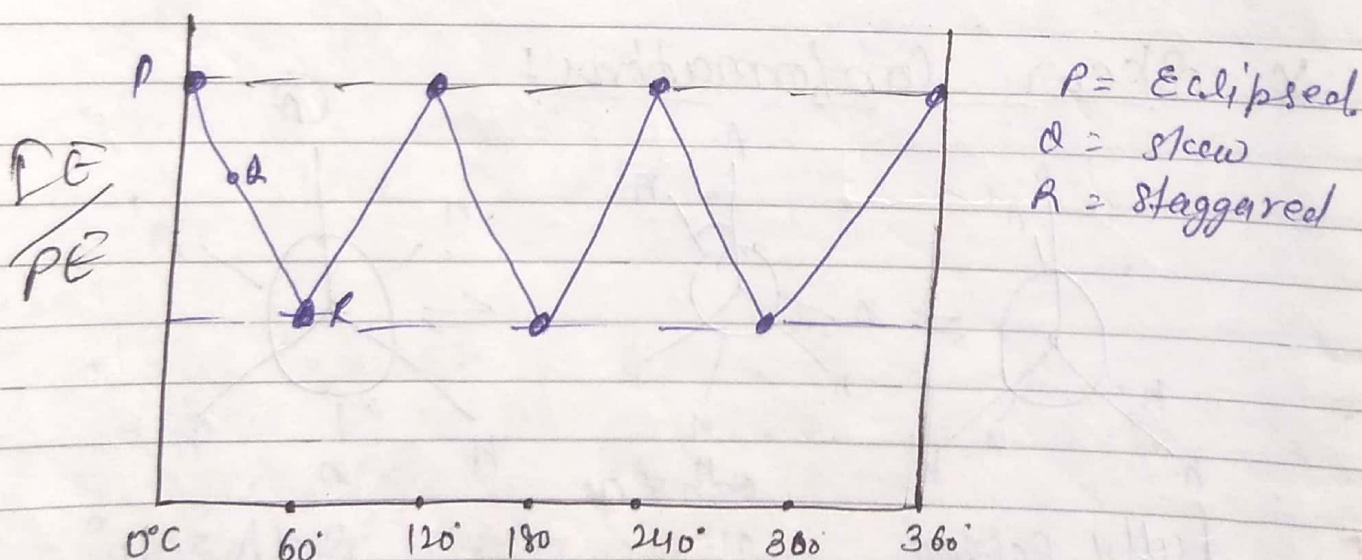
→ Extreme cases = 2

→ E
→ S

→ Internal/Potential Energy order: $E > S$

→ Stability order: $S > E$

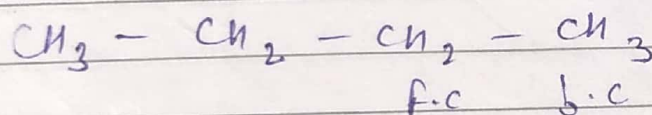
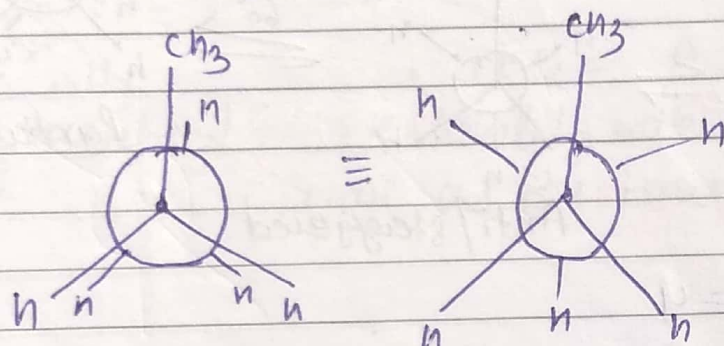
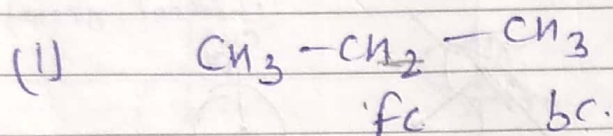
* Potential Energy graph:



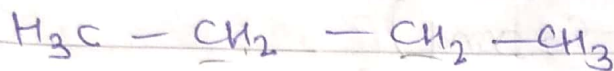
conformation of ethane

Ques: Write Conformational, PEO of the following

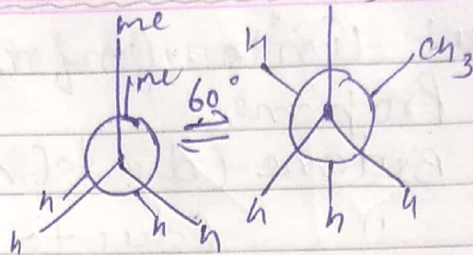
- 1) Propane 2
- 2) Butane (due to $C_1 - C_2$ bond) 2
- 3) " (due to $C_2 - C_3$ bond) 2
- 4) 1,2-Difluoroethane (5) 2-fluoroethanol.



* Conformation of Butane!

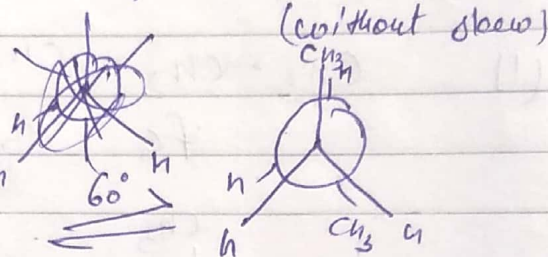


fully eclipsed

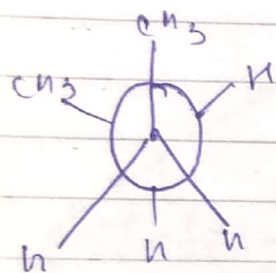


Conformation total = ∞
extreme cases =

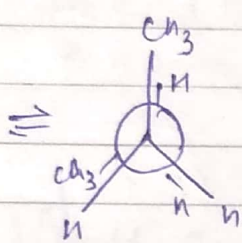
$\uparrow 60^\circ$



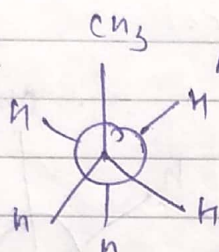
Partial eclipsed



Gauche

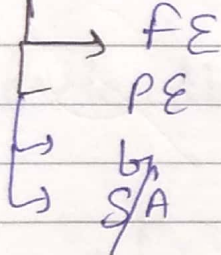


P.E



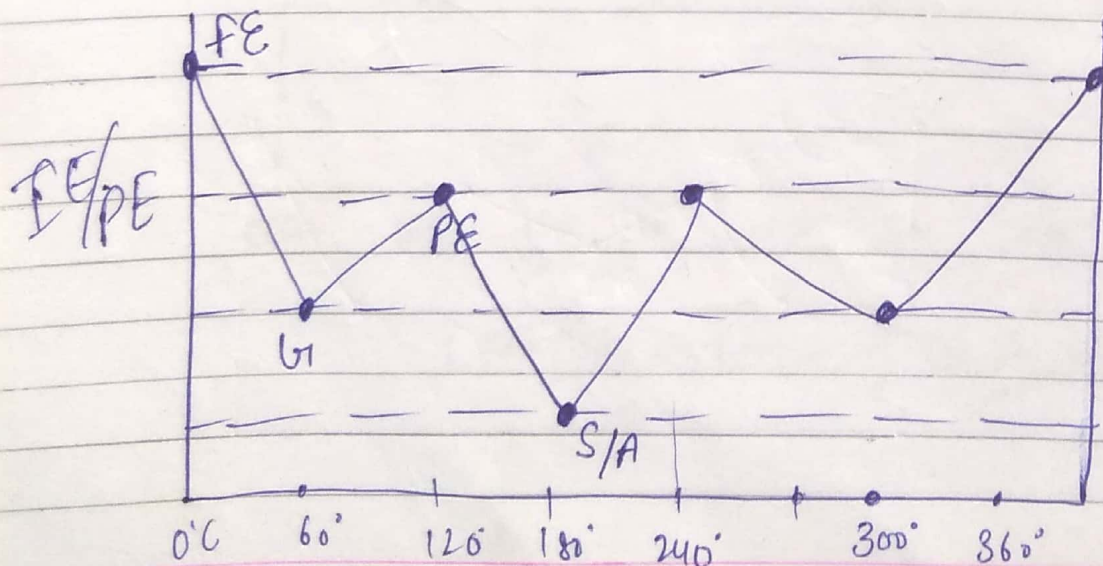
Anti/staggered

Extreme cases = 4

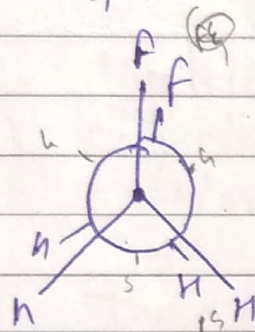
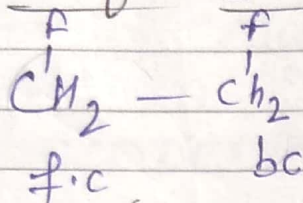


$$\text{F.E.O. / P.E.O.} = \text{FE} > \text{PE} > \text{G} > \text{S/A}$$

$$\text{Stability order} = \text{S/A} > \text{G} > \text{PE} > \text{FE}$$



* Conformation of 1,2 difluoro ethane :



fully eclipsed

Conformations

→ total = ∞
→ Extreme Case = 4

- FE
- PE
- G
- S/A

• IEO = $FE > PE > G > S/A$

• Stability order = $S/A > G > PE > FE$

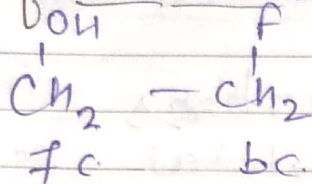
Same as Butane.

$60^\circ \Rightarrow$ ~~branch~~ FE
 $240^\circ \Rightarrow$ G
 $30^\circ \Rightarrow$ PE
 $60^\circ \Rightarrow$ S/A

4 - S > PE
 2 - FC7S

n.B = G/or S/A.

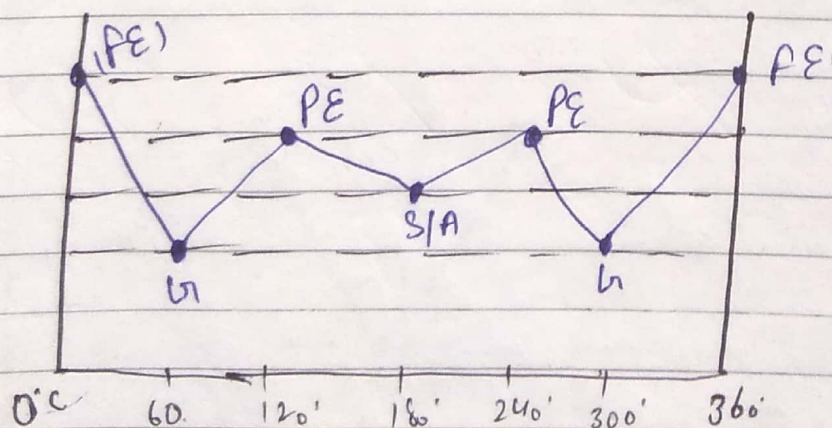
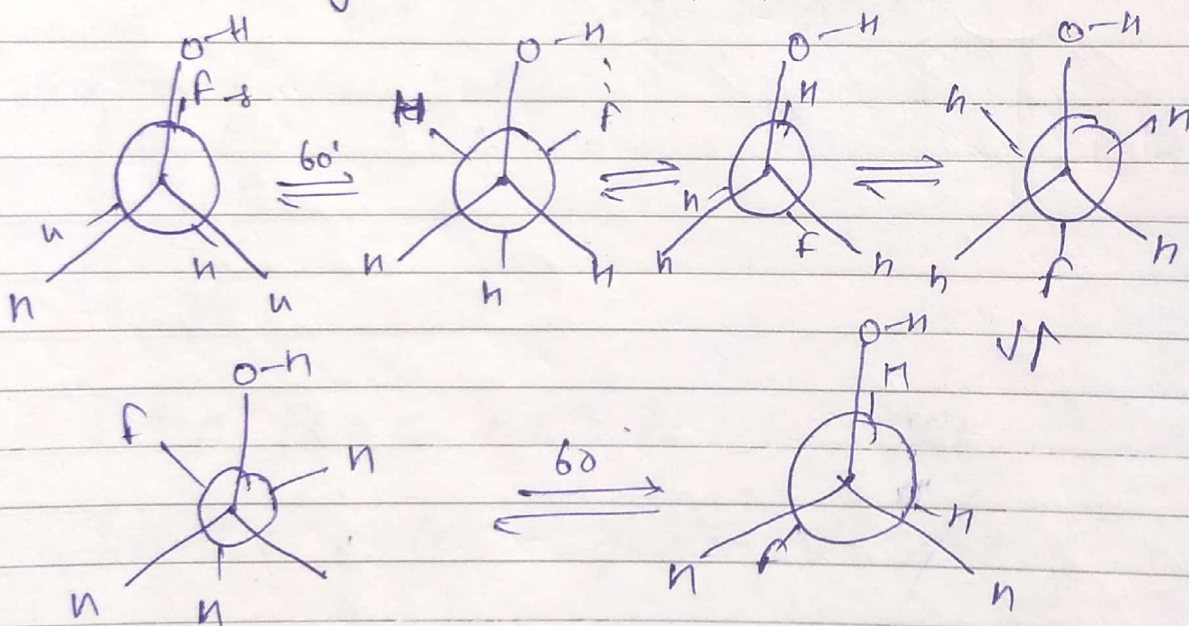
* Conformations of 2-fluoroethanol?



Total Conformation = ∞
 Extreme Cases = 4

↳ FE
 ↳ PE
 ↳ G
 ↳ S/A

- IEO/PEO = FE > PE > S/A > G
- Stability order = G > S/A > PE > FE.

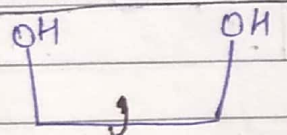
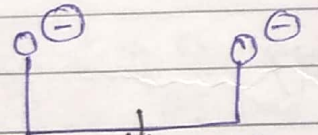
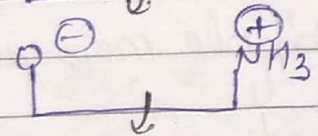
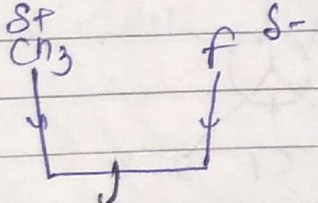
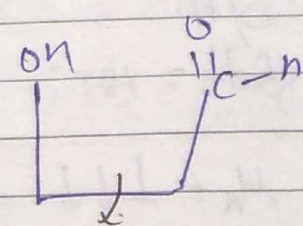


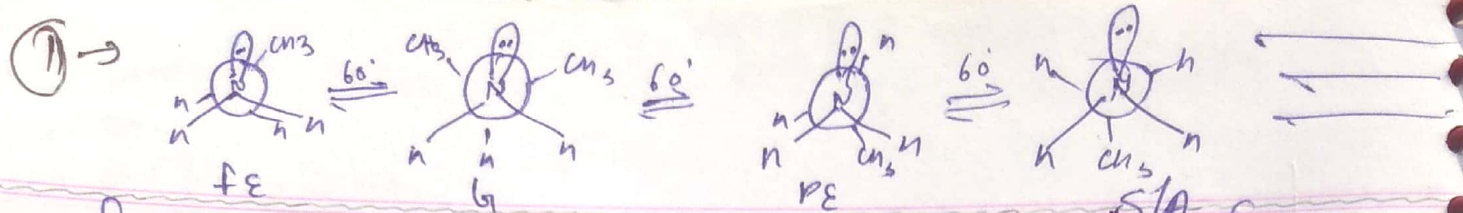
Note: Generally Staggered Conformation is more Stable than others.

But in following cases Gauche Conformation becomes more Stable than Staggered.

1. Hydrogen bonding (Intra molecular H-bonding).
2. Dipole - Dipole Attraction.
3. Cation - anion Attraction.

Q. Decide the most stable and least stable conformation of following molecule or ion.

Compound/Ion	Most stable	least stable
1)  Ethylene glycol	G	F
2) 	S	F.E
3) 	G	F
4) 	G	F
5) 	G	F.E



6) Pentane (C_1-C_2 bond)

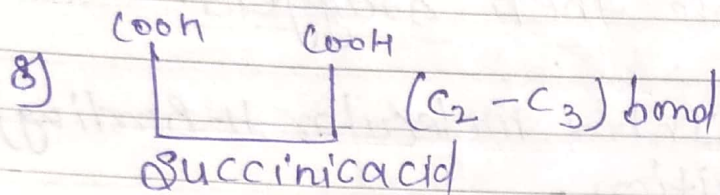
S

S/A f

7) Pentane (C_2-C_3 bond)

S

F



n-s
G/S

n-s
F

9) Succinic acid (C_2-C_3 bond)
at $pH = 3.0$

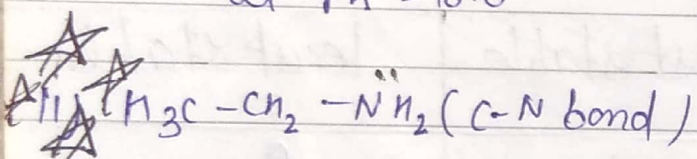
G

F

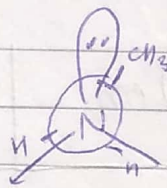
10) Succinic acid (C_2-C_3 bond)
at $pH = 10.0$

S

F



G

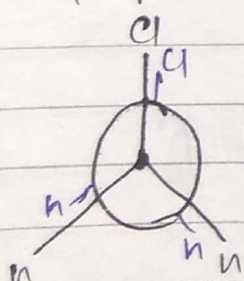


PE

* Physical Property of Conformational :

1) Stability = Pata hai (known)

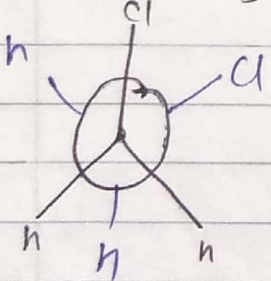
2) Dipole moment = μ / Polarity ($P \propto$ Dipole moment) =



fE

$\Delta\theta = 0^\circ$

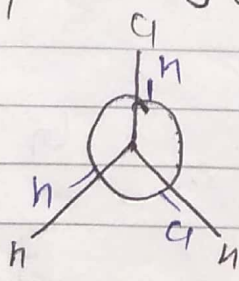
$\mu_R = \uparrow$



G

$\Delta\theta = 60^\circ$

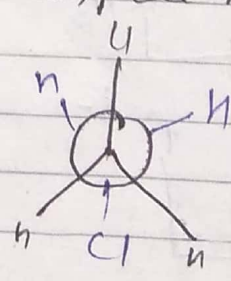
$\mu_R \neq$



PE

$\Delta\theta = 120^\circ$

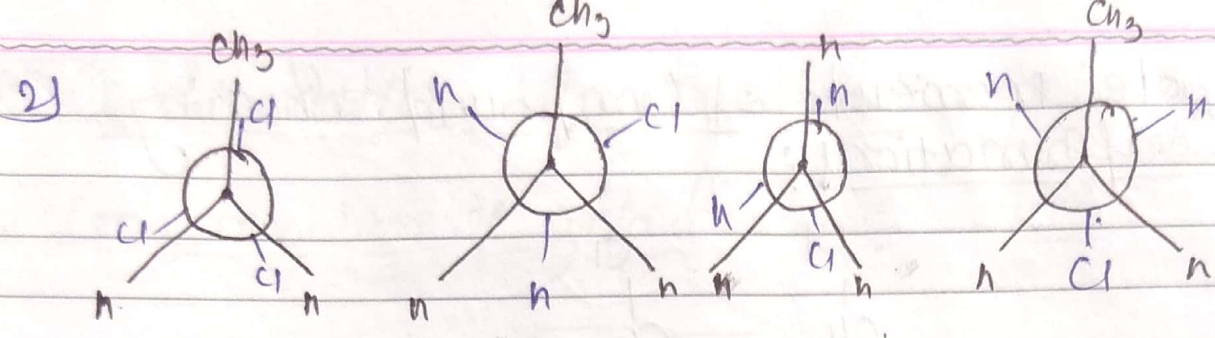
$\mu_R = \downarrow\downarrow$



S/A

$\Delta\theta = 180^\circ$

$\mu_R = \downarrow\downarrow\downarrow$



$\text{Odl} = 0^\circ$ $\text{Odl} = 60^\circ$ $\text{Odl} = 120^\circ$ $\text{Odl} = 180^\circ$

$\mu_R \uparrow$ $\mu_R \uparrow \uparrow$ $\mu_R \uparrow \uparrow \uparrow$ $\mu_R \uparrow \uparrow \uparrow \uparrow$

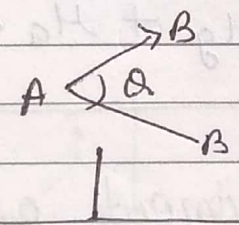
* for similar T.G.

$$\mu_R \propto \frac{1}{\theta}$$

when two polar bonds are at 0°

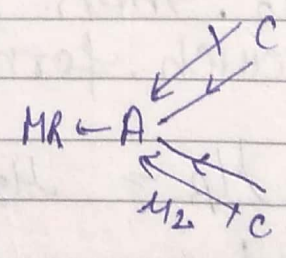
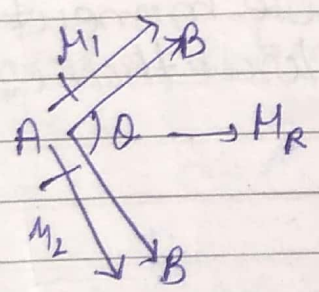
* for diff. sbs are

$$\mu_R \propto \theta$$



when both terminal gp are either +I and -I

when one gp is +I other is -I



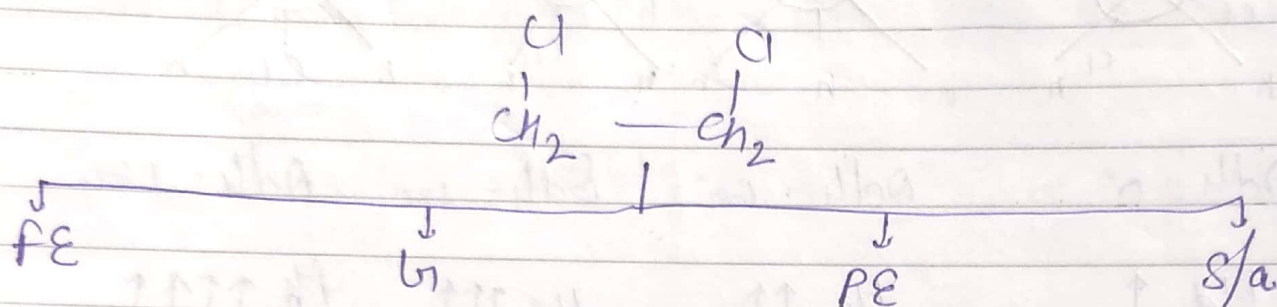
$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

$\theta \uparrow \Rightarrow \cos \theta \downarrow \Rightarrow \mu_R \downarrow$

$\theta \uparrow \Rightarrow \cos \theta \downarrow \Rightarrow \mu_R \uparrow$

* Dipole moment of compound showing Conformation:



$$\mu_R = \sum \mu_i \cdot n_i$$

$$\mu_R = \mu_{fE} \cdot n_{fE} + \mu_G \cdot n_G + \mu_{PE} \cdot n_{PE} + \mu_{s/a} \cdot n_{s/a} \quad \text{--- (1)}$$

Hence Since n_{PE} & $n_{fE} = 0$

$$\boxed{\mu_R = \mu_G \cdot n_G + \mu_a \cdot n_a} \quad \text{--- (2)}$$

$\frac{2}{25} \times 100$

Ques: Net dipole moment of ~~that~~ 1,2-dichloroethane is ~~to~~ 2 debye and mole fraction of anti conformation of 1,2-dichloroethane is 0.75. then Calculate the Dipole moment of gauche form of 1,2-dichloroethane.

Ans:

$$\begin{array}{ccccc} \mu_R & = & \mu_g \cdot n_g & + & \mu_a \cdot n_a \\ \downarrow & & \downarrow & & \downarrow \\ 2.0 & & ? \times 0.25 & & 0 \times 0.75 \end{array}$$

$$2.0 = \mu_g \times 0.25 \quad = \quad \frac{2}{25} \times 100 = 8$$

$$\mu = 8$$

* Conformation of cyclohexane cyclic compound.

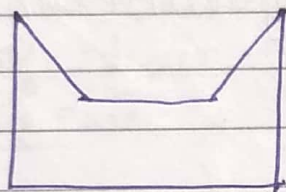
1) Conformation of cyclohexane:



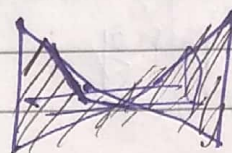
$$\theta = 120^\circ$$



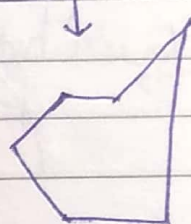
Chair form



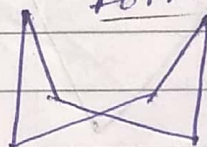
Boat form



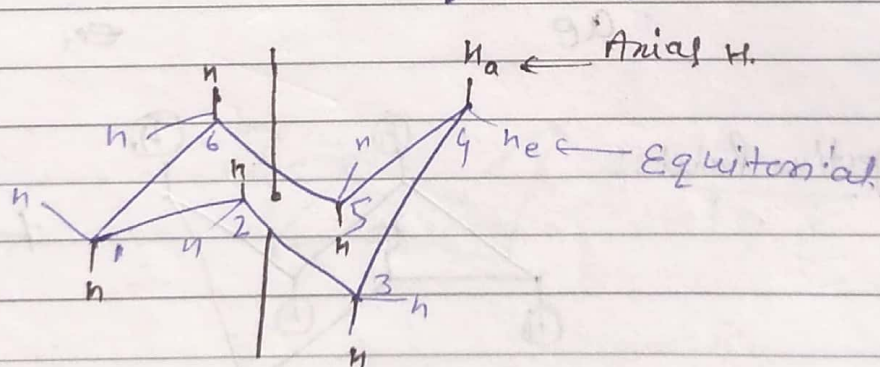
Twist Boat form



Half chair form



* Chair form:



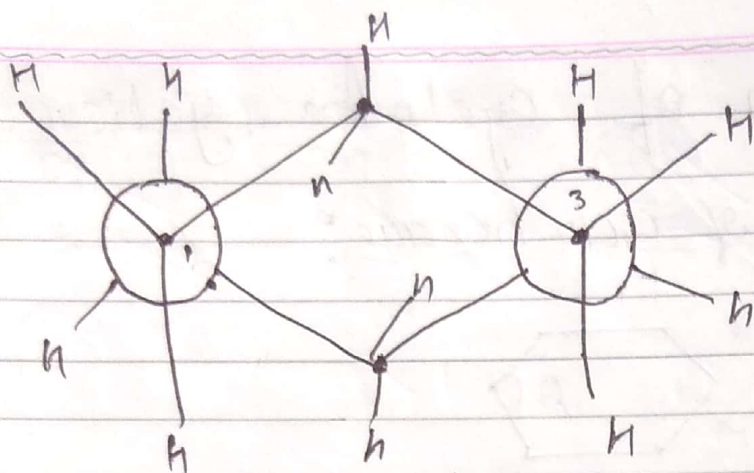
1) Total C-H bond = 12

↳ 6, C-H = a

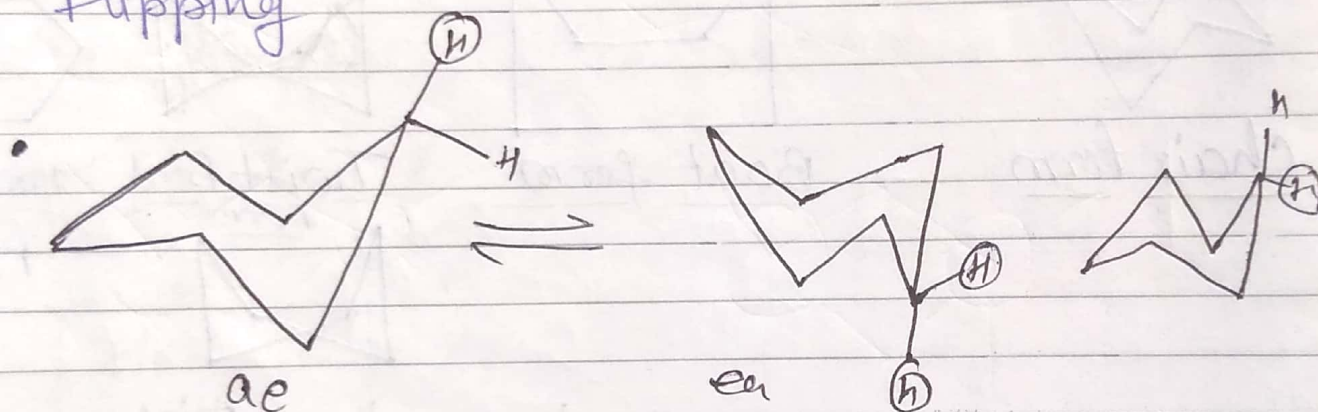
↳ 6, C-H = e

2) The carbon hydrogen form in ~~cy~~ chair form of cyclohexane are present as gauche conformation.

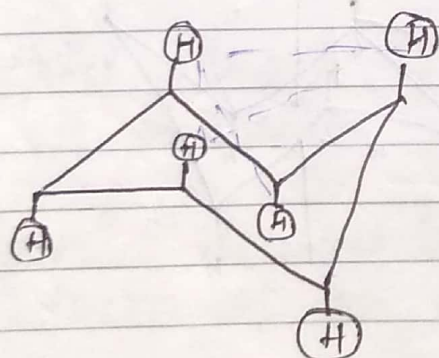
3) making chair form stable.



* Chair form of cyclohexane show flipping.

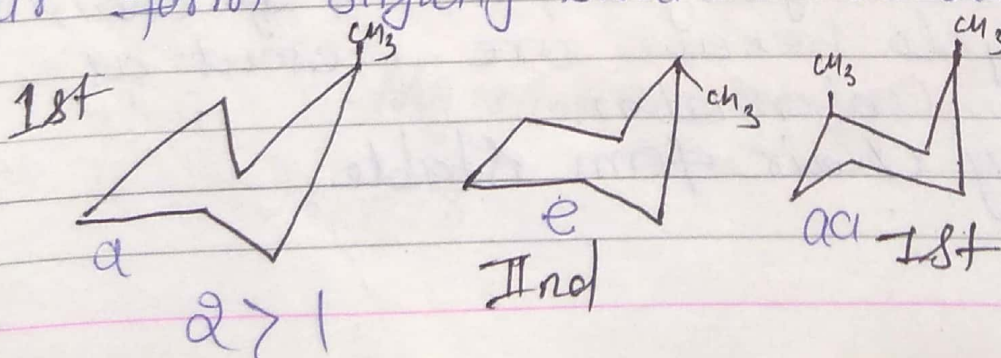


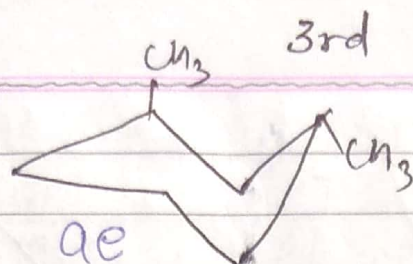
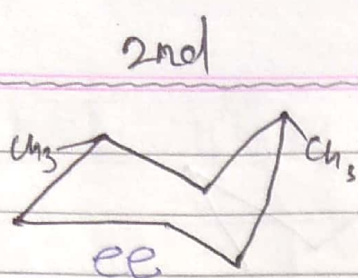
Negative Points:



1-3 Repulsion

* Every axial hydrogen repel to axial hydrogen of 3rd atom (1-3 repulsion) making chair form slightly strained & less stable





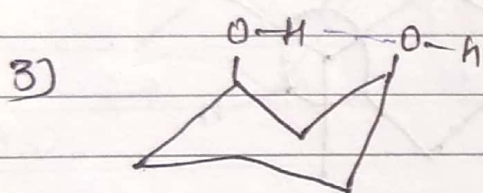
2 > 3 > 1

*Note: Greater the large gp at axial position lesser with stability of chair form. except the case of (1) Hydrogen bonding (2) Dipole Dipole attraction (3) cation-anion attraction.

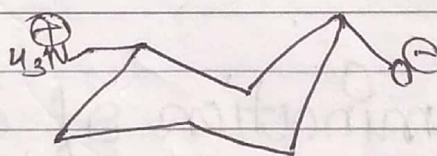
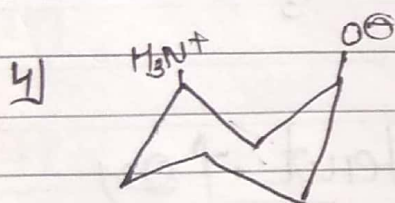
Ques: Decide the stability order of following Cyclohexane of chair form

1) — in intro. the Page.

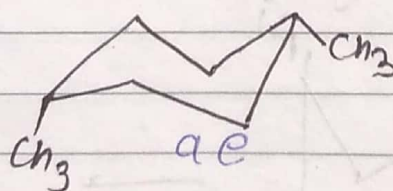
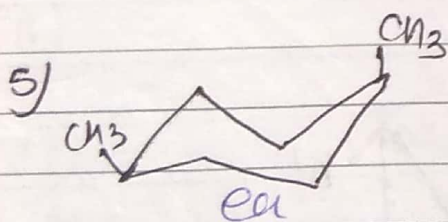
2) — in Previous Page.



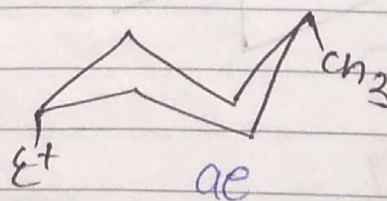
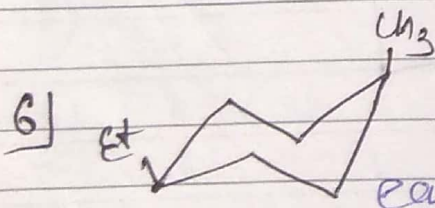
1 > 2



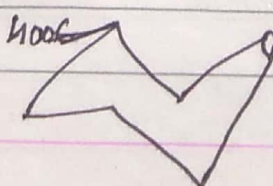
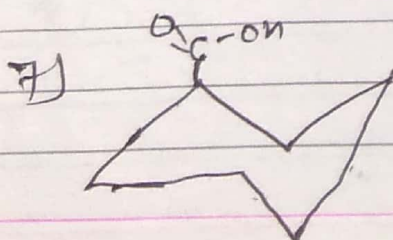
1 > 2



1 = 2

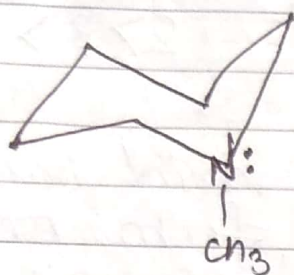


1 > 2

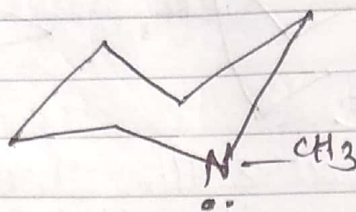


1 > 2

(8)

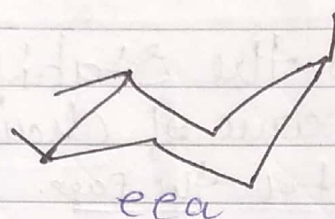


2 > 1



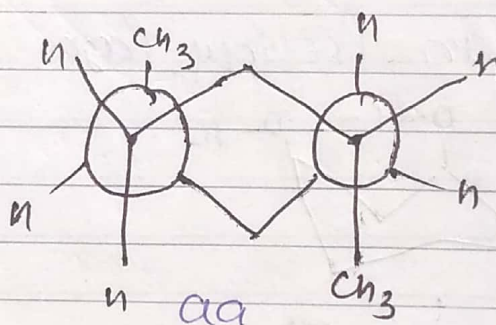
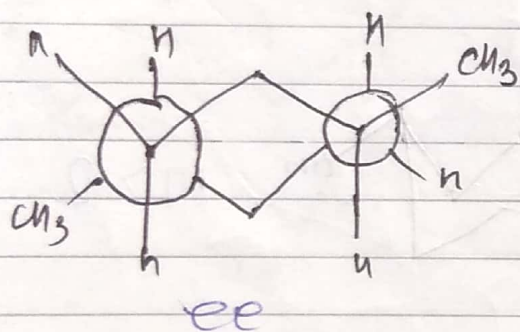
N-methyl piperidine

(9)

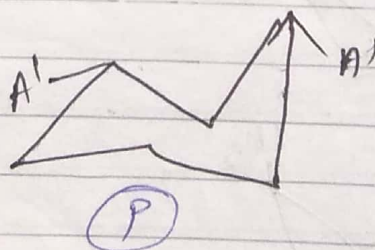
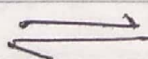
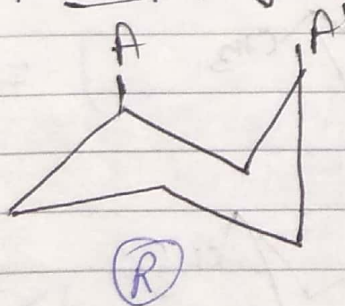


2 > 1

(10)



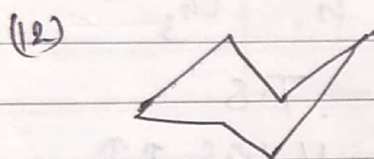
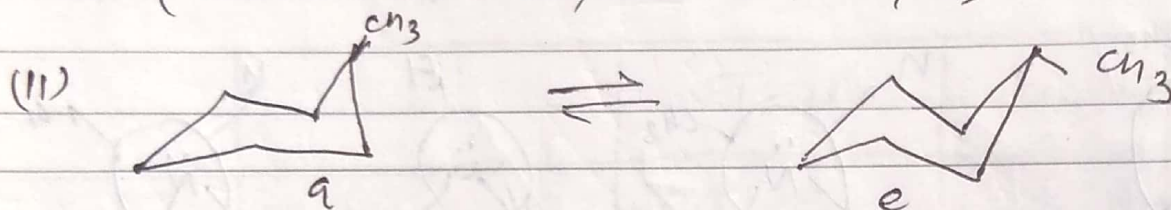
* Determination of eqb constant for
flipping



$$K_{eq} = \frac{[P]}{[R]}$$

- let stability of $P > R$, then $[P] > [R]$ $K_{eq} > 1.0$
- " " " $[P] < [R]$ $K_{eq} < 1.0$
- " " " $P = R$ $[P] = [R]$ $K_{eq} = 1.0$

Ques: Decide K_{eq} for following flipping process (more than one, less than one, equal to one)



(13)

(14)

(15)

(16)

(17)

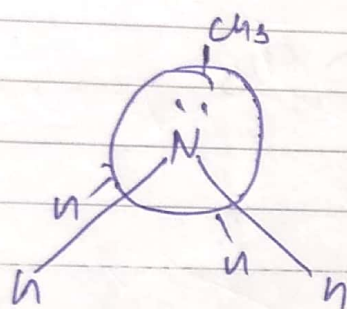
(18)

(19)

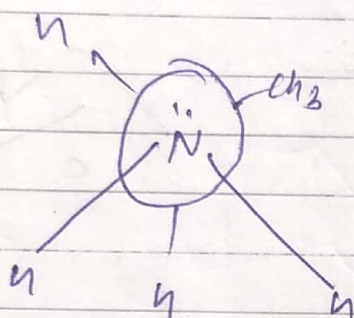
(20)

Bauch effect! Generally staggered is

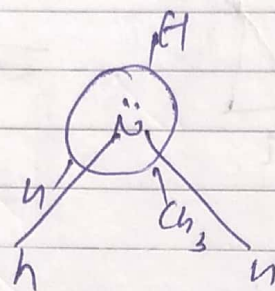
more stable than other. But if large gp present to 60° of lone pair (Brauch condition) then this conformation becomes more stable than staggered.



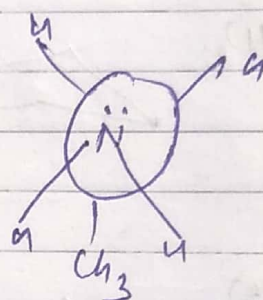
T.S. ↑
V.W.S. ↑↑↑



T.S.
V.W.S. ↑



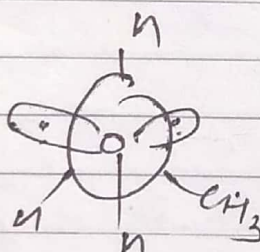
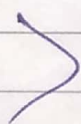
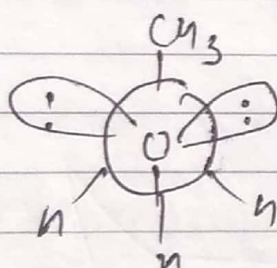
T.S. ↑
V.W.S. ↑↑↑



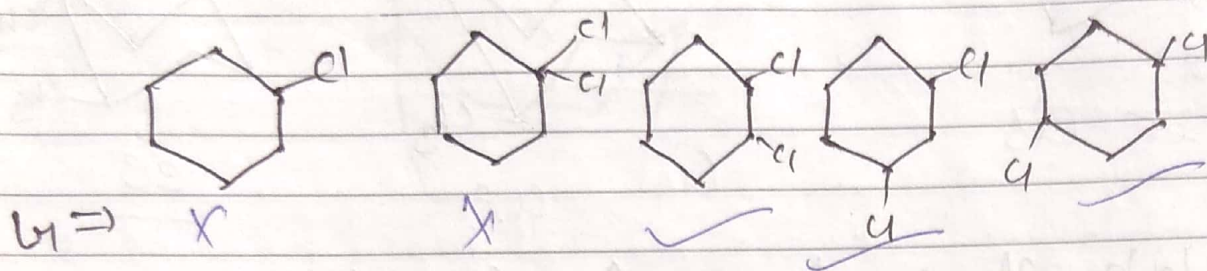
T.S.
V.W.S. ↑↑

Full

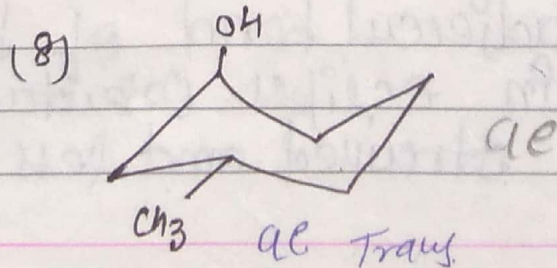
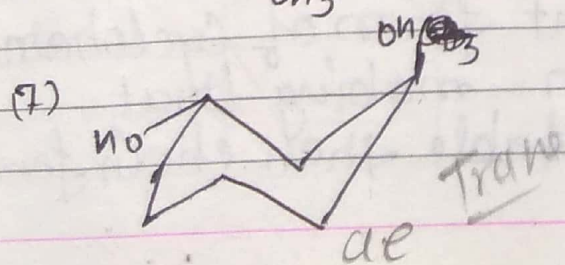
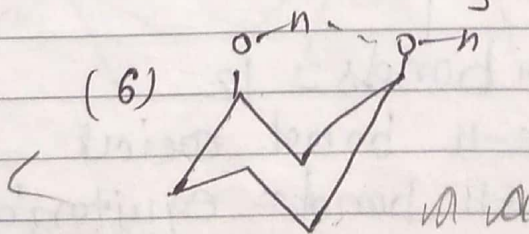
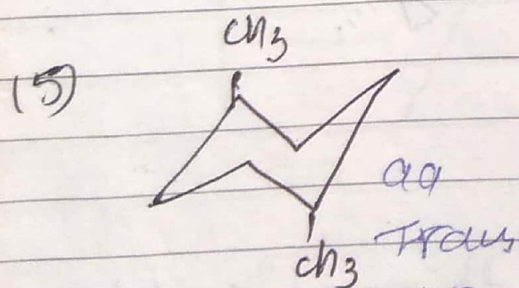
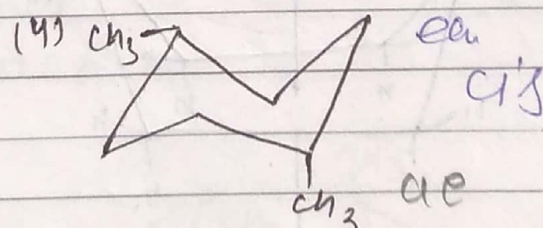
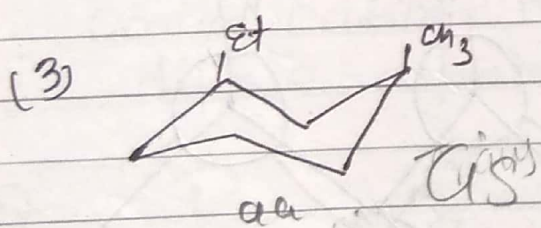
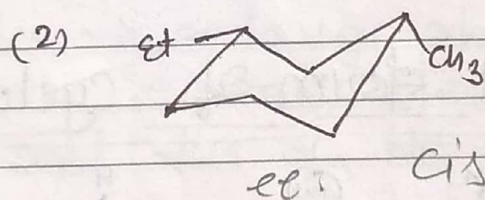
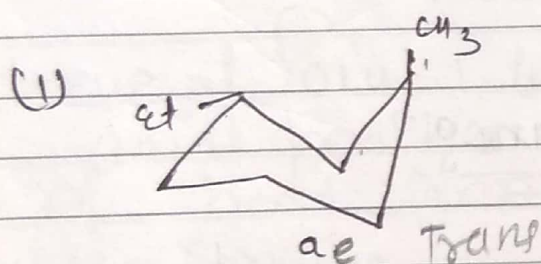
Que!



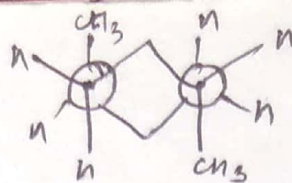
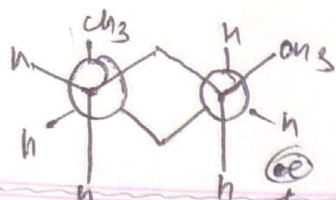
Ques: b.f in chair form of ~~en~~ cyclohexane



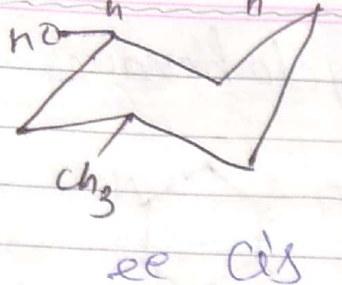
	Trans	Cis
1,2- / 1,4- / 1,6	ae/ee	ae/ea
1,3- / 1,5	ae/ea	aa/ee



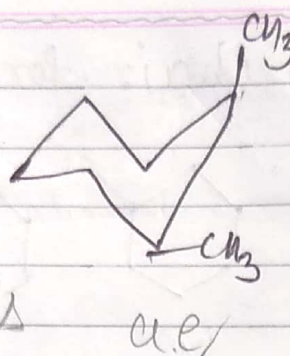
(12)



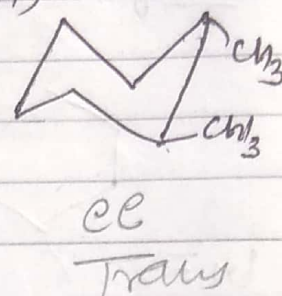
9)



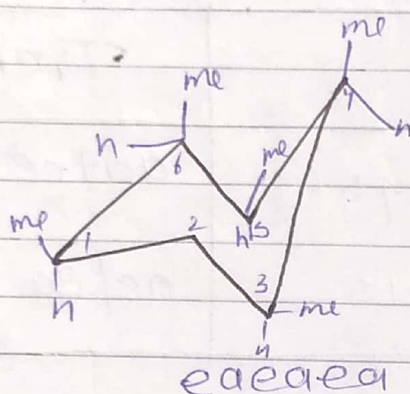
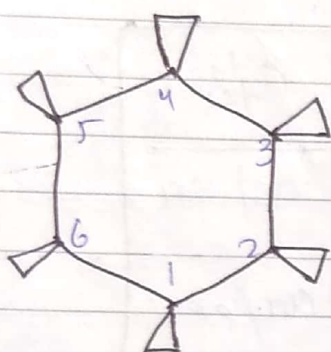
(10)



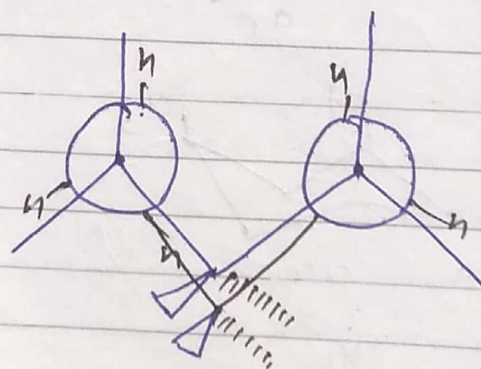
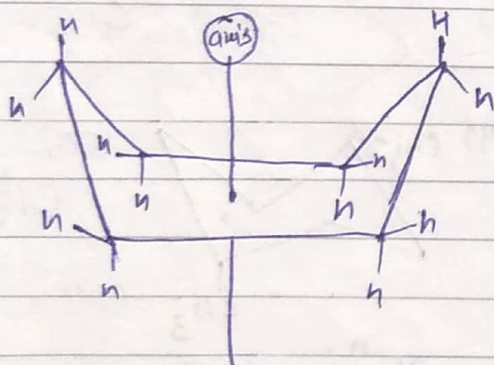
(11)



Que: Make chair form for following



* Boat form of Cyclohexane



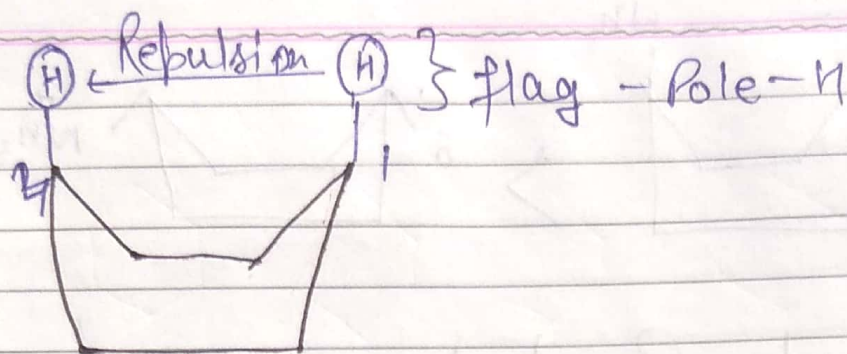
- Total C-H bonds = 12

→ 6, C-H bond axial

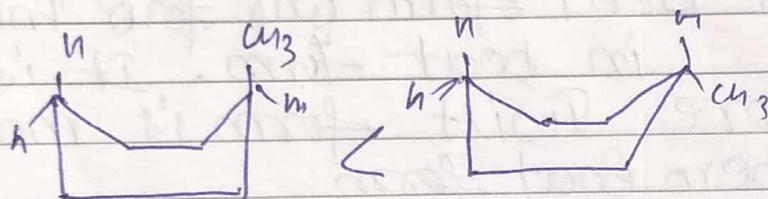
→ 6, C-H bond = equatorial

- The adjacent bond of boat form of cyclohexane lies in eclipsed orientation making boat form strained and less stable than chair form.

Negative Point:

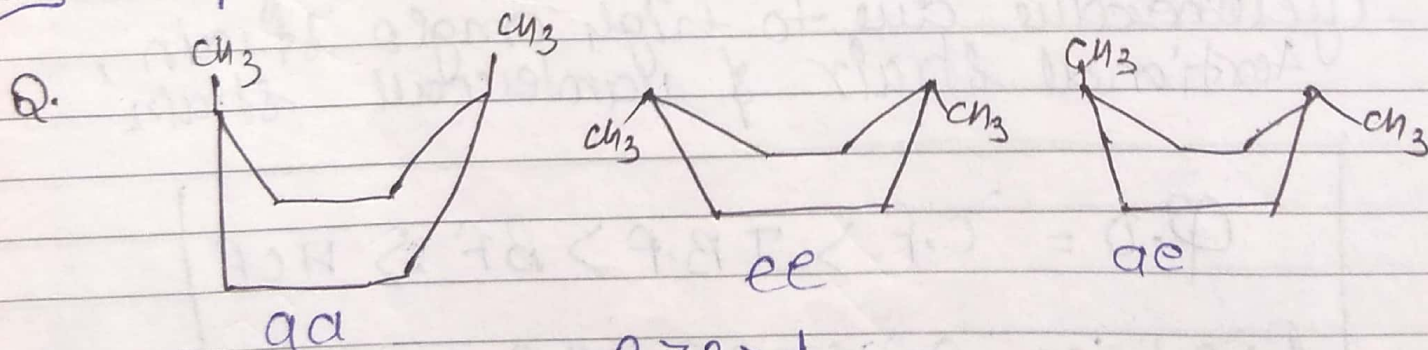


- The axial H of 1 and 4 carbon repels to each other (Flag-pole-Flag-pole Repulsion) making boat form less stable.

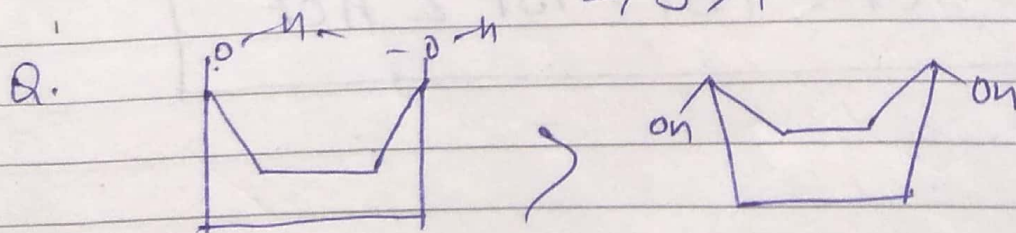


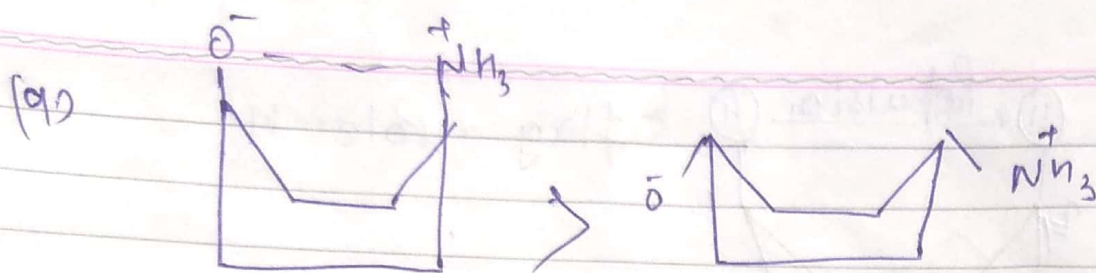
General Point: Greater the large gp at axial position lesser becomes stability of boat form except the of H-B

- 1) H-Bonding
- 2) anion cation Attraction
- 3) dipole-dipole Attraction



273 > 1

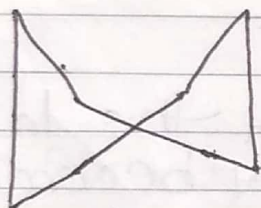




* Twist Boat form of cyclohexane :

Twist Boat differ from boat by one-four interaction.

In Twist Boat form one four interaction absent in boat form. It is present. Therefore Twist form is most stable than Boat form.



SBG STUDY

* Half Chair

It is a least stable conformation of cyclohexane due to high angle strain, torsional strain & van der Waals strain.

$$Q.D = C.F > TBF > BF > HCF$$

$$P.EO / PEO = C.F < TBF < BF < HCF$$