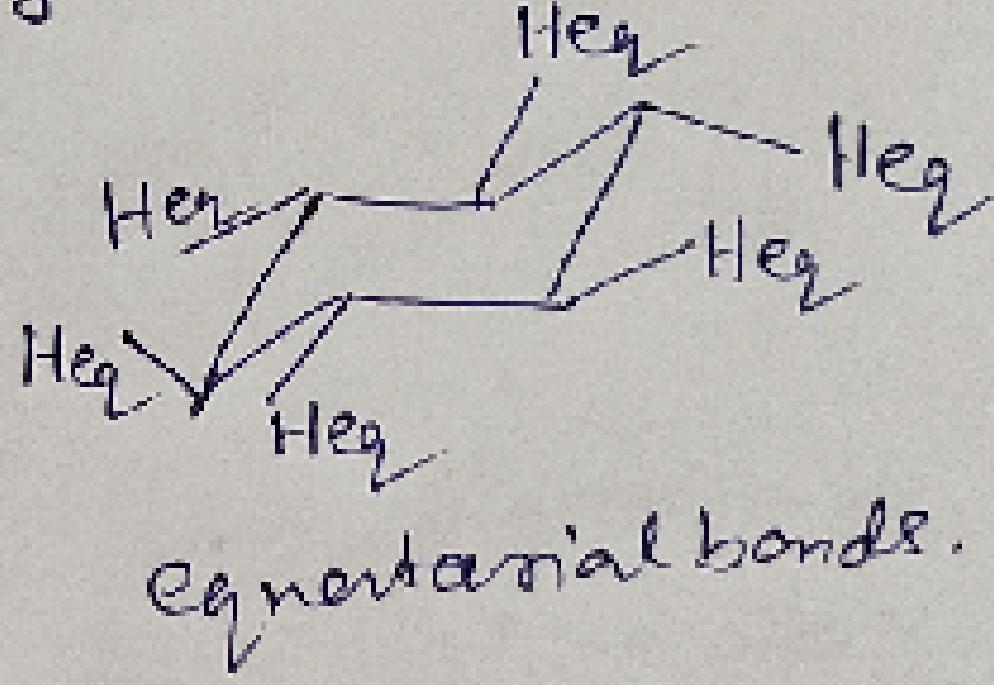
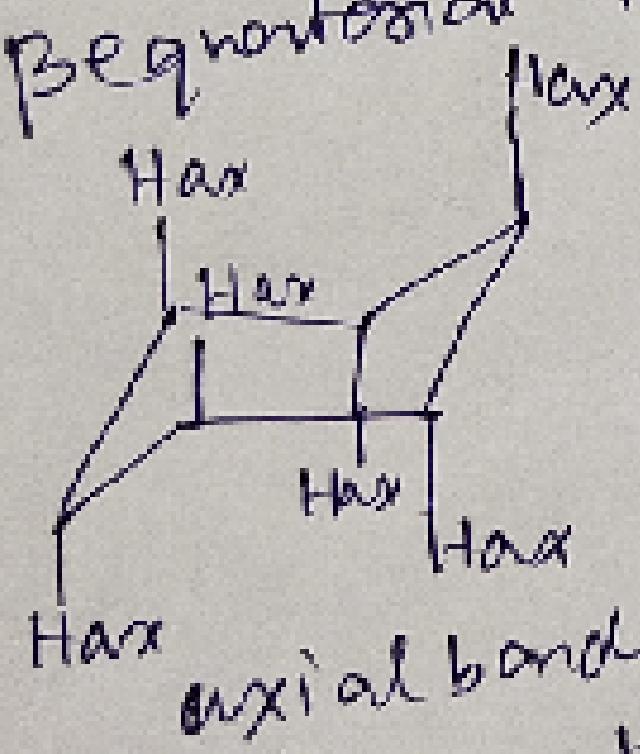


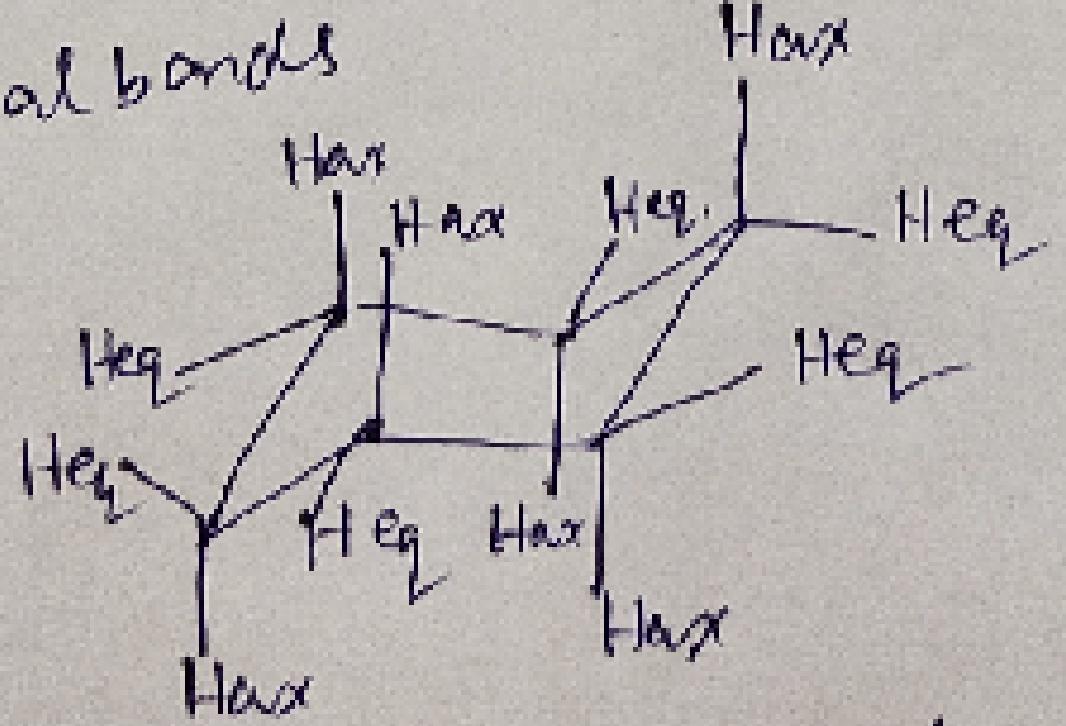
: Cyclohexane:

The most stable form of cyclohexane is its  $\pm$  chair form. In chair form of cyclohexane, it has two geometrically different set of C-H bonds. In one set, six C-H bonds perpendicular to the horizontal plane containing any three alternate carbon atoms of ring. They are called axial bonds. Three axial bonds are directed upward & the other three downward. Upward bonds are called  $\alpha$ -axial & downward bonds are called  $\beta$ -axial.

In the another set the six C-H bonds make an angle  $19^{\circ}28'$  with the horizontal plane containing any 3 alternate carbon atoms of ring. These are called equatorial bonds. 3 are projected upwards called equatorial bonds & other 3 projected downwards is called bonds.



equatorial bonds.

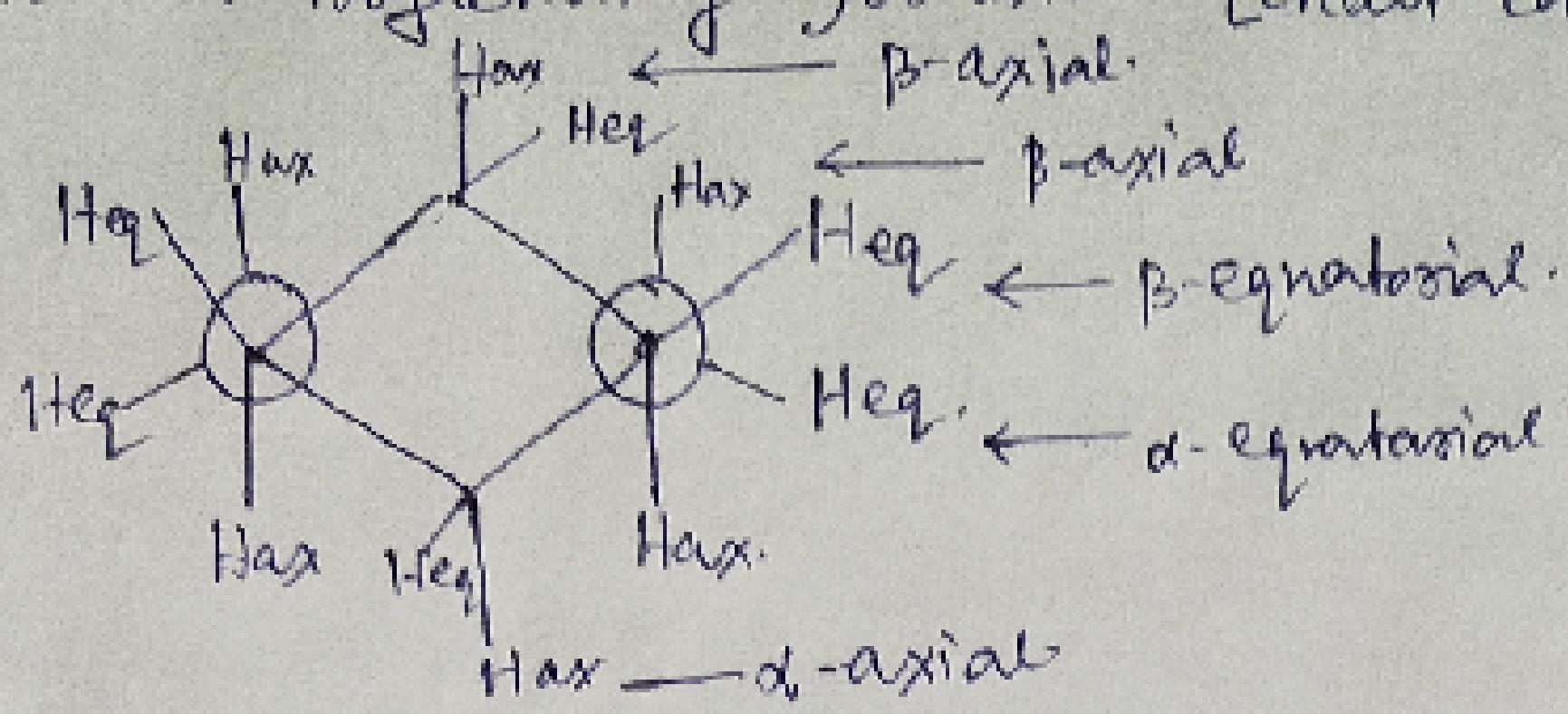


3 carbons (slightly above)  
 $\Rightarrow$  upward  $\Rightarrow$  axial bond.  
 3 carbons (slightly below)  
 $\Rightarrow$  downward  
 $\Rightarrow$  axial bond.

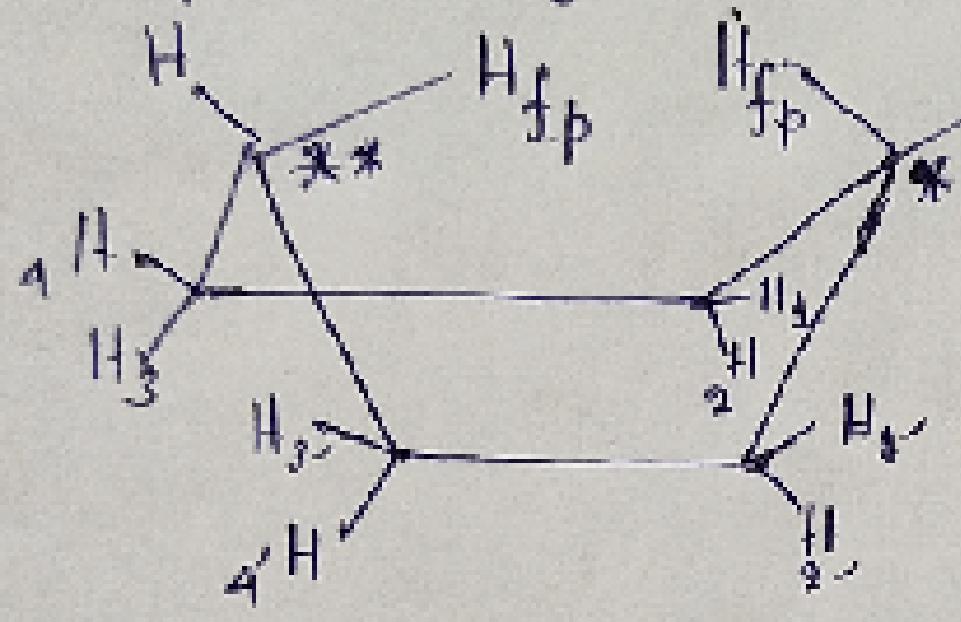
chair form of cyclohexane & other type of C-H bonds are called equatorial bonds.

Newman projection of cyclohexane [chair conformation].

2



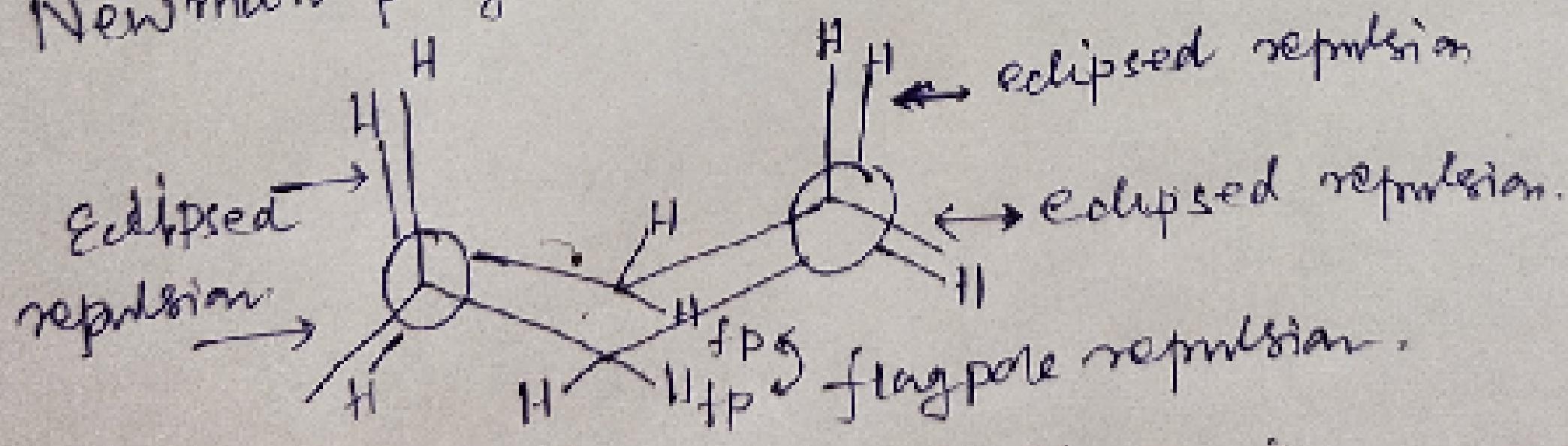
Boat form of cyclohexane:



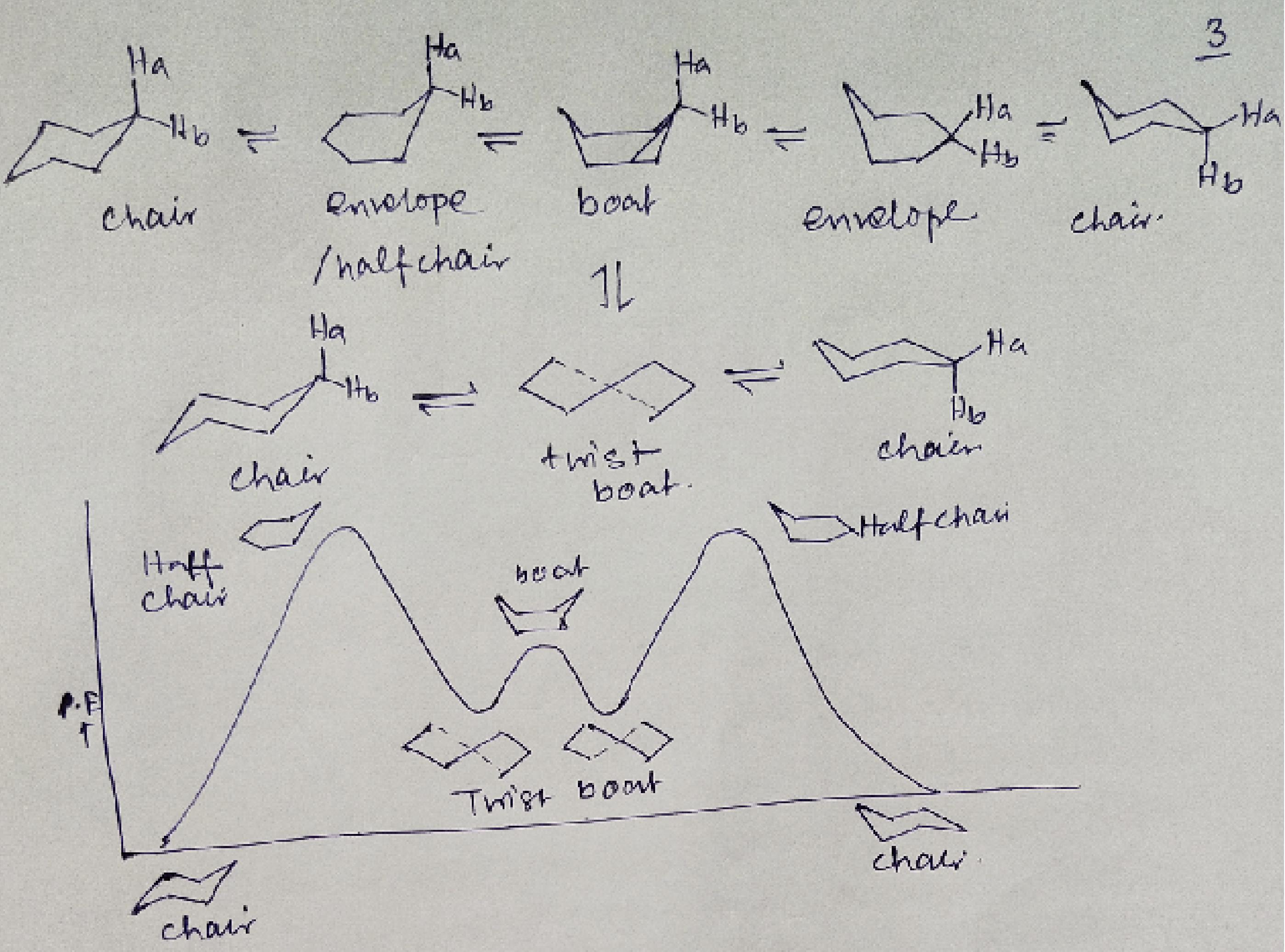
Compare to chair conformation  
boat conformation has  
form pair of eclipsed C-H  
bond repulsion. Also there  
is a strong steric repulsion

between the flagpole hydrogens at C<sup>1</sup> & C<sup>2</sup>. This is called  
flagpole repulsion. As a result of these interactions,  
the total strain in boat conformation is greater  
than that in chair conformation. So boat form  
is less stable than chair form.

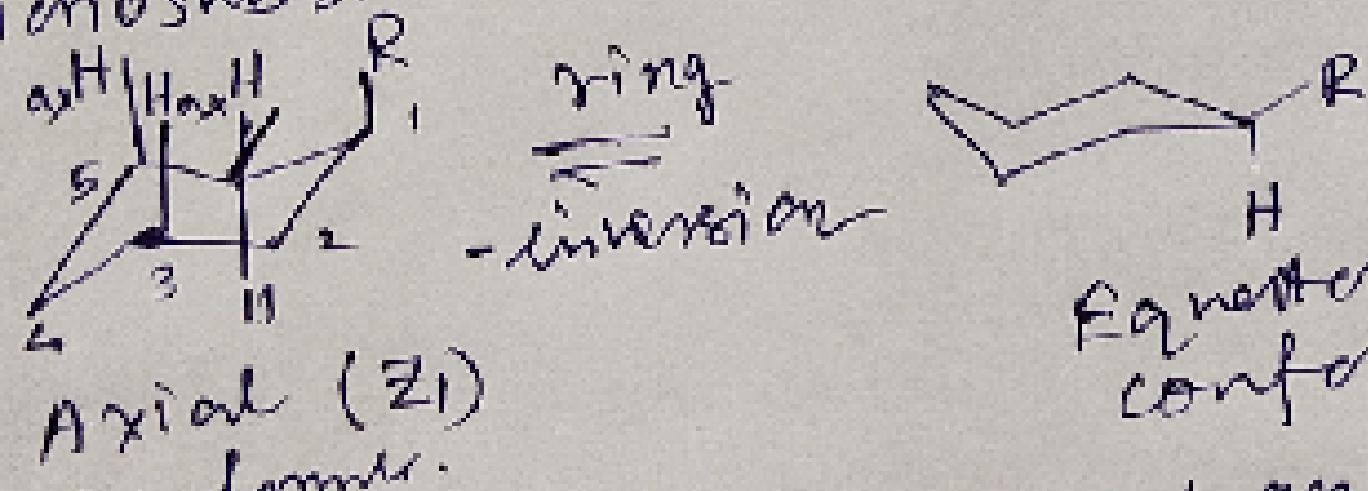
Newman projection of boat conformation



During inversion of one chair form with an equivalent  
chair form, axial Hydrogen becomes equatorial &  
vice versa. The transition state involves several  
conformations e.g. half chair, boat, twice boat etc.



Monosubstituted cycloalkane:

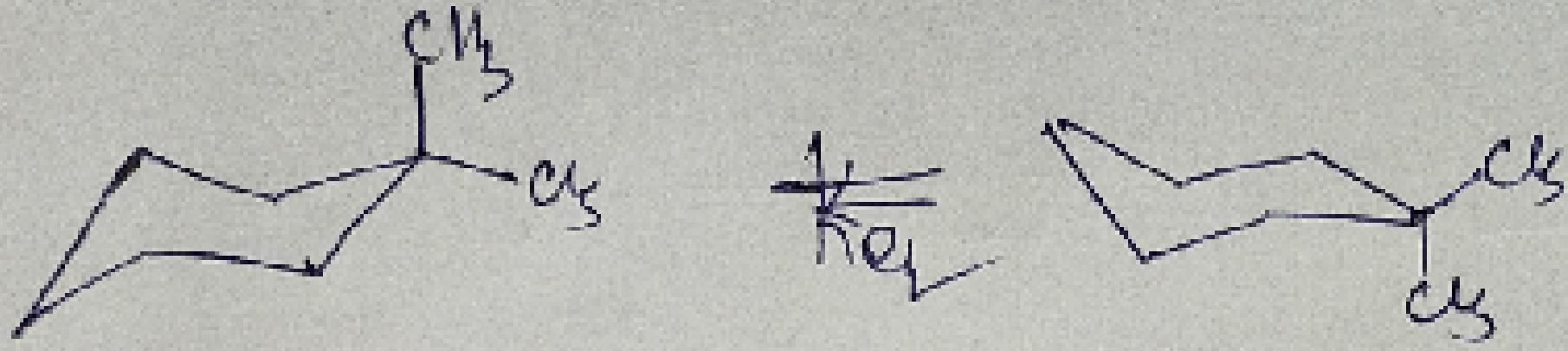


Equatorial ( $Z_2$ ) conformer.

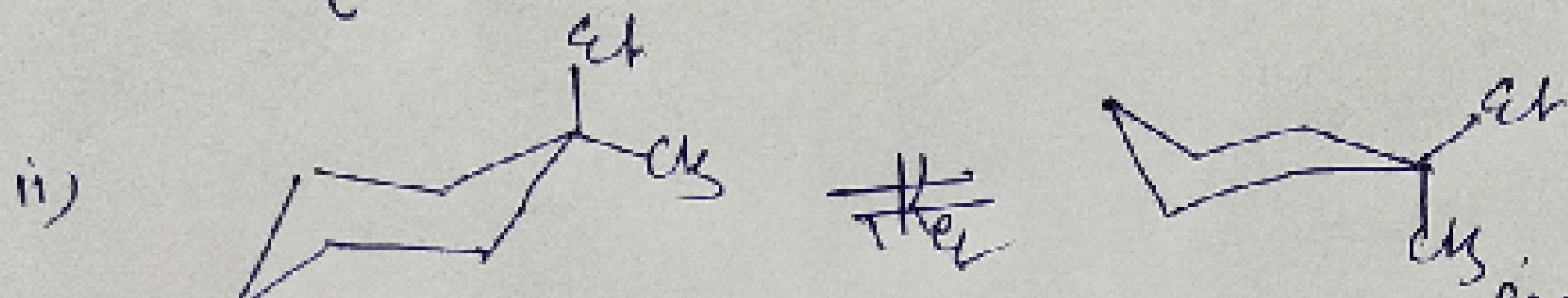
Axial conformer is less stable than equatorial conformer because a sterically bulky group ( $R$ ) in an axial position interacts with 2H atoms in C-3 & C-5 position which is called 1,3 diaxial repulsion.

$Z_2$  will be more than  $Z_1$ .  $K_{eq} > 1$ .

4



$K_{eq} = 1$ , when two group are identical  
(1,1 disubstituted cyclohexane)

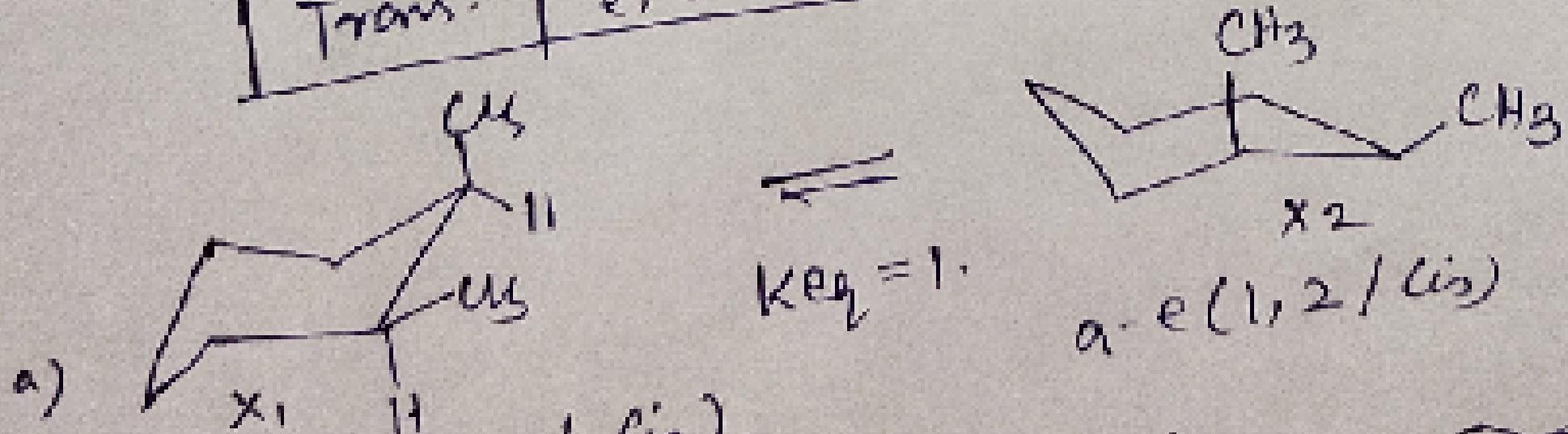


$K_{eq} > 1$ . If here bulky groups preferentially occupy at equatorial position to minimize steric repulsion.

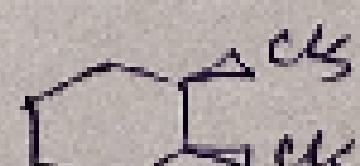
→ Monosubstituted & 1,1 disubstituted cyclohexane can not show geometrical isomerism - but can show conformational isomerism.

For dimethyl cyclohexane [1,2 ; 1,3 ; 2,4] For cis & trans isomer, the positioning of the groups should be given in the following table.

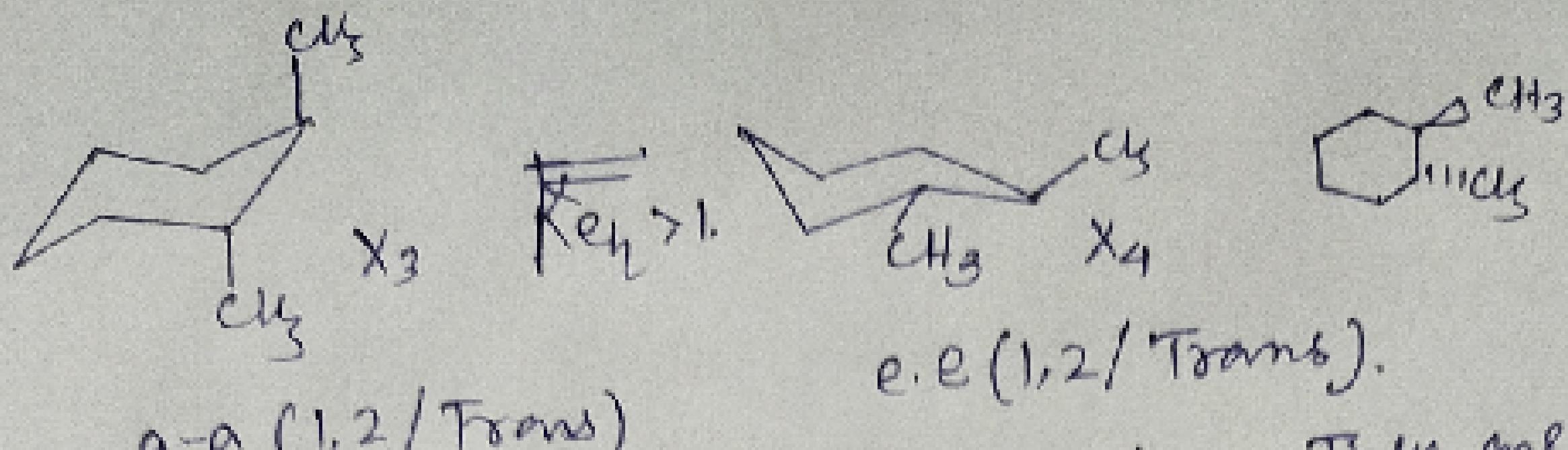
|       | 1,2        | 1,3        | 1,4        |
|-------|------------|------------|------------|
| Cis   | a,e<br>e,a | a,a<br>e,e | a,e<br>e,a |
| Trans | a,a<br>e,e | a,e<br>e,a | a,a<br>e,e |



$\alpha \cdot e(1,2 / \text{cis})$ .  
Both are examples of cis isomer.  
 $x_1$  &  $x_2$  are related as C.I.



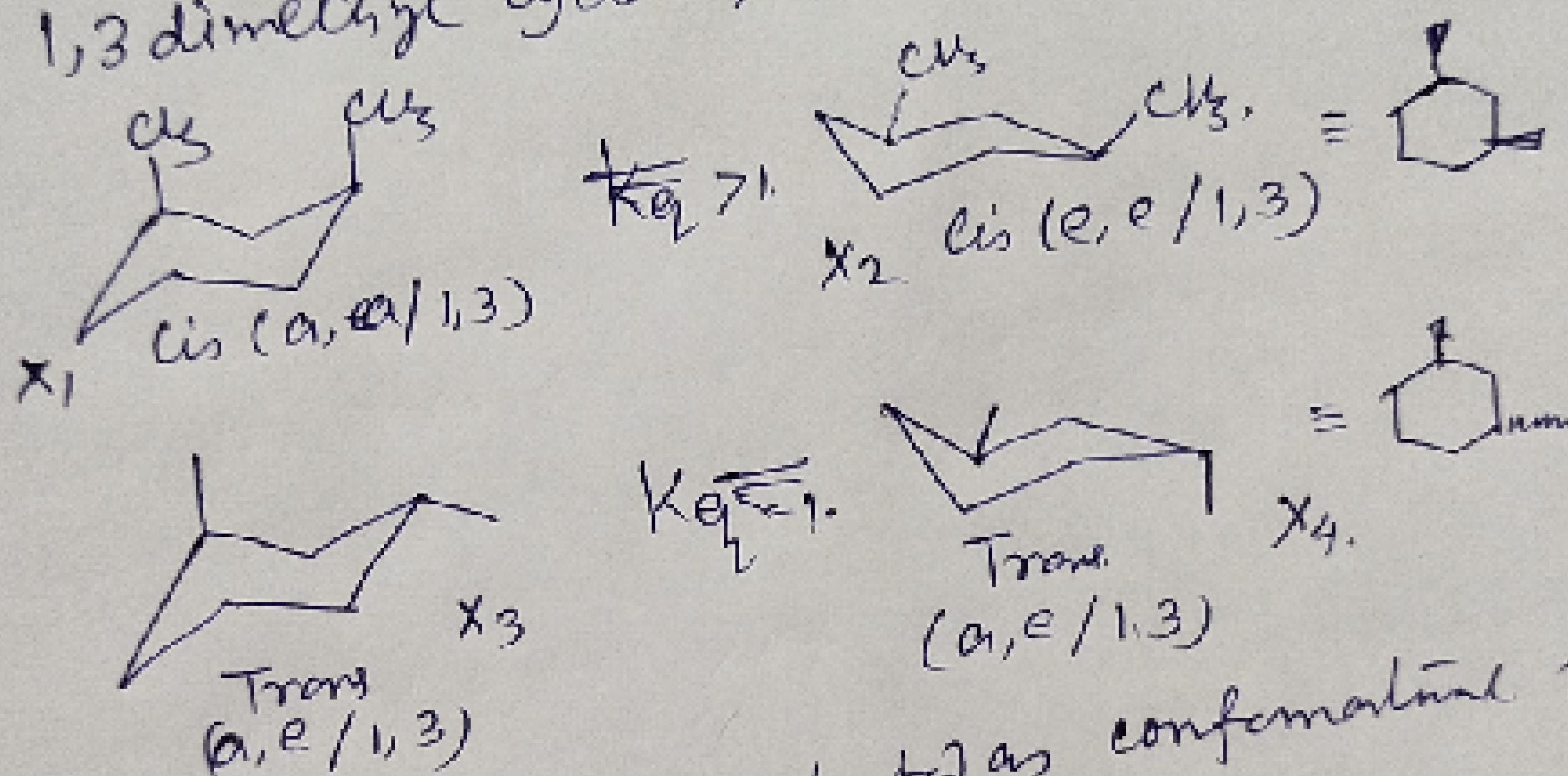
5



Both are examples of trans minima. They are related as conformational mirror.

The stability order:  $x_4 > x_1 = x_2 > x_3$ .

1,3 dimethyl cyclohexane:



$x_1, x_2$ ;  $x_3, x_4$  are related as conformational mirror.  
 $x_1, x_2$ ;  $x_3, x_4$  are related as G.I.

The stability order  $x_2 > x_3 = x_4 > x_1$

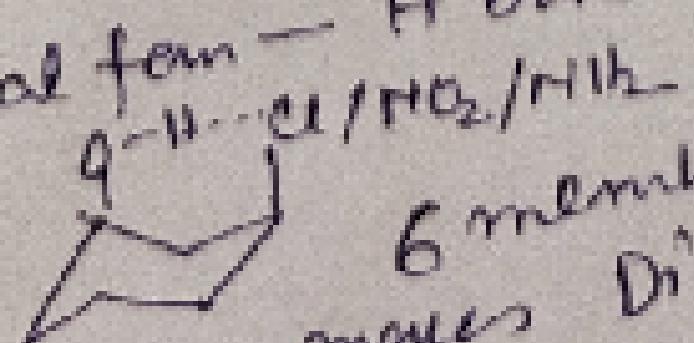
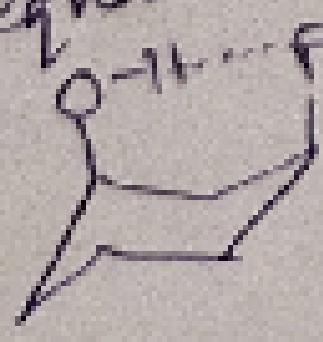
Cis mirror exists mainly in Diastereom. Trans exists

axial-equatorial form

for the molecule we

Di equatorial form is less stable than diaxial form.

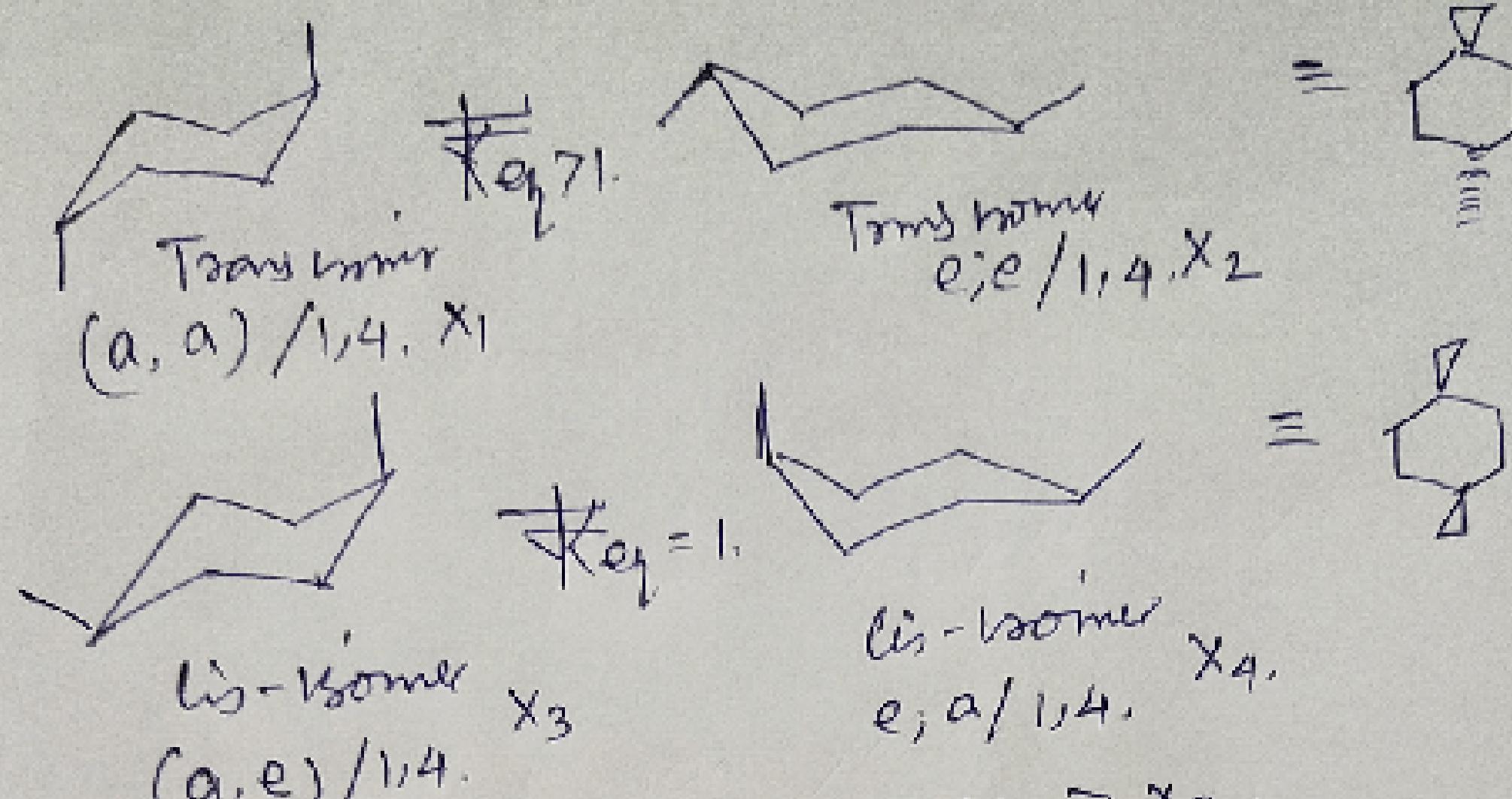
(diaxial form - H bonding takes place)



6 membered chloroform  
molecules Diaxial more stable.

1,4 dimethyl cyclohexane.

6



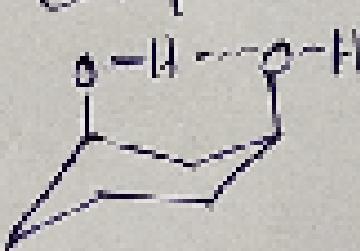
Mitability obs:  $x_1 > x_3 = x_4 > x_2$ .

Trans isomer is more populated in x<sub>2</sub> form.

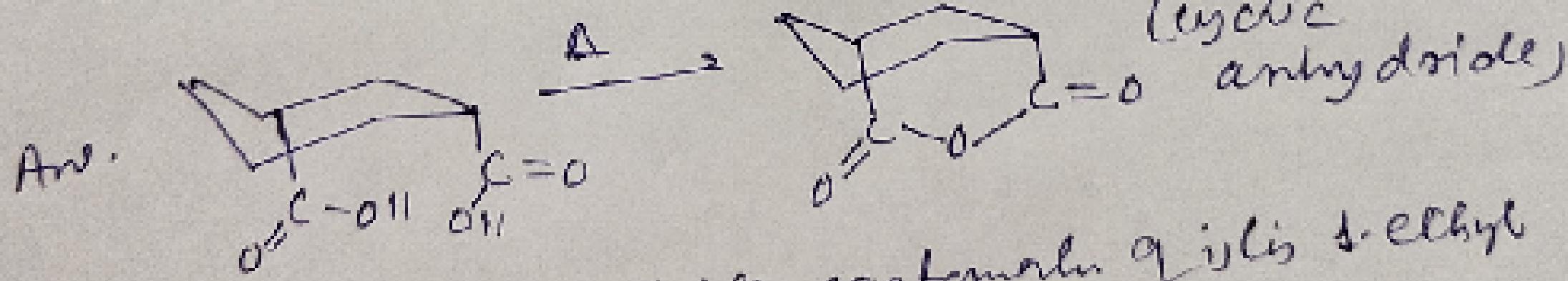
Trans isomer is more populated in x<sub>2</sub> form.

Q. What is the most stable conformation of cyclohexane 1,3-diol.

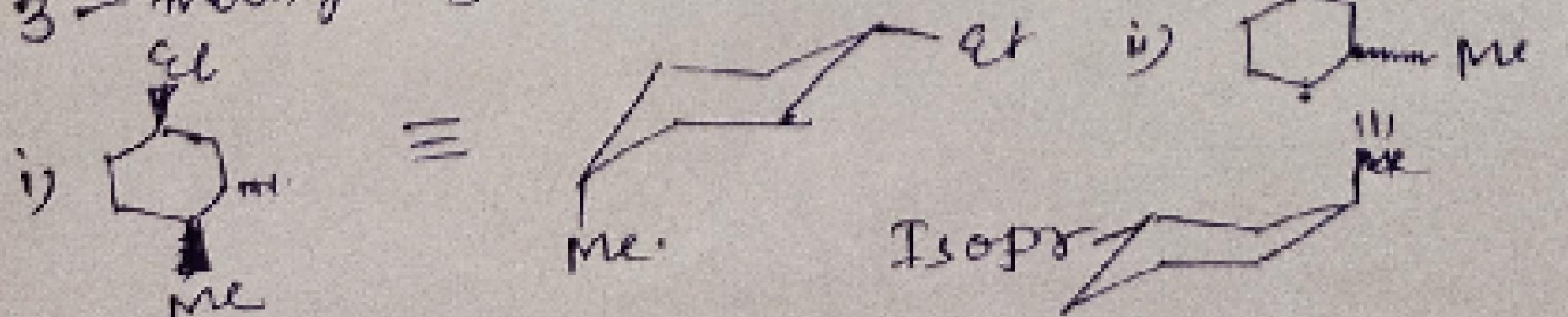
Q. Ans:



Q. What is the product on heating monoisopropyl 1,3-dicarboxylic acid undergoes heating?



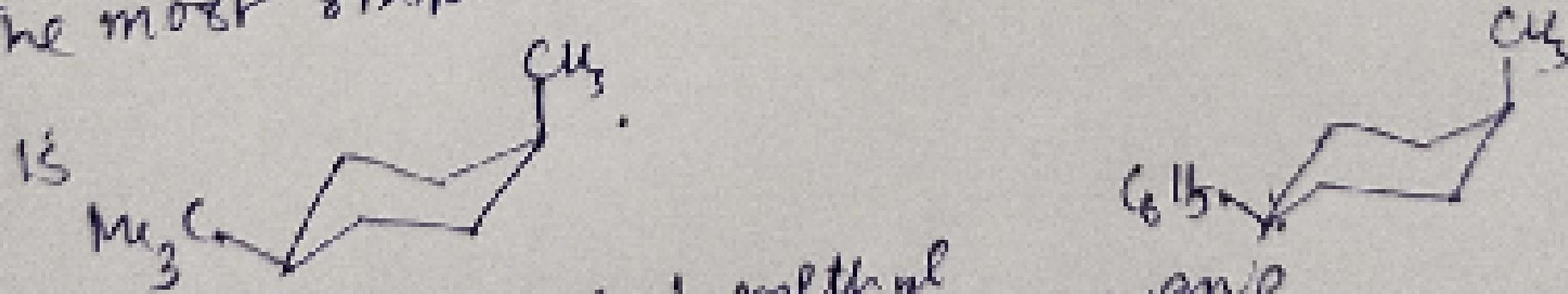
Q. What is the more stable conformation of i) cis-1-ethyl 4-methyl cyclohexane ii) Trans-1-isopropyl 3-methyl cyclohexane.



Points to be noted:

The activation energy for cyclohexane ring inversion is 10 Kcal/mol<sup>2</sup>. It is a rapid process with a half life of around  $10^{-5}$  s. at 25°C.

- ⇒ All bonds are staggered. The dihedral angle is 56°.
- ⇒ In half chair form is least stable form whereas the twist boat form is chiral
- ⇒ The ring flipping is fast & occurs  $10^8$  times / sec at room temp.
- ⇒ Cyclohexane when poured into water it floats because its density is less than water.
- ⇒ At 25°C, in methyl cyclohexane 95% of the molecules have the equatorial methyl str. & 5% of have axial C<sub>6</sub>H<sub>5</sub>
- ⇒ Groups like tertiary butyl group is so bulky that extreme strong repulsion exists in axial position & 99.9% of tert butyl cyclohexane is maintained in equatorial form. It's called locked conformation.      4-methyl
- ⇒ The most stable conformer of cis 1-tert butyl cyclohexane



⇒ Most stable form of cis 1-tert-butyl-4-phenylcyclohexane

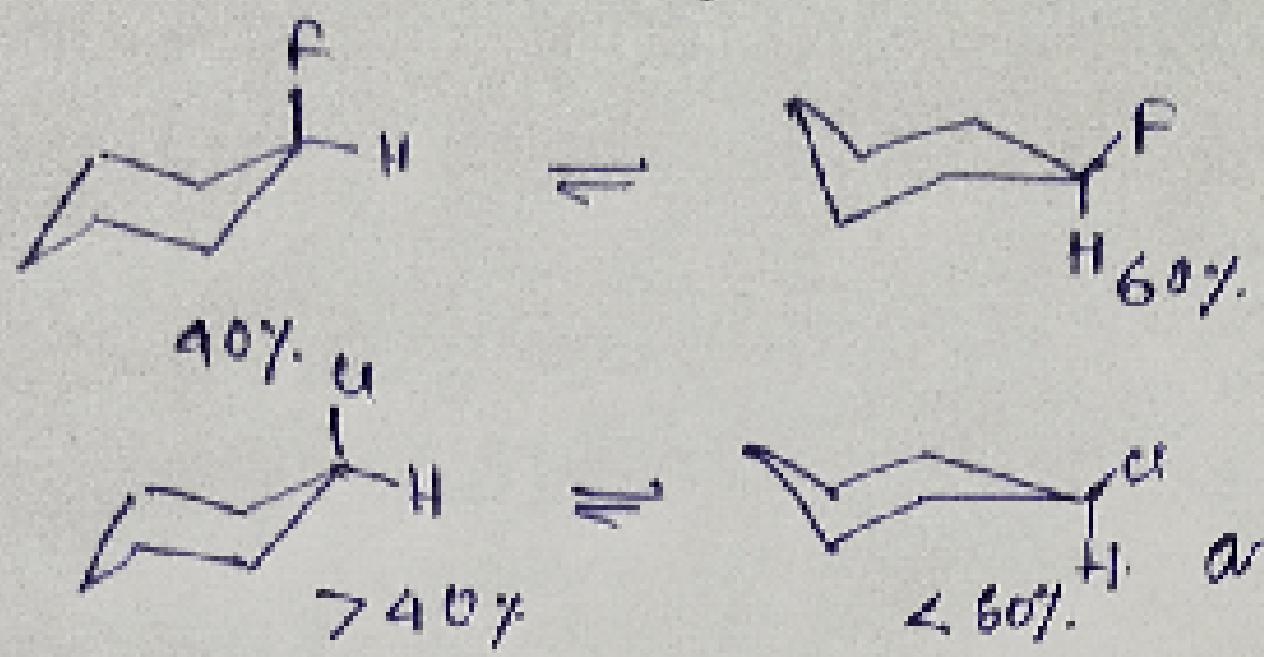
⇒ Most stable form of Trans-1-methyl-4-phenylcyclohexane

⇒ In cis 1,2-dimethylcyclohexane, during ring flipping one enantiomer is converted into another enantiomer.

⇒ In Trans, during ring flip di-equatorial form is converted into diaxial form. They are conformational isomers.

⇒ The cis & trans dimethyl cyclohexane are related as 8 configurational diastereomers. (1,2', 1,3'; 1,4).

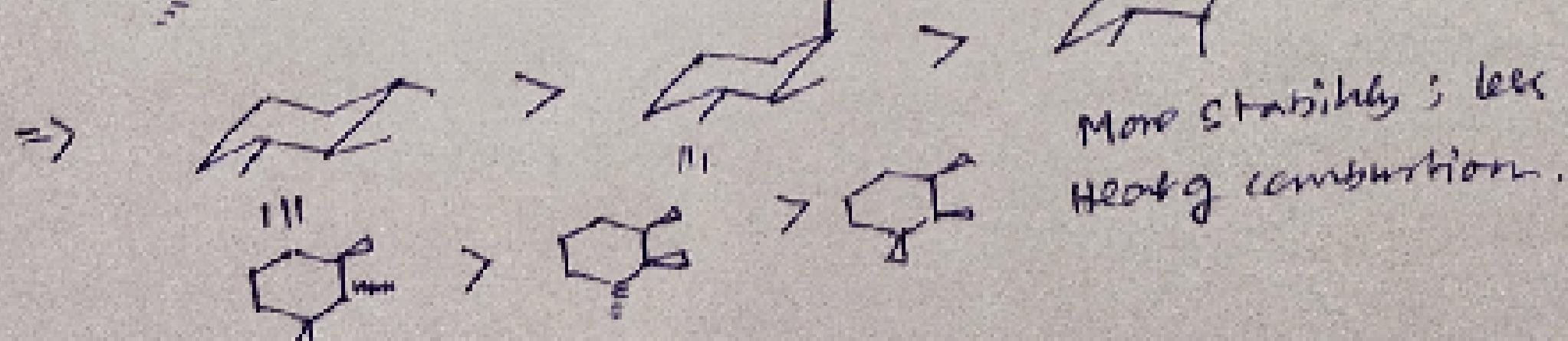
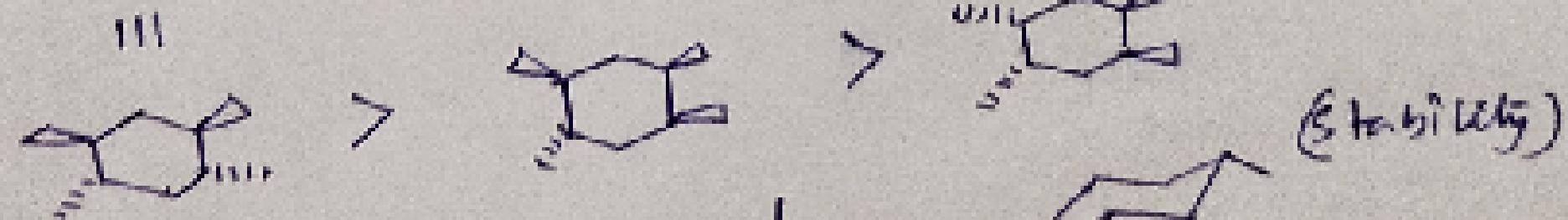
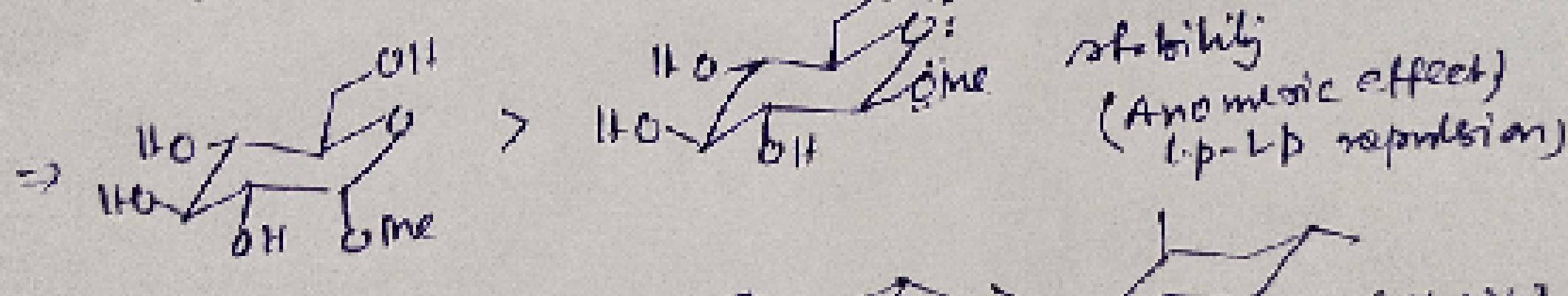
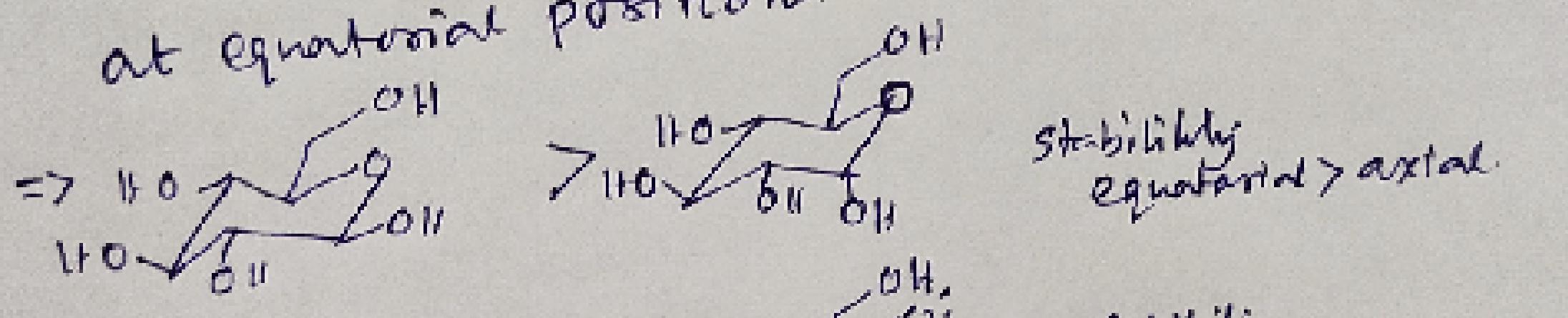
⇒ For halo substituted cyclohexane.

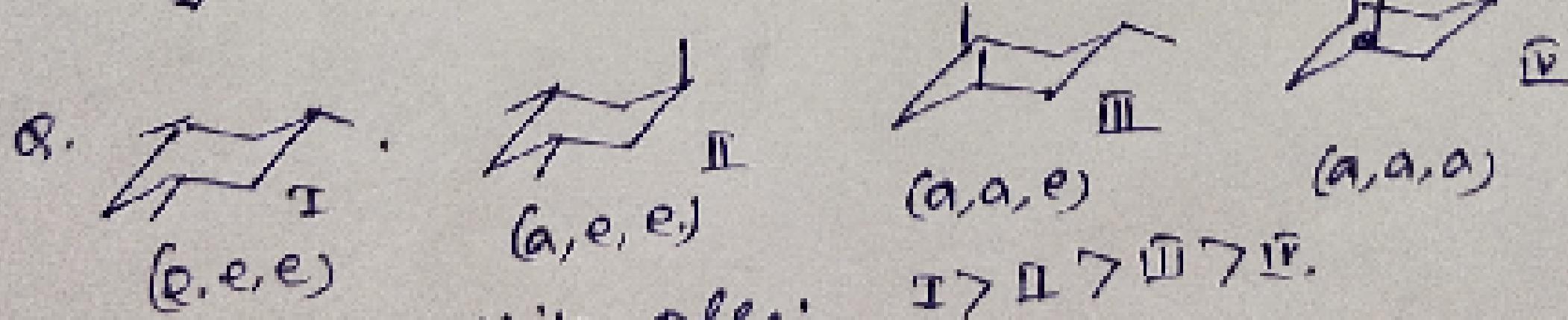
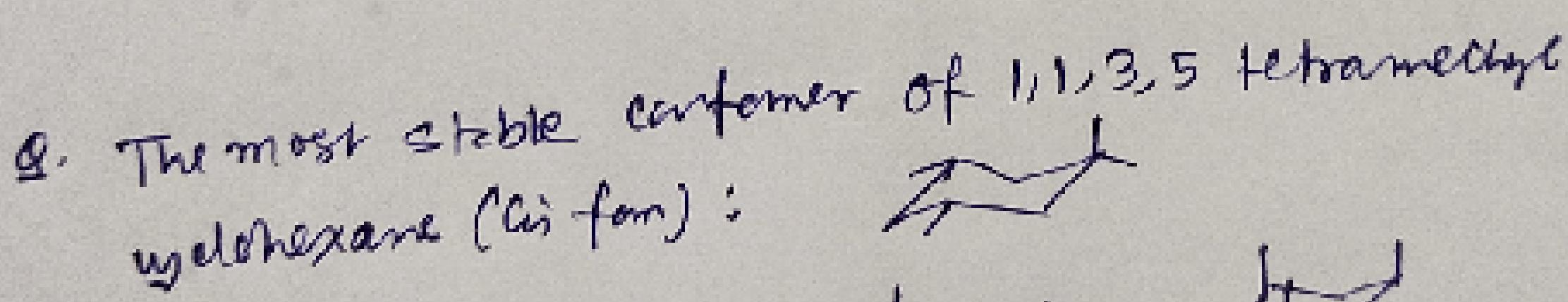
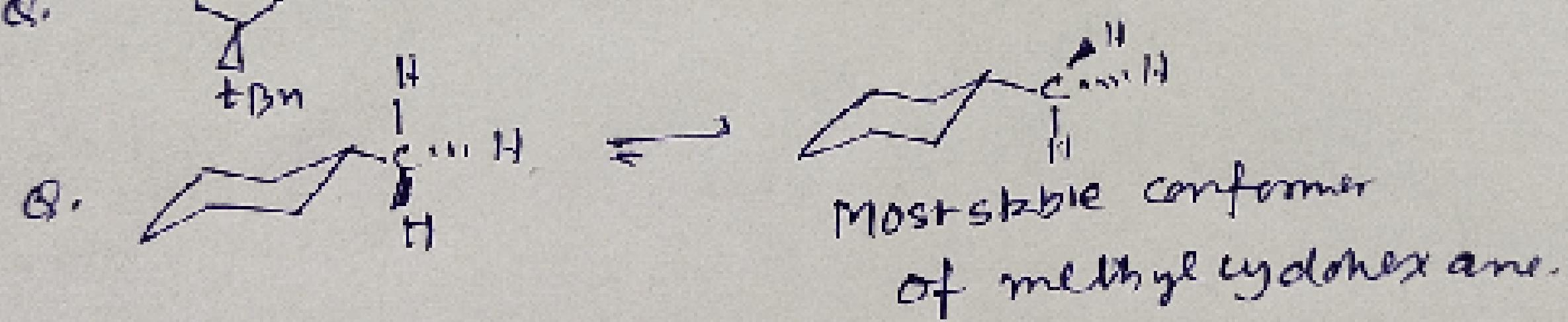
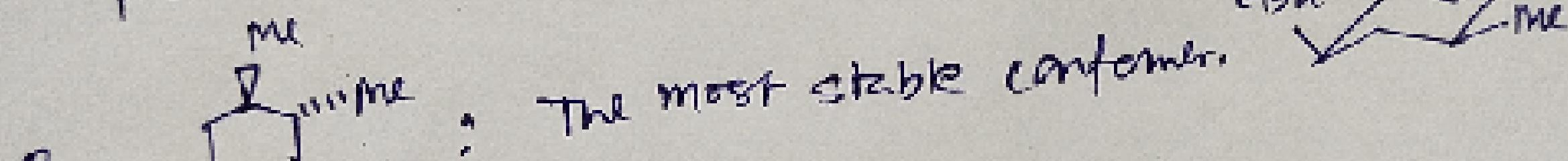
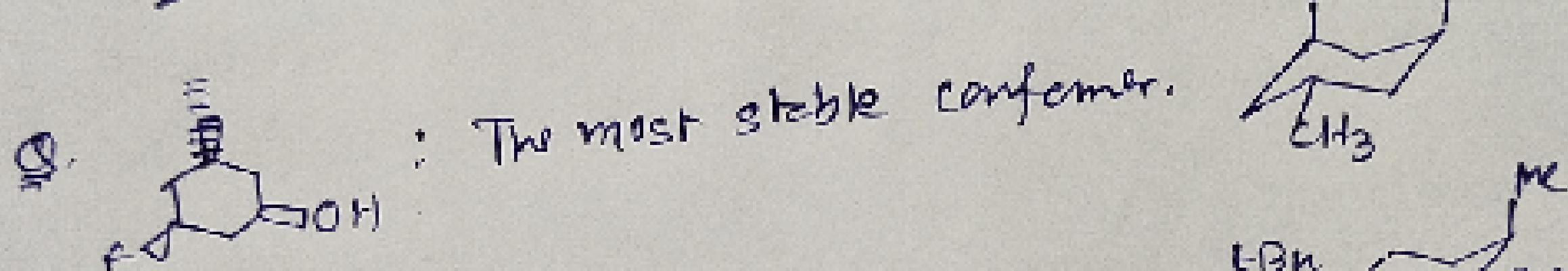
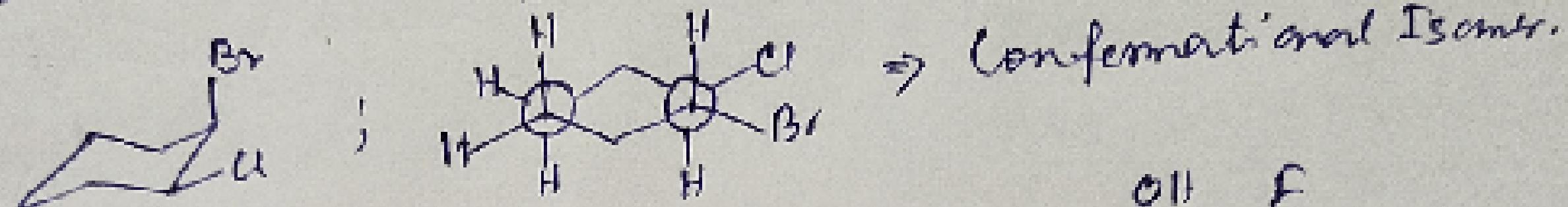
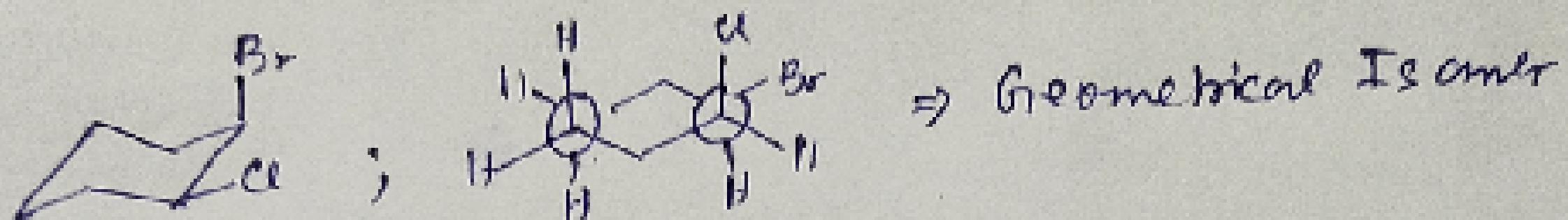
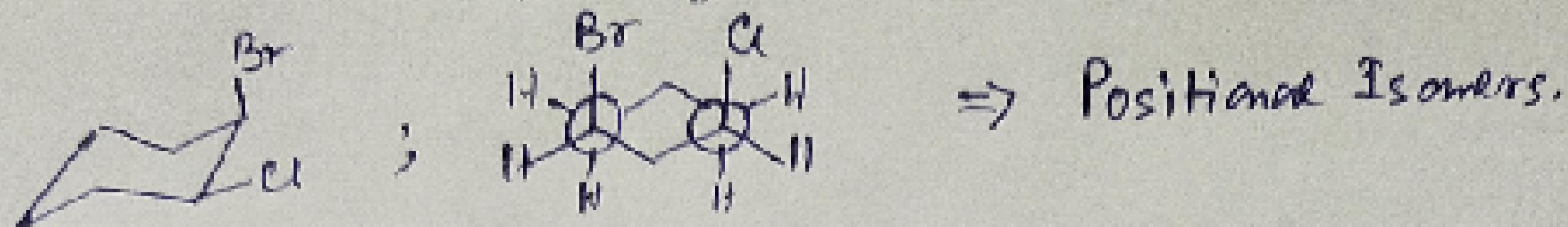
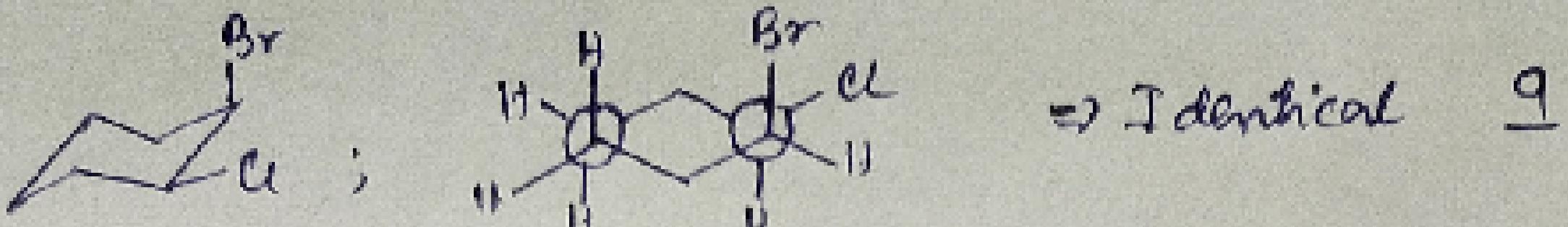


[A halogen does not require more space, moreover F & H are nearly similar in size thus the preference of F to take up

is less. As the size of halogen increases  $F < Cl < Br < I$ , so does the carbon-halogen bond distance. So the net repulsion will be less for Cl. w.r.t F.

⇒ The most stable conformer of N-methyl piperidene methyl group should occupy at equatorial position.



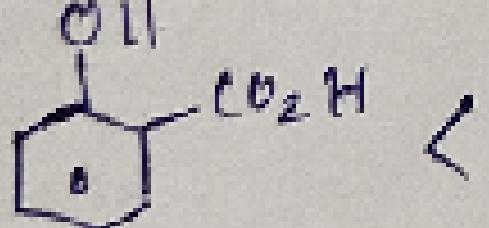
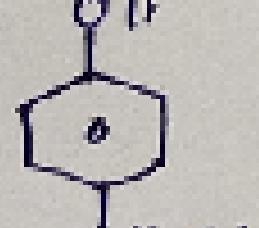
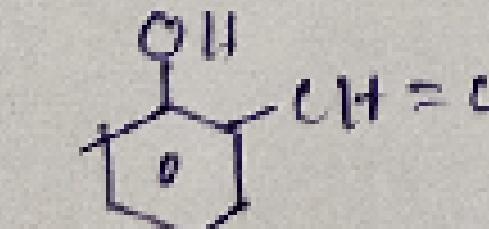
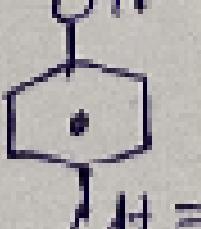
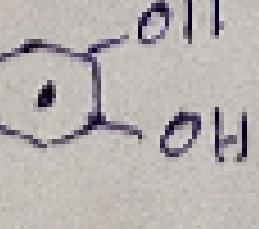


The stability order:

a. Stereoisomers separated by high energy barrier ( $> 100 \text{ kJ/mol}$ ) are called configurational isomers & they can be separated at room temp & if separated by low energy difference ( $< 60 \text{ kJ/mol}$ ) are called conformational min & cannot be separated.

: Boiling point order of compounds:

10

- i)  $\text{CH}_3-\text{C}_2\text{H}_5-\text{OH} > \text{CH}_3-\text{CH}_2-\text{OH} > \text{CH}_3-\text{O}-\text{CH}_3$
- ii) n-pentane, > isopentane; > neopentane. (Branching)
- iii) m( $\text{C}_4\text{H}_9\text{NH}_2$ ) > ( $\text{C}_2\text{H}_5$ )<sub>2</sub>NH >  $\text{C}_2\text{H}_5\text{N}(\text{CH}_3)_2 > \text{C}_2\text{H}_5\text{CH}(\text{CH}_3)_2$
- iv) Methane; Ethanol; Propan-1-ol. Butan-1-ol,  
butan-2-ol; Pentan-1-ol.  $6 > 4 > 5 > 3 > 2 > 1$ .
- v) Pentan-1-ol; Pentanal; ethoxyethane. n-butane
- vi) Propan-1-ol; > Acetone; > Propanal; > Methoxy  
methane, > n-butane.
- vii)  $\text{ROH} > \text{RSI}$   $(R = \text{Me})$  [H bonding].
- viii)  $\text{RS-R} > \text{R-O-R}$   $(R = \text{Me})$  [M.wt].
- ix)  $\text{C}_2\text{H}_5\text{CH}_2-\text{OH} < \begin{cases} \text{CH}_3\text{OH} \\ \text{CH}_2\text{OH} \end{cases} < \begin{cases} \text{CH}_2\text{OH} \\ \text{CH}_3\text{OH} \end{cases} < \begin{cases} \text{CH}_3\text{OH} \\ \text{CH}_2\text{OH} \end{cases}$  more no.  
+ OH comp.
- x) Salicylic Acid   $<$    $\beta$ -hydroxy benzoic acid  
Intra > Inter.
- xi) Salicylaldehyde   $<$    $\beta$ -hydroxy benzaldehyde
- xii)   $<$   More no. of -OH groups.
- xiii) a)  $\text{HF} > \text{HCl} > \text{HBr} > \text{HgCl}_2$ . b)  $\text{H}_2\text{O} > \text{HgTe} > \text{HgSe} > \text{HgS}$ . c)  $\text{SbH}_3 > \text{NIB}_3 > \text{AsH}_3 > \text{PH}_3$
- a)  $\text{CH}_3\text{SiH}_3 < \text{CH}_3\text{Hg} < \text{SnH}_3 < \text{PbH}_3$   
b)  $\text{CH}_3\text{Br} > \text{CH}_3\text{I} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$   
c)  $\text{SbH}_3 > \text{NIB}_3 > \text{AsH}_3 > \text{PH}_3$  [M.wt].

: Points to be noted:

- ⇒ More is the molecular weight, more is the boiling point
- ⇒ With H bonding > Without H bonding
- ⇒ Intra H bonding > Intra H bonding.
- ⇒ More is the branching, less is the boiling point. (Isomeric)
- ⇒ More is the dipole moment, more is the compound boiling point (Isomeric compound)
- ⇒ Compounds having more -OH group has more boiling point.
- ⇒ Extent of H bonding:  $\text{CH}_3\text{CH}_2\text{H} > \text{CH}_3\text{CH}_2\text{OH}$ .
- ⇒ Extent of H bonding:  $\text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$ .
- ⇒ Extent of H bonding:  $(\text{R} = \text{Me})$   $\text{1}^{\circ} \text{Amine} > \text{2}^{\circ} \text{Amine} > \text{3}^{\circ} \text{Amine}$ .

