

Semester - II
Organic - Chemistry

by Madhavi
Lecturer in chemistry

UNIT - 01

Carbon - Carbon sigma bonds
(Alkanes and Cycloalkanes)

Hydrocarbons :

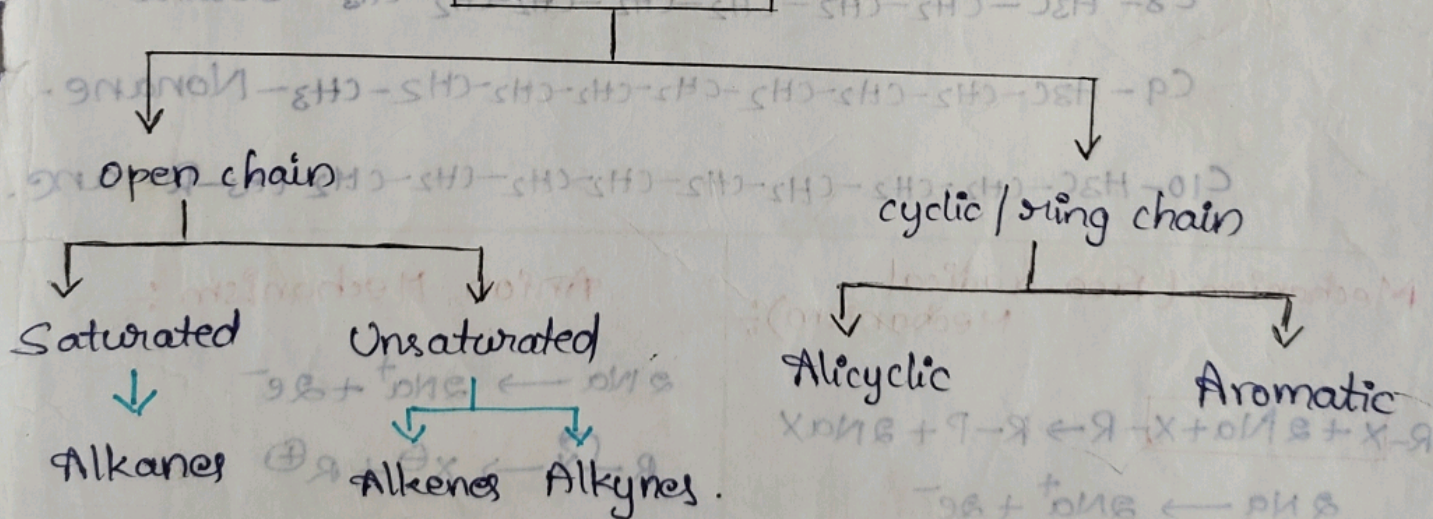
Compounds which contain carbon and hydrogen

atoms only are called Hydrocarbons.

* Depending upon the carbon framework; hydrocarbons may have either open chain (or) ring structure.

* Further depending upon the nature of C-C bonds, hydrocarbons may be saturated (or) unsaturated.

Hydrocarbons



* C-C single bonded hydrocarbons are called the saturated hydrocarbons / Alkanes.

* General formula of alkanes is C_nH_{2n+2}

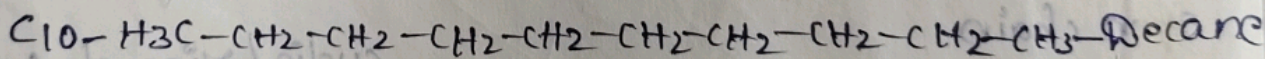
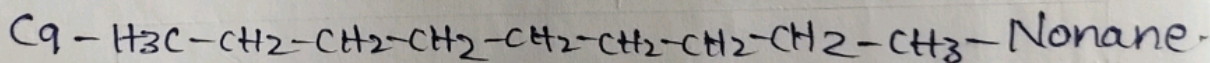
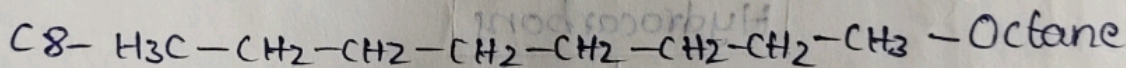
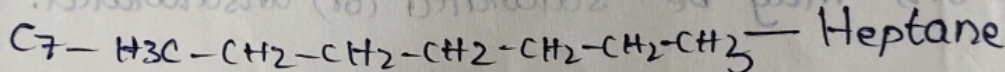
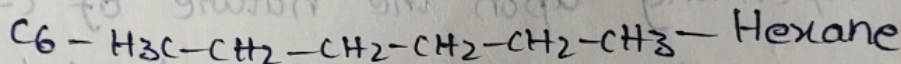
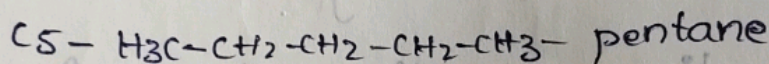
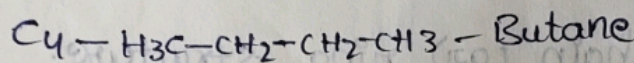
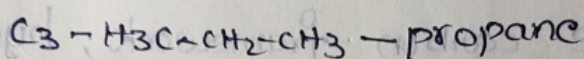
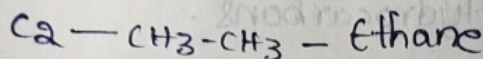
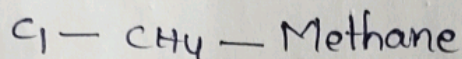
$\therefore n = \text{no. of 'C' atoms.}$

Alkanes each carbon atom is sp^3 hybridised and hence forms four σ bonds.

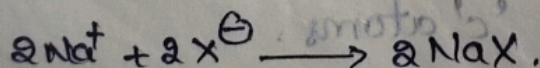
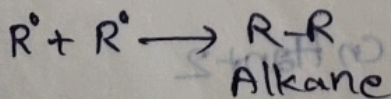
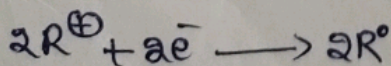
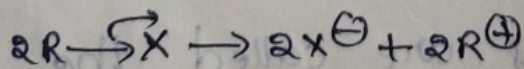
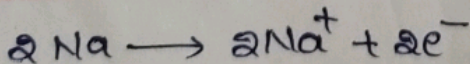
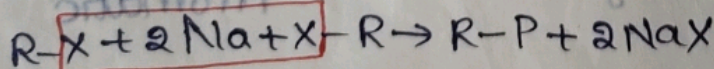
* Alkanes are generally inert towards most of the reagents, i.e., why alkanes are also called paraffins.

* The chief source of alkanes is crude petroleum and Natural gas.

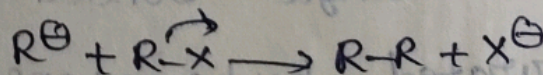
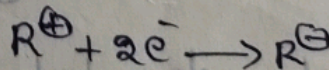
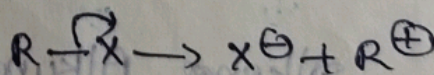
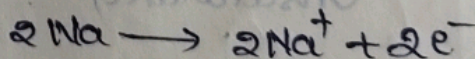
Ex:-



Mechanism (Free-radical Mechanism):-



Anion Mechanism:-



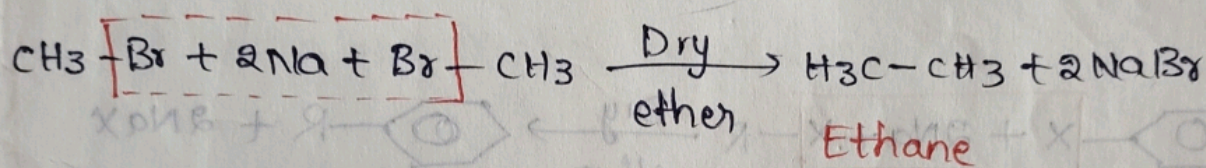
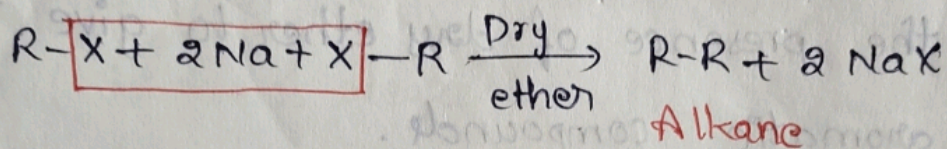
Nucleophilic

substitution.

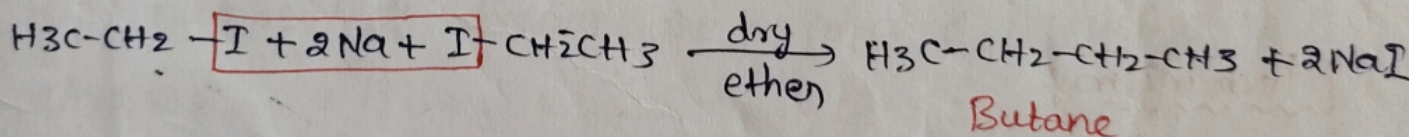
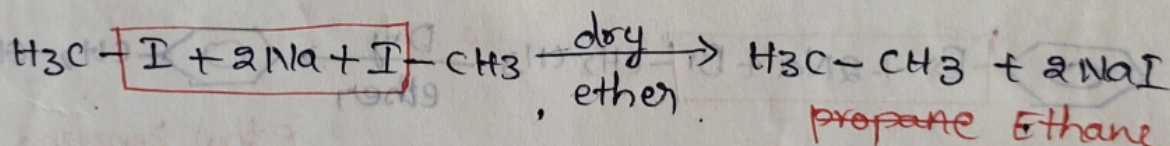
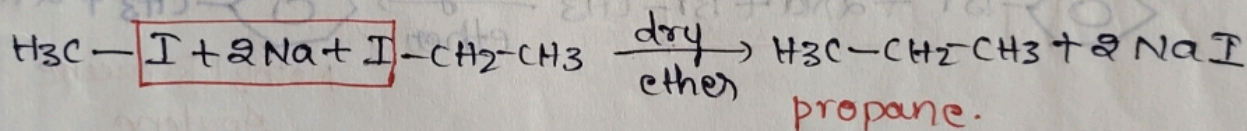
General Methods of preparation of alkanes:

Wurtz reaction:- (even no. of carbons) formed.

Two moles of alkyl halides react with sodium metal in the presence of dry ether to form alkanes is called wurtz reaction.



Mechanism:-



Unsymmetrical alkyl halides:-

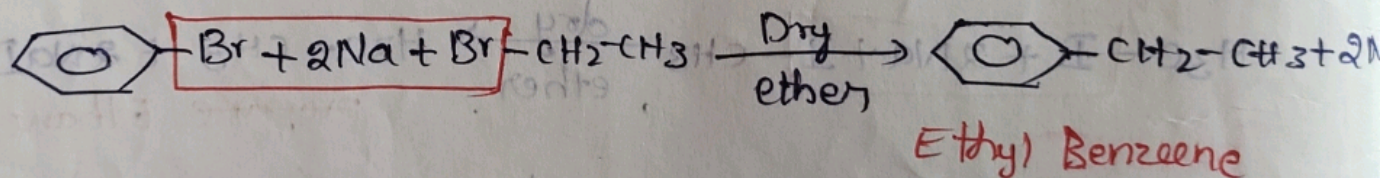
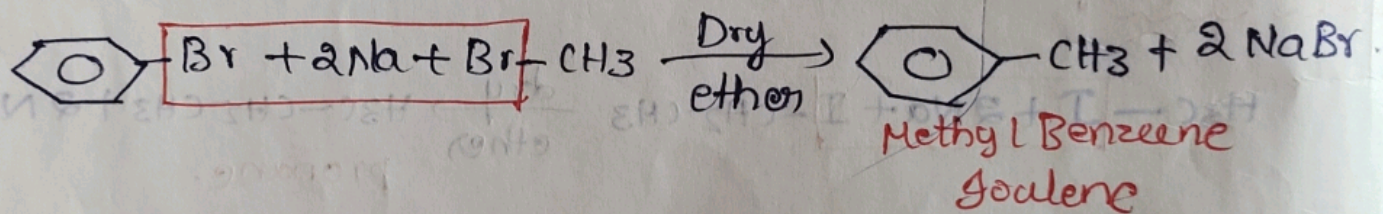
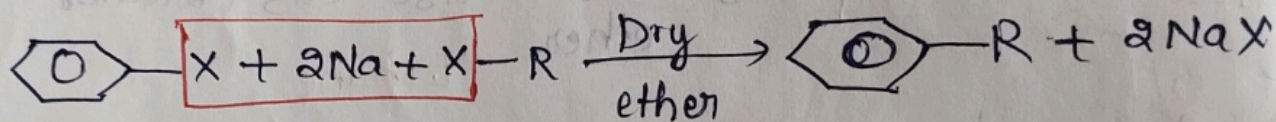
In unsymmetrical alkyl halides three products are formed. The formed products are having similar 'b.p.' that's why they can't be separated by the fractional distillation. (difficult to separate).

This is the reason the wurtz rxn is only

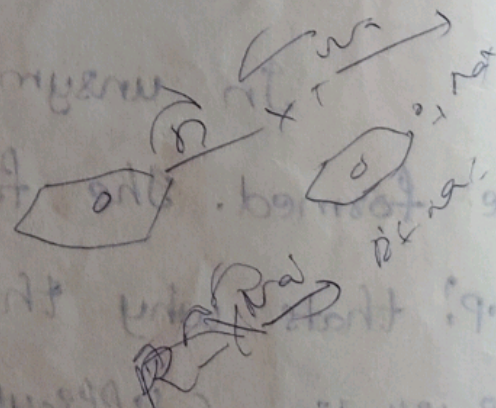
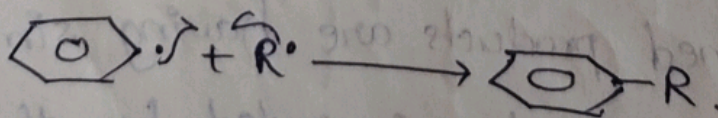
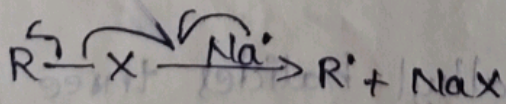
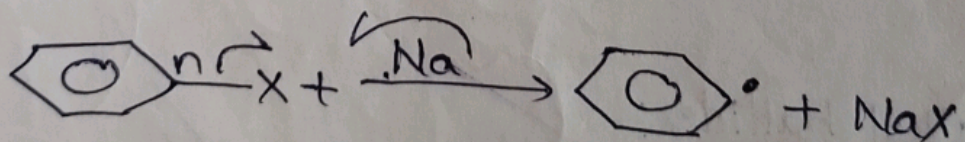
for symmetrical alkanes preparation. i.e. alkanes, containing even no. of carbon atom such as ethane, n-butane etc.---

2. Wurtz-Fittig reaction:

Aryl halides and alkyl halides reacts with 'Na' Metal in the presence of dry ether to give the substituted aromatic compounds.



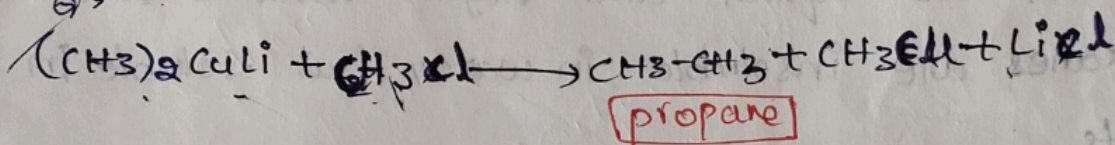
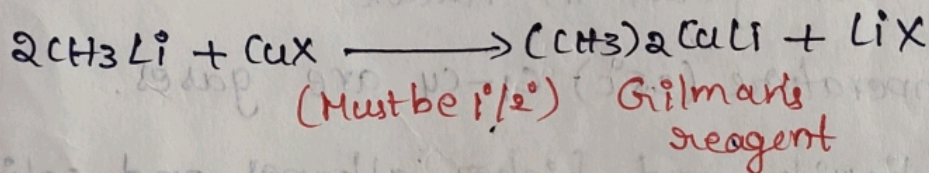
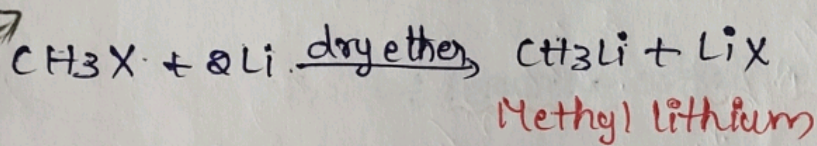
Mechanism:



Corey House Synthesis :-

Alkyl halides are treated with Li Metal and solvated dry ether \rightarrow which converts alkyl halide into alkyl lithium compounds.

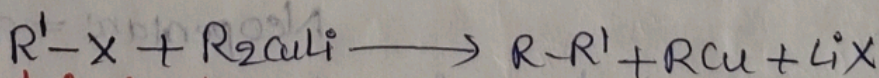
Alkyl lithium compound to be treated with cuprous chloride results in the formation of Lithium dialkyl cuprate (Gilman's reagent)



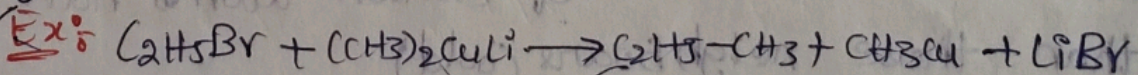
* Odd number of alkanes are prepared by using this synthesis.

3. Corey-House synthesis :-

Alkyl halides react with lithium dialkyl cuprate to form a new alkane and organo copper compound and lithium halide.



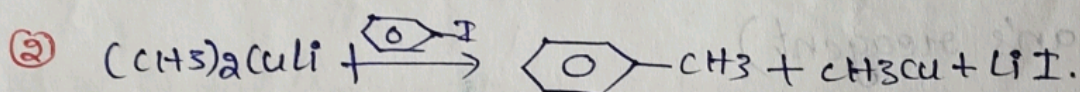
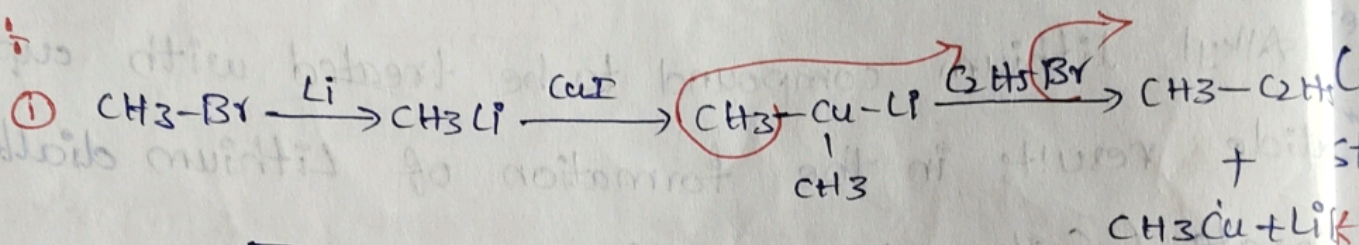
\downarrow 1°, 2° not 3°



* Used for preparing symmetrical and unsymmetrical alkane (i.e. even (or) odd no. of carbons).

* Used haloalkane, must be aliphatic/aromatic/alicyclic.
In aliphatic it must be 1°/2° not 3°.

Eg:



Physical properties of alkanes:

* Alkanes are non-polar in nature.

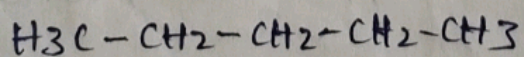
* At room temperature (25°C) C₁-C₄ are gases.

* C₅-C₁₇ are liquids and higher alkanes are solids.

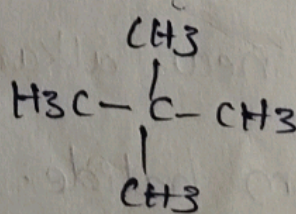
* Alkanes are insoluble in water, but soluble in non-polar solvents.

* Melting points, boiling points, viscosities and densities rise with increasing molecular weight (chain length), but ↓ with ↑ in the branching.

* The B.P. of n-pentane is 36.1° and Neopentane is 9.5° respectively.

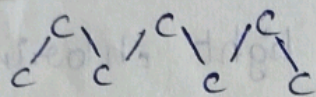


n-pentane = 36.1°

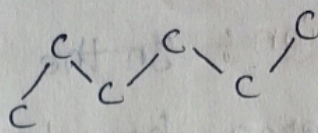


Neopentane = 9.5°

* Alkanes with even number of carbon atoms have more m.p. than those neighbours (odd)



Same side (c-c)



opposite (c-c)

Chemical properties of alkanes:-

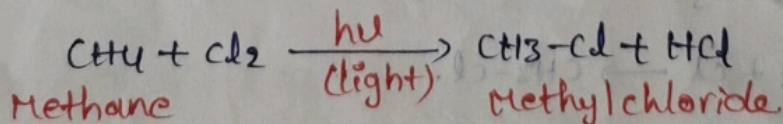
* Because of their saturated character, paraffins (para-little, affine - attraction) are stable and inert substances.

* Due to small difference in the electronegativities of carbon and hydrogen alkanes are non polar. They are not react with acids, bases, oxidising and reducing agents, and exhibits inert nature. Alkanes are not react with reagents like electrophille, nucleophilles, but in strong conditions in presence of light, they involved in free radical substitution reaction.

Free-radical substitution:-

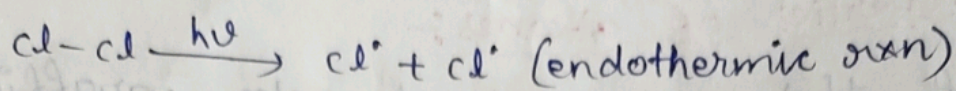
Ex:- Halogenation:- (Replacement of hydrogen atom by halogen) atom

Methane reacts with halogens (Cl_2, Br_2) in presence of u.v light to form corresponding substituted product.

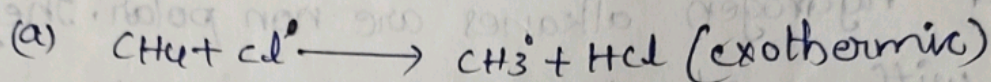


Mechanism:- Halogenation of alkanes takes place by free radical mechanism. It involves three steps namely.

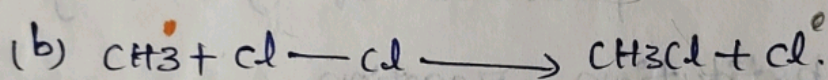
(1) chain initiation :- In the presence of light chlorine molecule undergo homolysis to form chlorine free radical.



(2) chain propagation :- chlorine free radical attacks methane molecule breaking one of the C-H bonds and generating Methyl free radical with the formation of HCl.

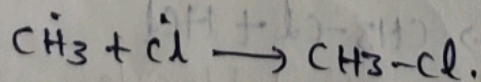
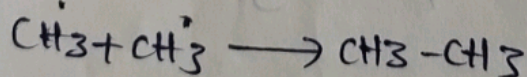
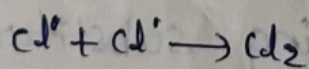


The methyl radical thus obtained attacks second chlorine molecule to form CH_3Cl with the liberation of another chlorine free radical.



(a) & (b) repeated till the total reaction to the mixture is consumed.

(iii) chain termination :- When 2 free radicals directly combine, the chain reaction terminates.



Same type of reaction is given by other halogen (Br). but fluorination is highly exothermic, so this rxn is not done in laboratory.

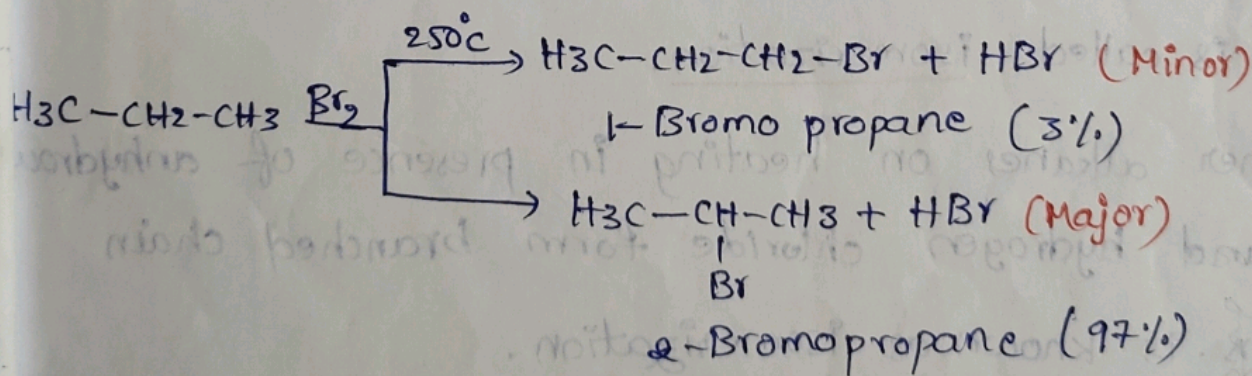
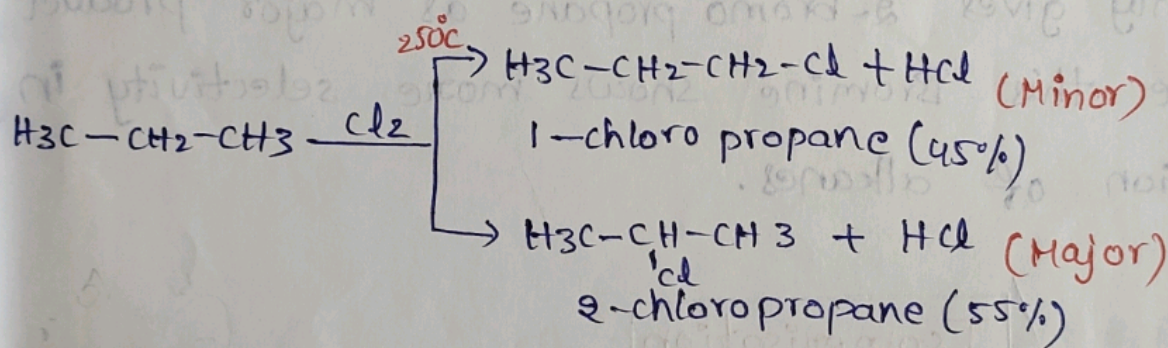
Iodination is also having some problem. In propagation⁵ rxn. It is highly endothermic.

And another problem in iodination is reversible & HI is strong reducing agent.

Concept of relative reactivity v/s Selectivity :-

In halogenation of alkanes selectivity of Br₂ is more than Cl₂.

Ex:- Reaction of propane with Cl₂ and Br₂.



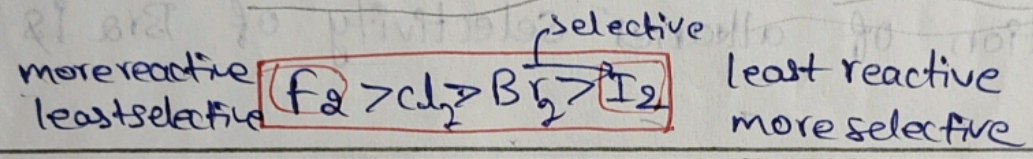
The order of reactivity of 'H' atoms is $3^\circ > 2^\circ > 1^\circ$

* Cl₂ is more reactive than Br₂, so it cannot differentiate both 1°, 2°-hydrogen atoms in propane gives

1-chloro propane (45%) and 2-chloro propane (55%) in almost equal ration. but bromine is less reactive more selective than chlorine.

Note:-

The relative reactivity of halogens towards halogenation is more reactive and least selective

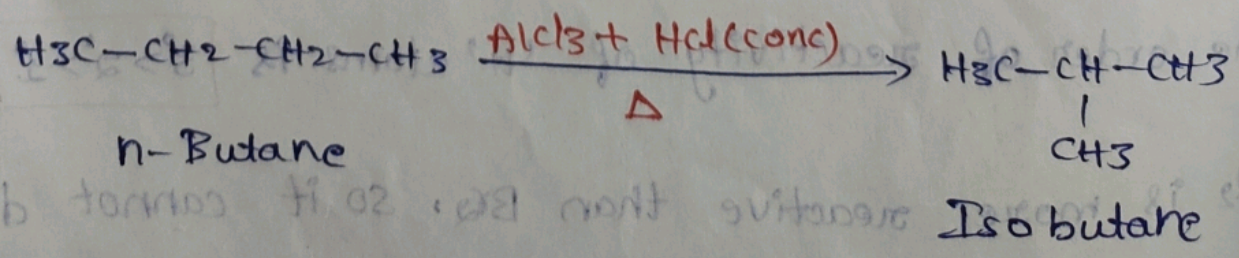


so, it can selectively reacts with 2° hydrogen atom propane only gives 2-bromo propane as major product (97%) like this Bromine shows more selectivity in Halogenation of alkanes.

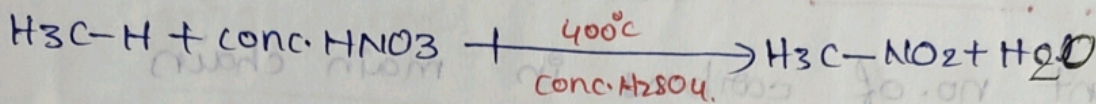
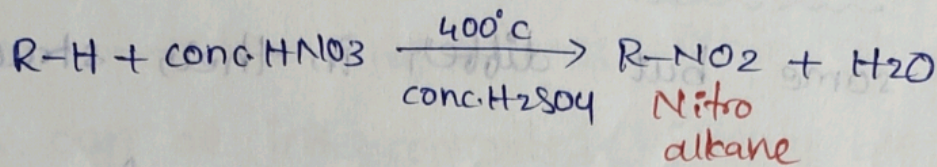
Isomerisation

The process of conversion of one isomer into another isomer is called isomerization.

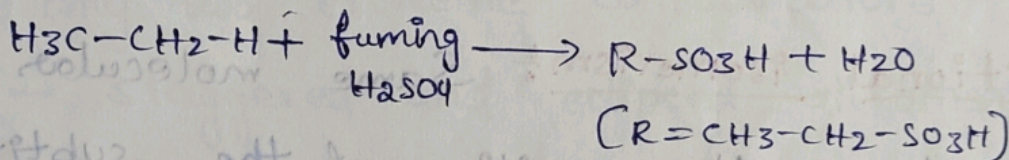
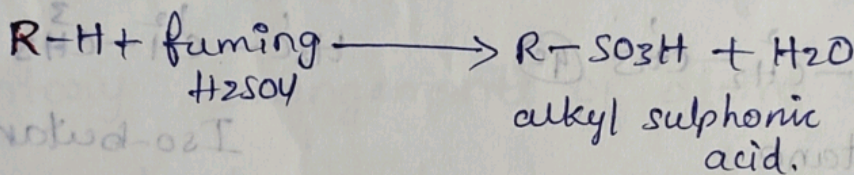
* Higher alkanes on heating in presence of anhydrous $AlCl_3$ and hydrogen chloride form branched chain isomers. is known as isomerization.



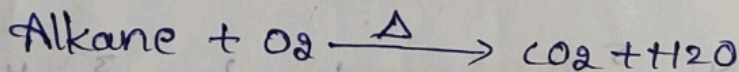
1) Nitration :-



2) Sulphonation :-



3) Combustion / oxidation :-



↑ isomerism

Compounds having same molecular formula for (or) same number of atoms but differ in their physical and chemical properties are called "isomers" and the phenomenon is known as isomerism, and the process is called isomerisation.

* Isomerism in alkanes is of two types.

1. Structural isomerism

→ chain isomerism

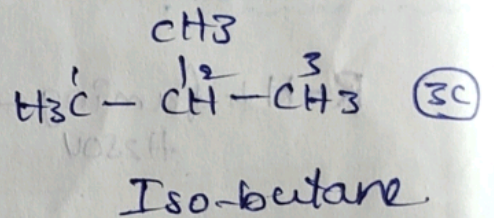
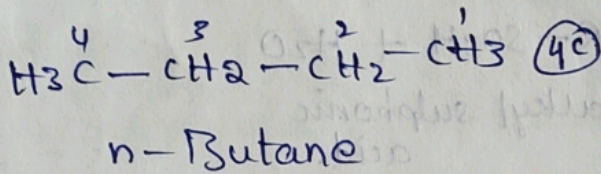
2. Stereo isomerism

→ position isomerism.

01. Structural isomerism :- In this the molecular formula is same but differ in their structure.

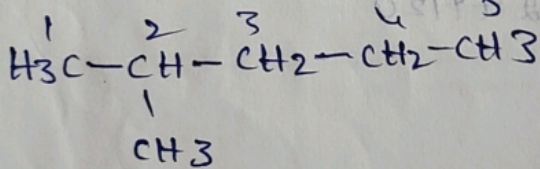
(a) chain isomerism :- Same molecular formula but different no. of carbons in main chain.

Ex:- Butane — 2 isomers.

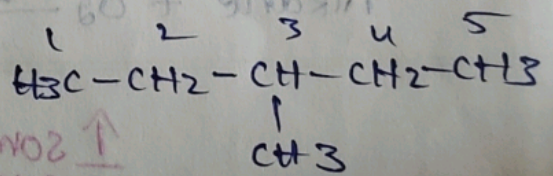


(b) positional isomerism :- Same molecular formula but differ in the position of the substituent.

* Compounds must have same parent chain



2-Methyl pentane



3-Methyl pentane

Stereo isomerism :- (stereo)

Same molecular formula but have different relative arrangements of atoms (or) groups in the

space. They are 2 types

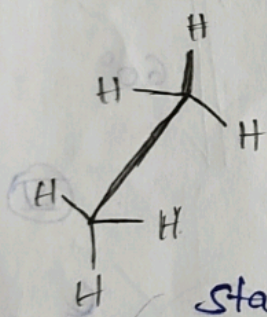
1) configurational isomers [seperable, Non interconvertible]

2) conformational isomers [Interconvertible, Non-seperable]

Conformational isomers \div stereoisomers which differ in relative positions of atoms within the molecule and which can be interconverted simply by rotation about sigma bonds.

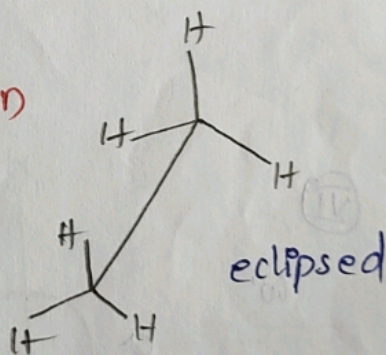
For ex: \div Conformations of ethane \div

Out of infinite numbers of (momentary arrangements of atoms in space) of ethane, only two extreme conformations are important — staggered and eclipsed. All other are called Skew (or) gauche forms.

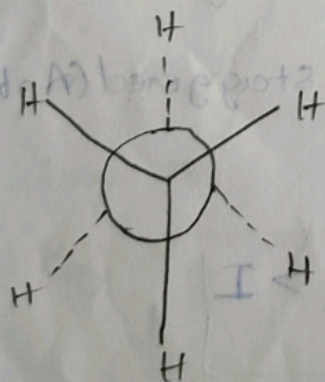


Staggered.

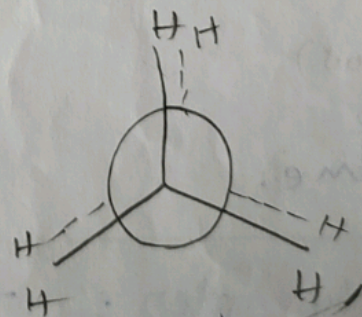
Sawhorse Representation



eclipsed



Newman representation



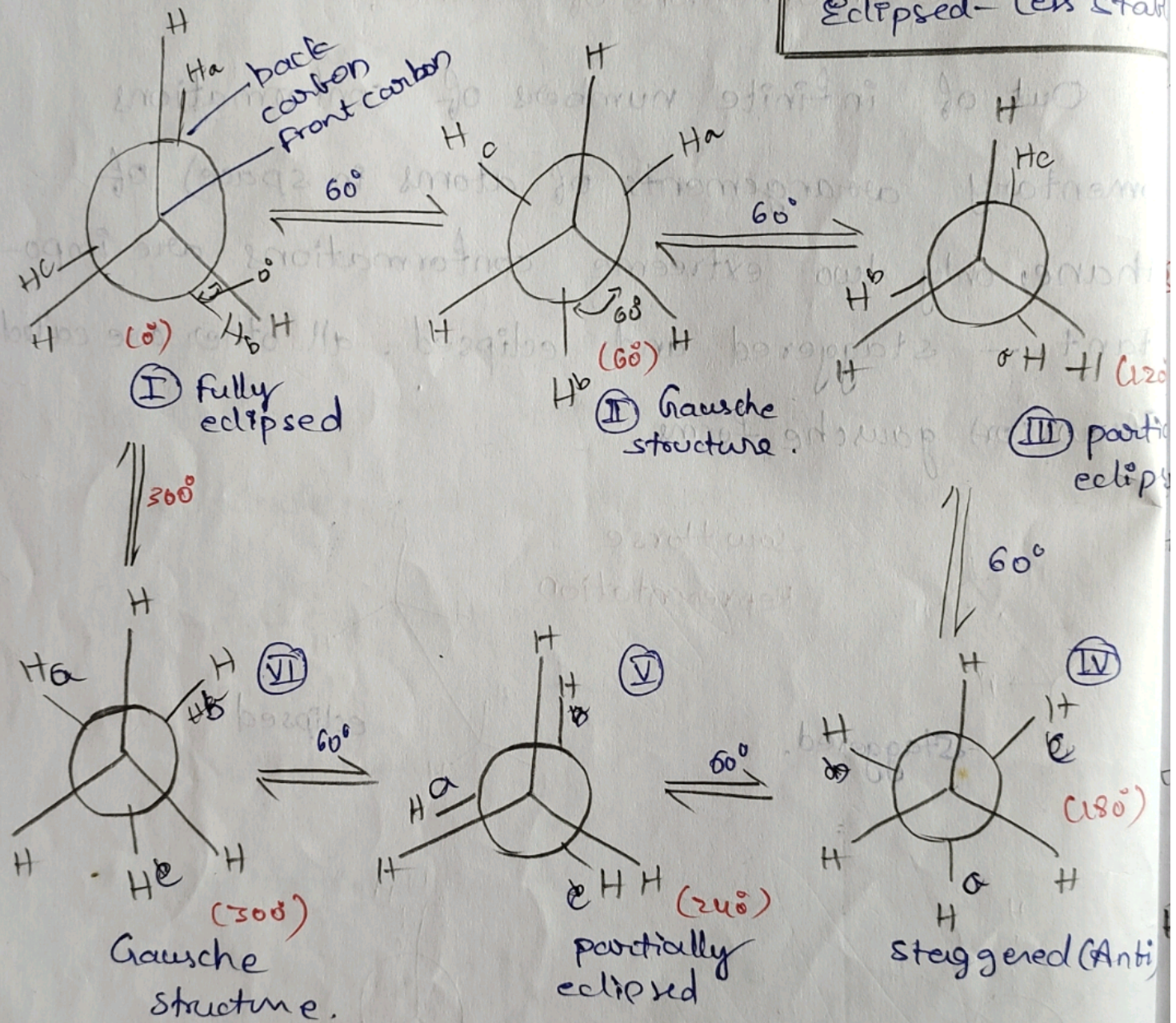
Conformational analysis of alkanes \div rebo pgs 113

The study of stability and energy

differences between different conformational isomers of a saturated compound is called as the conformational analysis.

Ethane conformation

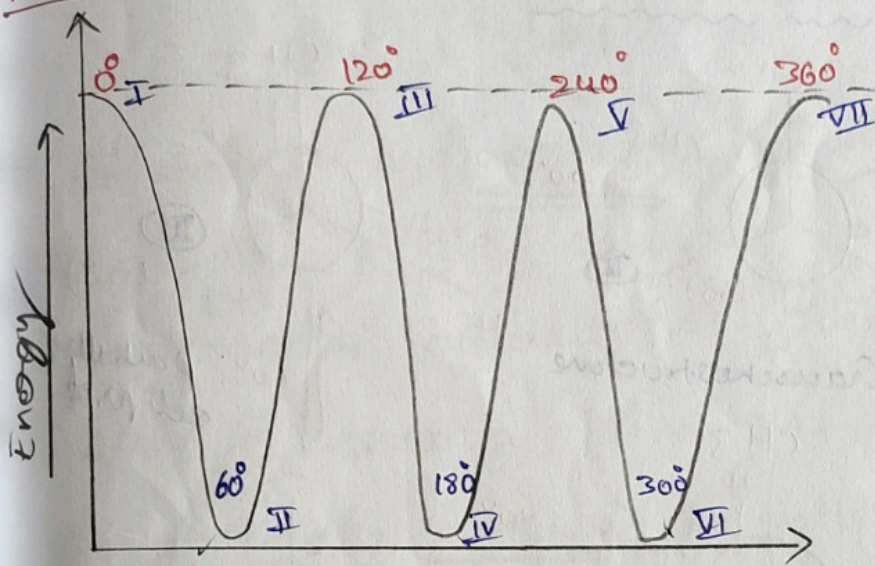
Note:
 Staggered - More stable
 Eclipsed - Less stable



Stability order : $\text{IV} > \text{II} > \text{III} > \text{I}$

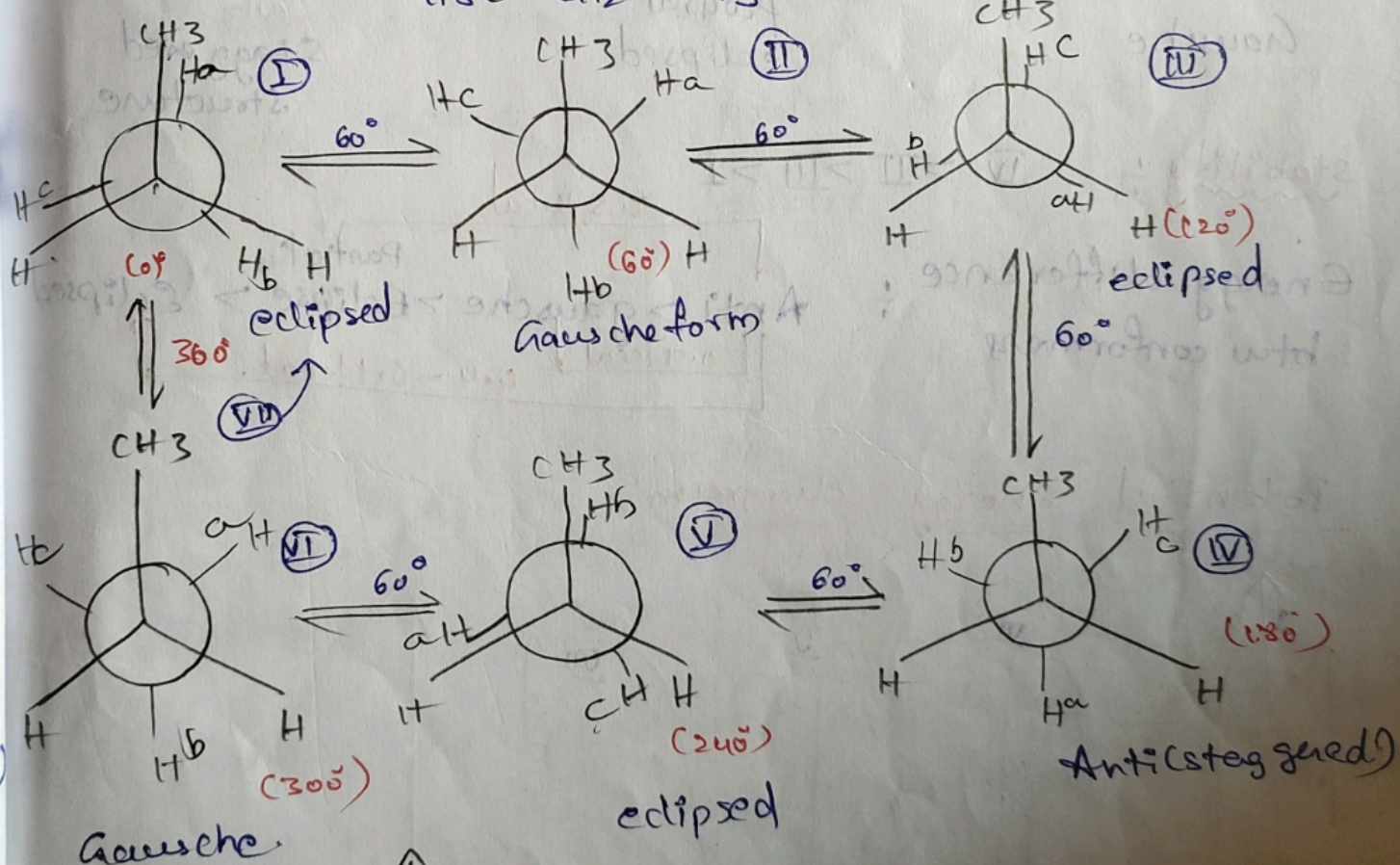
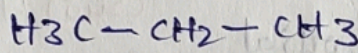
Energy order : $\text{I} > \text{III} > \text{II} > \text{IV}$

Potential Energy diagram

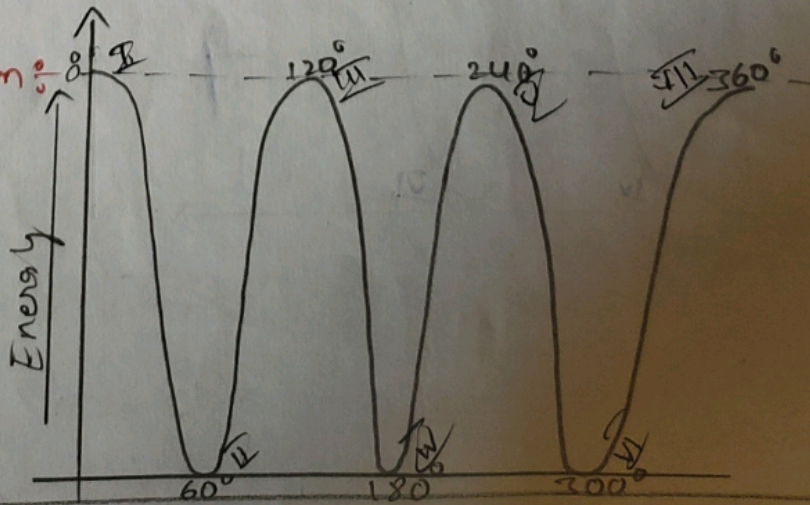


eclipsed
↑
Gausche / skew
↓
staggered

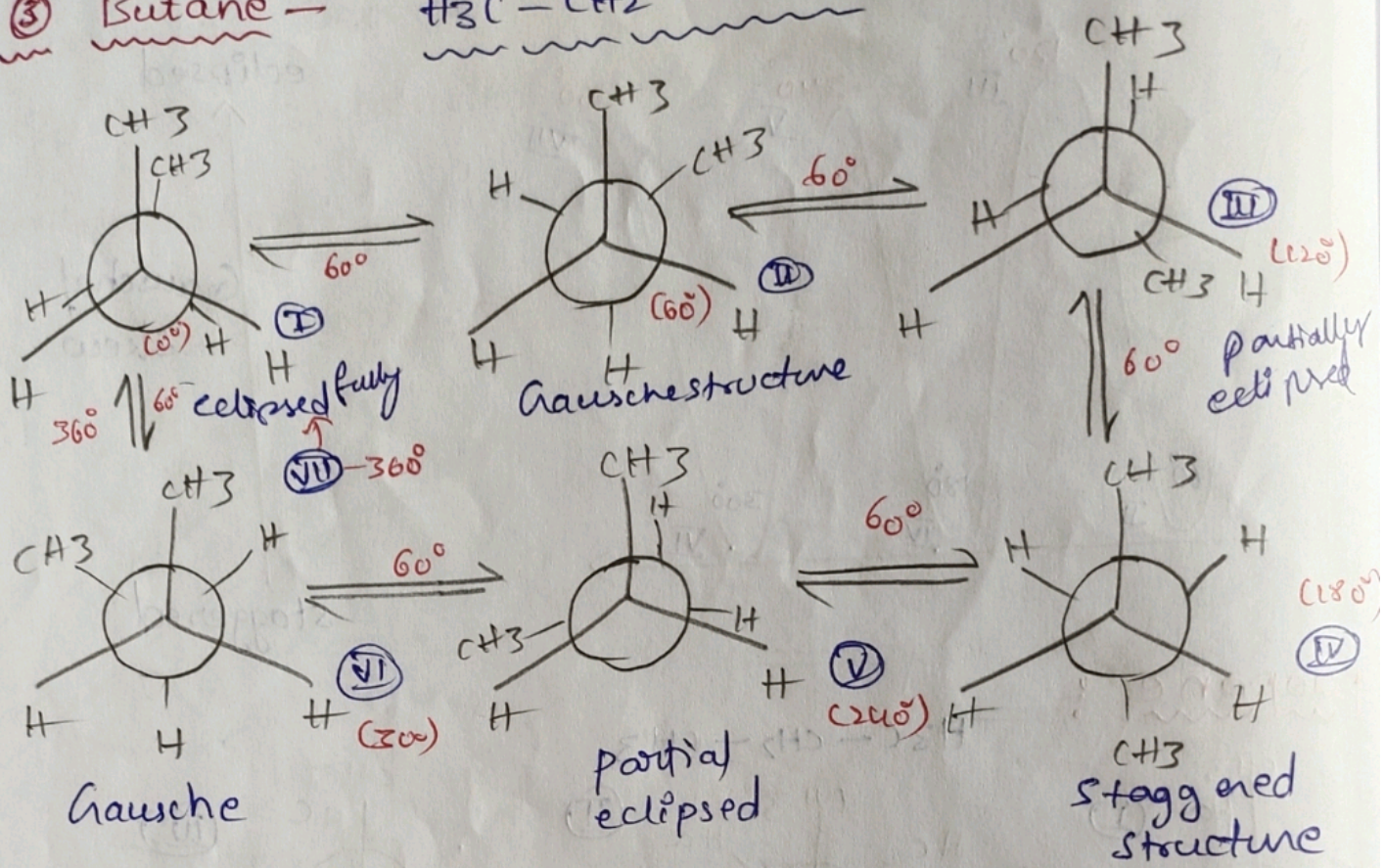
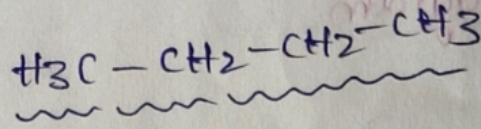
③ propane :-



Energy diagram :-



③ Butane —

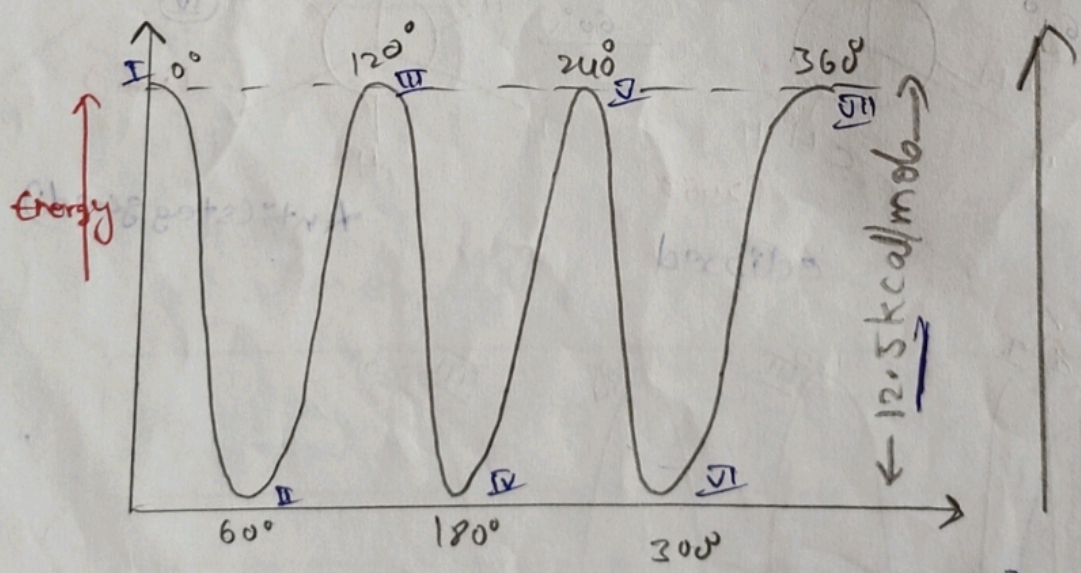


stability : $\text{IV} > \text{II} > \text{III} > \text{I}$

Energy difference : $\text{Anti} > \text{gauche} > \text{Eclipse} > \text{Eclipse}$
 btw conformers

Energy differences:
 - Anti to gauche: 0.9 kcal
 - Gauche to Eclipsed: 3.5 kcal
 - Eclipsed to Eclipsed: 6.0 kcal

Potential Energy diagram



a. Alicyclic hydrocarbons

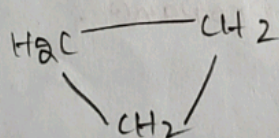
(9)

[Cycloalkanes]

Saturated hydrocarbons in which the carbon atoms are joined by single covalent bonds to form rings are known as cycloalkanes. Alicyclic compounds occur widely in essential oils. also called cycloparaffins. the general formula is C_nH_{2n} .

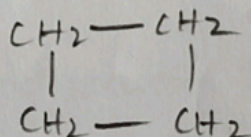
Nomenclature :-

* The name of the unsubstituted cycloalkanes is obtained by adding the prefix cyclo to the name of the corresponding alkane.

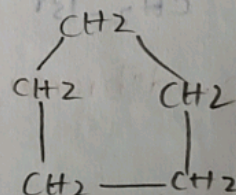


IUPAC
type :- cyclopropane

common :- Trimethylene

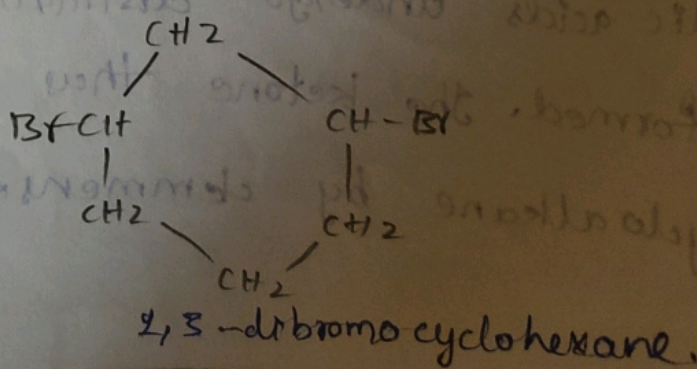
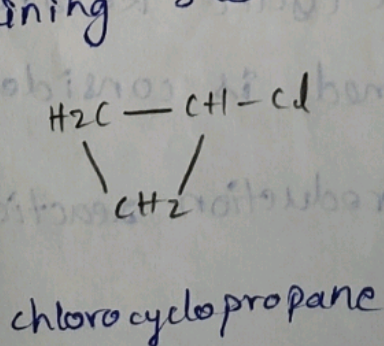


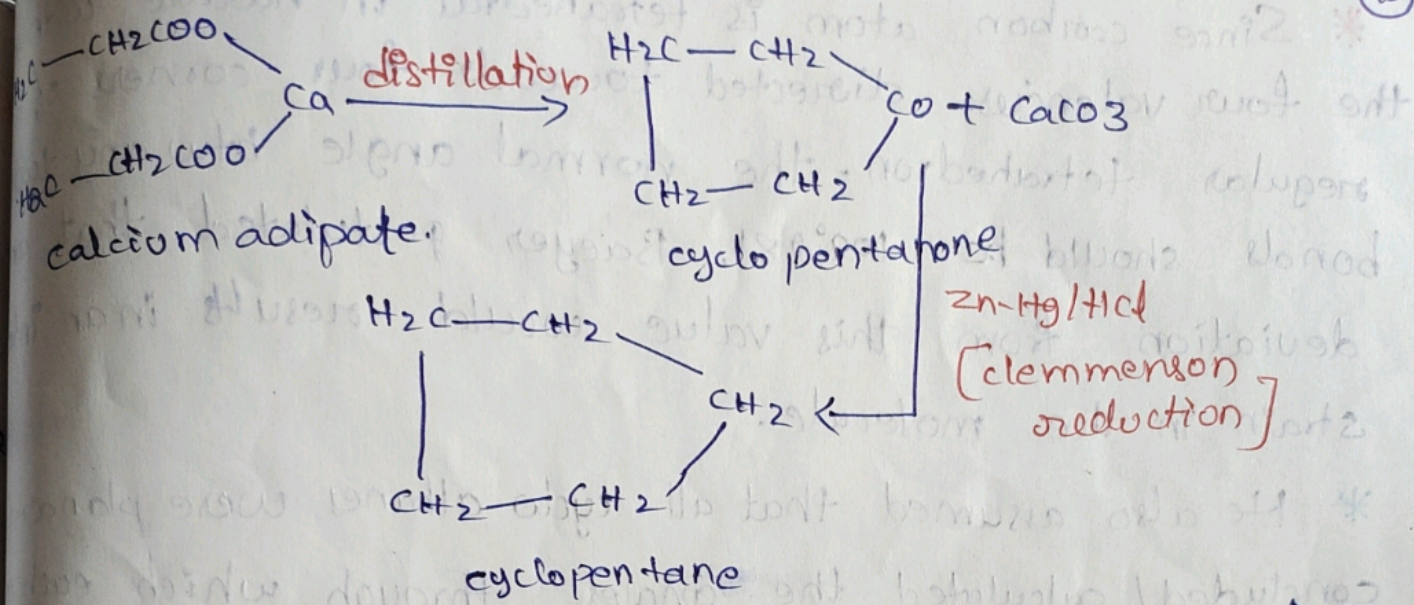
cyclobutane
Tetramethylene



cyclopentane
penta methylene

* For Naming the substituent cycloalkanes ring carbon atoms are to be given numbers and that the carbon containing substituent gets lowest possible number.





This method can't be used for the preparation of cyclopropane / its derivatives.

Physical properties: * The first two members cyclopropane & butane are colourless, pleasant smelling gases. While upto cycloheptane are liquid & higher ones are solids.

- * Insoluble in water and soluble in ether & ethanol
- * Their M.P & B.P ↑ses with ↑sing molecular weight.

Q. Stability of cycloalkanes - Baeyer's Strain theory

To explain the relative stability of few cycloalkanes "adolf von Baeyer" proposed a theory which was named after him. His theory is based on the following assumptions.

* Since carbon atom is tetrahedral in nature with the four valencies directed towards four corners of regular tetrahedron. the normal angle btw any two bonds should be $109^{\circ}28'$. Baeyer postulated that a deviation from this value would result in an internal strain in the molecule.

* He also assumed that all cycloalkanes were planar. He concluded/calculated the angles through which each of the valency bond was deflected from the normal angle. is called angle strain which determines the stability of the ring.

* Thus greater the deviation of the bond angle of the ring from $109^{\circ}28'$, greater the strain & more unstable (more reactive) is the ring.

$$\text{Bond angle strain} \propto \frac{1}{\text{stability}}$$

* Baeyer showed the deviation (d) in cycloalkanes from the normal tetrahedral angle can be calculated as follows.

$$d = \frac{1}{2} (109^{\circ}28' - \alpha)$$

α = bond angle in the cycloalkanes

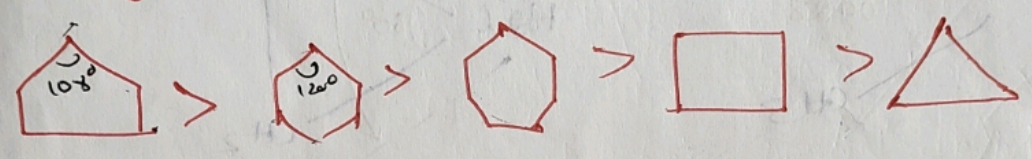
d = angle of deviation.

*) Angle of deviations in various cycloalkanes

The +ve & -ve values of valence angle deviation indicate whether the bond angle is lower/greater than the normal tetrahedral bond angle.

Limitations: Baeyer's strain theory explains the relative stability of cycloalkanes upto 5 but it fails beyond six | five.

Acc to Baeyer's theory the stability order of cycloalkanes is:



* Conformations of cyclohexane:

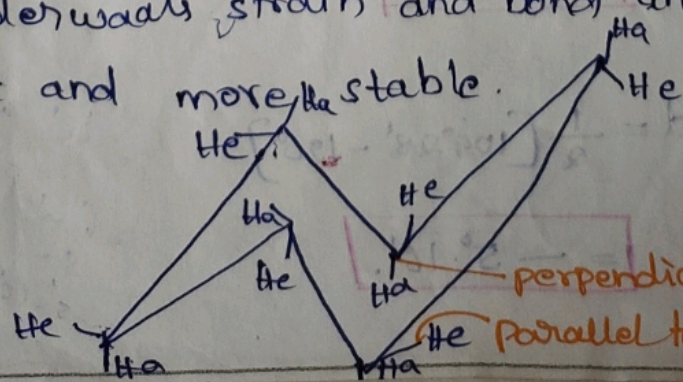
* cyclohexane (planar form)

Due to angle strain planar form of cyclohexane is unstable and it exist in different conformations.

- 1. chair form
- 2. Boat form
- 3. Twist boat
- 4. Half chair form.

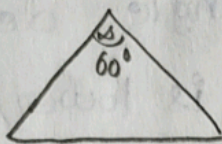
Among the four conformations chair and boat forms are important.

chair conformation: In this form the six carbon atom are in different planes (up & down) due to this there is no eclipsed strain between hydrogen atoms and there is no vanderwaals strain and bond angle strain. It is less energetic and more stable.



Ha → axial hydrogen
 He → equatorial hydrogen
 perpendicular to plane of the ring
 parallel to the plane of the ring

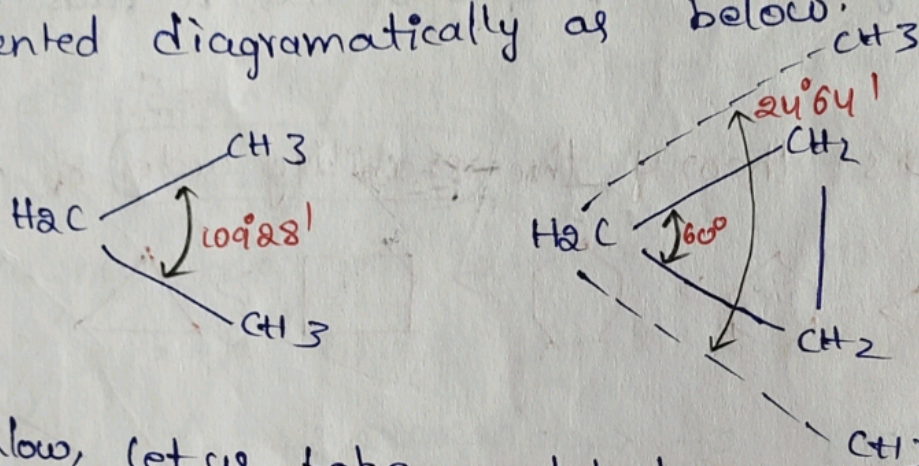
① For ex:



$$d = \frac{1}{2} (109^{\circ}28' - 60^{\circ})$$

$$= 24^{\circ}64'$$

The deviation of $24^{\circ}64'$ developed in cyclopropane during the conversion of propane to cyclopropane can be represented diagrammatically as below.



Now, let us take cyclobutane, pentane & hexane on the assumption these rings are planar, the value of bond angle & hence the valence angle deviation i.e., internal strain in the various cycloalkanes as calculated below.

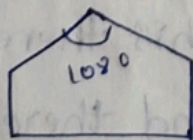
②



$$d = \frac{1}{2} [109^{\circ}28' - 90^{\circ}]$$

$$= +9^{\circ}.44' \Rightarrow [+9^{\circ}.44']$$

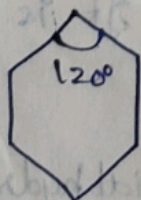
③



$$d = \frac{1}{2} [109^{\circ}28' - 108^{\circ}]$$

$$= +0^{\circ}.44'$$

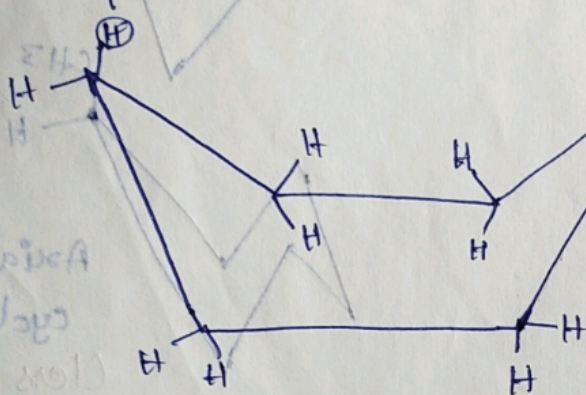
④



$$d = \frac{1}{2} [109^{\circ}28' - 120^{\circ}]$$

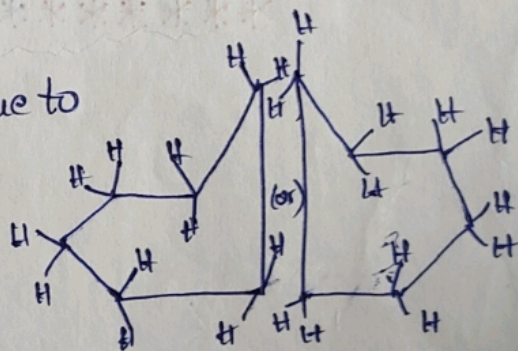
$$= -5^{\circ}.16'$$

Boat form: In boat form out of six carbon atoms (12) 4-carbons are in same plane due to this hydrogens these carbons involved in eclipsed strain and there is vanderwaal's strain also present in boat form. It is more energetic, less stable.



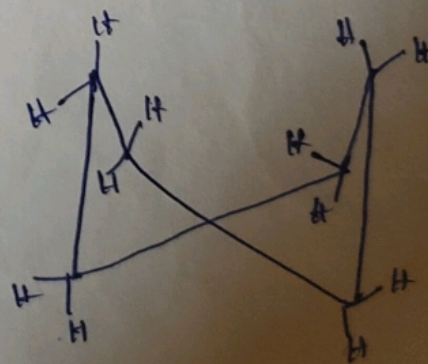
3. Half-chair form:

This is less stable conformation due to eclipsed strain, vanderwaal's strain and angle strain.



4. Twist boat form:

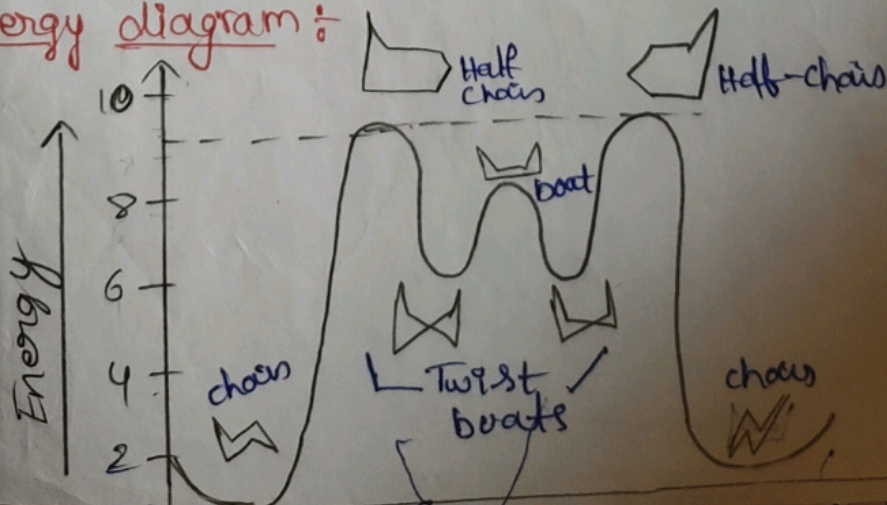
Twist boat conformation is much more stable than their boat conformation.



Stability:

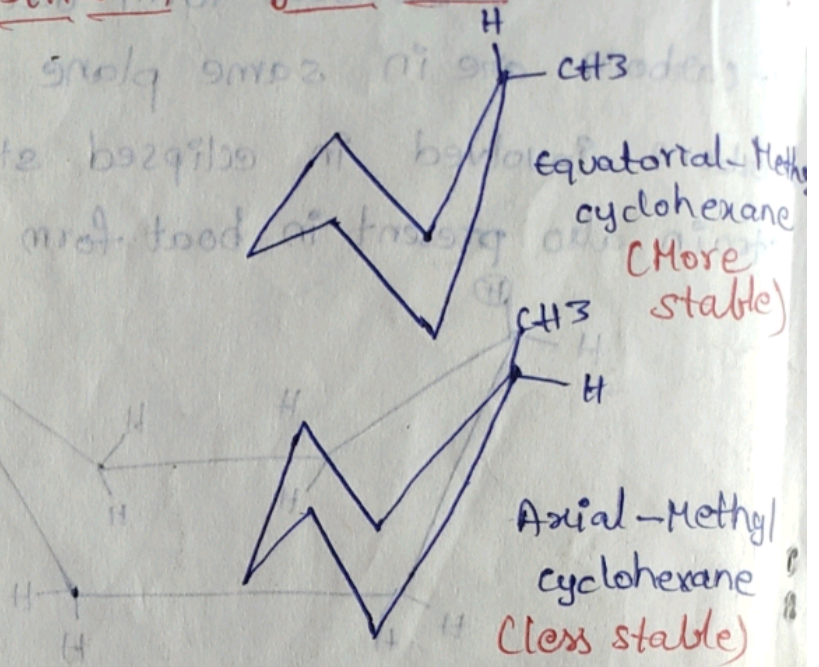
chair > Twistboat > Boat > Half chair

Energy diagram:

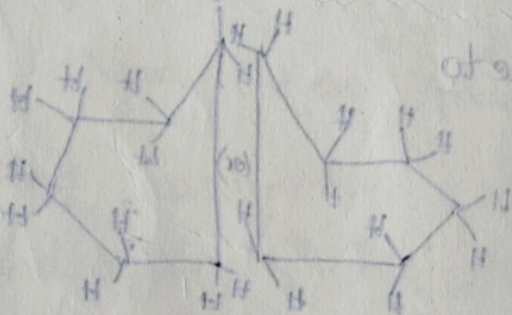


Conformations of monosubstituted cyclohexanes:

In Mono substituted cyclohexane like methyl cyclohexane the conformation with Methyl group of equatorial position is more stable than axial isomer.

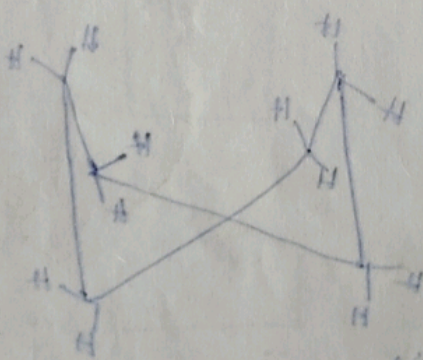


Chair - chair form:



This is less stable conformation due to eclipsed strain, van der Waals strain and angle strain.

Twist boat conformation is much more stable than chair form.



Chair > Twist boat > Boat > Half chair

Half-chair

Boat

Twist

Chair

Twist boat

Boat