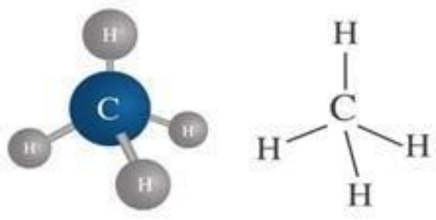
UNIT- I

ALKANES & CYCLO ALKANES

HYDROCARBONS:-

1. A hydrocarbon molecule contains only carbon and hydrogen. These are further divided into , alkanes, alkenes, alkynes and aromatics.
2. Alkanes having only sigma bonds, and general formula is $C_nH_{2n+2.}$ (n = number of c – atoms) .
3. Alkanes exist in straight chains, chains with branching, and cycles.
4. The carbon atom in an alkane has four sp3 hybridized and forms four single bonds that are equidistant from each other. The shape is referred to as tetrahedral with a C-C bond length of 1.54 Å and bond angles of $109^0.28''$



CH_4 Methane

Preparation Methods of Alkanes:-

1. WURTZ REACTION:-

In wurtz reaction a solution of alkyl halide in ether solvent on heating with sodium gives alkane. In this reaction symmetrical alkanes with even number of carbon atoms are formed as products.

$$2R\text{-}X + 2Na \rightarrow R\text{-}R + 2Na^+ X^-$$

If different types of alkyl halides produce all possible alkanes(Both even and odd number carbon containing alkanes) as given below

$$CH_3X + Na + C_2H_5X \rightarrow CH_3CH_2CH_3 + CH_3CH_3 + CH_3CH_2CH_2CH_3$$

The different involved are steps are:

$$CH_3X + 2Na + C_2H_5X \rightarrow CH_3CH_2CH_3 + 2NaX$$
$$CH_3X + 2Na + C_2H_5X \rightarrow CH_3CH_3 + 2NaX$$
$$C_2H_5X + 2Na + C_2H_5X \rightarrow C_2H_5C_2H_5 + 2NaX$$

The separation of mixture into individual members is not easy because their boiling points are near to each other and thus Wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atoms.

Limitations:-

a. Methane cannot be obtained by this method

b. The reaction fails in case of tertiary halides

c. In this reaction if Zn – metal used as catalyst this is called as Frankland Reaction.

***Mechanism*:**

The mechanism of Wurtz reaction is although not clear however two mechanisms are proposed for this reaction.

1. Through the formation of intermediate Organo metallic compound

$$RX + 2Na \rightarrow \underset{\text{Intermediate}}{[RNa]} + NaX$$

$$RX + [RNa] \rightarrow R\text{-}R + NaX$$

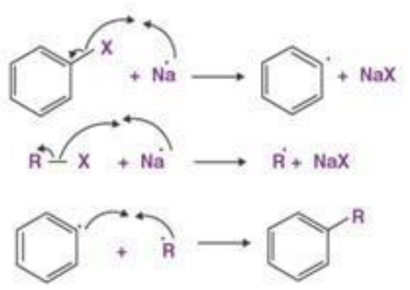
2. Through the formation of Intermediate free radicals.

$$RX + Na \rightarrow \underset{\text{Free radicals}}{R^{\cdot}} + Nax$$

$$R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R$$

2. WURTZ - FITTIG REACTION:-

The chemical reaction of aryl halides with alkyl halides and sodium metal with dry ether solvent to yield substituted aromatic compounds is called the Wurtz-Fittig reaction.

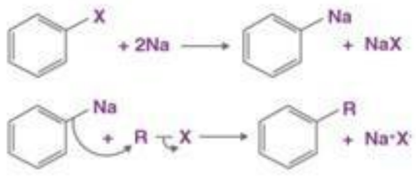


If the alkyl halide has more chemical reactivity than the aryl halide, it will form the carbon sodium bond first and act as a nucleophile to the aryl halide, helping the reaction in forming asymmetrical products.

Mechanism:-

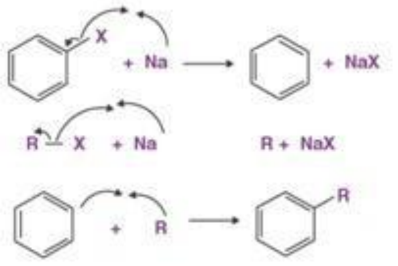
1. *The Organo Alkali Mechanism*:-

When the aryl halide is reacted with sodium metal, an intermediate organo-alkali compound is formed, which is followed by a nucleophilic attack of the alkyl halide as shown below. Thus, the required alkyl-aryl is formed.



2. *The Radical Mechanism*:-

The sodium atom acts as a moderator for the formation of alkyl radicals and aryl radicals. These alkyl and aryl radicals now combine to form a substituted aromatic compound as shown below.



The reaction can also be conducted using metals other than sodium (such as potassium, iron, copper, and lithium). The reaction can also be called a coupling reaction. It requires an aprotic solvent as the reaction medium for which dry ether is quite suitable as it is a good non-polar aprotic solvent.

3. **COREY HOUSE REACTION:-**

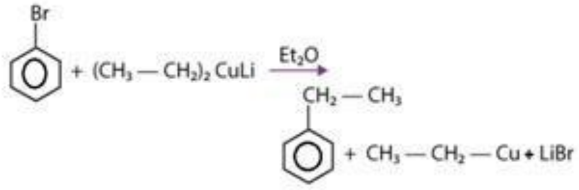
The coupling reaction is to join two alkyl groups together to produce higher alkanes. This versatile method is known as the Corey-House reaction.

The Gilman reagent (Lithium di alkyl cuprate) reacts with alkyl halide to give higher alkane, the reaction is known as Corey-House synthesis.

$$R_2CuLi + R''\text{-}X \rightarrow R\text{-}R'' + R\text{-}Cu + LiX$$

(R and R‟ may be same or different)

1. In this reaction R''-X may be methyl halide, 1^oalkyl halide (or) 2^o alkyl halide. The alkyl group of dialkyl lithium cuprate may be methyl, 1^o, 2^o (or) 3^o.
2. In this reaction dialkyl lithium cuprate also reacts with aryl halide, alkyl halide and vinyl halide.
3. The ***Corey-House reaction*** is limited to a 1^o alkyl halide and the alkyl groups in the Gilman reagents may be 1^o, 2^o or 3^o.



<u>For example</u>:-

$CH_3CH_2CH_2Br + (CH_3)_2CuLi$ e $CH_3CH_2CH_2CH_3 + CH_3Cu + LiBr$

This reaction can be used for preparing symmetrical, unsymmetrical, straight chain (or) branched chain alkanes. For a better yield the alkyl halide used should be primary where as lithium dialkyl copper may be primary, secondary or tertiary.

***Synthesis of Gilmans Reagent*:-**

Alkyl halides react with lithium in dry ether to form alkyl lithium.

R-X + 2Li e R-Li + LiX

This alkyl lithium reacts with CuI to give Dialkyl Lithium Cuprate known as Gilman reagent.

2R-Li + CuI e R_2CuLi + LiI

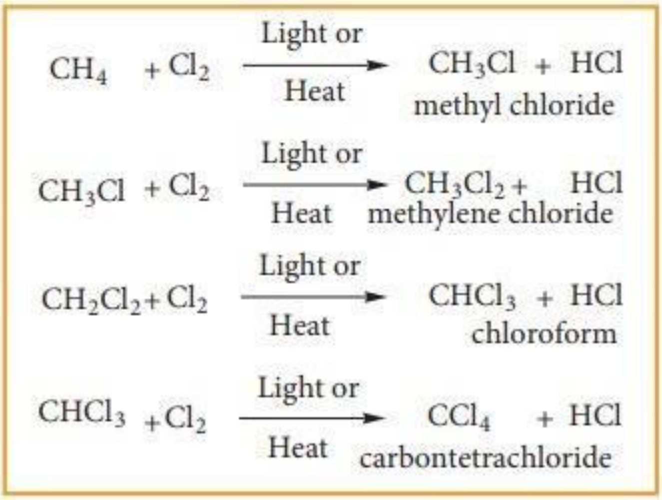
CHEMICAL REACTIVITY:-

Alkanes contain strong C – C single bonds and strong C - H bonds. The C - H bonds are slightly polar. Therefore, there is no portion of the molecule that carries positive (or) negative charge, which is required for other molecules to be attracted to it. For example, many organic reactions start because an ion (or) a polar molecule is attracted to a portion of an organic molecule. This attraction does not occur with alkanes because alkane molecules do not have this separation of charge. These are also known as ***Paraffins.***

1) HALOGENATION:-

Halogenation reaction is the chemical reaction between an alkane and halogen in which one (or) more hydrogen atoms are substituted by the halogens.

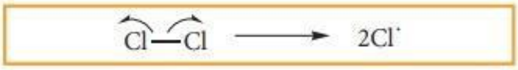
Chlorination and Bromination are two widely used halogenation reactions. Fluorination is too quick and iodination is too slow. Methane reacts with chlorine in the presence of light (or) when heated as follows.



***Mechanism*:**

The reaction proceeds through the free radical mechanism. This mechanism is characterized by three steps initiation, propagation and termination.

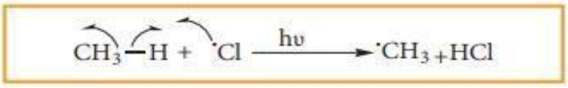
i) **CHAIN INITITATION**: The chain is initiated by UV light leading to homolytic fission of chlorine molecules into free radicals (chlorine atoms).



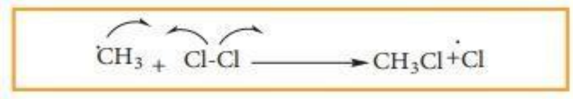
Here we choose Cl-Cl bond for fission because C-C & C-H bonds are stronger than Cl-Cl.

ii) **PROPAGATION:** It proceeds as follows,

A. Chlorine free radial attacks the methane molecule and breaks the C-H bond resulting in the generation of methyl free radical

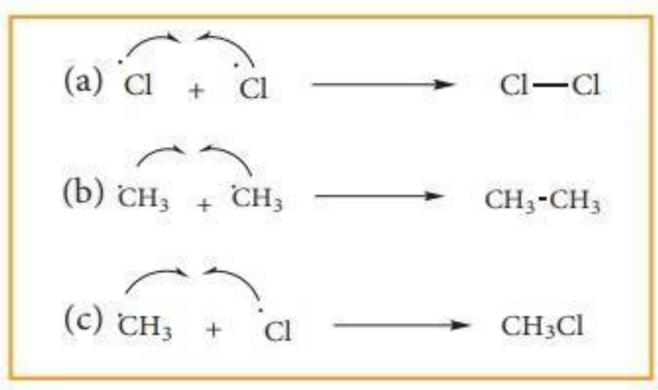


B. The methyl free radical thus obtained attacks the second molecule of chlorine to give chloromethane (CH_3Cl) and a chlorine free radical as follows.



C. This chlorine free radical then cycles back to step (a) and both step (a) & (b) are repeated many times and thus chain of reaction is set up.

iii) **CHAIN TERMINATION:-** After sometimes, the reactions stops due to consumption of reactant and the chain is terminated by the combination of free radicals.



Reactivity Vs Selectivity in Halogenation of Alkanes:-

1. The halogenation of alkanes with three and more carbon atoms may give two products, of unequal stability. For example

$$CH_3CH_2CH_3 + Br_2 \rightarrow 3\%\ CH_3CH_2CH_2Br + 97\%\ CH_3CH(Br)CH_3$$

2. The factors that determining the products in halogenation are:

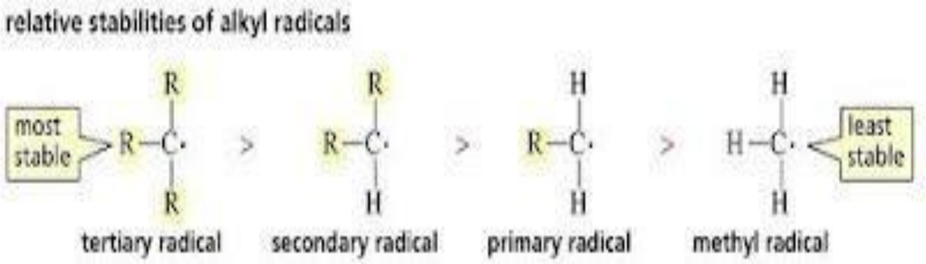
(a) Reactivity of R-H system.
(b) Reactivity of halogen radical.

(a) Reactivity of R-H system.:-

1. The differences in reactivity of alkanes is due to the differences in C- H bond dissociation energies.The bond dissociation energies for

Methyl :- CH_2-H: 435 kJ mol^{-1}
Ethyl :- CH_3CH_2-H (1° carbon): 410 kJ mol^{-1}
Isopropyl :- $(CH_3)_2$CH-H (2° carbon): 397 kJ mol^{-1}
Tert-butyl :- $(CH_3)_3$C-H (3° carbon): 380 kJ mol^{-1}

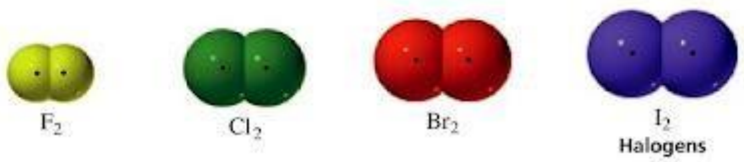
2. The weaker bonds are more easier to be broken than stronger bonds. So, the relative order of reactivity for alkanes: *methyl* $< 1^o < 2^o < 3^o$
3. The differences in bond dissociation energies can be explained the differences in the stability of alkyl radicals.



4. The *__more stable__* the radical, the *__easier__* it will form. Hence it is easier to remove a hydrogen atom from carbon atom to form a radical.

__(b) Reactivity of halogen radical:-__

a. The order of reactivity of halogens: $F_2 > Cl_2 > Br_2 > I_2$



b. The *fluorine radical is the most reactive* but the *iodine radical is the least reactive* in fact, it is unable to abstract a „H‟ atom from an alkane.
c. The bromination is a *slower* reaction than chlorination. The activation energy for abstraction of a „H‟ atom by a bromine radical to be about *4.5 times greater* than that for abstraction of a „H‟atom by a chlorine radical.
d. Bromine radical is *__less reactive__* and *__more selective__*. But the chlorine radical is *__more reactive__* and *__less selective__* in its reaction.

e. For example, the bromination of butane gives 98% of 2-bromobutane, compared with the 71% of 2-chlorobutane for chlorination of butane. Thus, *bromination is more highly regioselective than chlorination*.

CONFORMATIONAL ANALYSIS OF ALKANES:-

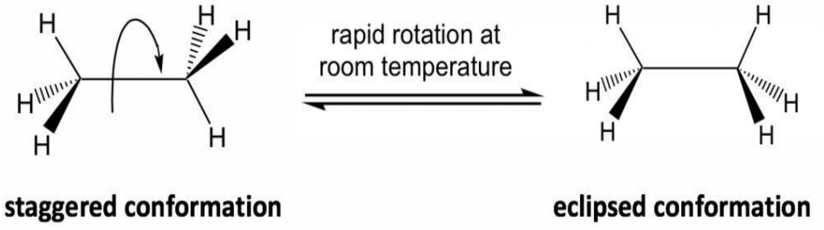
Conformation analysis is an investigation of the energy differences and relative stabilities of the different conformations of a compound.

Conformation:-

The different spatial arrangements of the atoms/groups that result from the single bond rotation are called conformations. Molecules with different conformations are called conformational isomers **(**or) conformers (or) rotamers.

At a molecular level, σ (sigma) bonds in alkane is keep on rotating. For example ethane (CH_3CH_3), one methyl (CH_3) group is able to rotate around the C-C bond freely which gives the two extreme conformations of ethane

1. Staggered Confirmation. (All the„H‟atoms spread out)
2. Eclipsed Confirmation. (All the„H‟atoms overlapped).

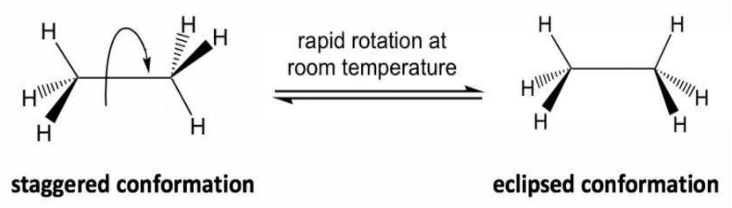


Based on dihedral angle the conformational isomers are named as follows

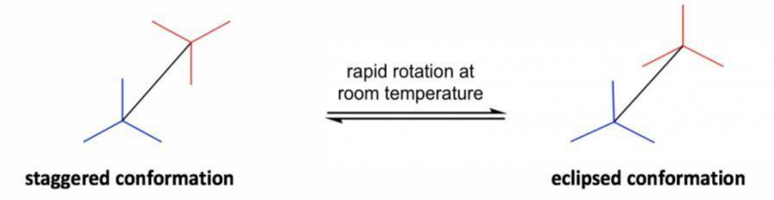
SI NO	DIHEDRAL ANGLE	CONFORMER
1	0^0	ECLIPSED
2	60^0	GOUCHE
3	180^0	STAGGERED
4	EVERY 1^0	SKEW

For the study of conformations, we use certain structural formulas. Like

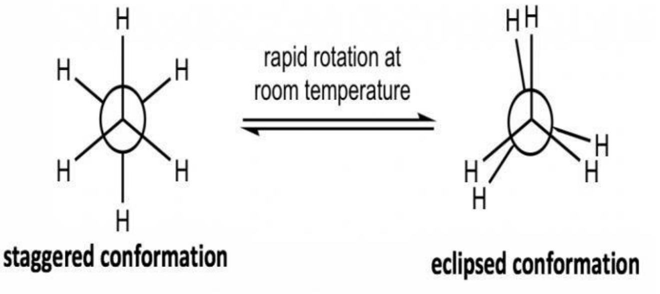
1. **Wedge formula.**



2. **Sawhorse formula.**

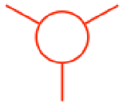


3. **Newman projection formula.**

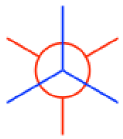


Newman Projection is the widely used representation for the study of conformations of alkanes. It visually represents the bonding of atoms from front to back. A Dot represents the first carbon atom (Near). The other carbon (Back) atom is a circle. At each C-atom groups are separated by 120° with each other. Lines show the hydrogen atoms bonded to each carbon atoms. This clearly indicates the dihedral angles.

Front C-atom



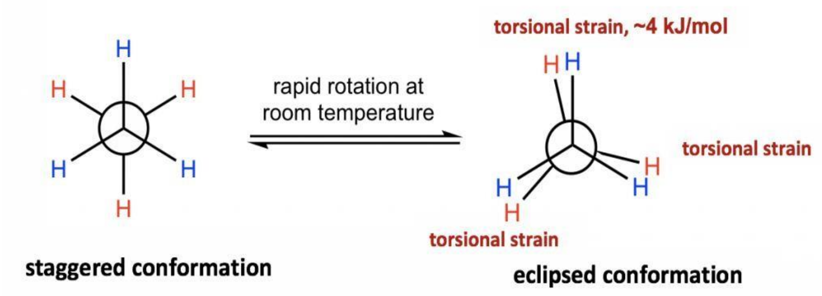
Back C-atom

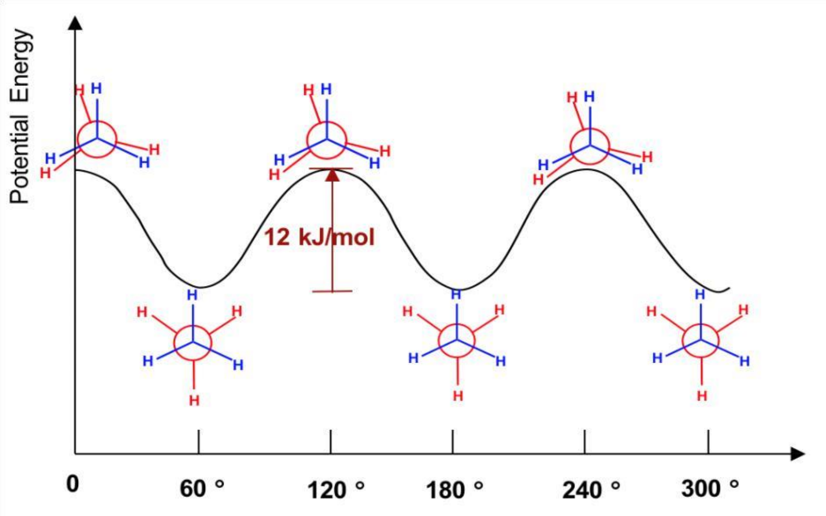


Both C-atoms

CONFORMATION ANALYSIS OF ETHANE:-

1. The two conformations of ethane are staggered and eclipsed, are different and having different energy levels.
2. The staggered conformation is more stable and is lower energy because the C-H bonds are arranged as far apart as possible in that conformation.
3. In eclipsed conformations, the „H‟ atoms on the front carbon are overlapping with the „H‟ atoms on the rear carbon, and this arrangement causes the repulsion between the electrons of C-H bonds of the two carbons. This type of repulsion is called **torsional strain**, also known as eclipsing strain.
4. Due to torsional strain, the eclipsed conformer is in an energy level that is 12 kJ/mol (or about 2.9 kcal/mol) higher than the staggered one. This can be represented graphically in a potential energy diagram as shown given below



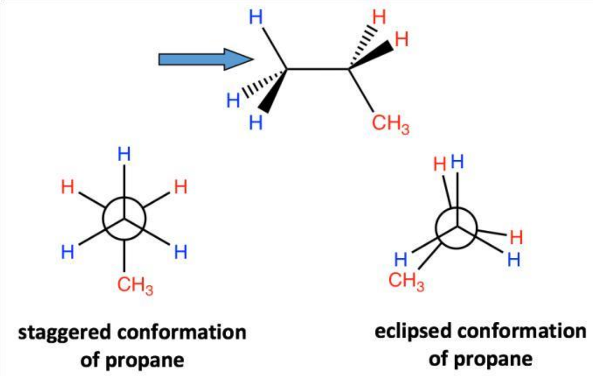


Potential Energy Vs Angle of Rotation

Energy difference in the confirmations of ethane is small. So, at room temperature, the changes from staggered to eclipsed conformers occur millions of times per second. Because of this continuous inter conversions, these two conformers cannot be separated from each other. However, at any given moment, about 99% of the ethane molecules will be in a staggered conformation because of their higher stability.

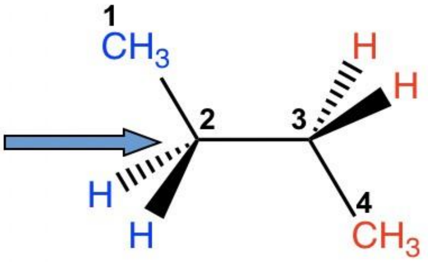
CONFORMATION ANALYSIS OF PROPANE:-

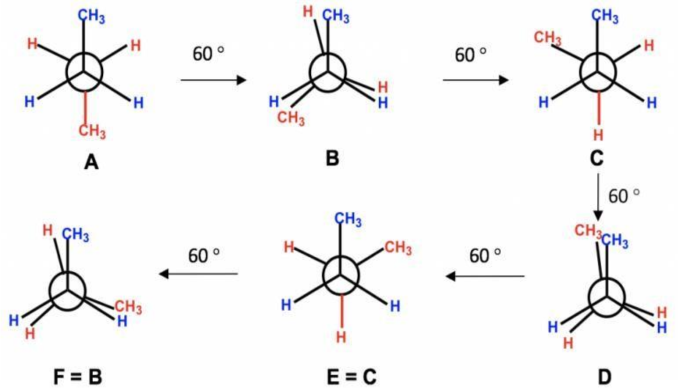
In propane also two types of conformations are formed i.e.. staggered and eclipsed by the rotation around C_1-C_2 bond in propane. The difference between propane and ethane is that there is a methyl (CH_3) group connected on the rear carbon for propane. However, that does not affect the relative stability, and the staggered conformer is more stable and lower energy.



CONFORMATION ANALYSIS OF BUTANE:-

There are three C-C bonds present in butane, C_1-C_2 ; C_3-C_4 and C_2-C_3 and rotation can occur about each of them. In butane we consider the rotation about the C_2-C_3 bond. For both carbon atoms, C_2 and C_3, there are two „H‟ atoms and one CH_3 group bonded. We can start with the conformer in which the two CH_3 groups are **opposite** to each other, then fix the front carbon and do 60° rotations of the rear/back carbon towards clock-wise direction to investigate **all** the possible conformations

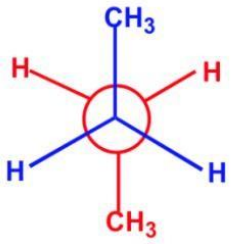




Among all six conformers obtained, there are three staggered and three eclipsed. Staggered conformations „**C'** and „**E'** should be in the same energy level because the groups are arranged in an equivalent way between these two conformers. Similarly, eclipsed conformations „**F'** and „**B'** are also in the same energy level. So, we analyze four conformers: **A, B, C** and **D**, having different in terms of energy and stability.

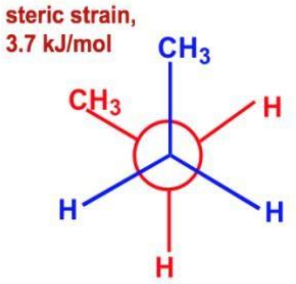
Between the two staggered conformers „**A'** and „**C', 'A'** is more stable than „**C'** because the two methyl CH_3 groups in „A‟ are as far apart as possible. This most stable staggered conformation is called the **anti**–conformation ("opposite"). In **anti**–conformations, the largest groups on the front and rear carbon are 180° opposite to each other.

The other staggered conformation „**C’** is called a **gauche** conformation, in which the two CH_3 groups are separated by 60° to each other. Hence the CH_3 groups being close to each other in gauche conformers, so the molecule experiences **steric strain,** this strain decreases the stability of confirmation **‘C.** steric strain does not apply in anti-conformations. The magnitude of steric strain also depends on the size of the group: the larger the size, the higher the steric strain.



anti

lowest in energy,
most stable

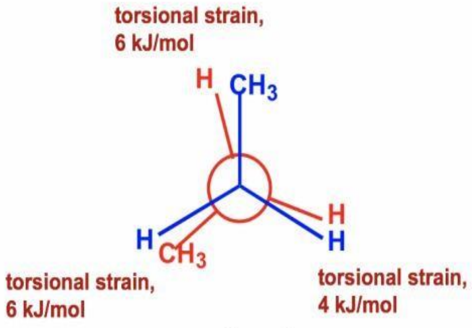


steric strain,
3.7 kJ/mol

gauche

2^{nd} low in energy

Between the two eclipsed conformers „**B’** and „**D’**, „**D’** is less stable than „**B’** because the two CH_3 groups are eclipsing (overlapping) each other in „**D’**, causing both torsional and steric strains.

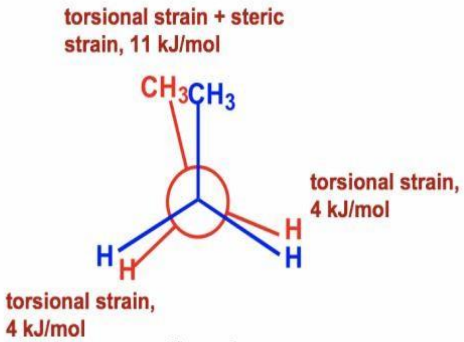


torsional strain,
6 kJ/mol

torsional strain,
6 kJ/mol

torsional strain,
4 kJ/mol

eclipsed



torsional strain + steric
strain, 11 kJ/mol

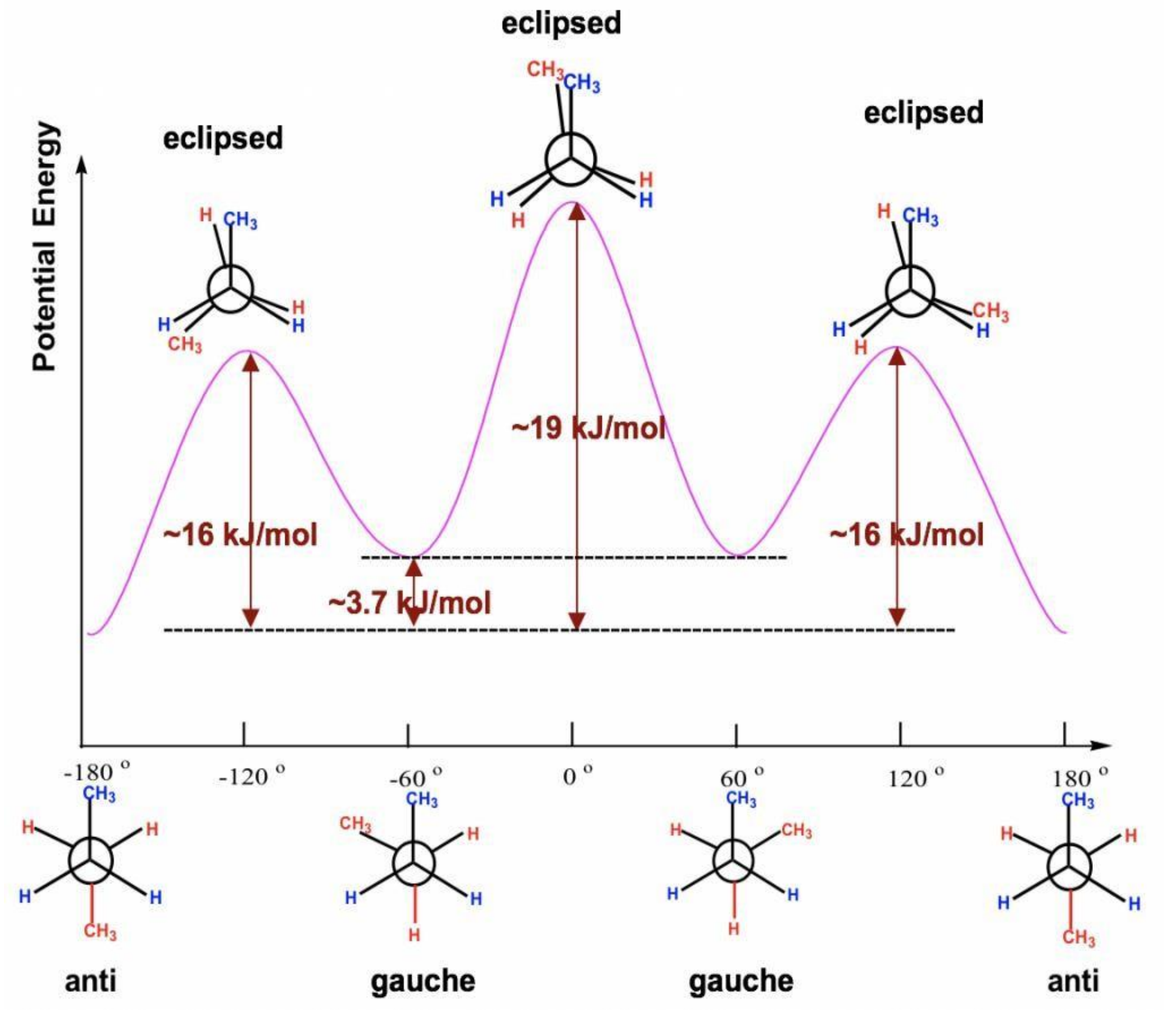
torsional strain,
4 kJ/mol

torsional strain,
4 kJ/mol

eclipsed

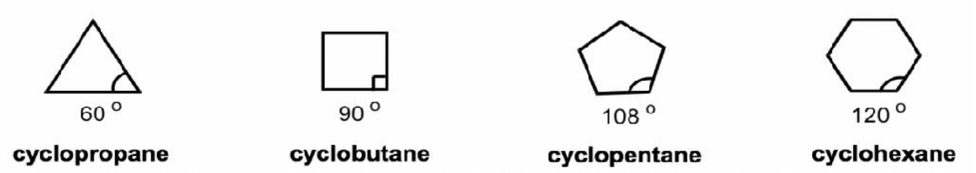
highest energy,
least stable

The energy difference of all the conformers are shown in the potential energy diagram given below. The curve is more complex than that of ethane since there are four different energy levels corresponding to four conformers with different stabilities. Even the energy barriers for the rotations are larger than that of ethane.

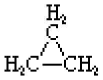
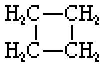
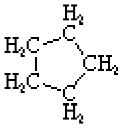
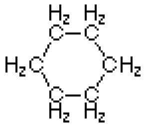
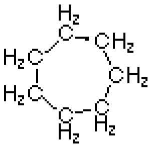
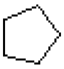
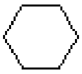
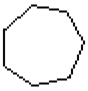
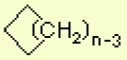


CYCLO - HYDROCARBONS

These are the cyclic (or) ring, analogues of the alkanes. These are referred to **as** alicyclic compounds, (or) cyclo alkanes. Their general formula is C_nH_{2n} (where n = no. of C – atoms)



Examples of Simple Cycloalkanes

Name	Cyclopropane	Cyclobutane	**Cyclopentane**	Cyclohexane	Cycloheptane	Cycloalkane
Molecular Formula	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_7H_{14}	C_nH_{2n}
Structural Formula						$(CH_2)_n$
Line Formula						

STABILITY OF CYCLO ALKANES:-

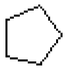
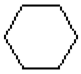
Stability of cycloalkanes can be explained by

1. Heat of combustion values.
2. Bayer‟s strain Theory.
3. Sachse – Mohr Theory.

1. BAYER'S STRAIN THEORY:-

- According to Bayer‟s strain theory all Cycloalkanes exist as planar confirmation, and in planar confirmation we observe that bond angle deviation.
- In all Cycloalkane ring carbons undergoes *sp* ^{3} hybridisiation, as similar to normal alkanes, hence the bond angles are equal to 109°28‟, and the expected shape is tetrahedral.
- But the Cycloalkanes are not tetra hedral because there is a bond angle deviation from tetra hedral bond angle, this angle deviation causes some strain in the molecule, this is called **Angle strain** and it is first observed by scientist Bayer, hence it is also known as **Bayer's strain**.
- The small size Cyclopropane (60°), Cyclobutane (90°) has more bond angle deviation from 109°28‟, hence more strain observed in the molecule, due to this reason energy of molecule increase.
- Cyclopentane have a bond angle 108°, which is very close to the tetrahedral angle. As a result of this, ring system possesses little angle strain. The angle deviation can be calculated by using following formula.

D = ½ (109^{0}28‟ - ϴ) (Where ϴ = Bond angle in alkane)

SI NO	**NAME**	**STRUCTURE**	**BOND ANGLE**	**ANGLE DEVIATION D = ½ (109^{0}28' - ϴ)**
1	Cyclo Propane		60^{0}	½ (109^{0}28‟ - 60^{0}) = +24^{0}44‟
2	Cyclo Butane		90^{0}	½ (109^{0}28‟ - 90^{0}) = +9^{0}44‟
3	Cyclo Pentane		108^{0}	½ (109^{0}28‟ - 108^{0}) = 0^{0}44‟
4	Cyclo Hexane		120^{0}	½ (109^{0}28‟ - 120^{0}) = -5^{0}16‟

The positive sign indicates that the C-C bonds are bent inwards and the negative sign indicates that the C-C bonds are bulged outwards from the tetrahedral angle. Whether the angle strain is positive (or) negative, its magnitude only determines the extent of strain in the ring.

- According to Baeyer‟s strain theory, Cyclopropane has the maximum angle strain should be highly strained molecule and consequently most unstable.

- The angle strain is minimum in the case of Cyclopentane, therefore, it is a less strained molecule and consequently should be a most stable molecule.
- The angle strain increases with the increase in the number of carbon atoms further from Cyclohexane onwards. Hence according to Baeyer‟s strain theory, Cyclohexane and other higher members should be unstable and therefore more reactive.

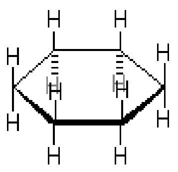
Limitations of Baeyer's strain theory:-

1. According to Baeyer strain theory Cyclopentane is stabler than Cyclohexane. In fact Cyclohexane is more stable than Cyclopentane.
2. Baeyer‟s theory is suitable only for Cyclopropane, Cyclobutane and Cyclopentane.3. The theory proposes planar structures to all Cycloalkanes.

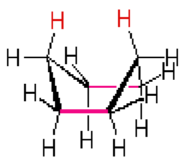
2. SACHSE-MOHR THEORY:-

To explain the stability of Cyclo hexane and higher members, Sachse and Mohr proposed that rings (Cyclo alkanes) are become free from strain. If the ring assumed a „folded‟ (or) „puckered‟ structure, the tetrahedral angle 109^0 28‟ is retained, as a result, the strain within the ring is relieved.

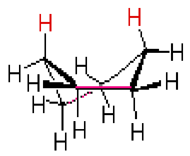
For example, Cyclo hexane can exist in five non-planar puckered conformations all those are completely free from strain. These are Chair, Twist-Boat, Boat, Half-Chair, Half-Boat forms. In these non planar, strain-free rings, the carbons are have tetrahedral angles($109^0$28‟).



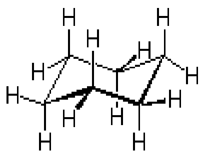
Planar Structure
severe angle strain (120°)
severe eclipsing strain (all bonds)
small steric strain



Boat Conformation
slight angle strain
eclipsing strain at two bonds
steric crowding of two hydrogens



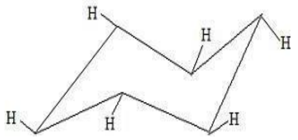
Twist Boat Conformation
slight angle strain
small eclipsing strain
small steric strain

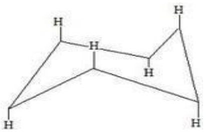


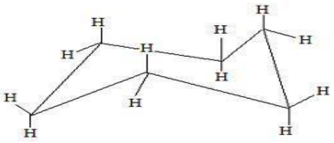
Chair Conformation
no angle strain
no eclipsing strain
small steric strain

The chair form of Cyclohexane is more stable than any other form. Under ordinary conditions, Cyclo hexane molecules will mostly exist in the chair form. The chair confirmation have twelve hydrogens, can be divided into two categories namely.

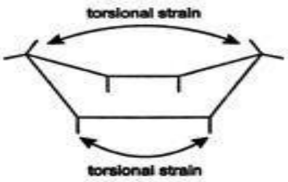
1. Axial Hydrogens.(6 H_a)
2. Equatorial Hydrogens.(6 H_e)



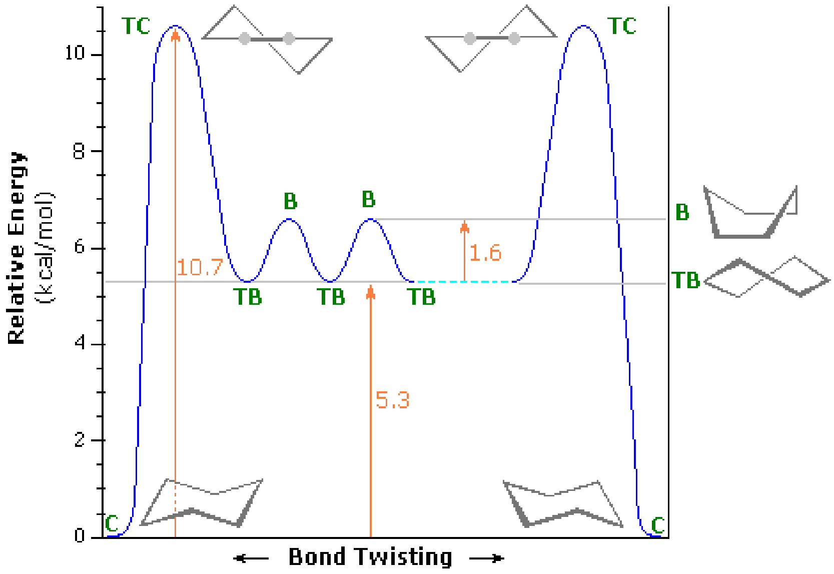




The chair form of Cyclohexane is more stable than its boat form. This is due to in the boat form of Cyclohexane the 1,4 axial hydrogen atoms (or) flag- pole hydrogen atoms are in close proximity (1.83A^0), hence the steric-hidrance can cause torsional strain between the flagpole hydrogens in boat confirmation.



Although there are five confirmations of Cyclohexane, the most stable and major conformer is the chair, because it has a lower activation barrier from the energy diagram.



Conformational Energy Profile of Cyclohexane.

The transition state structure is called a **half chair**. This energy diagram shows that the chair conformation is lower in energy; therefore, it is more stable, because it does not have any **steric hindrance (or) steric repulsion** between the hydrogen atoms.

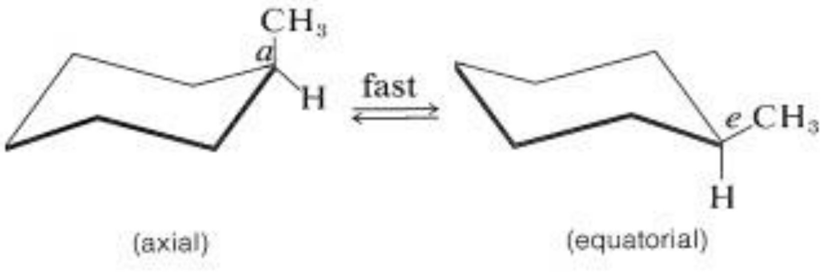
CONFIRMATION OF METHYL CYCLO HEXANES:-

The Hydrogen atom of Cyclohexane is replaced by a bulky group, like –CH_3 group, crowding occurs. The severe crowding is among atoms by the three axial bonds on the same side of the molecule. The methyl group in the axial position and the axial hydrogens repel each other. These interactions are called „**Axial-Axial (or)1,3-diaxial interaction’**. This causes a steric strain in the molecule.

In methyl (-CH_3 group) Cyclohexane, if the substituent placed at equatorial position, it reduces the repulsion. Hence, the energy of the equatorial conformation is lower. At room temperature is more stable than the axial confirmation by 1.7 kcal/ mol − 11.7 kcal/ mol.

At room temperature, about 95% of methyl Cyclohaxane molecules are in the equitorial conformation. When the two chair forms inter convertable to each other, the axial bonds become equatorial and vice-versa is known as **ring-flipping** (or) **ring inversion.**

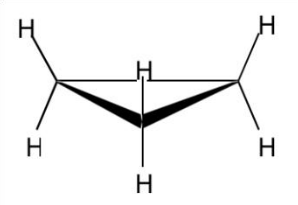
In Cyclohexane, ring inversion is so fast at room temperature, on an average, the molecules, flip about 100,000 times per second, over an energy barrier of about 11 – 111 kcal/ mol.



COMPETATIVE CORNER

CYCLOPROPANE:-

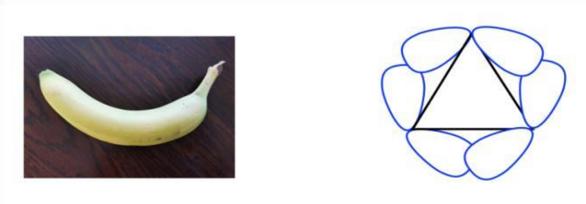
Always Cyclopropane exist in planar confirmation. The bond angle in cyclopropane is 60°, it is significantly deviated from an angle of $109^{0}.28''$, so it has very high angle strains. The sp^3-sp^3 orbitals can overlap partially because of the angle deviation, so the overlapping is not effective as a result of this, the C-C bond in Cyclopropane is relatively weak.



effective overlap,
normal strong bond

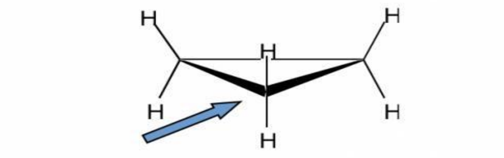
poor overlap,
weak bond in cyclopropane

Because of the poor overlapping of sp^3-sp^3orbitals, the bonds formed in cyclopropane resemble the shape of a banana and are sometimes called banana bonds.

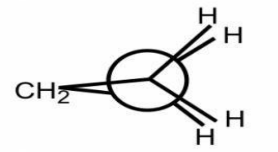


“Banana bonds” of cyclopropane

Other than the angle strains, all the adjacent C-H bonds are eclipsed in cyclopropane; therefore, the torsional strains are applied as well. Such strains can be “viewed” more clearly from the Newman projection of cyclopropane.



viewing along the C-C bond with blue arrow to draw the Newman projection

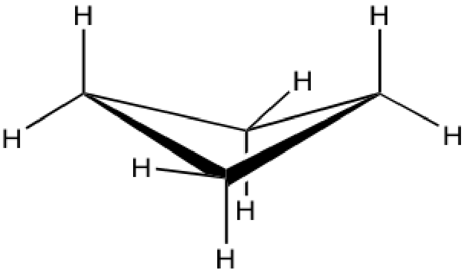


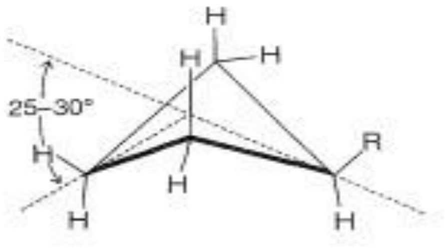
Newman projection of cyclopropane

Because of the high level of angle strains and torsional strains, 3-membered rings are unstable. They rarely exist in nature and undergo ring-opening reaction easily to release the strains.

CYCLOBUTANE:-

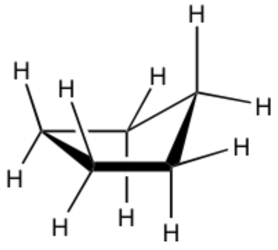
Cyclobutane is not planar. The ring puckers (or folds) slightly due to the efforts of releasing some torsional strain. Mean while, Cyclobutane still has a considerable number of angle strains as the internal angles become about 88° with the folded shape. Overall, Cyclobutane is an unstable structure with a high level of strains.



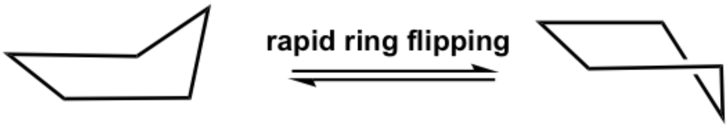


CYCLOPENTANE:-

Cyclopentane is also not planar, and the total level of strain is significantly lowered. It also puckers and adopts a bent conformation where one carbon atom sticks out of the plane of the others, which helps to release the torsional strain by allowing some hydrogen atoms to become almost staggered.



This bent shape of cyclopentane is also called the “envelope” conformation. The envelope conformation can undergo a process called “ring flipping” as a result of C - C bond rotation. Further discussion about ring flipping will be included in the section on cyclohexane.



STABILITY OF CYCLO ALKANES:-

1. HEAT OF COMBUSTION:-

The heat of combustion is the amount of heat released when the compounds burns completely with oxygen.

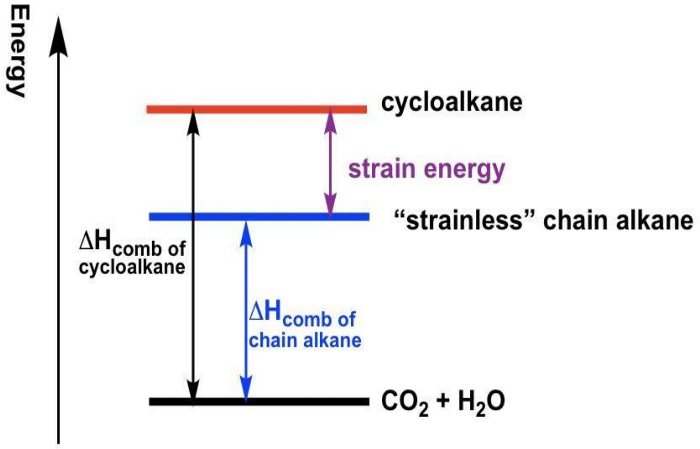
Combustion reaction: $(CH_2)_n$ + $3_{n/2}$ $O_2 \rightarrow$ n CO_2 + n H_2O + heat

To measure the relative stability of Cycloalkanes, the heat of combustion (ΔH_{comb}) for each Cycloalkane was measured. The Cycloalkanes will be in higher energy levels than corresponding chain alkanes because of strain energy.

Therefore,when Cycloalkane burns, more heat will be released, so the difference of ΔH_{comb} between Cycloalkane Vs the chain alkane is just the amount of strain energy.

The larger the difference, the higher the strain energy of the Cycloalkane. The strain energy for different Cycloalkanes are listed below

	cyclopropane	cyclobutane	cyclopentane	cyclohexane
Strain Energy (KJ/mol)	114	110	25	0



The relationship between heat of combustion and strain energy

SYNTHESIS OF ALKANES

DECARBOXYLATION:-

De carboxylation refers to the process of removal of CO_2 from the molecules having -COOH group. Saturated mono carboxylic acid salt of sodium potassium on dry distillation with soda lime gives alkane.

$$RCOONa \xrightarrow[-CO_2]{SodaLime} R-H$$

- The alkane formed by de carboxylation process always contains one carbon atom less than the original acid. The yield is good in case of lower members but poor for higher members.
- Soda lime is prepared by soaking quick lime (CaO) in caustic soda (NaOH) solution and then drying the products. It is generally written as NaOH + CaO.
- Its reaction is milder than caustic soda. Otherwise the reaction will occur violently. Also CaO used along with NaOH keeps it dry to aid fusion.

Examples:- $HCOONa + NaOH \xrightarrow{CaO} H_2 + Na_2CO_3$

$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$

1. REDUCTION OF ALKYL HALIDES:-

Alkyl halides on reduction with nascent hydrogen form alkanes.

$R\text{-}X + 2[H] \rightarrow R\text{-}H + HX.$

The nascent hydrogen may be obtained by any one of the following

1. Zn + HCI
2. Zn + CH_3COOH
3. Zn-Cu couple in ethanol
4. Red „P‟ + HI
5. Al-Hg + Ethanol

Alkyl halides can also be reduced catalytically to alkane by using H_2/Pd (or) $LiAIH_4$ (or) by H_2/Ni. The yields are generally high and the hydrocarbons formed are pure.

Note : Zn-Cu couple is prepared by adding Zn granules in aqueous $CuSO_4$ solution where copper is deposited on the Zn pieces.

2. SABATIER AND SENDEREN'S METHOD:-

Alkenes and alkynes on catatlytic hydrogenation in presence of metal catalyst like Ni, Pt and Pd give alkanes

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni, 200^{o}C} CH_3\text{-}CH_3$$

$$CH\equiv CH + 2H_2 \xrightarrow{Ni, 200^{o}C} CH_3\text{-}CH_3$$

Catalyst „Ni‟ is used in finely divided form. If Pt (or) Pd are used as catalyst, reaction occurs at normal temperature. Sometimes Raney „Ni‟ is used as catalyst. It is obtained by boiling „Ni-A*l*‟ alloy with NaOH, when „A*l* dissolves leaving „Ni‟ in finely divided state. The filterate, washed and dried „Ni‟ is known as Raney Nickel. „Raney- Ni‟ is effective at room temperature and atmospheric pressure.

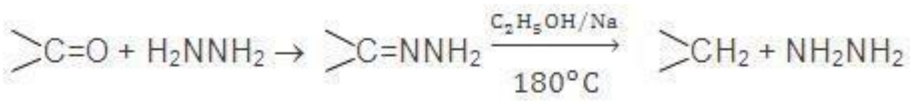
3. REDUCTION OF CARBONYL COMPOUNDS:-

The reduction of carbonyl compounds by Zn-Hg and conc. HC*l* yields alkanes. This is called as clemenson‟s reduction.

$$CH_3CHO + 2H_2 \xrightarrow{Zn+Hg/HCl} CH_3CH_3 + H_2O$$

$$CH_3COCH_3 + 2H_2 \xrightarrow{Zn+Hg/HCl} CH_3CH_2CH_3 + H_2O$$

Carbonyl compounds may also reduced to alkanes by Wolf Kishner reaction



$$>C=O + H_2NNH_2 \rightarrow >C=NNH_2 \xrightarrow[180^{o}C]{C_2H_5OH/Na} >CH_2 + NH_2NH_2$$

4. HYDROLYSIS OF CARBIDES:-

Only CH_4 can be obtained by the hydrolysis of Be (or) Al carbides.

$$Al_4C_3 + 12H_2O \xrightarrow{\Delta} 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \xrightarrow{\Delta} 2Be(OH)_2 + CH_4$$

Note :

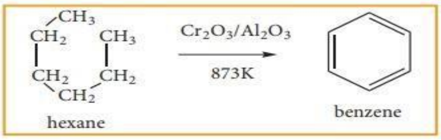
- Calcium carbide reacts with water to give acetylene.
  $CaC_2 + 2H_2O$ ------→ $C_2H_2 + Ca(OH)_2$
- Magnesium carbide reacts with water to give propyne.
  $Mg_2C_3 + 3\,H_2O$ --------→ $C_3H_4 + Mg(OH)_2$

PROPERTIES OF ALKANES

1. AROMATISATION:-

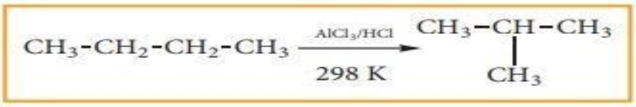
Alkanes with six to ten carbon atoms are converted into homologous of benzene at high temperature and in the presence of catalyst. This process is known as aromatization. It occurs by simultaneous cyclisation followed by dehydrogenation of alkanes.

n-Hexane passed over Cr_2O_3 supported on alumina at 873 K gives benzene.



2. ISOMERISATION:

Isomerisation is a chemical process by which a compound is transformed into any its isomeric forms. n- alkanes can be converted into branched alkanes in the presence of $AlCl_3$ and HCl at 298 k. This process is of great industrial importance. The quality of gasoline is improved by isomerising its components.



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[298\ K]{AlCl_3/HCl} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

3. Isomerism of alkanes:-

Alkanes with four (or) more carbon atoms can show structural isomersism, position isomerism and conformational isomerism. The carbon atoms can form a single un branched chain, (or) the primary chain of carbon atoms can have one (or) more shorter chains that form branches.

Example:- Butane (C_4H_{10}) has two possible structures. *n*-butane is $CH_3CH_2CH_2CH_3$ and *2-methylpropane* (*iso-butane*) is $(CH_3)_2CHCH_3$.

structural formula
of butane

structural formula
of isobutane

The given table shows us as the number of C- atoms increases the number of chain isomers increases.

Name	Formula	No of 'C' atoms	Number of Structural Isomers
Methane	CH_4	1	1
Ethane	C_2H_6	2	1
Propane	C_3H_8	3	1
Butane	C_4H_{10}	4	2
Pentane	C_5H_{12}	5	3
Hexane	C_6H_{14}	6	5
Heptane	C_7H_{16}	7	9
Octane	C_8H_{18}	8	13
Nonane	C_9H_{20}	9	36
Decane	$C_{10}H_{22}$	10	75