13. ORGANIC CHEMISTRY

II) ALKANES AND CYCLOALKANES

Synopsis :

- General molecular formula of alkanes is C_nH_{2n+2}.
- These are saturated hydrocarbons.
- They contain C – C and C – H bonds.
- They are commonly known as paraffins due to their less reactivity
- Carbon is sp^3 hybridised. Bond angle is 109°.28′ and bond length of C–H bond is 1.09 A°.
- Alkanes exhibit only chain isomerism among various types of structural isomerism.

ETHANE :

- Natural gas contains about 10 – 20% ethane.
- Both Carbons are sp^3 hybridised. C – C bond is formed by $sp^3 – sp^3$ overlapping and C – H bond is formed by sp^3 – s overlapping.

Conformational isomers of ethane

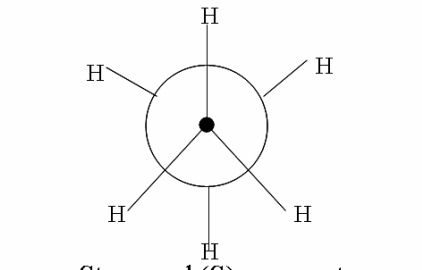
- For an alkane conformational isomers are obtained by rotation about C–C bond(single bond)
- Conformations are represented by
  (a) Newman projections
  (b) Line-Wedge
  (c) Sawhorse projections
- **In Newman projections**
- The molecule is viewed as if we were looking down the axis of C–C bond
- The lines radiating from the centre of the circle denote the bonds between the carbons closest to us and its attached atoms or groups.
- Those lines radiating from the circumference (outside) denote the bonds between the carbon farthest from us and its attached atoms or groups.



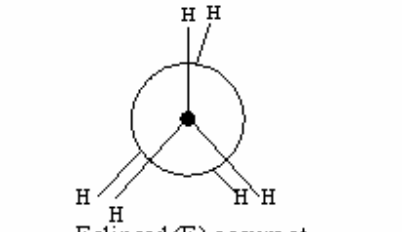
- The ratio of two conformations of a particular alkane in equilibrium at certain temperature T can be calculated by using the formula $\Delta G = RT ln K_{eq}$

  Here ΔG = Gibbs energy difference between two conformations
  R is universal gas constant
  K_{eq} is equilibrium constant
- Rotation about C–C bond in ethane is though very rapid not completely free.
- Though infinite number of conformations are possible with ethane only two conformations are important, they are
  (1) Staggered conformation (S)

(2) Eclipsed conformation (E)



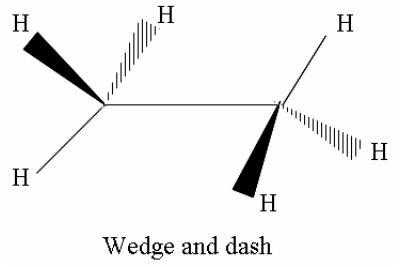
Staggered (S) occurs at
Dihedral angle of 60^0, 180^0, 300^0



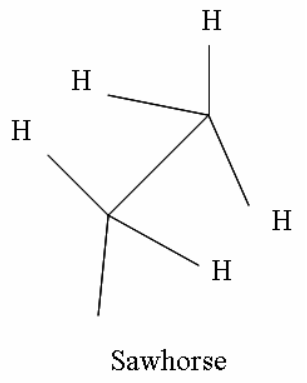
Eclipsed (E) occurs at
Dihedral angle of 0^0, 120^0 and 240^0

- In staggered conformation the C– H bonds are arranged as each one bisects the angle defined by two C–H bonds on adjacent carbon
- In eclipsed conformation each C–H bond is aligned with a C–H bond on adjacent carbon
- In staggered form the distance between the H–nuclei is $2.55A^0$ but in eclipsed form it is $2.29A^0$
- The staggered and eclipsed conformations are interconvertible by rotation of one carbon with respect to the other around the σ bond that connects them
- Different conformations of the same molecule are also called conformers or rotamers.

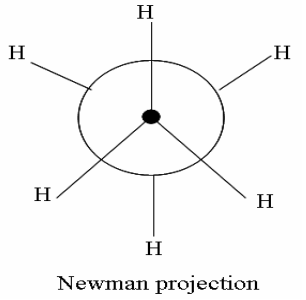
Representation of eathane conformations in different ways



Wedge and dash

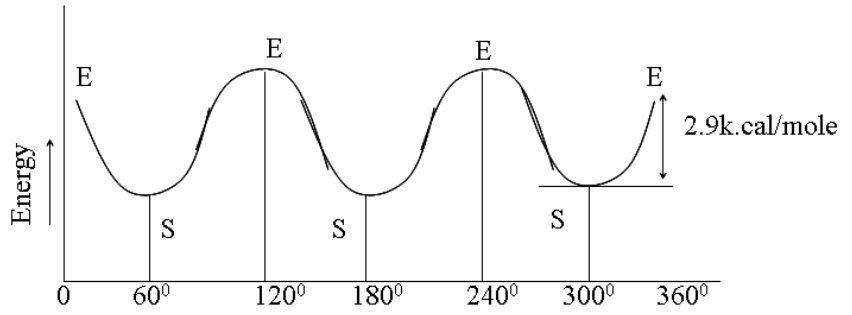


Sawhorse



Newman projection

- Each H–C–C–H unit in ethane is characterised by a torsion angle or dihedral angle
- It is nothing but the angle between the H–C–C plane and the C – C – H plane of H–C–C–H unit.
- Energy σ s dihedral angle ρ lot is



From the graph we can understand that staggered conformation is more stable than eclipsed.

This is because in staggered conformation bonds are at maximum separation. Hence bonded electrons have minimum repulsion.

But in eclipsed conformation bonds are close and repulsions are maximum. Hence it is less stable.

In eclipsed conformation the destabilisation is due to torsional strain.

- As the energy difference between E and S conformation of ethane is very small (2.9k.cal / mole) it can overcome this energy barrier easily even at ordinary temperature by getting sufficient thermal or kinetic energy through intermolecular collisions. So rotation about C–C in ethane is very rapid
- Any other intermediate conformation between staggered and eclipsed is called "a skew conformation."
- In all the conformations the bond angles and bond lengths remain the same

Preparation of ethane :

1. **Reduction of alkyl halides :** Ethyl iodide on reduction with Zn – Cu/alcohol gives ethane.

$$C_2H_5 - I + H_2 \xrightarrow[\text{alcohol}]{Zn-Cu} C_2H_6 + HI$$

2. **Decarboxylation :** Sodium propionate on heating with soda ash undergoes decarboxylation to give ethane.

$$C_2H_5 - COONa + NaOH \xrightarrow[\Delta]{CaO} C_2H_6 + Na_2CO_3$$

3. **Sabatier – Senderen's reaction :** Unsaturated hydrocarbons on addition of H_2 in presence of Ni will give saturated hydrocarbons.

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$$

$$CH \equiv CH + 2H_2 \xrightarrow{Ni} CH_3 - CH_3$$

4. **Kolbe's electrolysis :** Sodium or potassium salt of saturated mono carboxylic acids on electrolysis will give alkanes at anode

Electrolysis of sodium acetate will give ethane at anode.

$$2CH_3 - COONa + 2H - OH \xrightarrow{\text{Electrolysis}}$$

$$C_2H_6 + 2CO_2 + 2NaOH + H_2$$

5. **Wurtz reaction :** Alkyl halides react with sodium in presence of dry ether to give alkanes.

It is suitable to prepare alkanes containing even number of carbons because dimerisation occurs during the process.

Alkanes with odd number of carbons also can be prepared by taking mixture of two different alkyl halides.

$$2CH_3 - I + 2Na \xrightarrow{\text{ether}} CH_3 - CH_3 + 2NaI$$

$$2C_2H_5 - I + 2Na \xrightarrow{\text{ether}} C_2H_5 - C_2H_5 + 2NaI$$

$$CH_3 - I + C_2H_5 - I \xrightarrow{Na/\text{ether}}$$

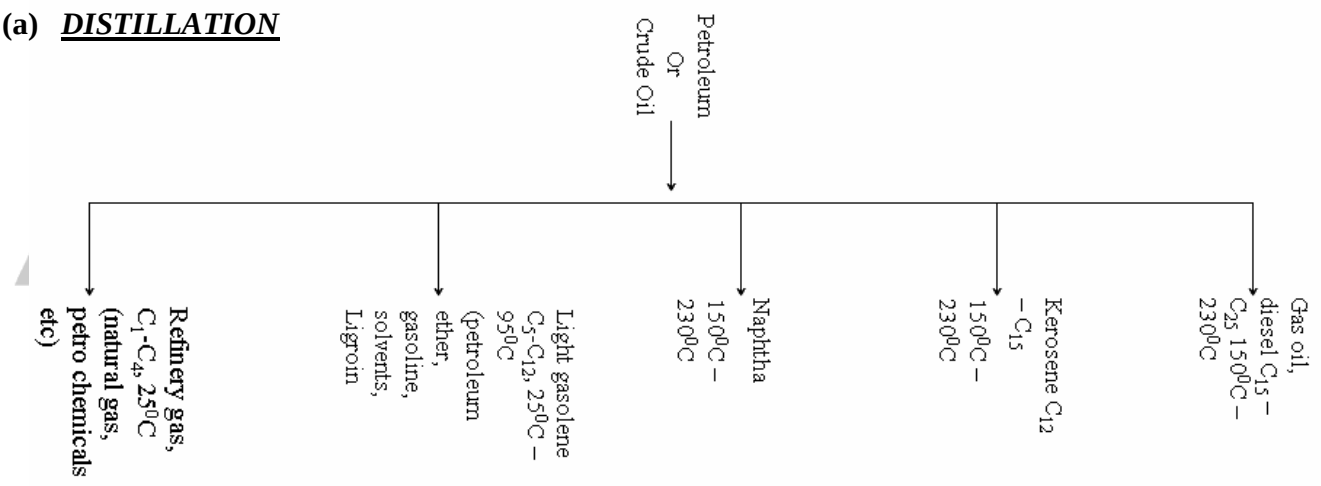
$$CH_3 - CH_3 + C_2H_5 - C_2H_5 + CH_3 - C_2H_5 + NaI$$

From natural gas and petroleum

- Natural gas is rich in methane and also ethane propane and low molecular weight alkanes
- Petroleum is a liquid mixture containing about 150 hydrocarbons and half of them are cycloalkanes
- Petroleum refining involves

  a) Distillation b) Cracking c) Reforming

(a) ***DISTILLATION***



(b) ***Cracking :*** Higher molecular weight hydrocarbons are broken at C–C bonds to form lower molecular weight hydrocarbons

This may be induced

(1) by heat (thermal cracking)

(2) by catalysis (catalytic cracking)

(c) ***Reforming :*** Reforming converts the hydrocarbons in gasolene and naphtha to aromatic hydrocarbons and highly branched alkanes

* Aromatic hydrocarbons and highly branched alkanes have less knocking tendency than unbranched alkanes 'or' cycloalkanes

* Leaves and fruits of many plants contain a waxy coating made up of alkanes, which prevents loss of water

Physical properties of alkanes : –

- Alkanes are nonpolar hence only weak Vanderwaals forces of attraction exist between their molecules.
- They possess very low B. Pts and M.Pts

  At 298K

  a) first four members (C_1–C_4)are gases

b) C_5-$C_{17}$are liquids and

c) above C_{17} are solids

- They are soluble in non-polar solvents

  Ex. Grease a mixture of higher hydrocarbons is soluble in petrol.

Chemical properties : C_2H_6 also undergoes only substitution reactions.

1. Halogenation :

$C_2H_6 + Cl_2 \xrightarrow{h\upsilon} C_2H_5Cl + HCl \quad C_2H_5 - Cl + Cl_2 \xrightarrow{h\upsilon} C_2H_4Cl_2 + ...C_2Cl_6 + HCl$

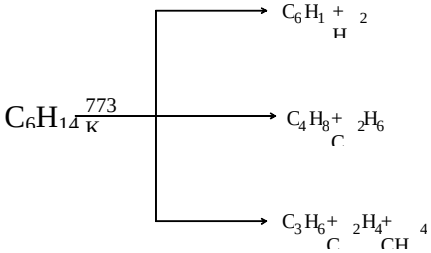
(excess)

2. Nitration : Ethane reacts with con.HNO_3 at 400^0C to give nitro ethane.

$C_2H_6 + HO - NO_2 \xrightarrow[\Delta]{400^0 C} C_2H_5 - NO_2 + H_2O$

3. ***Pyrolysis :-*** Strong heating in the absence of air is called pyrolysis 'or' cracking

a)



b) $C_{12}H_{26} \xrightarrow[973k]{Pt/Pd} C_7H_{16} + C_5H_{10}$ + other products

(Dodecane)

$C_2H_6 \xrightarrow{450^0 C} C_2H_4 + H_2$

4. ***Isomerisation :–***

Formation of branched chain isomers from higher alkanes on heating in the presence of anhydrous $AlCl_3$ and HCl gas is isomerisation

$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 \xrightarrow[HCl\ gas]{anhy\ AlCl}$

n–hexane

$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_2 - CH_3 + CH_3 + CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3$

2-Methylpentane 3-Methylpentane

5. ***Aromatisation or reforming:–***

$CH_3 - \underset{n-hexane}{(CH_2)_4} - CH_3 \xrightarrow[Cr_2O_3 \text{ or } V_2O_5 \text{ or } Mo_2O_3]{500^0 C, 10-20 atm} \underset{Benzene}{C_6H_6}$

6. Combustion : Any hydrocarbon on combustion gives CO_2 and H_2O

$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O; \quad \Delta H = -heat$

Uses:

It is used as fuel

It is used in the preparation of ethylene

It is used in the preparation of chloro ethanes

CYCLO ALKANES

SYNOPSIS:

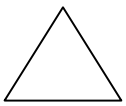
a) Hydrocarbons with one 'or'more carbon rings in their molecules with only C–C single bonds and sp^3 hybridised carbon atoms are cycloalkanes.

b) Cycloalkanes with only one ring have the general formula $C_n H_{2n}$

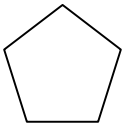
Nomenclature of cycloalkanes :

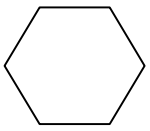
1) They are named by adding primary prefix cyclo before parent name alkane

Ex :

1) C_3H_6  Cyclo propane (first cycloalkane)

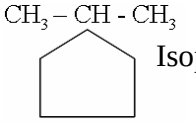
2) C_4H_8  Cyclo butane

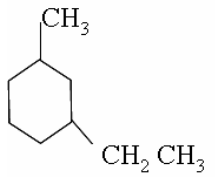
3) C_5H_{10}  Cyclo pentane

4) C_6H_{12}  Cyclo hexane

Alkyl substituted cycloalkanes :

In this case, (a) If the ring has more carbons than alkyl then it is the parent hydrocarbon

Ex :  Isopropyl Cyclo pentane

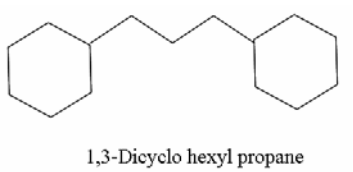
Ex : 

1 - Ethyl -3- Methyl cyclo hexane

(b) If the alkyl group has more carbons than ring then it is the parent hydro carbon

Ex : 

1 Cyclobutyl pentane

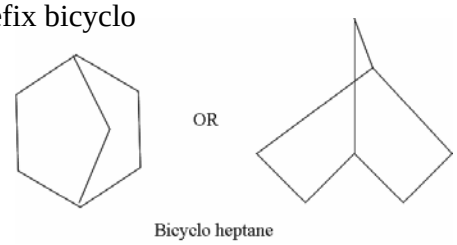
Ex : 

1,3-Dicyclo hexyl propane

Bicyclic compounds :

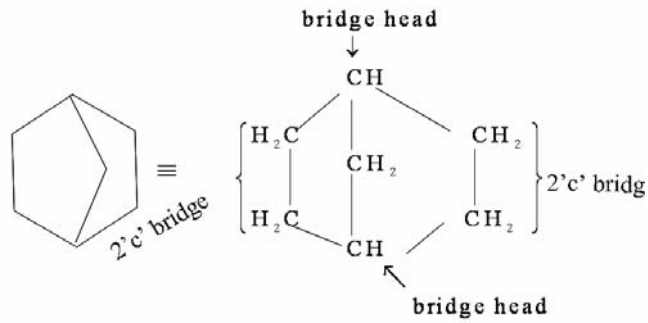
- If the molecule has twofused 'or' bridged rings they are named as bicyclic alkanes.
- Bicyclic compounds are named by using the alkane name(on the basis of total no of carbon atoms) and the prefix bicyclo

Ex :



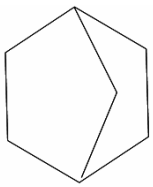
Bicyclo heptane

- In bicyclocompounds the carbon atoms common to both rings (either one or two) are called bridge heads.
- Each bond or chain of atoms connecting the bridge head atoms is called a bridge



- In naming these compounds, in between the words bicyclo and alkane, the no. of carbon atoms in each bridge is written(in descending order) in square brackets

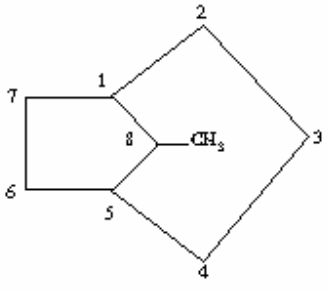
Ex :



Bicyclo[2, 2, 1]heptane

- Bicyclo[2, 2, 1] heptane in also known as 'NORBORNANE'
- If a substituent is present, the bicyclic ring system is numbered
- In substituted bicyclic alkanes, the numbering begins with one of the bridge head atoms proceeds first along the longest bridge, to the second bridge head atom continues along the next longest bridge to the first bridge head atom and finally completed along the shortest path

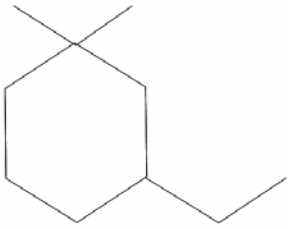
Ex :



8 — methyl bicyclo [3, 2, 1] octane

In cyclic compounds more branched chain carbon should be given the lowest number possible

Ex :

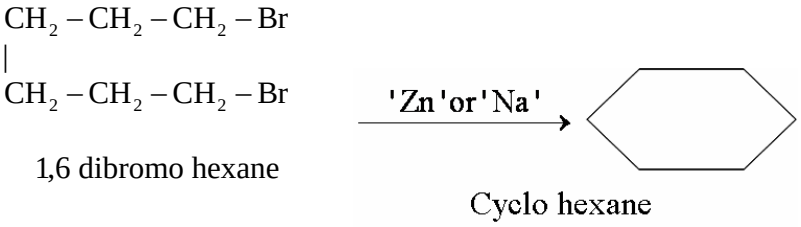


3-ethyl-1,1-dimethyl cyclo hexane

Cyclohexane Preparation

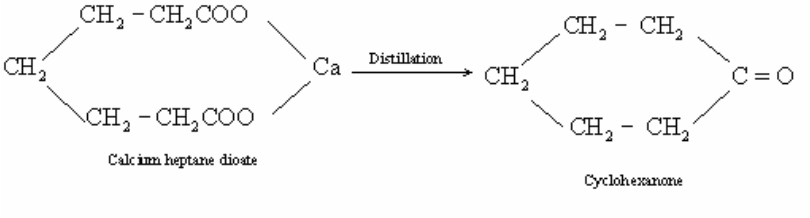
- **Freunds Method**

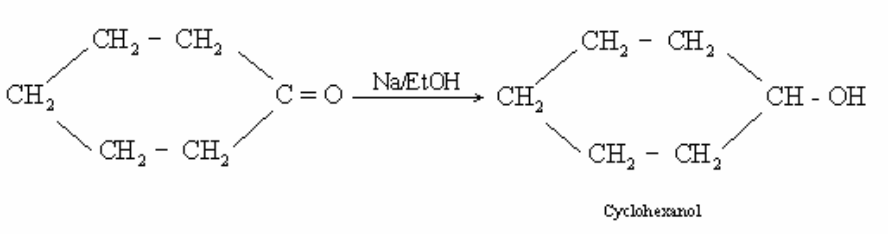
  In this method 1, 3 to 1,6-dihalo alkanes react with Na metal ‘or’ Zn metal to form corresponding cycloalkanes

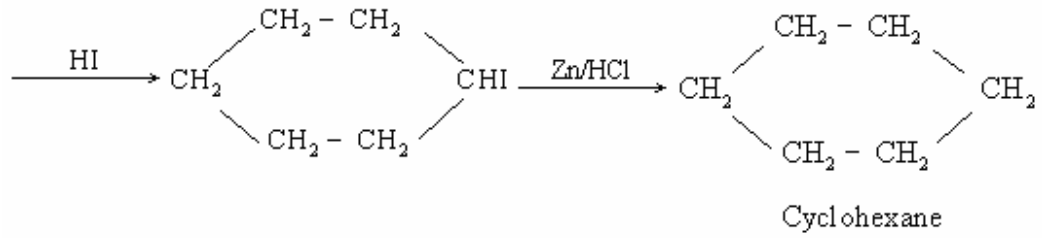


* But 1, 7 dihaloalkanes and higher alkanes undergo “Wurtz reaction” in these conditions

- **Wislicenus method :**

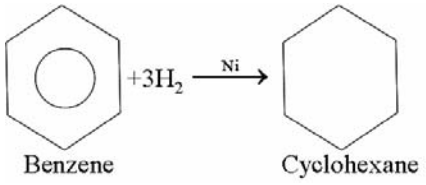






* Now-a-days higher cycloalkanes are prepared by heating thorium, cerium or yttrium salts of higher dicarboxylic acids with 'Cu' powder at 300^0c in vaccume

- **By the reduction of aromatic hydrocarbons**

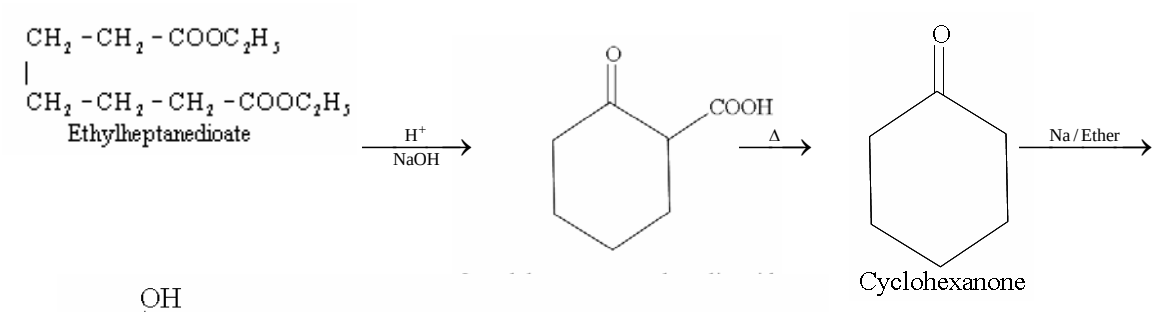


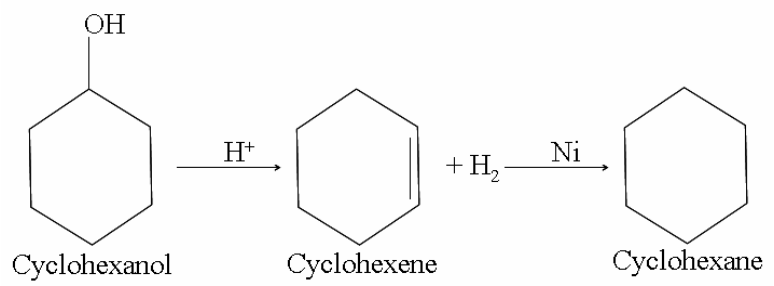
- **By Dieckmann condensation reaction**

This is an intramolecular condensation

*

5, 6, 7 membered rings can be prepared from esters of dicarboxylic acids





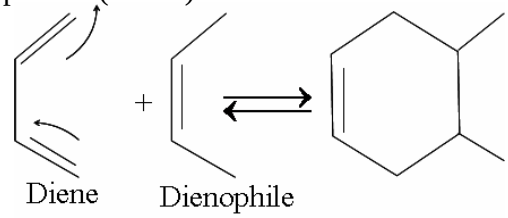
- **Diels - Alder reaction**

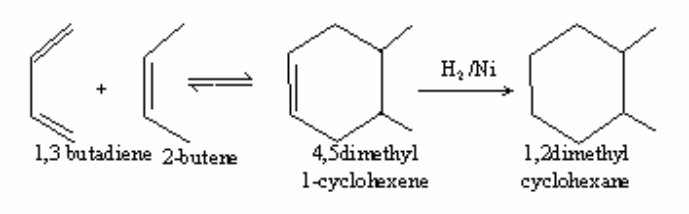
Generally this reaction is between 1) conjugated diene 2) dienophile

* Conjugated diene is a 4 - electron compound

* Dienophile in an ene compound (with double bond (or) 2electrons)

Here,Two new bonds are formed at the expense of two bonds of diene and dienophile. So the product(addict) contains a new six membered ring with a double bond





- **By Zieglar reaction**

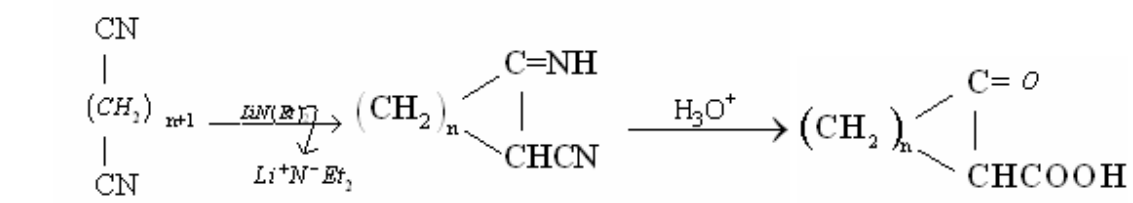
  It is a general method to prepare cyclic alkane

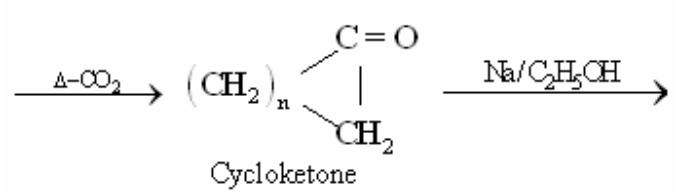
  a) A dinitrile is treated with diethyl lithium amide

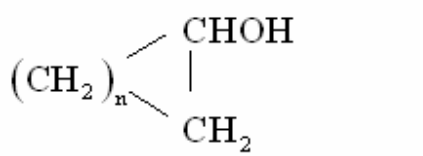
  b) An imminonitrile is formed

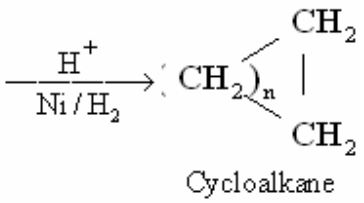
  c) This immino nitrile is converted to cycloketone by acid-catalysed hydrolysis and decarboxylation

  d) Cycloketone is then reduced to cycloalkene









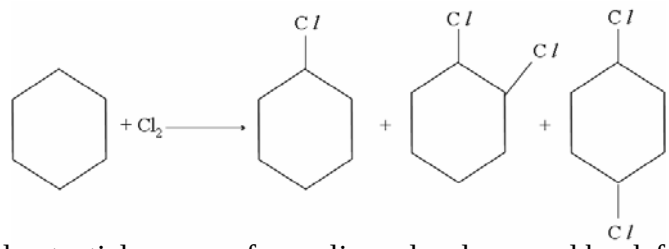
Properties

* Cyclohexane behaves like hexane

* Cyclopropane and cyclobutane are relatively more reactive due to "angle strain", Hence Cyclo propane and chclobutane are reduced to corresponding alkanes with H_2/Ni at 200^0c

But, cyclo pentane and cyclohexane do not react with H_2 / Ni because they have no "angle strain".

* Halogenation of cyclo hexane in free radical substitution similar to alkanes



Angle strain :

- It is the increased potential energy of a cyclic molecule caused by deformation of bond angle from its lowest energy value.
- For example : In cyclic alkanes 'C' atoms are 'sp^3' hybridised and hence the angle should be 109^0 28' but in cyclopropane with the shape of regular triangle the internal angle must be 60^0 i.e. they are compressed from 109^0"28' by almost 49.5^0.
- This compression of the bond angle causes some strain known as angle strain, which increases the potential energy of the molecule.
- In cyclopropane and cyclobutane in addition to angle strain there is one more strain known as torsional strain.
- Torsional strain is caused by repulsions between the aligned electron pairs of the "eclipsed bonds" in eclipsed conformations of a molecule"
- Due to (a) anglestrain and (b) torsional strain cyclo propane and cyclobutane are more reactive than 'cyclopentane' and 'cyclohexane'.