UNIT-V

CYCLOALKANES

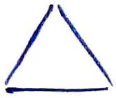
Cycloalkanes or cycloparaffins are saturated hydrocarbons in which the carbon atoms are joined by single covalent bonds to form a ring. They are also called as Alicyclic Compounds.

"Ali" – because similar to aliphatic compounds.

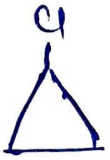
~~Unsub~~

Unsubstituted Cycloalkane form a homologous series with general formula – C_nH_{2n}, n = 3, 4, 5, 6 ----

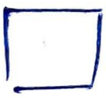
First member of a series is Cyclopropane  C_3H_6



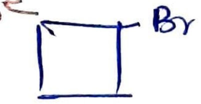
Trimethylene
Cyclopropane



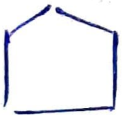
chlorocyclopropane



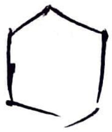
Tetramethylene
Cyclobutane



Bromocyclobutane



Pentamethylene
Cyclopentane



Cyclohexane
Hexamethylene

PHYSICAL PROPERTIES

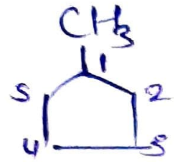
① Nature = liquid = remaining are
= Gas → Cyclopropane & Cyclobutane

② ~~MP~~ :

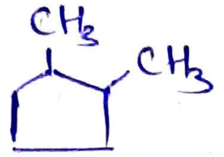
	MP	BP
Cyclopropane	-127.4 °C	-32.8
Cyclobutane	-90.7 °C	12.5
Cyclopentane	~~4~~ -13.9	49.3
Cyclohexane	6.6	80.7

↓ Increase

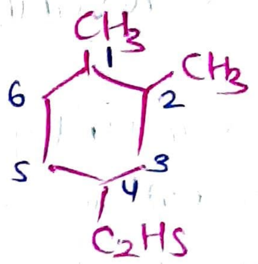
Some Derivatives & Nomenclature



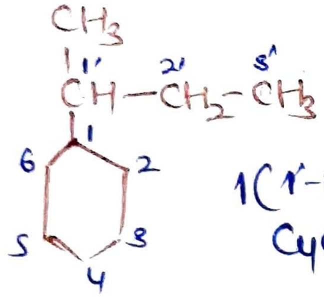
1-methyl
cyclopentane



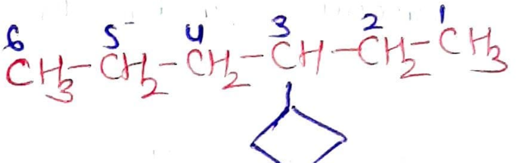
1,2-dimethyl
cyclopentane



4-ethyl-1,2-dimethyl
Cyclohexane



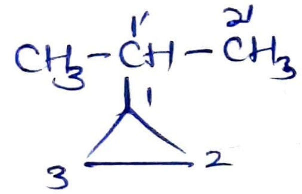
1(1'-methylpropyl)
Cyclohexane



3-Cyclobutyl hexane

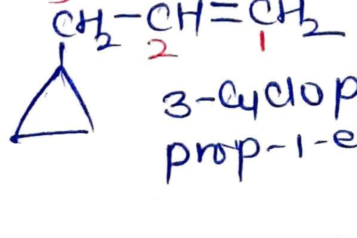
If side alky chain > cyclic alkane

no of C-atm ring = side chain

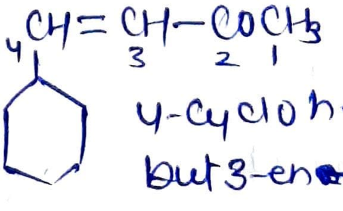


1(1'-methyl ethyl)
- Cyclopropane

If side chain contains a multiple bond or functional group, ~~alkyl~~ alicyclic ring is treated as substituent

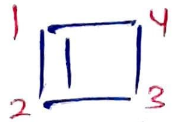


3-Cyclopropyl
prop-1-ene

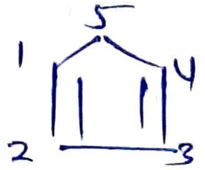


4-cyclohexyl
but3-en 2-one

If multiple bond present at ring, the numbering is done in such way that multiple bond get lowest number

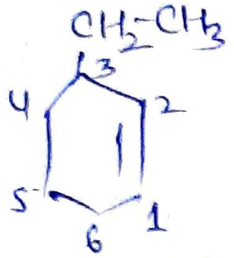


Cyclobut-1-ene

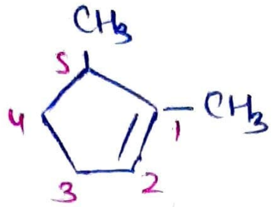


Cyclopent-1,4-diene

If multiple bond & side chain both present, bond is preferred

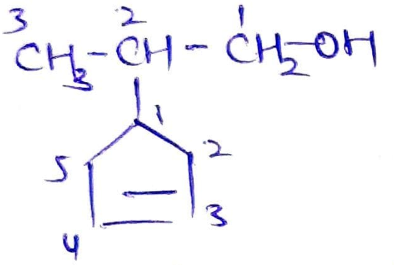


3-ethyl-cyclohex-1-ene

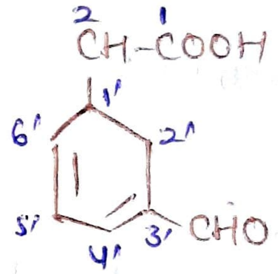


1,5-dimethyl cyclopent-1-ene

side chain contains ~~multiple bond~~ functional group & ring contains multiple bond, side chain should give preference



2(cyclopent-3-en 4yl) propan-1-ol



2-(3'-formyl cyclohex-3',5'-diene) ethan-1-oic acid

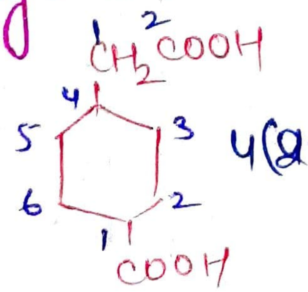
Functional group directly attached to ring

cyclopentane carbaldehyde

Cyclohexane carboxylic acid

If ring & side chain both contains same functional group

" no. of carbon atom"

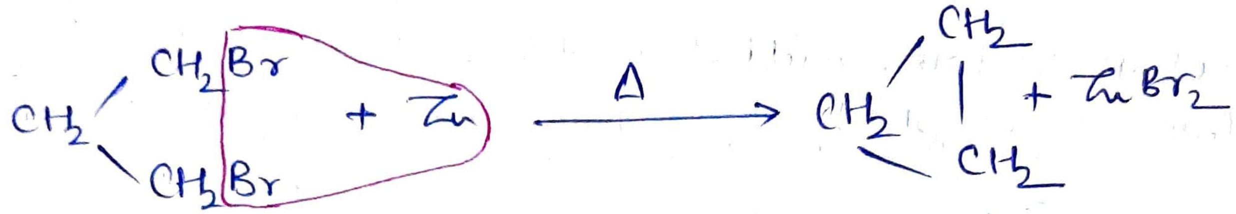


4(2-carboxylmethyl) cyclohexane-1-carboxylic acid

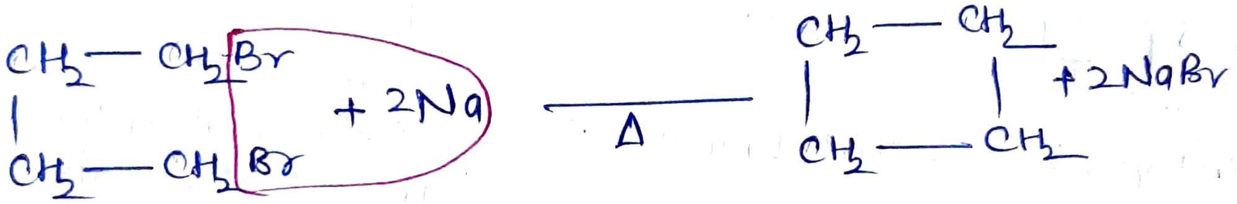
SYNTHESIS

① From Dihalide

Ⓐ Freund's Method → 1,3 or 1,4 dihalogen derivative of alk. react with Na or Zn



1,3-dibromo propane

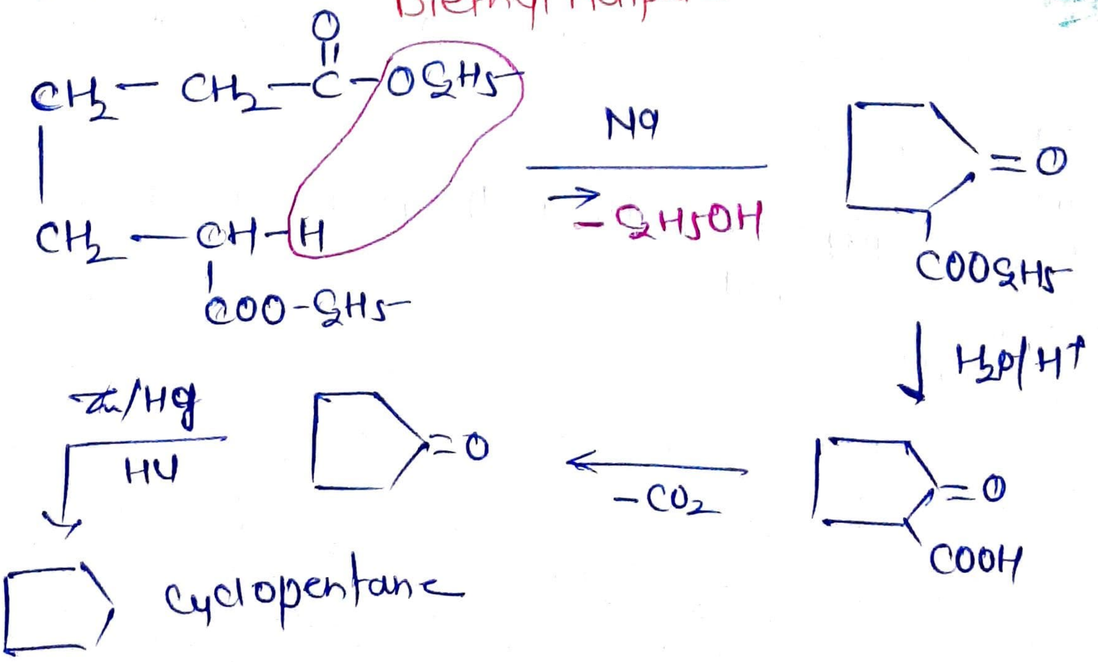


1,4-dibromo butane

- If halide is not 1,5 & 1,6 carbon then reaction forms open chain alkene
- mainly prepared Cyclopropane

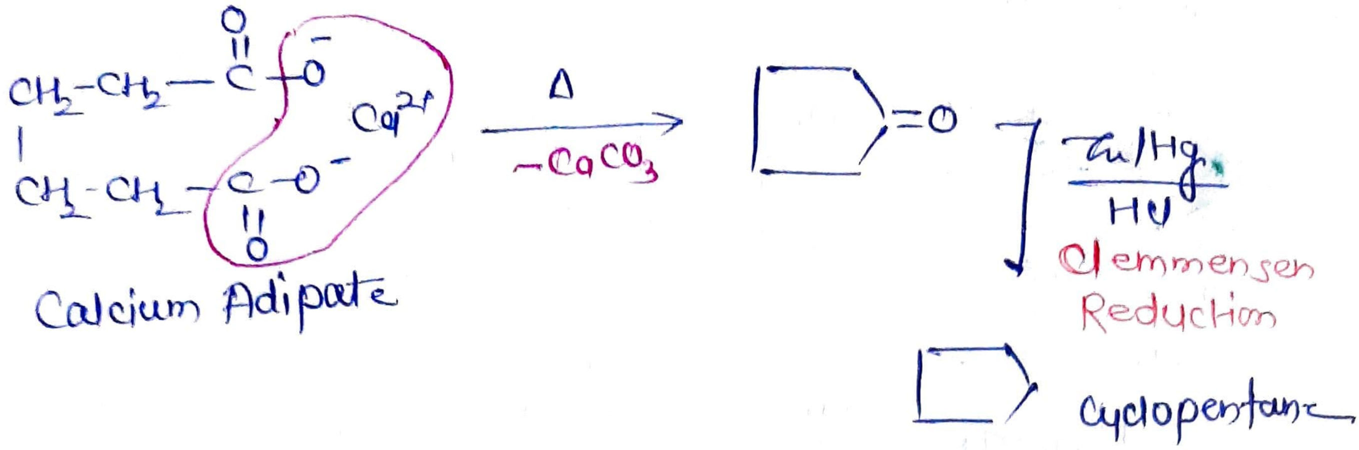
② Dieckmann Condensation - from ester of dicarboxylic acid.

Diethyl Adipate

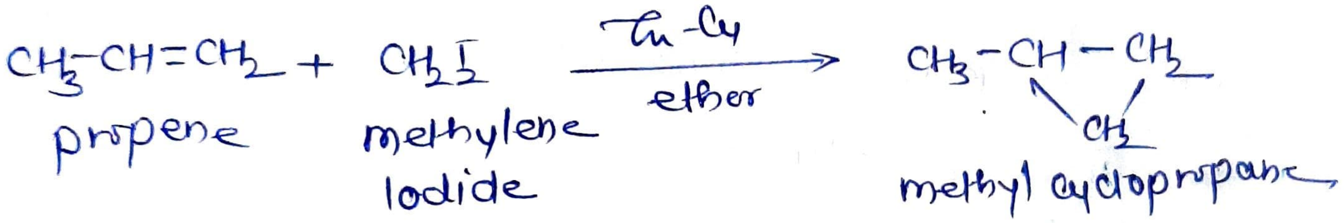


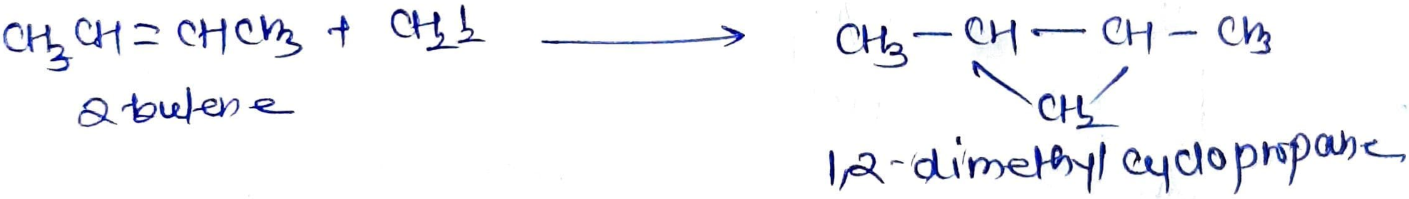
- mostly suitable for 5 & 6 membered ring

③ from Calcium Salt of Dicarboxylic acids (Wislicenus Method)

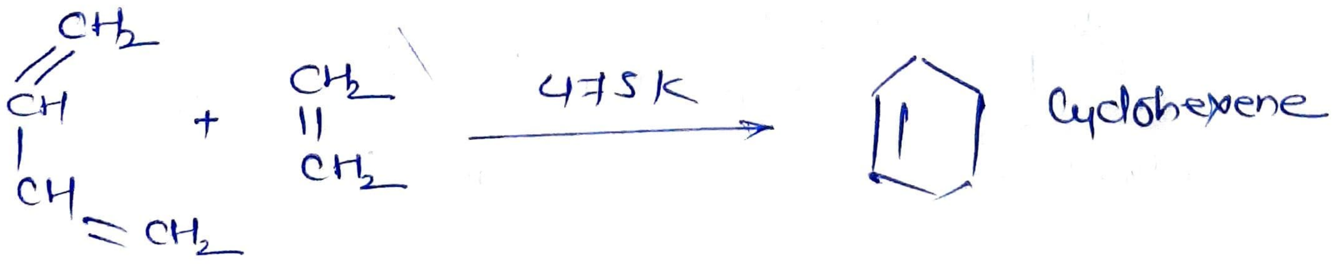


④ Simmons-Smith Reaction - from Alkene

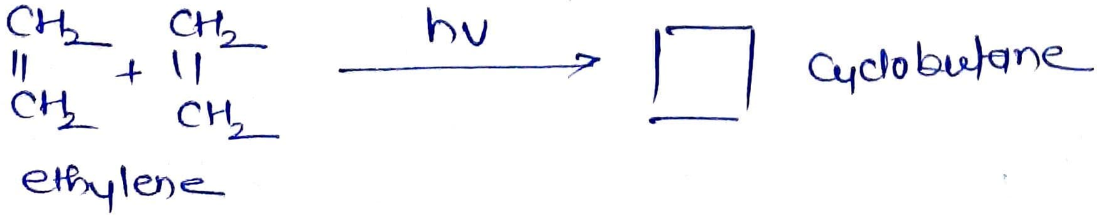




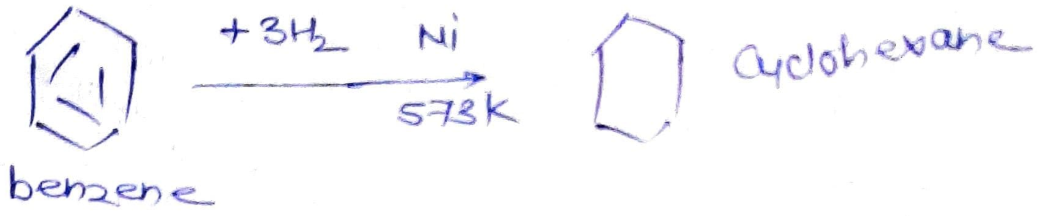
⑤ Diels-Alder Reaction - 4+2 Cycloaddition Reaction

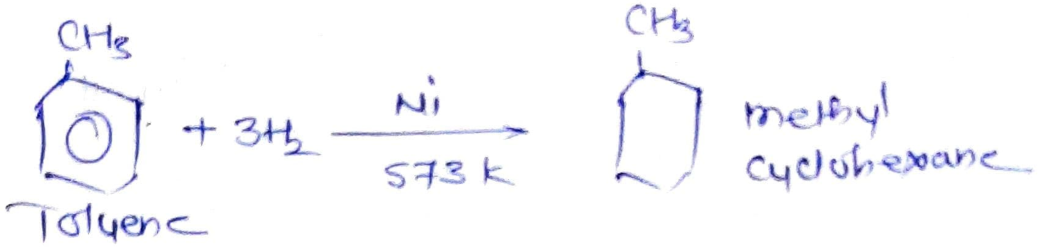


⑥ 2+2 Cyclo addition Reaction



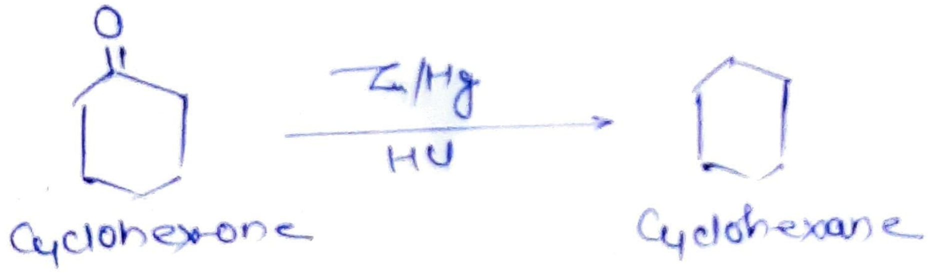
⑦ Hydrogenation of Aromatic Compound



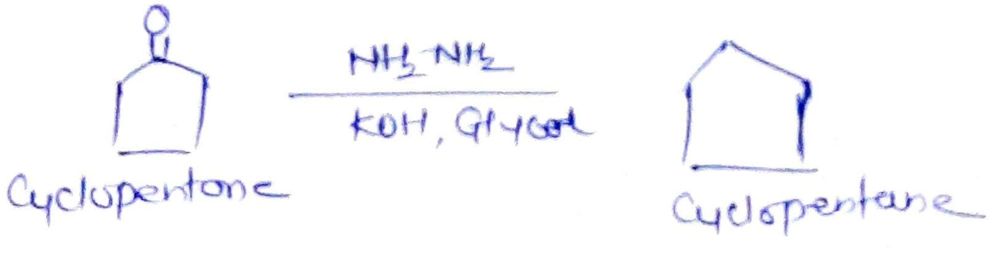


⑧ Reduction of cyclic carbonyl compounds

Ⓐ Clemmensen's Reduction



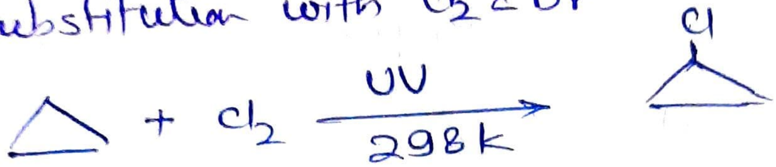
ⓑ Wolf-Kishner Reduction —



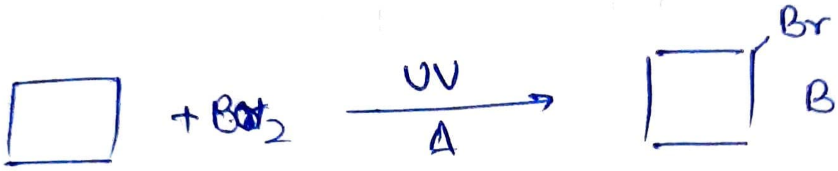
CHEMICAL REACTION

Ⓐ Substitution Reaction - free Radical Sub. Reactn

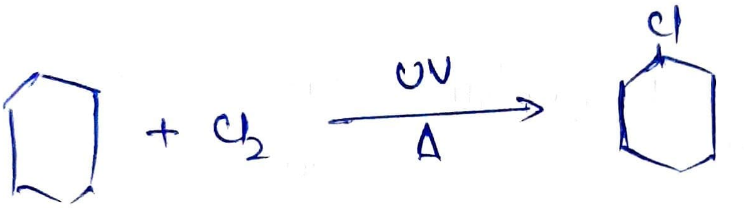
① Substitution with Cl_2 & Br



chlorocyclopropane



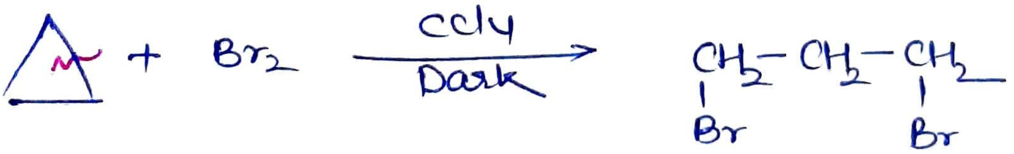
Bromocyclobutane



chlorocyclohexane

Ⓑ Addition Reaction → "Ring Opening Reaction"

② Add^n of Cl_2 & Br_2 → produce open chain product, CCl_4 used as solvent



$$\underset{Br}{CH_2}-CH_2-\underset{Br}{CH_2}$$

1,3-dibromopropane

$$\underset{Cl}{CH_2}-CH_2-CH_2-\underset{Cl}{CH_2}$$

1,4-dichlorobutane

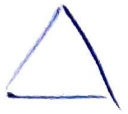
③ Add^n of Halogen acid HBr/HI → 1-halo product

$CH_3-CH_2-CH_2-Br$

1-bromopropane

* Higher member do not give this Reaction.

④ Addⁿ of Hydrogen - H_2/Ni

 $+ H_2 \xrightarrow[80°C]{Ni} CH_3-CH_2-CH_3$ Propane

 $+ H_2 \xrightarrow[200°C]{Ni} CH_3-CH_2-CH_2-CH_3$ n-butane

© Oxidation Reaction

 $+ 5(O) \xrightarrow[\Delta]{KMnO_4/OH^-}$ CH_2-CH_2-COOH | CH_2-CH_2-COOH Adipic Acid

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STABILITY OF CYCLOALKANE

BAEYER STRAIN THEORY

Based on ~~Ag~~ Angle strain of cycloalkane

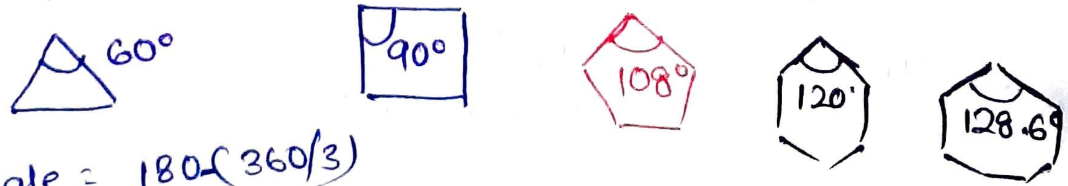
Angle - Interior Angle of polygon

Bond Angle = $180 - (360/n)°$ n = no. of side

OR

$$\frac{180(n-2)}{n}$$

As per this



Angle = $180-(360/3)$

= $180-120 = 60°$

OR

= $\frac{180(3-2)}{3}$

= $60°$

The main postulate of Baeyer Strain Theory (1885)

Proposed by Adolf Baeyer in 1885 to explain the relative stability of first few Cycloalkane

① Carbocyclic ring or Cycloalkane are planner like polygons. The proposed structure are

Cyclopropane – Equileteral Triangle
Cyclo butane – Square
Cyclopentane – Pentagon
Cyclo hexane – Hexagon

② In Cycloalkane each carbon atom is sp^3 hybridised and Angle betwen any pair of adjucent bond should be tetrahedral, Ideal bond Angle should be 109°28' OR 109.5°

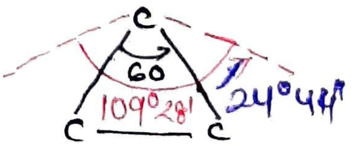
③ Due to cyclic in nature of cycloalkane, Bond angle of ring are not longer equal to normal tetrahydral angle 109.5°. The angle deviation varies with size of ring.

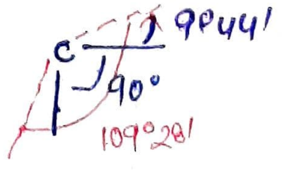
These Deviation in bond angle cause strain in the molecule called Angle Strain, which decrease Stability

$$\text{Deviation} \propto \text{Angle Strain} \propto \frac{1}{\text{stability}} \propto \text{Reactivity}$$

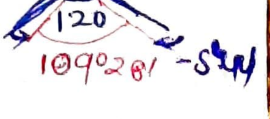
$$\text{Angle Strain} = \frac{1}{2}\left(109°28' - \text{Bond angle in planner ring}\right)$$

	Compound	Bond Angle	Angle Strain
①	Cyclopropan	60°	+24°44'
②	Cyclobutane	90°	+9°44'
③	Cyclopentane	108°	+0.44'
④	Cyclohexane	120°	−5.44'
⑥	Cycloheptane	128°26'	−9°33'





(+) - Indicate bond angle are compressed
(−) - Indicate bond angle are expanded



As per Baeyer Strain Theory Stability order

~~cyclopentane > Cyclobutane~~

cyclopentane > Cyclohexane > cycloheptane
> Cyclo butane > Cyclopropane

⇒ Not True At all

✓ Cyclohexane > Cyclopentane > cyclobutane
> Cyclo propane

hence cyclopropane undergoes ring breaking Reactn

Evidence in Favour of Baeyer's Strain Theory

① As earlier stated that
Angle strain → ↓ Stability

These can be explained on the basis of heat of combustion per methylene group in each cycloalkane

Heat Combustion per CH_2 group

- Cyclo propane — 697 kJ/mole
- Cyclo butane — ~~658.5~~ kJ/mole 686.5 kJ/mol
- Cyclo pentane — 664 kJ/mole
- Cyclo hexane — 658.5 kJ/mole

As we know that Higher energy less stable hence cyclopropane & cyclobutane are less stable and undergoes addn reactn & ring ~~fusion~~ fission.

- Cyclo butane is more stable and undergoes ring opening reactn but only in under more drastic condition.

Limitation -

① Not obey in more than 6 carbon atom ring

As per Baeyer strain theory intamediate ring size & higher are very strained and unstable

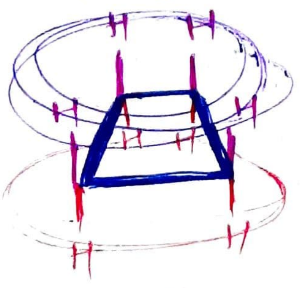
reality - cycloalkane of intamediate ring size have only modest strain & ring of 14-c or higher are strain free.

② BS Theory consider only Angle strain, assuming all cycloalkane to be planner.

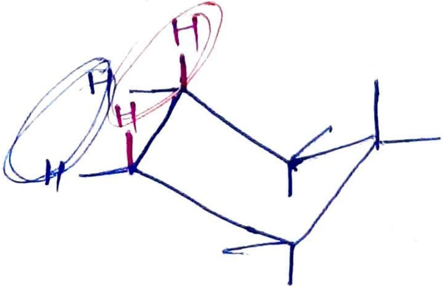
* Does not consider TORSIONAL STRAIN - The strain due to eclipsing of bond on neighbouring atoms.

* Does not consider Steric Strain - The strain due to repulsive interacton when atoms approach each other too closely also known as "Trans annular Strain"

\# Torsional Strain - excist when neighbouring carbon possess hydrogens that overlap in space (eclipse)



eclipse



SACHE MOHR THEORY

↳ Sache-Mohr proposed this theory in 1918 to explain the stability of cyclohexane & higher members.

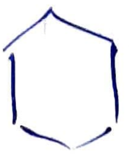
As we know that BST failed to explain the stability of cyclohexane & higher members.

Assumption. -

① Cyclohexane are not in plane.

② They are become free from strain if all rings carbons are not forced into one plane

hexagonal -



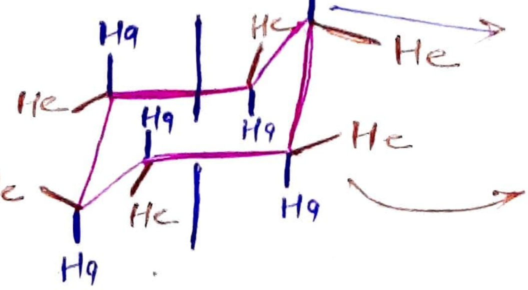
⇒ Not exectly as was assumed by Baeyer

③ They assumed that the ring are "Folded" or "Puckered" condition., And normal tetrahedral angle (109.5°) retained & as result, the strain within ring is relieved.

④ Cyclohexane may exist in two non-planar Puckered conformations. both of which are completely strain free → chair & boat

① chair form. → most stable

Ha -(axial Hydrogen)



a : axial bond (parallel to axis)

(equitorial Hydrogen) - He

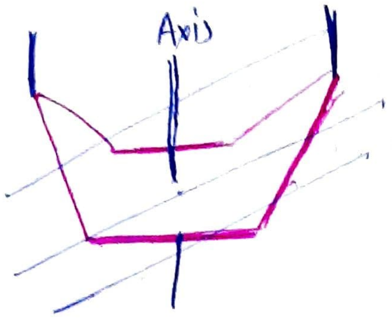
e : equitorial bond (109.5° to axis)

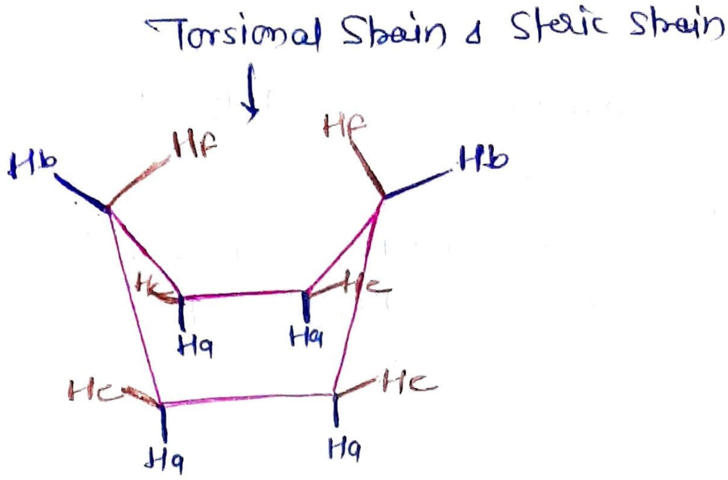
Free from Torsional strain & bond opposition strain

↳ 6 C-H → axial bond

↳ 6 CH → equitorial band

② Boat Form.



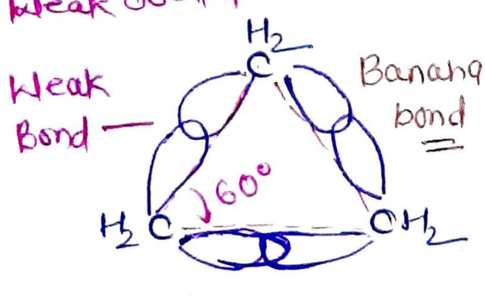


— Hb = Bow Spirit bond
— Hf = Flag pole bond
— Ha : axial bond
— He : equitorial bond

If see among the C-C bond then all CH bond are eclipsed with respect to each other hence this boat form conformatn has maximum torsional & ~~ste~~ ~~stern~~ steric strain

COULSON AND MOFFIT'S MODIFICATION

Cyclopropane has triangular planar structure with interval bond angle are 60°.

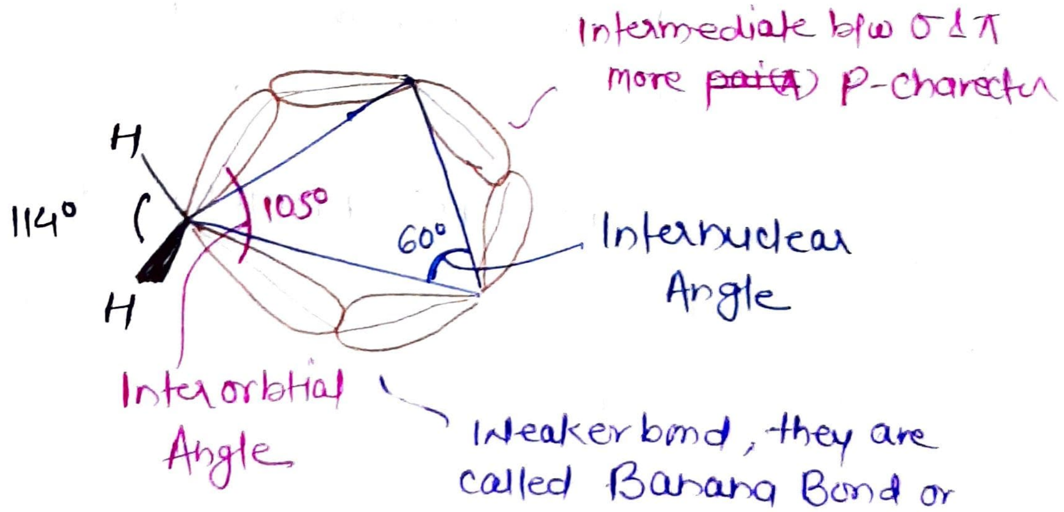


We know that a covalent bond b/w two atoms is formed by the overlap of orbitals of the atoms involved. The greater extent of overlap the stronger is the bond formed.

The atomic orbitals overlap to the maximum extent if they overlap ~~it~~ along their ~~axis~~ axes. As the axes of sp^3 orbitals are at angles of 109.5° or 109°28' to each other. The C-C bond will have their maximum strength if the C-C-C bond angles have value of 109°28'

In cyclopropane, sp^3 hybrid orbitals of carbon atom can not undergoes complete overlap with each other as shown in n-propane, because of this require a considerable deviation from the tetrahedral angles of 109° 28'

Due to considerable amount of ring strain in cyclopropane, In addition angular strain, cyclopropane also suffer additional Torsional Strain (due to co-planar arrangement of carbon atom where are leading to the eclipsed arrangement of the C–H bond



Weaker bond, they are called Banana Bond or Bent bond

"Coulson–Moffitt Model"

~~C–C → bon~~

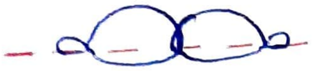
C–C bond → more p-character

C–H bond → s-character

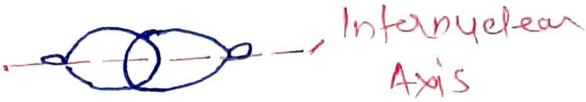
These reason cyclopropane is much more reactive than alkane or other higher ring system

Key Points of Coulson Moffitt Theory

- Concept based on maximum overlap of C-orbital
- Banana bond or Bent bond Theory - looks like that

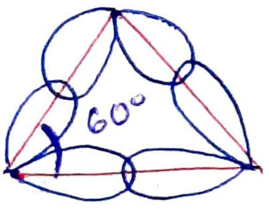


Bent bond
(Weaker)



Sigma bond
(Stronger)

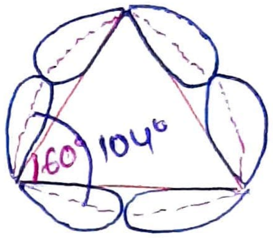
- Bent bond → Intermediate b/w σ & π

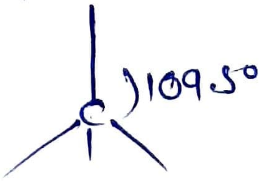


Angle = 60°

Force to 109.5°
normal tetrahydral

Thus formed bent
bond





SP^3 S = 25%
P = 75%

Internuclear Angle = 60°

Interorbital Angle = 104°

S = 16%
P = 84%
Character