Chapter 4

ALICYCLIC COMPOUNDS

PREPARATION OF CYCLOALKANES

- Following methods are commonly used for the preparation of cycloalkanes.
  - **From dihalogen compounds**: α-ω elimination from dihalides having halogen atoms on two ends of carbon chain (α-ω dihalides) with Na or Zn dust gives rise to the formation of cycloalkanes.

- The method can be regarded as intramolecular Wurtz reaction and is called Freund reaction. This can be used to prepare cycloalkanes from three to six carbon atoms.

- **By Clemmensen reduction**: The reduction of cyclic ketones by Zn-Hg/HCl gives cycloalkanes.

- **(c) From alkenes**: Alkenes on treating with CH₂I₂ in presence of Zn-Cu couple or by diazomethane (CH₂N₂) in presence of U.V. light gives derivatives of cycloalkanes.
(d) **By Dieckmann cyclisation**: Esters of dicarboxylic acids on heating in presence of sodium ethoxide undergo intramolecular Claisen condensation to gives cyclic β-keto esters. These β-keto esters on hydrolysis and subsequent heating gives cyclic ketones which are reduced by Zn-Hg/HCl to give cycloalkanes.

(e) **From aromatic compounds**: Six membered cyclo compounds can be easily obtained by the catalytic reduction of benzene and its derivatives.

**Baeyer strain theory**

- In 1885 adolf von baeyer proposed a theory to account for certain aspects of the chemistry of cyclic compounds.
- The theory deals with ring opening tendencies of cyclo propane & cyclo butane.
- Baeyers arguments state that:
• When carbon is bonded to 4 other atoms, the angle between any pair of bonds is the tetrahedral angle 109.5°.

• But the ring of cyclo propane is a triangle with three angles of 60°, & the ring of cyclo butane is a square with 4 angles of 90°.

• Therefore 1 pair of bonds to each carbon cannot assume a tetrahedral angle, it can be compressed to 60° or 90° to fit the geometry of the ring.

• These deviations of bond angle from the “normal” geometry tetrahedral value cause the molecule to be strained, & hence to be unstable when compared with the molecules in which the bond angles are tetrahedral.

• Cyclopropane & cyclobutane undergo ring-opening reactions since they relive the strain & yield more stable open-chain reactions.

• Cyclopropane is more highly strained, more unstable, & more prone to undergo ring opening reactions than cyclo butane.

• The angles of a regular pentagon(108°) are very close to the tetrahedral angle(109.5°).

• The angles of a regular hexagon(120°), are some what larger than tetrahedral angle.

• Baeyer incorrectly proposed there should be a certain amount of strain in cyclohexane & incorrectly suggested as 1 proceeded to cyclo heptane, cyclo octane, etc......

• The deviation of the bond angles from 109.5° would become progressively larger & the molecules would become progressively more strained.

Thus Baeyer considered that rings smaller or larger than cyclo pentane or cyclo hexane were unstable, it was because of this instability that the 3&4 membered rings underwent ring opening reactions, it was because of this instability that the great difficulty had been encountered in the synthesis of the larger rings.

By,

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