Carbocyclic Rings
Medium and Large Rings

Paper 4201 B
Organic Chemistry
(Special-II)
CHEMISTRY OF MEDIUM AND LARGE RING COMPOUNDS

- 8-11 C-atoms: Medium rings
- >12 C-atoms: Large rings

MACROCYCLES

CONFORMATION OF MEDIUM AND LARGE Sized RINGS

➢ Cyclooctane: boat-chair, chair-chair (crown) or boat-boat conformations
  • favored conformation - boat-chair due to minimum number of eclipsing ethane interactions (shown in blue), as well as torsional strain.
  • The chair-chair or crown conformation - less stable
  • boat-boat conformation - least stable

Cyclooctane

boat-chair conformation
favoured

Chair-Chair or Crown conformation

Ratio: 96:4 at r.t.

Boat-boat conformation
least favoured

Cyclononane

twist-boat-chair conformation

➢ Cyclononane: most favourable conformation - twist-boat-chair

➢ Cyclodecane: Boat-chair-boat and Chair-chair-chair conformation
  • Boat-chair-boat conformation - energetically minimized
  • Chair-chair-chair conformation - eclipsing interactions.

Cyclodecane

Boat-Chair-Boat conformation

Chair-Chair-Chair conformation
eclipsing interactions present
**SYNTHESIS OF MEDIUM AND LARGE SIZED RINGS**

**Challenges**
- Generally difficult to synthesize from open-chain compounds as the probability of reactive groups on the two ends of a long hydrocarbon chain undergoing cyclization is low.
- The reactions are carried out in very dilute solutions (*high-dilution technique*) to reduce the possibility of coupling of reactive groups on the ends of different molecules.

**THE DIECKMANN REACTION**
- Intramolecular reaction of diesters in the presence of base to give cyclic products.
- Usually used to prepare five- or six-membered rings.

**Mechanism**
- Products depend on the substrate and conditions. e.g., diethyl 3-ethoxycarbonylheptanedioate gives the 6-membered ring product with NaH in benzene and the 5-membered ring product with NaOEt in ethanol.

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*Paper 4201-B: Supramolecular chemistry and carbocyclic rings - Medium and large Rings*
7-membered and larger rings can also be prepared by this method (under high dilution techniques) and the yields can often be satisfactory.
• Reaction of α,ω-dinitrile with a base leads to cyclization.
• e.g., the reaction of adiponitrile with sodium ethoxide, lead to cyclization and formation of the imine-enamine mixture. Cyclic cyano-ketone obtained upon hydrolysis.

Disadvantages: The reaction has found much less general use than the Dieckmann reaction because dinitriles are less readily available than diesters and the resulting cyanoenamines are both more difficult to hydrolyze and less versatile in their transformation into other groups.
SYNTHESIS OF LARGE RINGS BY RING CLOSING METATHESIS (RCM) REACTION

- RCM, is a widely used for the synthesis of various unsaturated rings via the intramolecular metathesis of two terminal alkenes.
- Forms E- or Z- cycloalkenes
- **Advantages:**
  1. formation of rings, which were previously difficult obtain in good yields
  2. broad substrate scope
  3. Atom economical reaction- ethylene is the only major by-product

Examples

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RCM dimerization

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**Grubbs 1st Generation (Grubbs I)**

**Grubbs 2nd Generation (Grubbs II)**
Ring-closing metathesis is important in total synthesis.

Limitations: use of high dilution technique, selectivity issues, and unwanted isomerization.