ALICYCLIC CHEMISTRY (EHS) SYNOPSIS

Textbooks:

1. Ring Strain

(a) 1st Lecture: Angle (Baeyer) Strain.- As tetrahedral angle is compressed p-character of ring C-C bond increases. In cyclopropane internal bond $105^\circ$ with approx. $sp^{3.7}$ for C-C and $sp^{2.3}$ for C-H. Thus the C-H shorter and stronger shown by IR, CH acidity, $^{13}C$ NMR; C-C weaker and longer (p-like) shown by UV, $^1H$ NMR.

(b) Torsional (Pitzer) Strain.- Eclipsing of groups along a [-bond which cannot be relieved by rotation. Planar and puckered cyclobutanes.

(c) 2nd Lecture: Transannular Strain.- In medium rings groups project towards one another inside the ring.

(d) Cycloalkenes and Cycloalkynes.- Increase in angle strain is balanced to some extent by reduction in torsional strain. Trans-cycloalkenes – optical isomerism.

3rd Lecture: Strain measured by Ag$^{+}$ complexation. Cycloalkyne-Cycloallene equilibrium.

2. Conformational Analysis


(b) 4th Lecture: Kinetic Aspects.- (i) Steric control: Base hydrolysis of esters (TS more crowded than SM). Dichromate oxidation of alcohols (TS less crowded than SM).


3. Synthesis of Cyclopropanes and Cyclopropenes (Irreversible reactions only)

(a) Simmons-Smith – alkene + CH$_2$I$_2$ / Zn-Cu; cis –addition (Handout)

(b) Perkin synthesis – intramolecular displacement of leaving group by carbanion (Handout)

(c) Carbene additions – generation of carbenes – 5th Lecture: -stereospecificity of addition dependent upon multiplicity – singlet (concerted cis –addition) – triplet (biradical – stereochemistry depends upon rates of spin inversion and trapping).
4. **Reactivity of Cyclopropanes**
   
   (a) Olefin-like reactions; electrophilic, Markovnikov addition; Michael addition to conjugated cyclopropanes; hydrogenation.
   
   (b) Cyclopropyl cation – angle strain – electrocyclic reaction to allylic cations; cyclopropanones.

5. **6th Lecture: Synthesis of Cyclobutanes and Cyclobutenes** (Irreversible reactions only)
   
   (a) “[2 + 2]” – Cycloadditions – (i) \( h\beta \) + alkene + enone – non-stereospecific. Trapping of radical intermediates (Handout). (ii) Ketene + alkene – regiospecificity.

6. **Reactivity of Cyclobutanes and Cyclobutenes**
   
   (a) Cyclobutyl – cyclopropyl – homoallyl cation; i-cholesterol.
   
   (b) **7th Lecture**: Cyclobutenes – electrocyclic reaction to butadienes.

7. **Synthesis of Medium Rings**
   
   (a) Acyloin synthesis – comparison with Dieckmann – surface reaction.
   
   (b) \( \text{Ni}^0 \) – catalysed dimerisation of butadiene (Handout).
   
   (c) Cope rearrangement / expansion of smaller rings – chair transition states.

8. **8th Lecture: Reactivity of Medium Rings**
   
   (a) Transannular hydride shifts.
   
   (b) Transannular ring closures