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° 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 (π-like) shown by UV, $^1$H NMR.

(b) Torsional (Pitzer) Strain.- Eclipsing of groups along a σ-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. Oxirenes, 1H-azirines, 2H-azirines. Trans-cycloalkenes – optical isomerism.

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

2. Conformational Analysis ( Alicyclic only)


(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 Three-Membered Rings (Irreversible reactions only)

(a) 5th Lecture: Additions of “X” to a double bond: carbenes, carbenoids, nitrenes, oxene equivalents (peroxyacids)

(b) 6th Lecture: Intramolecular S$_2$2 displacements of leaving group by carbanions, oxyanions and amines.

4. Reactivity of Cyclopropanes, Epoxides and Aziridines

(a) Ring Opening by Electrophilic Attack

(b) 7th Lecture: Ring Opening by Nucleophilic Attack
5. **Synthesis of Four-Membered Rings** (Irreversible reactions only)
   “[2 + 2]” – Cycloadditions – (i) hv + alkene + enone (ii) Paterno-Buchi reaction (iii) Ketene + alkene (iv) ketene + imine, Staudinger reaction (v) chlorosulphonylisocyanate + alkene.

6. **Reactivity of Cyclobutanes, Cyclobutenes, Oxetanes and Azetidin-2-ones**
   (a) Cyclobutyl – cyclopropyl – homoallyl cation
   (b) Cyclobutenes – electrocyclic reaction to butadienes.
   (c) Nucleophilic attack on oxetanes and azetidin-2-ones.

7. **Synthesis of Medium Rings**
   (a) Acyloin synthesis.
   (b) Ni⁰ – catalysed dimerisation of butadiene.
   (c) Cope rearrangement / expansion of smaller rings.

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