

JCL 301 (Jan) (3-1-0)

Reaction Mechanisms

Instructor: Sridhar Rajaram

1. Introduction to Reaction Mechanisms

- Curved arrow formalism with examples from current literature.
- Chemical kinetics: Orders, approximations, case-study of Baylis-Hillman reaction
- Baldwin's Rules, Burgi-Dunitz trajectory, and Felkin-Ahn model.

2. Retrosynthetic Analysis

- Retrosynthetic transforms, role of symmetry, recognizing patterns: Wender's taxol synthesis.

3. Enzymatic Reactions

- Thermodynamic model of catalysis, non-covalent interactions, proximity effects, acid-base catalysis, small molecule mimics of bifunctional catalysis.
- Mechanism of proteases.
- Redox enzymes and their mechanisms.

4. Mechanism of Oxidation Reactions

- Chromium-based oxidants, DMSO-based oxidations, MnO_2 oxidation, oxidation to acids
- C-H oxidations: SeO_2 oxidations, oxaziridines, enolate oxidations.
- Hypervalent iodine oxidations: Periodinane, PIFA and SET

5. Introduction to Organometallic mechanisms

- Basic reaction mechanisms
- Mechanism of Schwartz reaction, Zeigler-Natta polymerization, Brookhart and Grubbs polymerization, hydroamination, enzyme-cyclization, hydrogenations, allylic substitution, and cross-coupling reactions.

6. Peptides and lactams

- Mechanistic ideas for coupling and prevention of racemization, mechanistic rationale for protecting groups, native chemical ligation, solid phase peptide synthesis
- Stereoselective synthesis of β -lactams, stereochemical models

7. Aldol reactions

- Diastereoselective aldol reactions, stereochemical models for selective enolization, soft enolization, Evans aldol, Crimmins aldol, anti-aldol reactions, aldol reactions of α -chiral aldehydes
- Enzymatic aldol reactions
- Organocatalytic aldol reactions

Reference Books:

1. Writing Organic Reaction Mechanisms by A. Miller and P. H. Solomon
2. Logic of Chemical Synthesis by E. J. Corey and X. M. Cheng
3. Introduction to Enzyme and Co-enzyme chemistry by Tim Bugg
4. The Organometallic Chemistry of Transition Metals by Robert H. Crabtree
5. Current literature