KOE 223/2 – Mechanisms in Organic Reactions

Course Objectives : 1) To understand the meaning of organic reaction mechanisms.
2) To learn the methods used to prove the mechanisms in organic reactions.

Topics	Contents	Number of Lecture Hours	Expected outcome – upon completion of this course, the student should be able to:
1. Introduction	• The meaning of 'reaction mechanisms' • Structure and reactivity	1	• Understand the meaning of 'mechanisms', and about what 'proposing' and 'writing' a mechanism means. • Relate structure to reactivity in many different situations.
2. Energetics and Kinetics	• Energy profile • Intermediates *vz*. transition states • Reaction rate and free energy of activation • Kinetics and the rate-determining step • Kinetic *vz.* thermodynamic control	4	• Distinguish between intermediates and transition states. • Recognize that individual reactions should be energetically favorable. • Predict the products(s) of a reaction under kinetic control and under thermodynamic control.
3. Methods of Determining Mechanisms	• Kinetic data and its interpretation • Kinetic and non-kinetic uses of isotopic labeling • Primary and secondary kinetic isotope effects • The study of reactive intermediates • The major types, their detection, isolation and trapping • Testing for possible intermediates • 'Cross-over' experiments • Stereochemical studies	12	• Use kinetics to rule out particular mechanisms. • Recognize that mechanisms cannot be deduced unequivocally from the kinetics. • Use isotope-labeling as a probe for reaction mechanisms, e.g. in mechanisms of hydration and elimination, ester hydrolysis, esterification, Claisen, Hofmann, Favorskii rearrangements and other rearrangement reactions. • Recognize the various types of intermediates generally encountered in organic reactions and their important characteristics. • Use techniques such as spectroscopy and trapping to establish the precise nature of the intermediates formed in a reaction. • Use 'Cross-over' experiments to determine if a rearrangement is inter-or intra-molecular. • Use stereochemical studies to provide some insights into the details of a mechanism, e.g. whether inversion or retention has taken place at the reaction site.

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4. Structure/Reactivity Correlations	• Hammett plots • The significance of σ and ρ • The use of Hammett plots • Limitations and deviations from Hammett plots • The Taft equation	3	• Recognize the significance of σ and ρ, particularly the sign and magnitude of ρ. • Use the Hammett equation to decide between two alternative mechanisms.
5. Molecular Rearrangements	• Neighboring group participation • Electron-deficient and electron-rich skeletal rearrangements • Rearrangements on an aromatic ring	4	• Write mechanisms for certain rearrangement reactions and understand the use of the above techniques in the support of these mechanisms.
	TOTAL	**24**	