Midterm I Study Guide for Chemistry 109C

(Kahn, Spring 2007)

In general, exam questions are based on topics that we covered in the lectures. However, in some cases the textbook provides more detailed examples of these topics and you are expected to be familiar with this material as well. Topics covered in quizzes and vitamin problems may be revisited in the exam. I anticipate that you are familiar with basic concepts of organic nomenclature, stereochemistry, and reactivity that were taught in Chem 109A and Chem109B.

Molecular Orbital Theory

Acids, bases, electrophiles, nucleophiles: connection with their electronic structure
Familiar examples from Chem 109A, B (addition of HBr to alkenes, hydroboration)
Bonding, nonbonding, and antibonding orbitals
Drawing molecular orbital diagrams
Frontier orbital theory; recognizing HOMO and LUMO orbitals in ground state molecules
Description of chemical reactions as flow or electrons from one orbital to another
Electron delocalization
Stability of the allyl cation; reactions of allyl halides
Conjugated vs. non-conjugated π systems
Conjugation in amide; properties of the amide bond
Properties and molecular orbitals of dienes; the Diels–Alder Reaction

Ultraviolet Spectroscopy

Lambert–Beer law (not covered in lecture; you should know it!)
$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions
Effect of conjugation in π system on λ_{max}
London dispersion as the main force between nonpolar solute and solvent
Dipole–diple interaction as the force between polar solute and polar solvent
MO-based explanation for the red shift in $\pi \rightarrow \pi^*$ transitions in apolar alkenes
MO-based explanation for the blue shift in $n \rightarrow \pi^*$ transition in carbonyl compounds

Reactivity due to the α-carbon in carbonyl compounds.

The acidity of the α-hydrogen in different systems
Keto-enol tautomerization
Reactivity of enols and enolates as good nucleophiles
Halogenation at the α-carbon in aldehydes, ketones, and esters
Halogenation at the α-carbon in carboxylic acids
Alkylation of the β-carbon in α,β-unsaturated aldehydes and ketones.
Aldol addition and aldol condensation: basic mechanisms
Claisen condensation of esters: basic mechanism
Possibility of formation of product mixtures in mixed Aldol and Claisen condensations
What is so special about benzyl aldehyde?
Structure and properties of LDA
Modern synthetic strategies for carbon-carbon bond formation using enolate chemistry.
Decarboxylation of 3-oxocarboxylic acids; relevance in biochemistry

Carbohydrates

Structural aspects:

General formula and functional groups
Classification based on number of carbons
Classification based on the nature of the carbonyl functionality
Classification based on the extent of polymerization (mono-, di-, oligo-, polysaccharides)
Classification into D- and L-isomers
Fisher projections, R, S nomenclature
Enantiomers, diastereomers, epimers
Structure of D-glyceraldehyde and L-glyceraldehyde
Structures of D-ribose, D-glucose, D-mannose, D-galactose and D-fructose (open chain)
Structures of D-ribose, D-glucose, D-mannose, D-galactose and D-fructose (cyclic, Haworth)
Aldonic acids and aldaric acids
Nomenclature of disaccharides: how to specify the linkage
Be able to recognize simple disaccharides: maltose, cellobiose, trehalose, lactose, and sucrose

Chemical reactions:

Oxidative chemistry of the aldehyde functionality: aldonic acids
Oxidative chemistry of the primary alcohol functionality: aldaric acids
Tollens test with aldoses and ketoses; enolization of ketoses
Reductive chemistry of the aldehyde functionality
Nucleophilic addition to carbonyl carbon
Chain elongation: Kiliani-Fisher synthesis
Chain shortening: Ruff degradation and Wohl degradation
Formation and properties of hemiacetals
Formation and properties of acetals, oxocarbenium ion mechanisms
Intramolecular hemiacetal formation: cyclic structures
α,β anomers; conformational stability in glucose
Furanoses and pyranoses
Formation of disaccharides
Reducing and non-reducing disaccharides
Acylation of free hydroxyl groups with acetic anhydride
Alkylation of free hydroxyl groups with methyl iodide
Reactions of 1,2-diols with periodic acids

Analysis and properties:

Chiral properties of polyhydroxyaldehydes
Chiral properties of aldonic acids
Chiral properties of aldaric acids
Identification of monosaccharides (e.g. Fisher's proof of glucose structure)
Mutarotation as tool to distinguish hemiacetals from acetals
Determination of ring size via exhaustive methylation analysis
Determination of disaccharide structures via exhaustive methylation analysis