EXAM 4 study guide

Organic Chemistry 2e chapters 16, 9-10

**DAY 22, Terms to know**:

Sections 16.1-16.5 Nuclear magnetic resonance, magnetic moment, alpha spin state, beta spin state, shielded, deshielded, resonance (in regard to spin states), free induction decay (FID), Fourier-transform (FT), chemical shift

**DAY 22, Specific outcomes and skills that may be tested on exam 4:**

Sections 16.1-16.5

* Be able to explain what happens to magnets and also the spin states of nuclei when atoms are placed in a magnetic field.
* Be able to explain what happens to the spin states when radio waves of the correct frequency excite nuclei in a magnetic field.
* Be able to explain why shielded atoms have smaller energy gaps between alpha and beta spin states.
* Be able to explain the relationship between the strength of the magnetic field the size of the energy gap between spin states.
* Be able to explain how modern NMR instruments are used to obtain a FID.
* Be able to explain how and why NMR samples are prepared including state of matter, solvent, spinning.
* Be able to determine when H atoms are equivalent or non equivalent.
* Be able to identify homotopic, enantiotopic, and diastereotopic protons and explain how such protons affect the number of signals and splitting patterns in the proton NMR.
* Be able to explain why TMS is added to many NMR samples.
* Be able to explain and use the terms upfield, downfield, shielded, deshielded, higher and lower energy and frequency and explain the relationships such as upfield is the area where shielded nuclei signals appear, etc.
* Be able to explain how electronegative atoms affect shielding and shifts of proton signals in NMR.
* Be able to give approximate predictions for where on the ppm scale proton signals will appear given the structure of a molecule.
* Be able to explain how aromatic rings affect the shifts of protons nearby.

**DAY 23, Terms to know**:

Sections 16.6-16.11 integration, splitting pattern or multiplicity, homotopic, enantiotopic, diastereotopic, internal standard, downfield, upfield, diamagnetic anisotropy, aromatic, coupling constant, exchangeable proton, decoupled

**DAY 23, Specific outcomes and skills that may be tested on exam 4:**

Sections 16.6-16.11

* Be able to explain what integration values represent in an NMR.
* Given a molecular structure, predict the integrations of each signal expected.
* Be able to label symmetrical splitting patterns such as singlet, double, triplet, etc.
* Be able to predict splitting patterns for each signal in a proton NMR based on the n+1 rule.
* Be able to identify H atoms that may have splitting patterns more complex than can be determined using the n+1 rule.
* Be able to explain how nonequivalent H atoms on adjacent carbons can split an atom with the same coupling constant giving a signal that would be predicted from the n+1 rule or with different coupling constants giving a more complex signal.
* Be able to identify some complex splitting patterns such as doublet of doublets, triplet of quartets, etc.
* Given a molecular structure, be able to predict some complex splitting patterns.
* Be able to explain how the NMR spectra is affected when a proton is exchangeable.
* Given a series of proton NMR peak data, be able to propose a reasonable molecular structure for the molecule.

**DAY 24, Terms to know**:

Sections 16.12-16.13, 9.1-9.4 Distortionless Enhancement by Polarization Transfer (DEPT), Addition reaction, hydrohalogenation, Markovnikov addition, anti-Markovnikov addition, hydration

**DAY 24, Specific outcomes and skills that may be tested on exam 4:**

Sections 16.12-16.13, 9.1-9.4

* Given a molecular structure, be able to predict how many 13C NMR peaks will be observed and their shifts.
* Given any or all of the data: IR, MS, proton NMR 13C NMR, DEPT, formula, be able to propose a reasonable molecular structure.
* Be able to explain how the number of pi and sigma bonds changes during an elimination reaction and identify where in an example reaction the bonds are that are breaking and forming.
* Be able to describe the relative reactivity as a base or a nucleophile of pi bonds versus sigma bonds and explain why.
* Be able to explain how addition reactions are at equilibrium with the reverse elimination reactions and what factors affect which side of the equilibrium is favored.
* Given a reaction and reaction conditions, be able to predict which side of an elim/addn equilibrium reaction is favored.
* Be able to predict whether the change in enthalpy for an addition reaction is positive or negative and WHY.
* Be able to predict whether the change in entropy for an addition reaction is positive or negative and WHY.
* Be able to explain how temperature can be increased or decreased to shift an addition equilibrium toward one side or another.
* Be able to predict the regioselectivity of addition reactions to asymmetrical alkenes.
* Be able to use the mechanism to explain WHY Markovnikov additions give the observed regioselectivity.
* Given addition products, be able to give a set of reactants, reagents, and conditions that will produce the desired product whether it be Markovnikov or anti-Markovnikov.
* Be able to predict a reasonable mechanism for Markovnikov addition reactions and explain how the mechanism gives the observed rate law.
* Be able to predict a reasonable reaction coordinate diagram for Markovnikov addition reactions and explain the energy changes during each step.
* Be able to explain how the stability of the intermediate and transition states during an addition reaction favor Markovnikov rather than anti-Markovnikov.
* Be able to predict the stereochemistry of Markovnikov addition products and use the mechanism to explain why products form with the predicted stereochemistry.
* Be able to predict when an addition reaction will involve a carbocation rearrangement step in the mechanism.
* Be able to give conditions that might favor non-rearrangement products over carbocation rearrangement products in Markovnikov addition reactions.

**DAY 25, Terms to know**:

Sections 9.5-9.8 Oxymercuration-Demercuration, Hydroboration-Oxidation, hydrogenation, halogenations, halonium ion, bromonium ion, halohydrin

**DAY 25, Specific outcomes and skills that may be tested on exam 4:**

Sections 9.5-9.8

* Be able to give reasonable reagents and conditions including an alkene that could be used to produce a desired addition product.
* Given an alkene and reaction conditions, be able to predict the product of an addition reaction including the proper stereochemistry and regiochemistry.
* Be able to explain why borane conditions yield anti-Markovnikov hydration products using sterics and electronics to explain regioselectivity and stereoselectivity.
* Be able to give the mechanism for each step of the Hydroboration-Oxidation reaction.
* Be able to explain the role of the metal catalyst in hydrogenation reactions.
* Be able to predict region- and steroselectivity in hydrogenation reactions.
* Be able to predict region- and steroselectivity in halogenation reactions.
* Be able to predict region- and steroselectivity in halohydrin reactions.
* Be able to draw a reasonable mechanism for **each** addition reaction mechanism covered in class.

**DAY 26, Terms to know**:

Sections 9.9-9.13, 10.1-10.3 dihydroxylation, diol, ozonolysis, carbonyl, Alkyne, acetylene, terminal alkyne, internal alkyne

**DAY 26, Specific outcomes and skills that may be tested on exam 4:**

Sections 9.9-9.13, 10.1-10.3

* Be able to give conditions for reactions to form epoxides. Be able to predict epoxide products given reaction conditions and reagents. Be able to give the mechanism for epoxidation formation.
* Be able to give the mechanism for the acid-catalyzed opening of an epoxide with water and predict the products with the correct regio- and stereoselectivity. Be able to give conditions for the opening of an epoxide to give a desired diol.
* Be able to give conditions for the formation of a syn diol, and be able to predict diol products given specific reagents.
* Be able to explain how reactions with KMnO4 give different major products depending on the temperature.
* Be able to predict the products for ozonolysis reactions. Be able to give conditions for the conversion of an alkene into two carbonyls using ozonolysis.
* Be able to give reagents or predict products to complete short 2-5 step syntheses using all of the reactions learned up to this point. Being able to predict correct regio- and stereoselectivity is very important here.
* Be able to predict and explain the geometry, hybridization, and reactivity (nucleophile or electrophile) of alkynes.
* Be able to name alkynes using IUPAC, and be able to draw structures of alkynes from a given IUPAC name.
* Be able to recognize by roughly how much alkyne p*K*a values are lower than alkenes and alkanes and explain why.
* Using ARIO or given p*K*a values, be able to identify bases that will deprotonate terminal alkynes, and be able to identify acids that can protonate the conjugate base of a terminal alkyne.

**DAY 27, Terms to know**:

Sections 10.4-10.11 geminal, vicinal, unimolecular, bimolecular, termolecular, enol, keto, tautomerization, carboxylates, alkynide ion

**DAY 27, Specific outcomes and skills that may be tested on exam 4:**

Sections 10.4-10.11

* Be able to predict alkyne products from dihalides reacting with base, and be able to give a dihalide and reaction conditions that could be used to give a specific alkyne.
* Given an alkyne and reaction conditions, be able to predict the product of an addition reaction including the proper stereochemistry and regiochemistry.
* Given an alkyne and reaction conditions, be able to draw a reasonable mechanism including not limited to the dissolving metal reaction.
* Be able to explain the factors including the rate and carbocation stability that suggests a termolecular hydrohalogenation reaction for alkynes rather than the standard mechanism seen with alkenes.
* Be able to predict enol and keto products for both Markovnikov and anti-Markovnikov hydration reactions of alkynes, and be able to give reagents necessary to produce ketones and aldehydes using such reactions.
* Be familiar with bulky borane reagents and why they are used in Hydroboration-Oxidation reactions.
* Be able to predict the products for ozonolysis reactions starting with alkynes. Be able to give conditions for the conversion of an alkyne into two carbonyls or carboxylates using ozonolysis.
* Give conditions for the formation of an alkynide ion, and be able to recognize when such ions form given specific conditions for forming them.
* Be able to give reagents necessary to convert alkynide ions into alkynes forming new carbon-carbon bonds, and be able to predict alkyne products from reactions between alkynide ions and alkyl halides.
* Be able to give reagents or predict products to complete short 2-5 step syntheses using all of the reactions learned up to this point. Being able to predict correct regio- and stereoselectivity is very important here.