

## What Do I Need to Remember from Organic I?

A brief chapter-by-chapter summary of the most important topics that you should remember from CH 310M appears below. Please come to office hours for help as quickly as possible if you have any questions!!!

### Chapter 1

- Be able to draw Lewis structures for molecules.
- Understand the difference between ionic and covalent bonds; be able to draw bond dipole moments and net molecular dipole moments for polar covalent molecules.
- Be able to calculate formal charge on atoms.
- Be able to draw resonance structures, using curved arrows to symbolize the flow of electrons. Be able to apply the octet rule. Know the exceptions to the octet rule. Be able to identify the resonance structure that contributes most to the “true” structure of the resonance hybrid.
- Know the organic functional groups (structure and name). Be able to indicate partial charges in polar functional groups.
- Know the various possible hybridization states for carbon ( $sp$ ,  $sp^2$ ,  $sp^3$ ) and how these different states are formed by mixing  $s$  and  $p$  orbitals in the valence shell of carbon. Be able to draw representations of these hybrid orbitals and to show how bonds can be formed for simple organic molecules by the overlap of these hybrid orbitals with orbitals on another atom. Know how the shape of a molecule (i.e. bond angles) corresponds to the hybridization of the central atom.
- Understand the distinction between a  $\sigma$  bond and a  $\pi$  bond.

### Chapter 2

- Be able to draw the structures of constitutional isomers using both condensed structural formulas and “line-angle” structures.
- Know the alkyl groups and the appropriate symbols for them (e.g.  $CH_3 = Me = methyl$ , etc.)
- Know how to use IUPAC nomenclature to name alkanes and haloalkanes; know the names of the commonly encountered alkyl groups (e.g. methyl, ethyl, propyl, isopropyl, etc.). Memorize the names of all of the parent hydrocarbons up to  $C_{12}$  (dodecane). Be able to name substituted monocyclic hydrocarbons, including cis/trans.
- Know how to classify carbon and hydrogen atoms ( $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ ,  $4^\circ$ ).
- Be able to draw conformational energy diagrams for acyclic molecules, illustrating the energy changes that occur upon rotation about carbon-carbon single bonds. Be able to draw the appropriate Newman projections for the conformers corresponding to energy maxima and minima.
- Know the difference between torsional, angle, and steric strain.
- Be able to draw chair representations of cyclohexane, showing the orientation of axial and equatorial bonds and substituents, using both Newman projections and line drawings. Be sure you can draw the result of a “chair flip.”
- Be able to predict relative stabilities of different conformations of mono- and disubstituted (including cis and trans) cyclohexanes. Know how to predict which conformer will be the major form.

### Chapter 3

- Know the differences between constitutional isomers, enantiomers, diastereomers, and meso compounds, and how to identify relationships between compounds irrespective of how they are drawn. You must be able to work with both cyclic and acyclic systems.
- Be able to use and give examples of chiral molecules, stereogenic centers, optical activity.
- Be able to draw 3 dimensional representations of stereoisomers.
- Be able to recognize compounds that will be optically active (i.e. that have enantiomers).
- Know the (R/S) system for nomenclature and be able to use it on acyclic or cyclic systems.

#### **Chapter 4**

- Know and be able to apply definitions of Brønsted-Lowry and Lewis acids and bases. Understand the definitions of nucleophile and electrophile
- Be able to apply your understanding of acidity and basicity towards predicting organic and inorganic reactions. Key idea = acids react with bases (electrophiles react with nucleophiles)
- Be able to use curved arrows to symbolize the flow of electrons in acid-base reactions.
- Be able to explain how structure affects acidity (using factors such as resonance, inductive effects, hybridization, etc.) that stabilize the conjugate base.
- What is the relationship of  $pK_a$  to acid strength? Be able to predict the outcome of acid-base reactions given  $pK_a$ 's. What side of the reaction is favored at equilibrium?

#### **Chapter 5**

- Know how  $sp^2$  orbitals are formed by mixing of s and p orbitals, and be able to draw representations of these hybrid orbitals and show how bonds are formed. Know shapes (bond angles) associated with  $sp^2$  hybridization.
- Know how to use IUPAC nomenclature to name alkenes.
- Know the sequence rules and be able to assign double bonds as *E* or *Z*.

#### **Chapter 6**

- Be able to distinguish between the terms rate (kinetic; reaction fast or slow) and equilibrium (thermodynamics; in what direction does the reaction go spontaneously).
- Know the difference between endothermic and exothermic reactions and be able to draw reaction energy diagrams for each reaction we studied. You should be able to include structures of reactants, transition state(s), intermediates, and products on such a diagram. Be able to label the curve with  $\Delta H$  (enthalpy change) and  $\Delta G^\ddagger$  (activation energy).
- Know how to predict and rationalize which regioisomeric product will be formed as the major product in the addition of an unsymmetrical reagent, such as  $H-X$  ( $X = \text{halogen}$ ),  $X_2/H_2O$  (or  $X_2/CH_3OH$ , etc.),  $H_2O/H_3O^+$ ,  $Hg(OAc)_2/H_2O$ , and  $BH_3$ , to an unsymmetrical alkene. Typically, the major product is formed via the more stable carbocation intermediate (i.e. Markovnikov's rule is followed) or by opening a bridged cation at the more substituted carbon (i.e. the carbon best able to accommodate the positive charge).
- Be familiar with the Hammond postulate and its consequences for predicting factors that are important in stabilizing transition states for a reaction.
- Know the relative stabilities of carbocations ( $3^\circ > 2^\circ > 1^\circ$ ). Remember that if a carbocation can rearrange to a more stable carbocation, it typically will, and the rearranged product is the major product.
- Be able to write the stepwise mechanisms for the electrophilic additions of  $HX$ ,  $H_2O/H_3O^+$ ,  $X_2$ , and  $X_2/H_2O$  to carbon-carbon double bonds symbolizing the flow of electrons with curved arrows.
- Know the stereochemical outcome of reactions such as the addition of  $X_2$  (*anti*),  $X_2/H_2O$  (or  $X_2/CH_3OH$ , etc.) (*anti*),  $Hg(OAc)_2/H_2O$  (*anti*),  $BH_3$  (*syn*),  $H_2/Pd$  (*syn*),  $OsO_4$  (*syn*) to alkenes.
- Be able to predict the regiochemistry for the net addition of water to an alkene by the sequence of oxymercuration/reduction or by hydroboration/oxidation. How does the regiochemistry of these processes compare to the direct acid-catalyzed hydration of an alkene? What advantage might there be to using the sequence of oxymercuration/reduction instead of the acid-catalyzed hydration of an alkene to prepare an alcohol?
- Memorize the reagents for oxymercuration/reduction, hydroboration/oxidation, hydrogenation, vicinal hydroxylation, and ozonolysis of alkenes. Be able to recognize and apply these reactions.
- Be able to determine whether an oxidation has occurred in a chemical reaction.
- Know relative stabilities of alkenes (more substituted is more stable).
- Be able to use electrophilic additions to alkenes in synthesis.

## Chapter 7

- Be able to name simple alkynes using the IUPAC nomenclature rules.
- Know what base to use to generate acetylide anions from terminal alkynes.
- Know how to use elimination (double dehydrohalogenation of 1,2-dihaloalkanes) and  $S_N2$  (alkylation of acetylide anions with primary  $R-X$ ) reactions to produce alkynes.
- Know how  $HX$ ,  $X_2$ , and  $H_2O$  [in the presence of  $Hg(II)$ ] add to alkynes. Be able to write reaction mechanisms (using curved arrows to show electron movement) and be able to predict the regiochemistry of the addition of unsymmetrical reagents to alkynes.
- Know how to use  $(sia)_2BH$  to achieve hydroboration of alkynes. Understand how treatment of the resulting alkenylborane yields an enol which rearranges to give a carbonyl compound.
- Know reaction conditions/stereochemistry of reduction of alkynes using  $H_2/Lindlar$  catalyst and  $Na$  (or  $Li$ )/ $NH_3$ .
- Be able to do synthesis problems using alkynes.

## Chapter 8

- Know how to name alkyl halides using IUPAC nomenclature.
- Be able to write the free radical halogenation of alkanes using “fishhook” arrows to symbolize the flow of electrons and identify the initiation, propagation, and termination steps.
- Be able to predict the major products of free radical chlorination and bromination of simple alkanes and alkenes (allylic bromination using  $NBS$ ). Understand the basis for the regioselectivity of free radical halogenation reactions.
- Given bond dissociation energies, be able to calculate  $\Delta H$  for any chemical reaction.
- Understand the observed trends for radical stability.
- Be able to rationalize why free radical chlorination is less selective than free radical bromination. Be familiar with the Hammond postulate and its consequences for predicting factors that are important in stabilizing transition states for a reaction.

## Chapter 9

- Know the reaction mechanisms (symbolizing the flow of electrons using curved arrows) for  $S_N1$  and  $S_N2$  reactions. Be able to draw reaction energy diagrams showing starting materials, transition states, intermediates, and products.
- Know the kinetic and stereochemical features of  $S_N1$  and  $S_N2$  reactions.
- Know how differences in structure of  $R-X$ , solvent, nucleophile, and leaving group affect the rates of  $S_N1$  and  $S_N2$  reactions. Be able to discuss and rationalize the mechanistic basis for differences.
- Know the structures of carbocations and be able to rationalize their relative stabilities.
- Be able to predict the products when structurally different alkyl halides undergo substitution reactions with a diversity of nucleophiles (bases) under different conditions.
- See Table 9.12 for a summary of  $S_N1$  and  $S_N2$  reactions.
- Know the reaction mechanisms (symbolizing the flow of electrons using curved arrows) for  $E1$  and  $E2$  reactions. Be able to draw energy diagrams showing starting materials, transition states, intermediates, and products.
- Know the kinetic and stereochemical features of  $E1$  and  $E2$  (antiperiplanar preferred) reactions.
- Know how differences in structure of  $R-X$ , solvent, base, and leaving group affect the rates of  $E1$  and  $E2$  reactions. Be able to discuss and rationalize mechanistic basis for differences.
- For different reactions of nucleophiles and bases with  $1^\circ$ ,  $2^\circ$ , and  $3^\circ$  halides, be able to predict whether substitution or elimination will be favored (or if a mixture will result). Remember, negatively charged bases favor elimination by the  $E2$  mechanism, even for  $3^\circ$  halides. See Table 9.14 for a summary of substitution versus elimination.
- Be able to use substitution and elimination reactions of alkyl halides in synthesis.

## Chapter 10

- Know how to name alcohols according to IUPAC nomenclature.
- Know how alcohols can serve as acids and bases (both in the Brønsted-Lowry and Lewis sense).
- Know the reactions of alcohols with active metals such as Na, Li, and K.
- Be able to write the mechanism of the reaction of H-X (H-Cl, H-Br, and H-I) with a 1°, 2°, or 3° alcohol, showing the flow of electrons with curved arrows. Be aware of rearrangements of the intermediate carbocations to form more stable carbocations!
- Know the reactions of alcohols with PBr<sub>3</sub> (milder conditions and less prone to rearrangement) and SOCl<sub>2</sub> (clean stereochemical inversion of a 2° R-OH).
- Know how to prepare alkyl sulfonates (e.g. tosylates).
- Be able to write the mechanism for acid-catalyzed dehydration of 1°, 2°, and 3° alcohols, using curved arrows to show the movement of electrons. Once again, watch out for carbocation rearrangements!
- Be able to write the mechanism of the pinacol rearrangement, using curved arrows to show the movement of electrons.
- Know H<sub>2</sub>CrO<sub>4</sub> as a reagent to oxidize 1° and 2° alcohols to carbonyl compounds.
- Know how to oxidatively cleave glycols using periodic acid (HIO<sub>4</sub>).
- Be able to do synthesis problems using the reactions of alcohols.

## Chapter 11

- Know how to prepare ethers using the Williamson ether synthesis. This requires that you know what combination of alkyl halide and alkoxide to use to avoid competitive elimination reactions!
- Know the mechanism for the acid-catalyzed dehydration of 1° alcohols to yield symmetrical ethers.
- Know the mechanism for the acid-catalyzed addition of alcohols to alkenes.
- Know the mechanism for the acid-catalyzed cleavage of ethers by concentrated HX.
- Know how to prepare epoxides from alkenes, using peracids (e.g. *m*CPBA), or via halohydrins.
- Be able to predict the regioselectivity in the opening of epoxides by acid-catalyzed reactions, and in the presence of a good nucleophile (e.g. alkoxides, acetylide anion, etc.)
- Be able to do synthesis problems using ethers and epoxides.