Learning Objectives

Chapter 8 (last semester)

1. Write an electron-pushing mechanism for an S_N2 reaction between an alkyl halide and a nucleophile.
2. Describe the rate law and relative rate of reaction of alkyl halides of different degree for an S_N2 substitution reaction.
3. Describe the mechanistic detail of the S_N2 mechanism relating the geometrical structure of the transition state to the stereochemistry of the reactant and product at the atom where substitution occurs.
4. Describe the effect of leaving group stability on the rate of an S_N2 reaction.
5. Describe the effect of strength of nucleophile on the rate of an S_N2 reaction.
6. Describe how nucleophilicity is influenced by solvent.
7. Describe how nucleophilicity is influenced by the size of the nucleophile.
8. Write an electron-pushing mechanism for an S_N1 reaction between an alkyl halide and a nucleophile.
9. Describe the rate law and relative rate of reaction of alkyl halides for an S_N1 substitution reaction.
10. Describe the mechanistic detail of the S_N1 mechanism relating the geometrical structure of the transition state to the stereochemistry of the reactant and product at the atom where substitution occurs.
11. Describe the effect of leaving group stability on the rate of an S_N1 reaction.
12. Describe the effect of strength of nucleophile on the rate of an S_N1 reaction.
13. Determine whether a carbocation will undergo rearrangement via a 1,2-hydride or alkyl shift and draw the resulting cation.
14. Explain, with mechanistic specifics and discussion of the solvent, how partial racemization (with more inversion) can occur in an S_N1 reaction.
15. Account for the non-reactivity of vinyl and aryl halides in nucleophilic substitution reactions.
16. Analyze information about alkyl halide, nucleophile, solvent, concentration, and temperature to predict whether a substitution will occur by an S_N1 or S_N2 mechanism.
17. Describe how the rate of a nucleophilic substitution reaction will be affected by an aprotic or a protic polar solvent.

Chapter 9 (last semester)

1. Write an electron-pushing mechanism for an E2 reaction between an alkyl halide and a base.
2. Describe the rate law and relative rate of reaction of alkyl halides of different degree for an E2 elimination reaction.
3. Describe the mechanistic detail of the E2 mechanism relating the geometrical structure of the transition state to the stereochemistry of the reactant and product at the atoms where elimination occurs.
4. Describe the effect of leaving group stability on the rate of an E2 reaction.
5. Describe the effect of the size of the base on distribution of products of an E2 reaction.
6. Predict the major product of an E2 reaction of an alkyl halide and a base, taking into account the size of the base and the identity of the halide.
7. Write an electron-pushing mechanism for an E1 reaction between an alkyl halide and a base.
8. Describe the rate law and relative rate of reaction of alkyl halides of different degree for an E1 elimination reaction.
9. Describe the mechanistic detail of the E1 mechanism relating the geometrical structure of the transition state to the stereochemistry of the reactant and product at the atoms where elimination occurs.
10. Predict the major product of an E1 reaction of an alkyl halide and a base, taking into account the possibility of a 1,2-hydride or alkyl shift.
11. Analyze information about alkyl halide, base, solvent, concentration, and temperature to predict whether a substitution will occur by an E1 or E2 mechanism.
12. Describe the stereoselective nature of the E2 reaction.
13. Describe the stereoselective nature of the E1 reaction.
14. Analyze substituted cyclohexanes to determine the reactivity and products in an E2 reaction.
15. Analyze information about alkyl halide, nucleophile/base, solvent, concentration, and temperature to predict whether the major product from reaction of the alkyl halide will arise by substitution or by elimination, and determine the likely mechanism.

Chapter 10 (sections 10.1 through 10.4; see more of chapter 10 below)

1. Write a chemical equation for the formation of an alkyl halide from an alcohol and a hydrohalic acid.
2. Write an electron-pushing mechanism for the S_N2 reaction of an alcohol.
3. Write an electron-pushing mechanism for the S_N1 reaction of an alcohol.
4. Determine from the degree of an alcohol whether it will react by an S_N1 or S_N2 mechanism.
5. Describe the effect of the halide on the rate of a reaction of a hydrohalic acid with an alcohol.
6. Describe the effect of the degree of the alcohol on the rate of a reaction of a hydrohalic acid with an alcohol.
7. Write a chemical equation for the reaction of an alcohol with PX_3 (with pyridine). (X = Cl, Br, or I)
8. Write a chemical equation for the reaction of an alcohol with $SOCl_2$ (with pyridine).
9. Write an electron-pushing mechanism for the reaction of an alcohol with PX_3 (with pyridine). (X = Cl, Br, or I)
10. Write an electron-pushing mechanism for the reaction of an alcohol with $SOCl_2$ (with pyridine).
11. Write a chemical equation for the formation of a sulfonate ester from an alcohol and a sulfonyl chloride (with pyridine).
12. Write an electron pushing mechanism for the formation of a sulfonate ester from an alcohol and a sulfonyl chloride (with pyridine).
13. Identify and distinguish between alkyl sulfonates (such as tosylates, mesylates, and triflates) and the analogous sulfonyl chlorides.
14. Know and understand the preparation of tosylates, reactions of tosylates, and chemicals similar to tosylates such as the methanesulfonates (mesylates).
15. Describe the relationship of the stereochemistry of the reactant and product in a reaction to form an alkyl sulfonate from an alcohol.
16. Describe the relationship of the stereochemistry of the reactant and product in a nucleophilic substitution reaction of an alkyl sulfonate.
17. Write a chemical equation for the dehydration reaction of an alcohol with sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), or a similar acid with a non-nucleophilic conjugate base (with pyridine) to form an alkene.
18. Write an electron-pushing mechanism for the dehydration reaction of an alcohol with sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), or a similar acid with a non-nucleophilic

conjugate base (with pyridine) to form an alkene, taking into account the potential for a carbocation rearrangement.

19. Write a chemical equation for the reaction of an alcohol with $P(O)Cl_3$ (with pyridine).
20. Write an electron-pushing mechanism for the reaction of an alcohol with $P(O)Cl_3$ (with pyridine).
21. Determine from the degree of an alcohol whether it will react by an E1 or E2 mechanism.

Chapter 4

1. Recall the general features (hybridization, typical bond angles etc) of alkenes, including restricted rotation, stereoisomerism and relative stability.
2. Apply the IUPAC nomenclature system to alkenes, including common names for groups derived from alkenes, in order to generate a chemical structure from a name provided.
3. Calculate degrees of unsaturation for a given organic formula that contains some or all of the following elements: C, H, N, O, X (X = F, Cl, Br, I) *(Chem 132)*
4. Name alkenes using the *cis* and *trans* prefixes, which are appropriate for disubstituted alkenes, and the *E* and *Z* prefixes, which are appropriate for all alkenes that show stereoisomerism at the double bond. *(Chem 132)*
5. Relate the physical properties of alkenes including solubility, melting point and boiling point trends to their structure. *(Chem 132)*
6. Recall the relative stability of 1°, 2° and 3° carbocations.
7. Justify the relative stability of 1°, 2° and 3° carbocations, making reference to inductive and hyperconjugation effects.
8. Recognize a situation where a carbocation shift (1,2-hydride shift and 1,2-alkyl shift) will occur. and draw the carbocation resulting from a shift.
9. Write a chemical equation for the reaction of an alkene with HX (hydrohalogenation; X = Cl, Br, I) considering stereochemistry and regiochemistry in predicting the product.
10. Write a chemical equation for the reaction of an alkene with H_2O (or an alcohol) and a catalytic amount of a non-nucleophilic acid (hydration) considering stereochemistry and regiochemistry in predicting the product.
11. Write a chemical equation for the reaction of an alkene with H_2O (or an alcohol) via oxymercuration–reduction (hydration) considering stereochemistry and regiochemistry in predicting the product.
12. Write a chemical equation for the reaction of an alkene with X_2 (X = Cl, Br; halogenation) considering stereochemistry and regiochemistry in predicting the product.

13. Write a chemical equation for the reaction of an alkene with X_2 and H_2O or ROH (X = Cl, Br; R = alkyl group; halohydrin) considering stereochemistry and regiochemistry in predicting the product.
14. Write a chemical equation for the reaction of an alkene with a peroxyacid considering stereochemistry and regiochemistry in predicting the product.
15. Write a chemical equation for the reaction of an alkene with BH_3 (or an alkylborane) followed by OH^- and H_2O_2 (hydroboration–oxidation) considering stereochemistry and regiochemistry in predicting the product.
16. Write a chemical equation for the reaction of an alkene with H_2 considering catalyst, stereochemistry and regiochemistry in predicting the product.
17. Describe the theoretical basis of the Markovnikov rule, with reference to carbocation intermediates and apply the Markovnikov rule to predict the constitutional isomer that forms from addition of a reagent to an unsymmetrical alkene.
18. Write an electron-pushing mechanism for the reaction of an alkene with HX (hydrohalogenation; X = Cl, Br, I) considering stereochemistry and regiochemistry in predicting the product.
19. Write an electron-pushing mechanism for the reaction of an alkene with H_2O (or an alcohol) and a catalytic amount of a non-nucleophilic acid (hydration) considering stereochemistry and regiochemistry in predicting the product.
20. Write an electron-pushing mechanism for the oxymercuration part of the oxymercuration–reduction considering stereochemistry and regiochemistry in predicting the product.
21. Write an electron-pushing mechanism for the reaction of an alkene with X_2 (X = Cl, Br; halogenation) considering stereochemistry and regiochemistry in predicting the product.
22. Write an electron-pushing mechanism for the reaction of an alkene with X_2 and H_2O or ROH (X = Cl, Br; R = alkyl group; halohydrin formation) considering stereochemistry and regiochemistry in predicting the product.
23. Write an electron-pushing mechanism for the reaction of an alkene with a peroxyacid considering stereochemistry and regiochemistry in predicting the product.
24. Draw and describe a transition state structure to explain the stereoselectivity observed in hydroboration of an alkene.
25. Explain the observed stereoselectivity (e.g. syn vs. anti addition) for addition reactions of alkenes referring to the details of the reaction mechanism.
26. Explain the observed regioselectivity of the halohydrin formation reaction on unsymmetrical alkenes.
27. Explain the relative stability of alkenes with reference to number of substituents and cis,trans isomerization.

Chapter 12 (sections 12.2 through 12.7)

1. Recall the relative stability of 1°, 2°, 3°, allylic, and benzylic radicals.
2. Justify the relative stability of 1°, 2°, 3°, allylic, and benzylic radicals, making reference to inductive, hyperconjugation, and delocalization effects as appropriate.
3. Write a chemical equation for for the halogenation of alkanes with X_2 (X = Cl, Br), considering stereochemistry and regiochemistry in predicting the product.
4. Write a chemical equation for the allylic halogenation with *N*-bromosuccinimide (NBS), considering stereochemistry and regiochemistry in predicting the product.
5. Write a chemical equation for the the hydrohalogenation of alkenes with HBr, considering stereochemistry and regiochemistry in predicting the product.
6. Write an electron-pushing mechanism for the halogenation of alkanes with X_2 (X = Cl, Br), including initiation, propagation, and termination.
7. Write an electron-pushing mechanism for allylic halogenation with *N*-bromosuccinimide (NBS), including initiation, propagation and termination.
8. Write an electron-pushing mechanism for the hydrohalogenation of alkenes with HBr, including initiation, propagation and termination.
9. Apply the reactivity–selectivity principle to explain the selectivity observed in radical halogenation of alkanes.
10. Use thermodynamic data provided to explain why radical hydrohalogenation of alkenes works for HBr but not for HCl or HI.

Chapter 20 (sections 20.7 and 20.9)

1. Write a chemical equation for the oxidation of alkenes to 1,2-diols (OsO_4 and H_2O_2), considering stereochemistry and regiochemistry in predicting the product.
2. Justify the observed regiochemistry in the oxidation of alkenes to 1,2-diols (OsO_4 and H_2O_2) by describing the cyclic osmate intermediate.
3. Write a chemical equation for the oxidative cleavage of alkenes by ozone (O_3) to aldehydes, ketones, and carboxylic acids, considering stereochemistry, regiochemistry, and type of workup (oxidative or reductive) in predicting the product.
4. Draw the cyclic intermediates (molozonide, ozonide) formed in the oxidative cleavage of alkenes by ozone (O_3).
5. Determine the structure of an alkene (or dialkene, trialkene, etc.) from an analysis of the ozonolysis products.

Chapter 6 (sections 6.1 through 6.12)

1. Know the general features (hybridization, typical bond angles, etc.) of alkynes.
2. Know the nomenclature of alkynes, including common names for groups derived from alkynes.
3. Know two reactions for the preparation of alkynes (via terminal alkynes and via alkenes).
4. Write a chemical equation for the preparation of acetylide anions using strong base and a terminal alkyne.
5. Write a chemical equation for the reaction of an alkyne with both 1 equiv and 2 equiv of HX (hydrohalogenation; X = Cl, Br, I) considering stereochemistry and regiochemistry in predicting the products.
6. Write a chemical equation for the reaction of an alkyne with H_2O and catalytic amounts of $HgSO_4$ and a non-nucleophilic acid (hydration) considering stereochemistry and regiochemistry in predicting the product (enol and keto form).
7. Write a chemical equation for the reaction of an alkyne with both 1 equiv and 2 equiv of X_2 (X = Cl, Br; halogenation) considering stereochemistry and regiochemistry in predicting the products.
8. Write a chemical equation for the reaction of an alkyne with BH_3 (or an alkylborane) followed by OH^- and H_2O_2 (hydroboration–oxidation) considering stereochemistry and regiochemistry in predicting the product (enol and keto form).
9. Write a chemical equation for the reaction of an alkyne with both 1 equiv and 2 equiv of H_2 considering selection of catalyst, stereochemistry and regiochemistry in predicting the product.
10. Apply the Markovnikov rule to predict the constitutional isomer that forms from addition to terminal alkynes.
11. For selected addition reactions of alkynes (hydrohalogenation, hydration, halogenation, and hydroboration-oxidation), be able to draw electron-pushing mechanisms for the reactions.
12. Know the stereochemistry of addition reactions of alkynes, (in the case of halogenation and hydrohalogenation, show the products of adding both 1 and 2 equiv of reagent) and be able to rationalize the observed stereochemistry (syn vs. anti addition) based on the details of the reaction mechanism.
13. Be able to draw the keto and enol forms of a tautomeric pair of isomers. Given one form, be able to draw the other. Know which form is the more stable form.
14. Know the reactions of acetylide anions with alkyl halides and epoxides, including stereo- and regiochemistry. (The epoxide reaction is in chapter 10.)

Chapter 10 (sections 10.6 through 10.8; see more of chapter 10 above)

22. Write a chemical equation for the reaction of an ether with 2 equiv of concentrated HBr or HI.
23. Write an electron-pushing mechanism for the reaction of an ether with 2 equiv of concentrated HBr or HI, being mindful that the type of mechanism is related to the degree of the alkyl groups of the ether.
24. Write a chemical equation for the formation of an epoxide: (a) via a peroxyacid *(Chapter 4)* or (b) via a halohydrin *(Chapter 8),* considering stereochemistry and regiochemistry in predicting the product.
25. Write a chemical equation for the reaction of an epoxide with an acidic reagent (e.g., HX or H_2SO_4 and an alcohol) considering stereochemistry and regiochemistry in predicting the product.
26. Write an electron-pushing mechanism for the reaction of an epoxide with an acidic reagent (e.g., HX or H_2SO_4 and an alcohol) considering stereochemistry and regiochemistry in predicting the product.
27. Write a chemical equation for the reaction of an epoxide a strong nucleophile under neutral of basic conditions, considering stereochemistry and regiochemistry in predicting the product.
28. Write an electron-pushing mechanism for the reaction of an epoxide a strong nucleophile under neutral of basic conditions, considering stereochemistry and regiochemistry in predicting the product.
29. Write a series of chemical equations for the formation of a quaternary trimethylalkylammonium hydroxide from an alkyl halide.
30. Predict the major product obtained from heating a quaternary trimethylalkylammonium hydroxide.
31. Write an electron-pushing mechanism for the reaction that occurs upon heating a quaternary trimethylalkylammonium hydroxide.

General.

1. Be able to integrate your knowledge of reactions that transform functional groups, so that given a starting material and a product, you can propose a reasonable multi-step synthesis (2-6 steps) to get from the starting material to the product.