Practice Sets, Organic Chemistry I Table of Contents

- Online Organic Chemistry I, Chem 350,
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- For full class website, see

https://collaborate.mnstate.edu/public/blogs/jasperse/online-organic-chemistry-i-350-fall-spring/

Test	Page
Test 1 PS#1: Arrow-Pushing/Mechanisms Practice Set	3
Test 1 PS#2: Acid Base Practice Set	7
Test 1 PS#3: 3-D Structure-Drawing Practice Set	11
Test 1 PS#4: Isomers Practice Practice Set	15
Test 1 PS#5: Newman Practice Practice Set	17
Test 1 PS#6: Cyclohexane Chair Practice Set	21
Test 2 PS#1: PS1: Radical Bromination Practice Set	25
Test 2 PS#2: PS2: Stereochemistry Practice Set	27
Test 2 PS3: 2 Extra Mechanisms + Product Predict Practice	31
Test 3 PS1: Miscellaneous and Mechanisms Principles	35
Test 3 PS2: Test 3 Extra Mechanisms Practice	39
Test 3 PS3: Test 3 Alkene Reactions Practice	43
Test 3 PS4: Test 3 Extra Synthesis Practice (6 pages)	45
Test 4 PS1: Test 4 HBr Addn to Dienes; NBS Allylic Bromination	51
Test 4 PS2: Test 4 Conjugation-Allylic-Diels-Alder Practice	55
Test 4 PS3: Aromatic Substitution Mechanisms (Products Provided)	57
Test 4 PS4: Aromatic Substitution Product Prediction/Mechanisms/Synthesis Design Practice	59

Organic Chemistry

Jasperse Mechanisms Practice. See Page 3 for a summary of mechanisms principles.

Arrow-Pushing Practice, Page 1:

- Draw arrows for each of the steps in the following reactions.
- I won't require this on tests, but you may find it useful to include all lone-pairs on atoms that react.
- I won't require this on tests, but you may find it useful to draw in all hydrogens on atoms that react. (It is not useful to draw in all H's on atoms that don't react.)
- Remember that <u>arrows track the movement of electrons</u>, so an arrow should go from the source of electrons and point directly to the atom that accepts them.

1.
$$\bigoplus_{H}^{O}$$
 + H-Br \bigoplus_{H}^{O} \bigoplus_{H}^{H} \bigoplus_{H}^{O} $\bigoplus_{H}^$

2.
$$S_N^2$$
 B_r + NaI I + NaBr

5. E1
$$\xrightarrow{\text{Br}}$$
 $\xrightarrow{\text{H}_2\text{O}}$ $\xrightarrow{\text{H}}$ $\xrightarrow{\text{H}_3\text{O}}$ $\xrightarrow{\text{H}}$ $\xrightarrow{\text{H}_3\text{O}}$

3.
$$H \xrightarrow{H_2O} + H_3O^+$$

$$4. \text{ Ph} \xrightarrow{\text{Br}} \longrightarrow \text{Ph} \xrightarrow{\text{Ph}} + \text{Br}$$

$$5.$$
 Ph $\xrightarrow{\text{Br}}$ $\xrightarrow{\text{OH}}$ $\xrightarrow{\text{OH}}$ $\xrightarrow{\text{Ph}}$ $+$ Br

7.
$$PH \oplus^D + Br \xrightarrow{Br} D$$

9.
$$\Theta_{OCH_3}$$
 OCH_3

$$10. \text{ Phr} \longrightarrow \text{ Phr} \longrightarrow$$

Some Arrow-Pushing Guidelines

- 1. Arrows follow electron movement.
- 2. Some rules for the appearance of arrows
 - The arrow must begin from the electron source. There are two sources:
 - a. An atom (which must have a lone pair to give)
 - b. A bond pair (an old bond that breaks)
 - An arrow must always point directly to an <u>atom</u>, because when electrons move, they always go to some new atom.
- 3. Ignore any Spectator Atoms. Any metal atom is always a "spectator"
 - When you have a metal spectator atom, realize that the non-metal next to it must have negative charge
- 4. Draw all H's on any Atom Whose Bonding Changes
- 5. Draw all lone-pairs on any Atom whose bonding changes
- 6. **KEY ON BOND CHANGES**. Any two-electron bond that changes (either made or broken) must have an arrow to illustrate:
 - where it came from (new bond made) or
 - an arrow showing where it goes to (old bond broken)

7. Watch for Formal Charges and Changes in Formal Charge

- If an atom's charge <u>gets more positive</u> ⇒ it's donating/losing an electron pair ⇒ <u>arrow must emanate from that atom or one of it's associated bonds.</u> There are two "more positive" transactions:
 - When an anion becomes neutral. In this case, an arrow will emanate from the atom. The atom has donated a lone pair which becomes a bond pair.
 - When a neutral atom becomes cationic. In this case, the atom will be losing a bond pair, so the arrow should emanate from the bond rather than from the atom.
- If an atom's charge <u>gets more negative</u> ⇒ it's accepting an electron pair ⇒ <u>an arrow must point to that atom</u>. Ordinarily the arrow will have started from a bond and will point to the atom.

8. When bonds change, but Formal Charge Doesn't Change, A "Substitution" is Involved

- Often an atom gives up an old bond and replaces it with a new bond. This is "substitution".
- In this case, there will be an incoming arrow pointing directly at the atom (to illustrate formation of the new bond), and an outgoing arrow emanating from the old bond that breaks

Organic Chemistry Jasperse Acid-Base Practice Problems

A. Identify each chemical as either an "acid" or a "base" in the following reactions, and identify "conjugate" relationships.

- -You should have one acid and one base on each side
- -You should have two conjugate pairs

$$CH_3CH_2OH + NaOH$$
 $CH_3CH_2ONa + H_2O$

$$_3$$
 CH₃CH₂CO₂H + CH₃MgBr \longrightarrow CH₃CH₂CO₂MgBr + CH₄

$$_{4}$$
 CH₃OH + H₃O⁺ \longrightarrow H₂O + CH₃OH₂⁺

$$_{5}$$
 CH₃CH₂NH₃⁺ + CH₃OH \longrightarrow CH₃CH₂NH₂ + CH₃OH₂⁺

B. Choose the More Basic for Each of the Following Pairs (Single Variable). You can use stability to decide.

$$NH_3$$
 $NaNH_2$

7. NaOH
$$H_2O$$

Test 1 PS#2: Acid Base Practice Set

C. Rank the basicity of the following sets: Multiple Variable Problems

12. CH₃MgBr CH₃NHNa

 CH_3NH_2

13 \\C)

ONa

15.

$$\sim$$
NH

D. Choose the More Acidic for Each of the Following Pairs: Single Variable Problems

16.

$$NH_{3} \\$$

$$\oplus$$
 NH₄

17.

$$\nearrow^{\oplus}_{\mathsf{OH}_2}$$

$$\nearrow$$
OH

18.

$$\nearrow$$
NH₂

NH₂

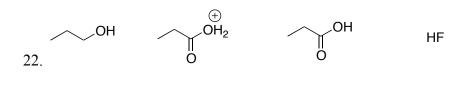
20.

21.

$$\nearrow$$
NH₂

Test 1 PS#2: Acid Base Practice Set

E. Rank the acidity of the following sets: Multiple Variable Problems



$$NH_2$$
 OH H_2O

OH OH
$$NH_2$$
 24.

OH
$$NH_3$$
 NH_2 NH_2

$$H_{e}O$$
 OH NH_{2} OH

F. Draw arrow to show whether equilibrium favors products or reactants. (Why?)

27.
$$\bigcirc$$
OH + HOH \bigcirc OH \bigcirc OH

- G. For the following acid-base reaction,
 - a. put a box around the weakest base in the reaction
 - b. put a circle around the weakest acid
 - c. draw an arrow to show whether the equilibrium goes to the right or left. (4pt)

Test 1 PS#2: Acid Base Practice Set

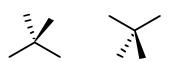
MOLECULAR STRUCTURE

For each of the following molecules, draw their 3-D structure. You will usually need to have converted the condensed structure into a Lewis structure. Draw in all hydrogens.

- For molecules involving lone-pairs, draw them with the lone pairs shown. While this may not be required for test questions, VSEPR is impacted by lone pairs, so they indirectly impact where atoms are located. For this exercise, try to show where in space the lone pairs will be. To do so, put a "double dot" on the end of a stick (in place), or wedge (in front) or hash (in back).

Guidelines for Drawing Models:

- A. 3-D Perspective
 - 1. Keep as many atoms as possible in a single plane (plane of the paper) by zigzagging. Connections within the paper are drawn with straight lines.
 - 2. Use wedges to indicate atoms that are in front of the plane.
 - 3. Use hashes to indicate atoms behind the plane.
- B. For any tetrahedral atom, only 2 attachments can be in the plane, 1 must be in front, and 1 behind.
 - -if the two in the plane are "down", the hash/wedge should be up
 - -if the two in plane are "up", the hash/wedge should be down.
 - -the hash/wedge should never point in same direction as the in-plane lines, or else the atom doesn't looks tetrahedral
 - -for polyatomic molecules, <u>it is strongly preferable to NOT have either of the in-</u> plane atoms pointing straight up. Straight-up in-plane atoms do not lend themselves to extended 3-D structures.



Good! Look tetrahedral



Bad! These don't look tetrahedral!

- 1. ALKANE. butane, CH₃CH₂CH₂CH₃-take the chain and wiggle around all the single bonds.
 -The most stable actual shape is the one with the carbons zig-zagged and co-planar.
 -Notice the symmetry possible.
- 2. ALKANE. Pentane, CH₃CH₂CH₂CH₂CH₃

- 3. HALOALKANE. 2-bromobutane, CH₃CHBrCH₂CH₃ -notice that if the 4 carbons are co-planar zig-zagged, the attached Br can't be in the same plane. -try to compare with a partner 2 cases in which Br is in front versus behind. Are they the same molecule, or isomers?
- 4. ALKENE. Draw both: a) trans-2-butene, CH₃CH=CHCH₃ and b) cis-2-butene (trans means the two CH₃ groups are on the opposite sides of the double bond; cis means they are on same side) -notice that not only the 2 double-bonded C's but also the four atoms directly attached are all co-planar.

- 5. ALKYNE. 2-butyne, CH₃CCCH₃ -draw Lewis structure first
- 6. WATER. H₂O
- 7. ALCOHOL. Ethanol, CH₃CH₂OH

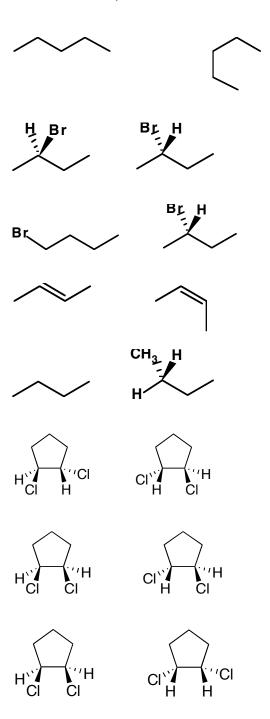
8. ETHER. Diethyl ether, CH₃CH₂OCH₂CH₃

- 9. FORMALDEHYDE. CH₂O.
- -for 9-16, make sure you draw the Lewis structure before you build models and draw the 3-D picture. If you don't know the connectivity, you have no chance!
- 10. ALDEHYDE. CH₃CH₂CHO.
- 11. KETONE. CH₃CH₂C(O)CH₂CH₃.
- 12. ACID. CH₃CH₂CO₂H.
- 13. ESTER. CH₃CH₂CO₂CH₃.
- 14. AMMONIA. NH₃
- 15. AMINE. (CH₃CH₂)₂NH
- 16. AMIDE CH₃CONH₂.

SAME OR DIFFERENT? Classify the following pairs as "same" or "isomers". Rules:

- 1. Structures which can be interchanged or made equivalent by <u>rotations around single bonds</u> are considered to be the <u>same</u>.
- 2. "<u>Isomers</u>" are things with the <u>same formula</u> that can't be made superimposable by simple rotations around single bonds.

(For class, we will eventually need to be able to distinguish "structural isomers" from "stereoisomers", so try to do that if possible. And within stereoisomers, by test two we'll need to distinguish between "enantiomers", which are mirror image isomers; versus "diastereomers", which are cis/trans isomers.)



Test 1 Isomers/Resonance Recognition Practice.

Note: You should be able to practice the first page fairly early during the class lectures.

The second page you won't be able to process until almost the end, after completion of the chapter dealing with Newman Projections and Cyclohexane Chair conformations.

For the following pairs, classify the relationship between each pair as either:

- same compound
- structural isomers
- resonance structures
- stereoisomers

For the following pairs, classify the relationship between each pair as either:

- same compound
 structural isomers
- resonance structures
 stereoisomers

Newman Projection Practice Test 1 PS#5: Newman Practice Practice Set

Organic Chemistry I – Jasperse Newman Projection Practice (See page 4 for some summary of operations/steps for handling Newman projections)

A. For each of the following, draw the best and worst Newman projection, relative to the bond indicated.

- 1. Butane, relative to the C2-C3 bond
- 2. 1-chloropropane, relative to the C1-C2 bond
- 3. 2-methylbutane, relative to the C2-C3 bond
- 4. 2,2-dimethylbutane, relative to the C2-C3 bond
- 5. 2-chloro-2-methylpentane, relative to the C2-C3 bond Note: Cl is smaller than methyl

B. Rotation Barriers.

- 6. Rank the rotation barriers relative to the indicated bonds, with 1 have the largest barrier
 - For convenience, Et = ethyl and iPr = isopropyl
 - Assume that a halogen, OH, or NH₂ is smaller than a CH₃ or any other alkyl group.

C. For each of the following, use the words torsional and/or steric to explain why the first conformation is more stable than the second. (The answer key and explaining video will be a bit more detailed as appropriate.)

- a. For each, note if any "total eclipse" steric interactions exist (two non-hydrogens eclipsing)
- b. For each, note if any "gauche" steric interactions exist (two non-hydrogens gauche)

7.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
8.	CH ₃ CH ₃ H H CH ₃	
9.	CH ₃ CH ₃ ICH ₃ H H H H	
10.	H H H H	
11.	CH ₃ CH ₃ H ₃ C H H H H iPr CH ₃	
12.	iPr iPr iCH ₃ HCH ₃ HCH ₃	
13.	CH ₃ CH ₃ H ₃ C H H CH ₃ CH ₃	

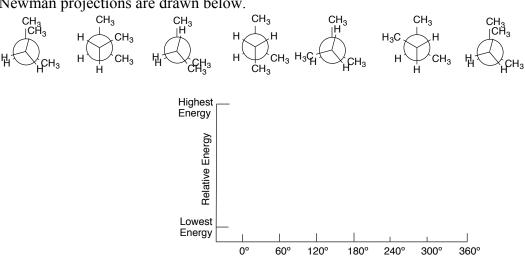
D. Newman Projection Energy Diagrams.

14. Draw a qualitative energy diagram for CH₃CH₂CH₂CH₂CH(CH₃)₂, relative to the bond between the two CH2 carbons. The Newman projections are drawn below, using "iPr" as an abbreviation for the isopropyl CH(CH₃)₂ group. Put "S" (for staggered) by any "staggered" conformation, and "E" (for eclipsed) by an eclipsed conformation.

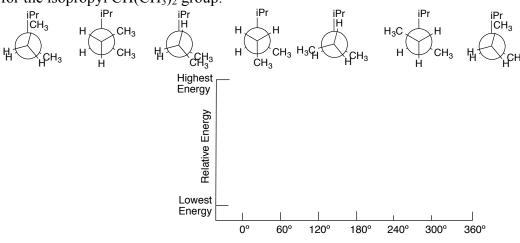
15. Draw a qualitative energy diagram for CH₃CH₂CH(CH₃)₂, relative to the C2-C3 bond. The Newman projections are drawn below.

180°

240°



16. Draw a qualitative energy diagram for CH₃CH₂CH(CH₃)CH(CH₃)₂, relative to the bond between the CH₂ and CH carbons. The Newman projections are drawn below, using "iPr" as an abbreviation for the isopropyl CH(CH₃)₂ group.



Steps for processing a di-substituted cyclohexane chair:

Summary: Draw chairs; install sticks; install substituents appropriately

- 1. Draw both "right-" and "left-handed" chairs
- 2. Draw in "axial" sticks on the relevant carbons; then draw in "equatorial" sticks on the relevant carbons
 - Use the left-most carbon for your first substituted carbon
- 3. On the left-most carbon, put your first substituent in on both chairs.
 - It should be equatorial in the "right-handed" chair, and axial in the other.
- 4. Use "upper/downer" logic to decide whether the second substituent belongs eq or ax on the first chair (then make it the opposite on the second chair)
 - Draw in the H's on the relavent carbons
- 5. Are the two substituents eq/eq, eq/ax, or ax/ax? This will help recognize relative stability
- 6. If one subst. is forced axial, the preferred chair has the bigger subst. equatorial
- 7. The best cis vs trans isomer has both substituents equatorial.
- 8. Note: To draw and identify the best cis versus trans, just draw a chair with both groups equatorial, and then identify whether that is cis or trans

Steps for Drawing the Best Newman projection

Summary: Draw staggered sticks; install substituents appropriately

- 1. Draw a staggered Newman projection, with three sticks on the "back" carbon and three on the "front". Have a stick up on the back carbon, and one down on the front.
- 2. Draw your biggest substituent on the back carbon on the "up" stick
- 3. Draw your biggest substituent on the front on the "down" "anti" stick
- 4. Fill in the other two back attachments on the other two back-carbon sticks.
- 5. Fill in the other two front attachments on the other two front-carbon sticks.

Steps for Drawing the Worst Newman projection

Summary: Draw eclipsed sticks; install substituents appropriately

- 1. Draw an eclipsed Newman projection, with three sticks on the "back" carbon and three on the "front". Have a stick up on both the back and front carbons.
- 2. Draw your biggest substituent on the back carbon on the "up" stick
- 3. Draw your biggest substituent on the front on the "up" "totally eclipsed" stick
- 4. Fill in the other back and front attachments.

Note: The more severe the eclipsing in the "worst" projection, the greater the rotation barrier

Tips for creating a Newman Projection Energy Diagram

- 1. Use the "worst" (totally eclipsed version) as 0° and 360°.
- 2. 120° and 240° will be the other "eclipsed" conformations => energy crests.
- 3. 60°, 180°, and 300° will be the staggered conformations => energy valleys
- 4. 60° and 300° will be the other two staggered conformations (gauche) => energy valleys.
- 5. To compared the relative energies of the eclipsed crests, evaluate the sizes of the eclipsing substituents (when two non-hydrogens eclipse) and
- 6. To compare the relative energies of the staggered valleys, evaluate the number/severity of gauche interactions

1

Test 1 PS#6: Cyclohexane Chair Practice Set

Cyclohexane Chair Practice

A. Draw the two chair conformations for each of the following di-substituted cyclohexanes. Circle the more stable one.

• For convenience, you may abbreviate the substituents (Me, Et, Pr, Bu, iPr, tBu, or the like rather than drawing out methyl, ethyl, propyl, butyl, isopropyl, t-butyl....)

	 rather than drawing out methyl, ethyl, propyl, butyl, isopropyl, t-butyl) Assume that a halogen, OH, or NH₂ is smaller than a CH₃ or any other alkyl group. Remember to draw in the hydrogens on each of the "substituted" carbons
1.	Cis-2-bromo-1-methylcyclohexane
2.	Cis-3-isopropyl-1-methylcyclohexane
3.	Cis -4-ethyl-1-hydroxycyclohexane
1	trans-2-butyl-1-isopropylcyclohexane
т.	trans-2-outyr-1-isopropyreyeronexane

- 5. trans-3-t-butyl-1-methylcyclohexane
- 6. trans -4-chloro-1-propylcyclohexane

Cyclohexane Chair Practice Test 1 PS#6: Cyclohexane Chair Practice Set

3	For	each	of the	following,	do	two	things:	
J.	TOI	cacii	or the	ionowing,	uv		unings.	

- A. draw the most stable chair form for the more stable stereoisomer for the molecule
- B. identify whether the more stable stereoisomer is cis or trans.
- 7. 1-butyl-2-methylcyclohexane
- 8. 3-t-butyl-1-methylcyclohexane
- 9. 1,4-diethylcyclohexane

C. For each of the following, do two things:

- A. draw the most stable chair form
- B. identify whether the more stable stereoisomer would be the cis or the trans stereoisomer
- 10. Cis-2-chloro-1-ethylcyclohexane
- 11. trans-3-butyl-1-isopropylcyclohexane

12. trans -4-hydroxy-1-t-butylcyclohexane

Test 1 PS#6: Cyclohexane Chair Practice Set

Organic Chemistry I Jasperse Newman Projections and Cyclohexane Chairs. Steps.

Steps for processing a di-substituted cyclohexane chair:

Summary: Draw chairs; install sticks; install substituents appropriately

- 1. Draw both "right-" and "left-handed" chairs
- 2. Draw in "axial" sticks on the relevant carbons; then draw in "equatorial" sticks on the relevant carbons
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- 3. On the left-most carbon, put your first substituent in on both chairs.
 - It should be equatorial in the "right-handed" chair, and axial in the other.
- 4. Use "upper/downer" logic to decide whether the second substituent belongs eq or ax on the first chair (then make it the opposite on the second chair)
 - Draw in the H's on the relavent carbons
- 5. Are the two substituents eq/eq, eq/ax, or ax/ax? This will help recognize relative stability
- 6. If one subst. is forced axial, the preferred chair has the bigger subst. equatorial
- 7. The best cis vs trans isomer has both substituents equatorial.
- 8. Note: To draw and identify the best cis versus trans, just draw a chair with both groups equatorial, and then identify whether that is cis or trans

Steps for Drawing the Best Newman projection

Summary: Draw staggered sticks; install substituents appropriately

- 1. Draw a staggered Newman projection, with three sticks on the "back" carbon and three on the "front". Have a stick up on the back carbon, and one down on the front.
- 2. Draw your biggest substituent on the back carbon on the "up" stick
- 3. Draw your biggest substituent on the front on the "down" "anti" stick
- 4. Fill in the other two back attachments on the other two back-carbon sticks.
- 5. Fill in the other two front attachments on the other two front-carbon sticks.

Steps for Drawing the Worst Newman projection

Summary: Draw eclipsed sticks; install substituents appropriately

- 1. Draw an eclipsed Newman projection, with three sticks on the "back" carbon and three on the "front". Have a stick up on both the back and front carbons.
- 2. Draw your biggest substituent on the back carbon on the "up" stick
- 3. Draw your biggest substituent on the front on the "up" "totally eclipsed" stick
- 4. Fill in the other back and front attachments.

Note: The more severe the eclipsing in the "worst" projection, the greater the rotation barrier

Tips for creating a Newman Projection Energy Diagram

- 1. Use the "worst" (totally eclipsed version) as 0° and 360°.
- 2. 120° and 240° will be the other "eclipsed" conformations => energy crests.
- 3. 60°, 180°, and 300° will be the staggered conformations => energy valleys
- 4. 60° and 300° will be the other two staggered conformations (gauche) => energy valleys.
- 5. To compared the relative energies of the eclipsed crests, evaluate the sizes of the eclipsing substituents (when two non-hydrogens eclipse) and
- 6. To compare the relative energies of the staggered valleys, evaluate the number/severity of gauche interactions

Test 1 PS#6: Cyclohexane Chair Practice Set

Organic Chemistry I Jasperse

Test 2, Radical bromination: Extra Radical Bromination Product Prediction and Mechanism Practice Problems

Note: In each of the following, draw the MAJOR mono-brominated product, and/or draw the mechanism (full arrow-pushing) for the propagation steps in the radical mechanism. Initiation need not be illustrated..

$$2.$$
 Br_2, hv
 Br

Note: Was error in original draft of this problem. And answer key is corrected, but the explanatory video will not really fit this specific structure.

Organic Chemistry I

Test 2

Extra Stereochemistry Practice Problems

Page 1: Designate R/S Page 2: Chiral or Achiral? Page 3: Same, Enantiomer, or Diastereomer?

A. Designate the R/S configuration for any chiral centers in the following molecules.

H Br

H₂N H

$$_{10.}$$
 HO $\stackrel{\text{H. Br}}{\smile}$ OH

B. Identify each of the following molecule as chiral or achiral. (By circling the chiral ones.) Write "meso" where it applies. (In other words, if it is achiral despite having chiral centers).

C. Mark the relationships between the following structures as either "same", "enantiomers", or "diastereomers".

Note: In each of these cases, I am asking you to draw the mechanism for the product shown. In some cases where both elimination and substitution may occur, there may be another product in addition to the one shown. And in cases where elimination is happening, there may be an additional structural isomer that could form. Regardless, you should be able to draw the mechanism for how the product that IS shown would have actually formed.

3.

9.
$$Br_2$$
, hv Br

$$Br_2$$
, hv Br

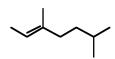


In these problems, both predict the major product and draw the mechanism for its formation. If you expect both substitution and elimination to occur, draw both (bit if there is more than one alkene isomer possible, just draw the one that would form to greater extent,) and draw the mechanism for both. ASSUME ANYTHING THAT STARTS CHIRAL IS OPTICALLY ACTIVE TO START.

Organic Chemistry I

Jasperse Some Chapter 7 Quiz-Like Practice, But NOT REQUIRED. Answer key available: http://web.mnstate.edu/jasperse/Chem341/Quizzes/Quiz -341-alkenes + mech-Answers.pdf

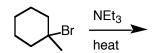
- 1. How many elements of unsaturation are present for a molecule with formula C₅H₅NO₂?
 - a. 0
 - b. 1
 - c. 2
 - d. 3
 - e. 4
 - f. 5
- 2. Provide the proper IUPAC name for the alkene shown below.



3. Which of the following is correct for the geometry of the double bond shown below?



- a. E
- b. Z
- c. Neither E nor Z
- 4. Draw and all structural and stereoisomeric <u>alkenes</u> (no alkanes or cyclic compounds) with the formula C_4H_8 . (stereoisomers included)
- 5. Choose the most stable alkene among the following. (may help to draw each of them out first...)
 - a. 1-methylcyclohexene
 - b. 3-methylcyclohexene
 - c. 4-methylcyclohexene
 - d. They are all of equal stability
- 6. a) Draw and circle the major alkene product that would result from the following reaction.
 - b) In addition, draw any other minor isomers that would form, but don't draw the same isomer twice.



- 7. a) Draw and <u>circle the major alkene product</u> for the following reaction. (There may be a lot of $S_N 2$ product that forms as well, but you need not draw that.)
 - b) In addition, draw any other minor isomers that would form, but don't draw the same isomer twice.

- 8. a) Draw and <u>circle the major alkene product</u> for the reaction shown. (There may be some S_N1 product that forms as well, but you need not draw that.)
 - b) In addition, draw any other minor isomers that would form, but don't draw the same isomer twice.
 - c) Draw a detailed, step-by-step mechanism for the pathway to the major product.

9. Provide the chemicals necessary for transforming 2-methylheptane (**A**) into 2-methyl-1-heptene (**C**), and draw the structure for the chemical **B** which you can make from **A** and which serves as a precursor to **C**. Above the arrows write in recipes for the $A \rightarrow B$ transformation and for the $B \rightarrow C$ transformation.

For each of the following reactions, write whether the mechanism would be radical, cationic, or anionic?

$$\bigcap_{1.} \bigcap_{1.} \stackrel{\mathsf{HNO}_3}{\bigcap_{1.}} \bigcap_{1.} \bigcap$$

$$O_2$$
 O_2 O_2 O_2 O_3 O_4 O_4 O_5 O_4 O_5 O_6 O_7 O_8 O_8

$$H_2O, H^+$$
 OH OH

8.
$$H_3CO \rightarrow OCH_3 \rightarrow H_2O, H^+ \rightarrow O$$

9.
$$\stackrel{\text{OLi}}{\longleftarrow}$$
 $\stackrel{\text{OLi}}{\longleftarrow}$ $\stackrel{\text{OLi}}{\longleftarrow}$

Draw the arrow(s) for each of these steps.

$$4. \text{ Ph} \xrightarrow{\text{Br}} \longrightarrow \text{Ph} \xrightarrow{\text{Ph}} + \text{Br}$$

7.
$$PH \oplus D + Br \ominus \longrightarrow PH \oplus D$$

9.
$$\Theta_{OCH_3}$$
 OCH_3

$$10. \text{ Ph} \longrightarrow \text{Br-Cl} \longrightarrow \text{Ph} \longrightarrow \text{Ph} \longrightarrow \text{Br}$$

Test 3 Extra Mechanism Practice Problems

Page 1: Eliminations to make Alkenes. Page 2+3: Reactions of Alkenes

Note: In each of these cases, I am asking you to draw the mechanism for the product shown, even if in some cases there may be other products formed as well. In these problems I'm telling you what type of mechanism is involved; I won't on a test! \odot

Ch. 7 Elimination Reactions

E2, Small/Normal Base

E2, Bulky Base

E2, Bulky Base using Neutral NEt₃

H⁺-Catalyzed Dehydration

7. HO
$$H_2SO_4$$

Ch. 8 Reactions.

Ionic H-X Addition

11. Ph
$$\stackrel{\text{H+, H}_2O}{\longrightarrow}$$
 Ph

H⁺ catalyzed H₂O Addition

$$H^+, H_2O$$
 OH

X₂ addition

X₂ addition

14.

15.

$$\begin{array}{c|c} & \text{CI}_2 & \text{CI} \\ \hline & \text{H}_2\text{O} & & \\ \hline & \ddot{\text{O}}\text{H} \end{array}$$

X₂/H₂O addition

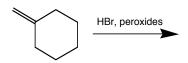
H⁺ catalyzed H₂O addition

Organic Chemistry I

Test 3 Extra Alkenes Reactions Practice Problems. (First half of the alkenes reactions only)

1. Draw the major product for the reaction shown. (There may be some side products or isomers formed in addition to the major products, but you don't need to draw them.) <u>Draw the mechanism</u>.

2. Draw the major product for the reaction shown. (There may be some side products or isomers formed in addition to the major products, but you don't need to draw them.) No mechanism required.



3. Draw the major product for the reaction shown. (There may be some side products or isomers formed in addition to the major products, but you don't need to draw them.) Draw the mechanism.

4. Draw the major product for the reaction shown. No mechanism required.

6. Draw the major product for the reaction shown. (There may be some side products or isomers formed in addition to the major products, but you don't need to draw them.)

7. Draw the major product for the reaction shown. Include stereochemistry. <u>Draw the mechanism, and make sure it accounts for the product stereochemistry.</u>

8. Draw the major product for the reaction shown. Include stereochemistry. <u>Draw the mechanism, and make sure it accounts for the product stereochemistry</u>. Also, make sure that your mechanism really gives the product that you show. (You may actually want to work the mechanism first, so you make sure you draw the product correctly.)

Test 3 PS4: <u>Test 3 Extra Synthesis Practice</u> (6 pages)

Organic Chemistry I

2.

Test 3 Extra Synthesis Practice Problems

Page 1: Synthesis Design Practice.

Page 2+3: Predict the Product Practice (including some that involve stereochemistry).

Page 4: Cis/trans Stereospecific reactions: which recipe to use; which E or Z alkene to use.

Page 5: Recognizing cationic/anionic/radical reactions, and reasonable intermediates/first steps

Page 6: Elements of unsaturation/hydrogenation problems; ozonolysis puzzle problems.

A. Provide reagents for the following transformations.

B. Draw the <u>major</u> product for each of the following reactions or reaction sequences. You needn't bother to show side products or minor products. For chiral molecules that are racemic, you needn't draw both enantiomers. BE CAREFUL TO SHOW THE CORRECT ORIENTATION, AND THE CORRECT STEREOCHEMISTRY IN CASES WHERE STEREOCHEM IS FACTOR. (3 points each).

2. NaBH₄

19.

$$21.$$
 \longrightarrow $\frac{Br_2}{}$

$$\begin{array}{c|c} & & \\ \hline 29. & & Ph \end{array} \begin{array}{c} \hline \begin{array}{c} CH_3CO_3H, \ H_2O \\ \hline \end{array}$$

$$\frac{1. O_3}{2. Me_2S}$$

C. Draw the alkene that would product the products shown. Make sure to make your drawing clear whether the starting alkene was E or Z.

35.
$$Cl_{2} \longrightarrow Ph \longrightarrow Cl$$

$$Br_{2}, H_{2}O \longrightarrow OH$$

$$Br_{3}CO_{3}H, H_{2}O \longrightarrow OH$$

$$OH$$
OH

41. OOPS, IGNORE THIS ONE
$$\frac{1. \ O_3}{2. \ Me_2 S}$$

D. What reagent(s) would you use to conduct the following transformations?

42. Ph
$$\stackrel{OH}{\longrightarrow}$$
 $\stackrel{OH}{\longrightarrow}$ $\stackrel{$

- E. Recognizing whether reaction mechanisms should be cationic, anionic, or radical; whether intermediates should be cationic, anionic, or radical; and recognizing what could be reasonably involved in the initial reaction step.
- 44. The transformation shown is common in many biological systems. Which of the following statements is definitely, absolutely **false**?
 - a. The first step in the mechanism probably involves protonation of the carbonyl oxygen.
 - b. The overall reaction involves an addition reaction
 - c. The mechanism is probably radical in nature
- 45. For the transformation shown, which of the following statements is definitely, absolutely **false**?
 - a. The first step in the mechanism probably involves protonation of a carbonyl oxygen.
 - b. The overall reaction involves a substitution reaction
 - c. The mechanism is probably anionic in nature
 - d. The first step in the mechanism involves ethoxide anion grabbing a hydrogen.
- 46. Shown is a reaction, and some possible intermediates along the mechanistic pathway. Given the reaction conditions shown, which of the following statements is true?
 - a. Structures **A** and **B** might be plausible intermediates; structure **C** definitely isn't
 - b. Structures **A** and **C** might be plausible intermediates; structure **B** definitely isn't
 - c. Structures **B** and **C** might be plausible intermediates; structure **A** definitely isn't
 - d. Structure **A** might be a plausible intermediates; structures **B** and **C** definitely aren't
- 47. Shown is a reaction, and some possible <u>intermediates</u> along the mechanistic pathway. Given the reaction conditions shown, which of the following statements is true?
 - a. Structures **A** and **B** might be plausible intermediates; structure **C** definitely isn't
 - b. Structures **A** and **C** might be plausible intermediates; structure **B** definitely isn't
 - c. Structures **B** and **C** might be plausible intermediates; structure **A** definitely isn't
 - d. Structure **A** might be a plausible intermediates; structures **B** and **C** definitely aren't

HO
$$\frac{H^+}{H_2O}$$
 OH

$$\begin{array}{c|c}
O & O \\
\hline
OEt & \frac{1. \text{ NaOEt}}{2. \text{ BrCH}_3}
\end{array}$$
OEt

$$\begin{array}{c|cccc}
OH & H^+ & O \\
\hline
NMe_2 & H^2O & H & + HNMe_2
\end{array}$$

$$\begin{array}{c|cccc}
OH & & OH & & & \\
\hline
NMe_2 & & NMe_2 & & & \\
\hline
A & & B & H & & C
\end{array}$$

Test 3 PS4: Test 3 Extra Synthesis Practice (6 pages)

F. Elements of Unsaturation/Hydrogenation Problems. For each problem there will be multiple satisfactory solutions.

- 48. Provide a possible structure for a compound with formula C₅H₈, given that it reacts with excess H₂/Pt to give C_5H_{10} .
- 49. Provide a possible structure for a compound with formula C₆H₈, given that it reacts with excess H₂/Pt to give C_6H_{12} .
- 50. Provide a possible structure for a compound with formula C₈H₁₀, given that it reacts with excess H₂/Pt to give C₈H₁₄.
- compound with formula C₆H₈, given that it reacts with excess H₂/Pt to give C_6H_{12} .

51. Provide a possible structure for a OOPS, IGNORE THIS ONE. IT'S SAME AS #49

G. Ozonolysis: Draw starting chemicals that will undergo ozonolysis to produce the products shown. In some cases there may be more than one satisfactory answer.

$$\begin{array}{c|c}
1. O_3 \\
\hline
2. Me_2S
\end{array}$$

53.

54.

55.

Organic Chemistry I Jasperse

Test 4: Extra Practice with HBr addition to Dienes (p 1,2) and Allylic NBS Brominations (p3,4).

Review on predicting products when H-X adds to a diene.

- 1. Always protonate first on an outside rather than inside carbon.
 - This will give an allylic rather than isolated cation
- 2. Is the diene symmetric or asymmetric?
 - If it's symmetric, it doesn't matter which outside carbon you add to first.
 - If it's asymmetric, then protonating at different ends will likely give allylic cations of unequal stability. Thus you should decide which protonation site will give the best allylic cation.
- 3. Is the allylic cation (once you have protonated) symmetric or asymmetric?
 - If it's symmetric, you'll get one structural isomer.
 - Is it's asymmetric, you'll get two structural isomers.

A. For each of the following:

- a. Predict products following HBr addition. (Will there be just one, or more than one?)
- b. Draw mechanisms. Be sure to draw both versions of the allylic cation.
- c. Identify 1,2 versus 1,4 addition products.
- d. Identify thermodynamic product.

Practice with NBS bromination of Alkenes.

Review on predicting products for NBS allylic radical bromination of an alkene.

- 1. Any allylic spot with an H could give up an H to product an allylic radical. How many allylic spots are there?
- 2. If there is more than one allylic spot, is the alkene symmetric or asymmetric? In other words, will the different allylic spots give the same allylic radical or unequal allylic radicals?
 - If there is more than one allylic radical, they may be of unequal stability. So one might lead to more product than the other. Still, you should expect to get at least some product from each of the allylic radicals.
- 3. One you have made an allylic radical, is it symmetric or asymmetric?
 - If it's symmetric, you'll get one structural isomer from it.
 - If it's asymmetric, you'll get two structural isomers out.
 - Note that if you your allylic radicals are asymmetric, you'll get two bromide products for each one. So if you have two different allylic sites each offering asymmetric allylic radicals, you'll get 2 x 2 = 4 isomer products.
- B. For each of the following:
 - a. Predict products following allylic NBS reaction. (Will there be just one, or two, or four?)
 - b. Draw all allylic radicals that could be intermediates.
 - c. For each allylic radicals, draw all resonance structures.
 - d. Be sure to note whether allylic radicals and allylic resonance structures are the same or different.

Draw products following NBS/peroxides bromination. Identify radicals, and draw all resonance structures for the radicals.



Organic Chemistry I Jasperse

Extra Practice Problems: Conjugated Systems, Dienes, Allylic Systems and the Diels-Alder Reaction

1. Rank the heats of hydrogenation for the following, 1 being most heat released and 4 being least heat. (Think: will the more stable isomer release more heat or less heat when it is hydrogenated)?

2. Rank the rate of reaction of the following toward S_N1 substitution (AgNO₃/CH₃CH₂OH), 1 being most reactive and 4 being least reactive. (Think: what determines the rates for S_N1 reactions?)

$$\nearrow$$
 Br \nearrow Br \nearrow CI

- 3. Products **A** and **B** combine to make up over 90% of the product mixture.
 - a. For each of the structures **A-D**, attach an H atom to the carbon that in fact added an H.
 - b. Classify each of the four structures as either a 1,2 or 1,4 addition product.
 - c. Draw the resonance structures for the cation that leads to both products A + B, and also draw the resonance structures for the cation that leads to both products C+D.

4. Draw the mechanism for formation of products A and B above.

5. 1,4-pentanediene is much more acidic than pentane. Explain why. (Think: what determines aciditiy?)

- 6. Draw the two major products for the following reaction.
 - Identify each as either a 1,2 or 1,4 addition product.
 - Write either "thermodynamic" or "kinetic" underneath each one.
 - Draw the two resonance structures for the intermediate from which both form.

7. Draw the major product or products for the following reaction. Draw the resonance structures for the intermediate from which both form.

8. Give the reactants (including stereochemistry) that would give the following Diels-Alder product.

9. Draw the major Diels-Alder product.

Organic Chemistry I Jasperse

Test 4 Extra Practice: Drawing Mechanisms when the Reactants and Products are Given

Aromatic Substitution Mechanism Practice. Product given.

• A subsequent practice set will give additional mechanism practice, but will also require you to predict the product as well. It will also to have a bunch of other product prediction problems that don't focus on mechanisms, and a bunch of synthesis design practice problems.)

3.
$$\frac{\text{HNO}_3, \text{H}_2\text{SO}_4}{\text{O}_2\text{N}}$$

Organic Chemistry I Jasperse

Test 4 Extra Practice: Predict product and draw mechanism (p 1,2); predict product (p 3,4); synthesis design (p5)

A. Aromatic Substitution Predict Product and Draw the Reaction Mechanisms

- Draw the major product and the mechanism for each of the following reactions, using detailed arrow-pushing.
- Draw the resonance structures for carbocationic intermediate.

Note: See pages 3 and 4 for more production prediction problems. See page 5 for some synthesis design problems.

$$Br_2$$
, FeBr₃

4.
$$HNO_3, H_2SO_4$$

5.

6.

$$HO_2C$$
 OCH₃ CI AlCl₃

$$CI$$
 CI $AICI_3$

B. Draw the major product for the following reactions.

$$H_2N$$
 NO_2 CI_2 $AICI_3$

$$3. \begin{tabular}{lll} \hline & 1. & HNO_3, H_2SO_4 \\ \hline & 2. & Br_2, FeBr_3 \\ \hline & 3. & Fe, HCI \\ \hline \end{tabular}$$

2.

$$4. \begin{array}{c} \begin{array}{c} \text{1. } \mathsf{HNO_3, H_2SO_4} \\ \text{2. } \mathsf{Fe, HCl} \\ \hline \\ \text{3. } \mathsf{Br_2, FeBr_3} \end{array}$$

$$\mathbf{Q} \qquad \qquad \boxed{ \qquad \qquad } \mathsf{OCH_3} \qquad \qquad \mathsf{bromocyclopentane, AlCl_3}$$

$$\begin{array}{c|c} O_2N & & \xrightarrow{\text{1. AICl}_3, \quad CI} & \xrightarrow{\text{0}} \\ \hline 2. \quad \text{AICl}_3, \quad \text{2-bromopropane} \\ 3. \quad \text{Zn(Hg), HCI} \end{array}$$

$$14. \begin{tabular}{ll} \hline & 1. & NBS, peroxides (or Br_2, hv) \\ \hline & \hline & 2. & NaOCH_3 \\ \hline \end{tabular}$$

1. NBS, peroxides (or
$$Br_2$$
, hv)

2. NEt_3

16. NBS, peroxides (or
$$Br_2$$
, hv)

2. NEt_3

17. NBS, peroxides (or
$$Br_2$$
, hv)

2. NaOCH₃

Design Syntheses for the following transformation:

$$O_2N$$
 H_2N

$$\begin{array}{c|c} & & & \\ \hline \\ & & \\ \hline \\ & & \\ \end{array}$$