

# Practice Set **Answer** Keys, Organic Chemistry I

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- Online Organic Chemistry I, Chem 350,
- Dr. Craig P. Jasperse, Minnesota State University Moorhead
- For full class website, see

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

- The website will include **explanatory videos** for each practice set, videos in which I talk through the process and logic involved in determining the correct answers.
- My recommendation would be to do a complete two-sided printout of all of the practice sets, and all of the practice set answer keys, at the start of the semester.

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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.

Watch for:

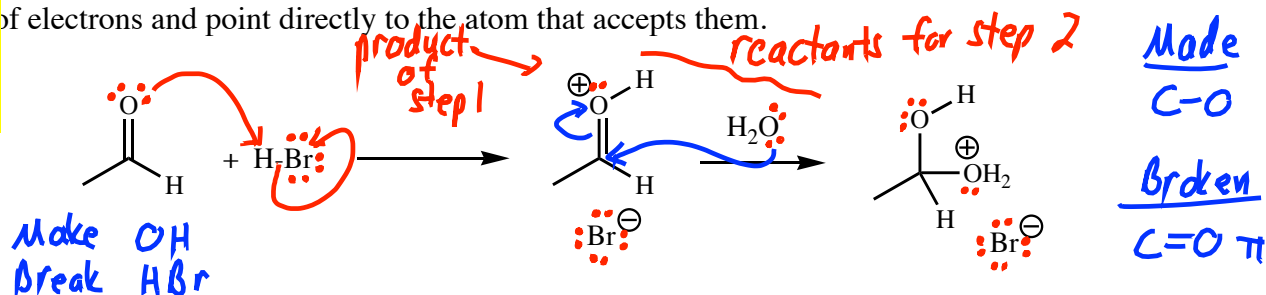
Changes in:

1. Bonds
2. Lone Pairs
3. Formal Charge

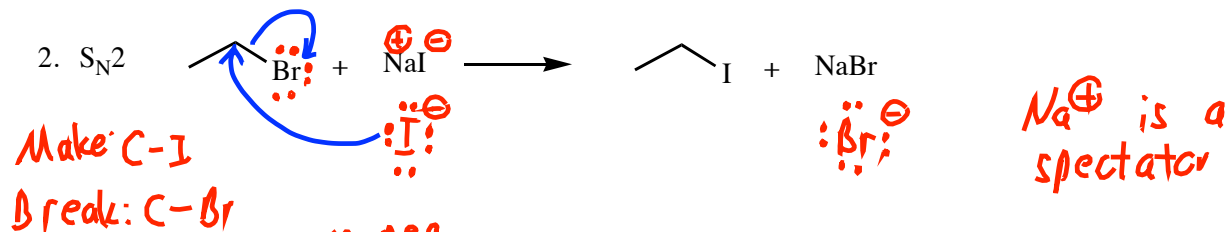
I won't require this on tests, but you may find it useful to draw in all hydrogens on atoms that react. (It is not useful to draw in all H's on atoms that don't react.)

Remember that arrows track the movement of electrons, so an arrow should go from the source of electrons and point directly to the atom that accepts them.

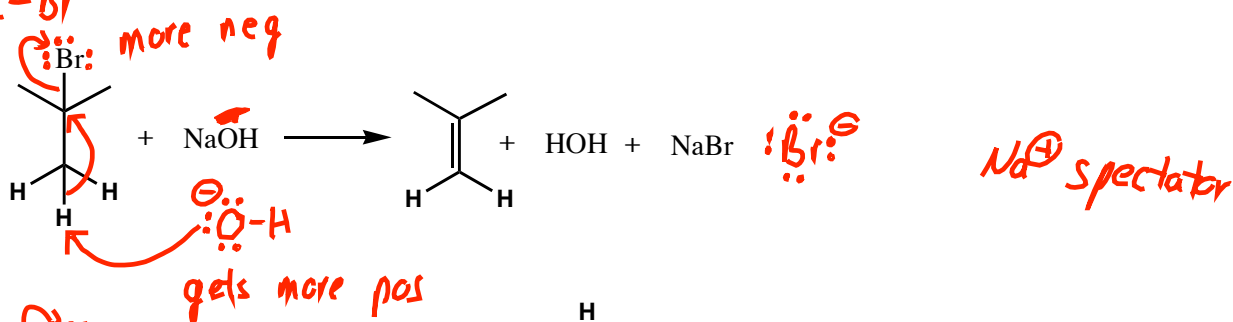
1.



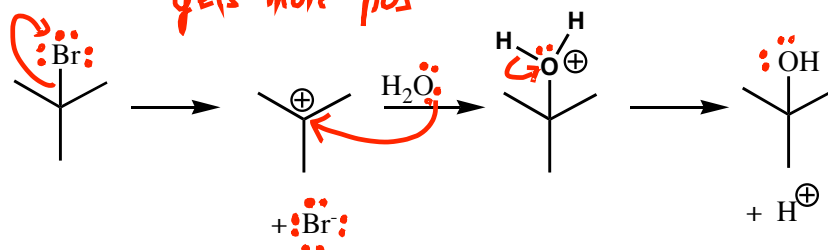
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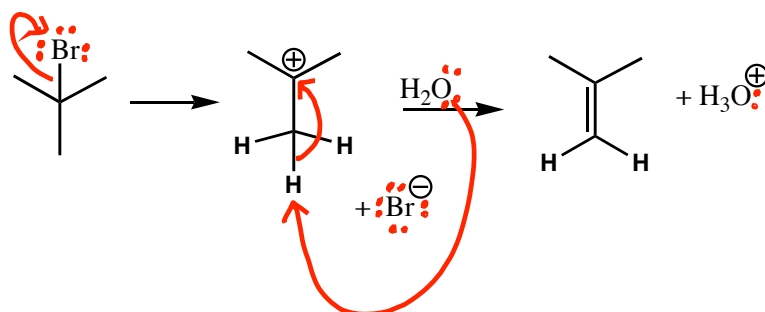
3. E2



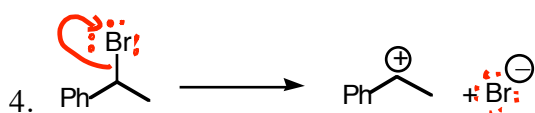
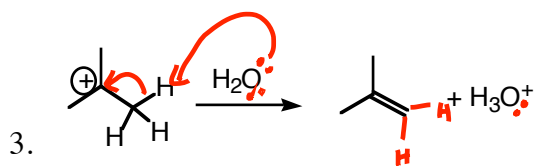
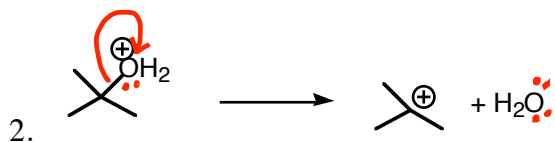
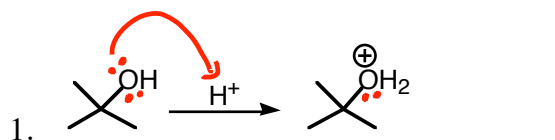
4.  $S_N1$



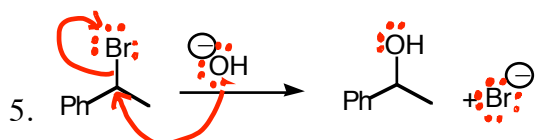
5. E1



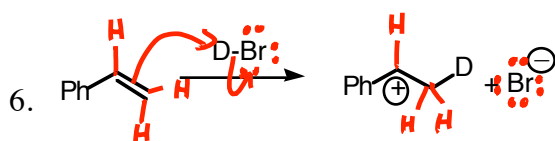
Page 2: Draw the arrow(s) for each of these steps.



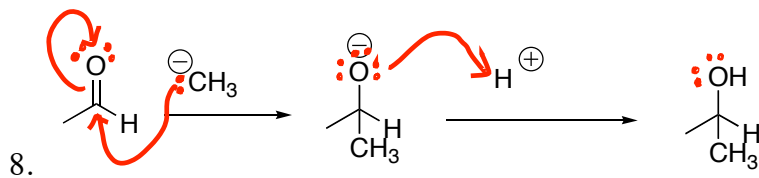
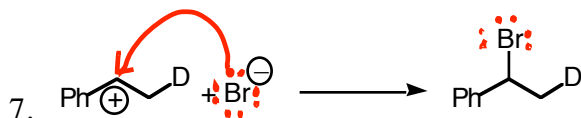
*S<sub>N</sub>1/E1 Mech step (Test 2)*



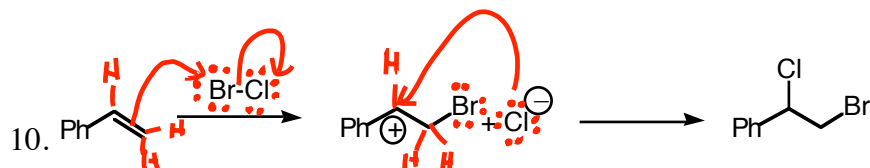
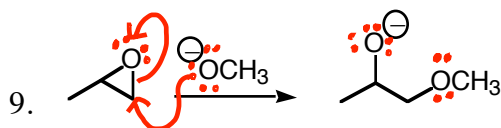
*S<sub>N</sub>2 Mech (Test 2)*



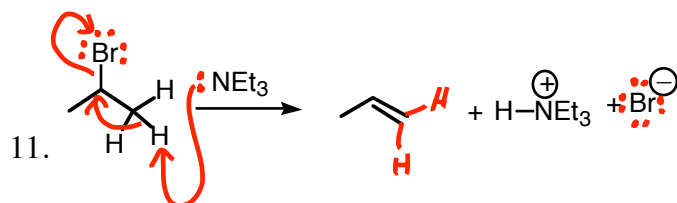
*Test 3 HX addn to alkenes*



*Organic 2  
Test 1*



*Test 3*



*Test 3*

**Some Arrow-Pushing Guidelines**

- Arrows follow electron movement.
- Some rules for the appearance of arrows
  - The arrow must begin from the electron source. There are two sources:
    - An atom (which must have a lone pair to give)
    - A bond pair (an old bond that breaks)
  - An arrow must always point directly to an atom, because when electrons move, they always go to some new atom.
- 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
- Draw all H's on any Atom Whose Bonding Changes
- Draw all lone-pairs on any Atom whose bonding changes
- 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)
- Watch for Formal Charges and Changes in Formal Charge**
  - If an atom's charge gets more positive  $\Rightarrow$  it's donating/losing an electron pair  $\Rightarrow$  arrow must emanate from that atom or one of its associated bonds. 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 gets more negative  $\Rightarrow$  it's accepting an electron pair  $\Rightarrow$  an arrow must point to that atom. Ordinarily the arrow will have started from a bond and will point to the atom.
- 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

3 types

① more pos (source)

② more neg (acceptor)

③ subst.



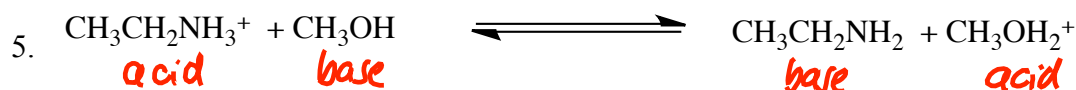
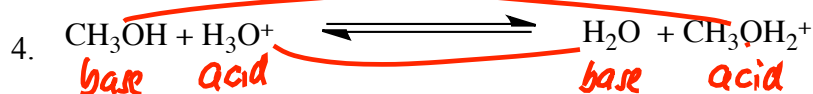
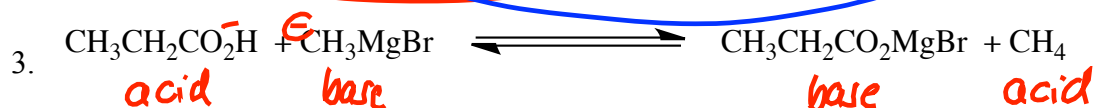
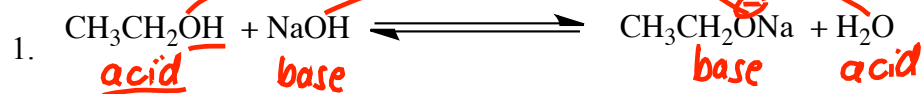
## Organic Chemistry Jasperse

## Acid-Base Practice Problems

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

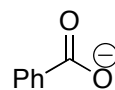
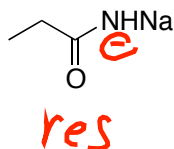
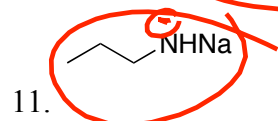
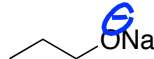
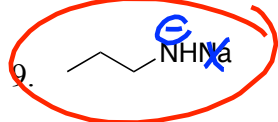
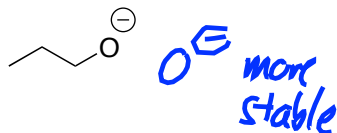
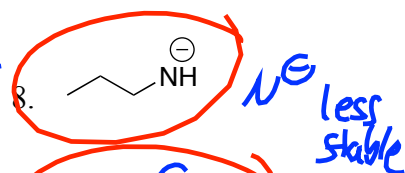
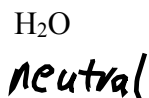
-You should have one acid and one base on each side

-You should have two conjugate pairs

**B. Choose the More Basic for Each of the Following Pairs (Single Variable). You can use stability to decide.**Base: less stable  $\Rightarrow$  more reactive

Keys:

1. Charge
2. Electronegativity
3. Resonance

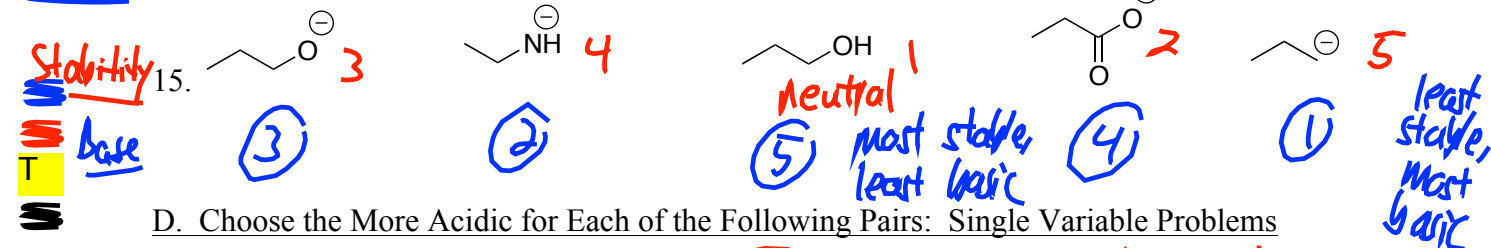
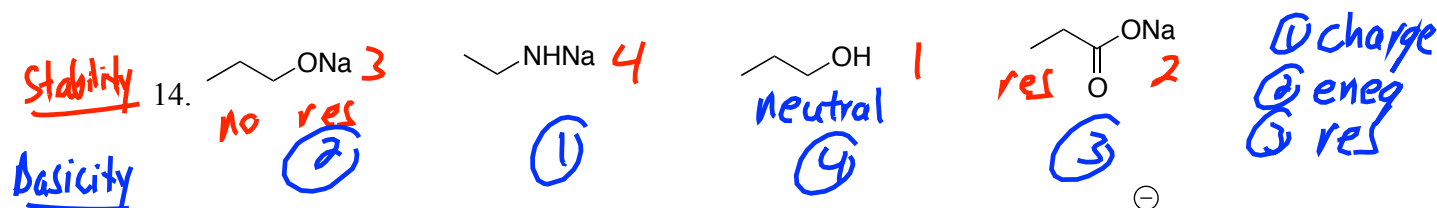
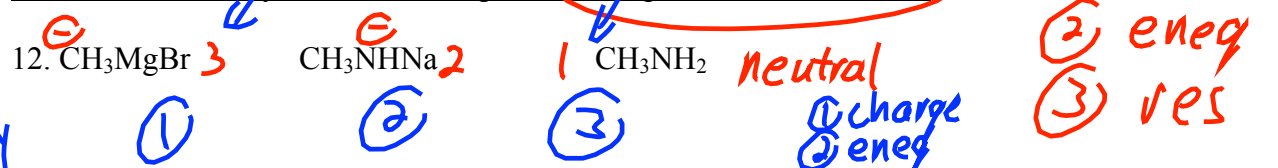
res  $\Rightarrow$  stabilizes

base  
 ① charge: anion more basic than neutral  
 ② eneg:  $\text{C}^-$   $\text{N}^-$   $\text{O}^-$   $\text{F}^-$   
 Stability  $\rightarrow$   
 ← basicity  
 ③ res anion stabilized  $\Rightarrow$  less basic

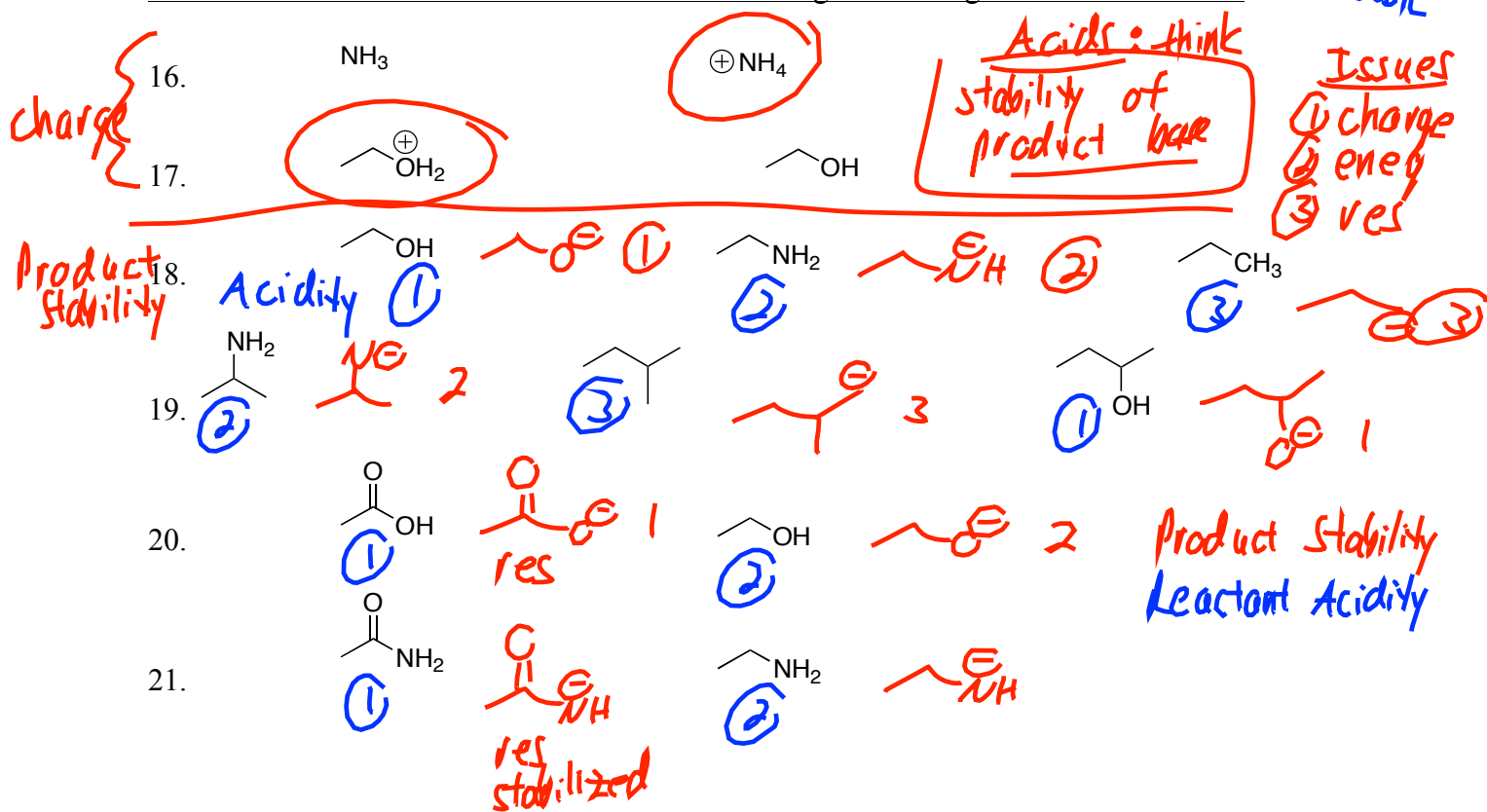
chargeenegres

1  
2  
T  
3

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

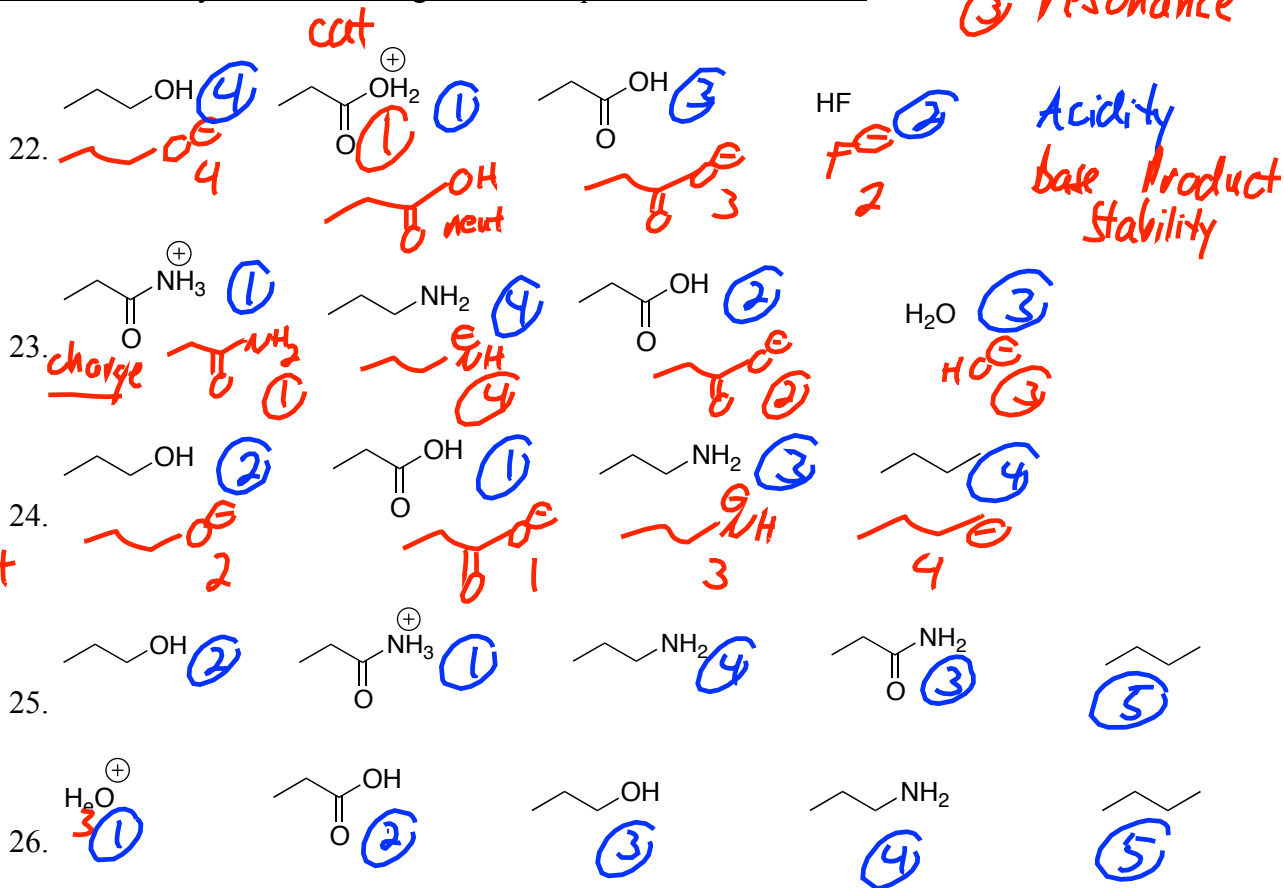


D. Choose the More Acidic for Each of the Following Pairs: **Single Variable Problems**



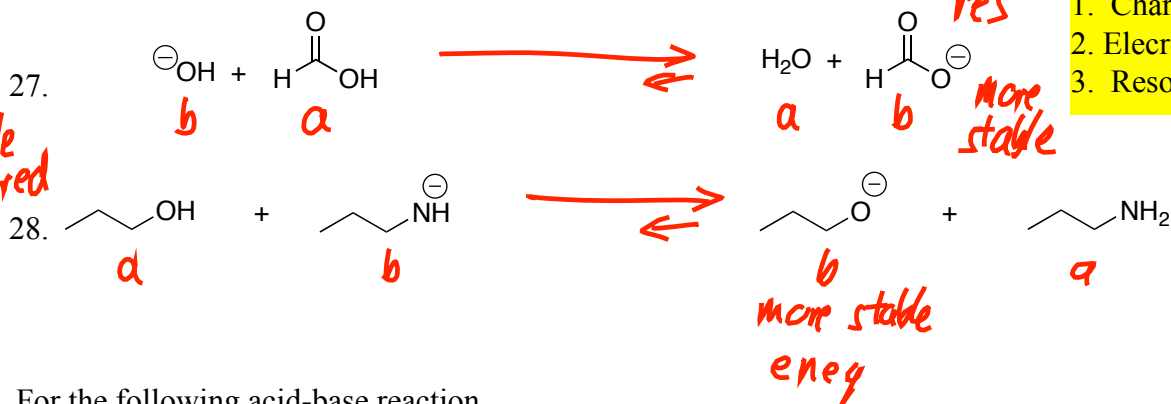
- ① charge  
② eneg  
③ resonance

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



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

Compare  
bases  
more stable  
base favored

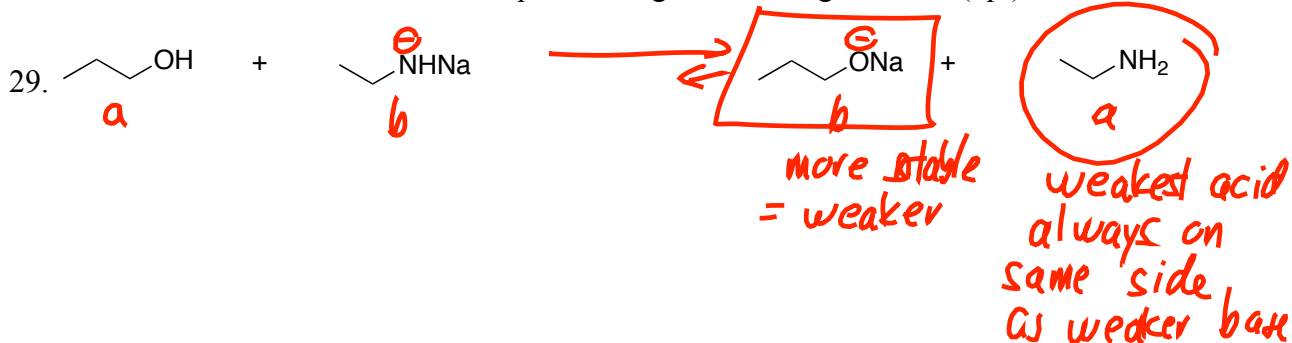


Keys:




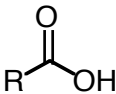
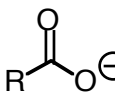
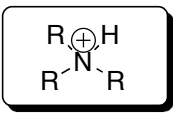
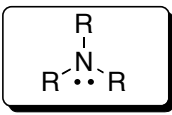
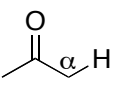
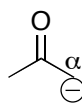
1. Charge
2. Electronegativity
3. Resonance

G. For the following acid-base reaction,

- put a box around the weakest base in the reaction  $\equiv$  more stable
- put a circle around the weakest acid
- draw an arrow to show whether the equilibrium goes to the right or left. (4pt)



Test 1 PS#2: **Acid Base Practice Set****Acid-Base Chemistry (Section 1.13-18)****Acidity/Basicity Table**

Entry	Class	Structure	K <sub>a</sub>	Acid Strength	Base	Base Strength	Base Stability
1	Strong Acids	H-Cl, H <sub>2</sub> SO <sub>4</sub>	10 <sup>2</sup>		Cl <sup>-</sup> , HO-SO <sub>3</sub> <sup>-</sup>		
2	Hydronium	H <sub>3</sub> O <sup>+</sup> , ROH <sup>+</sup> cationic	10 <sup>0</sup>		H <sub>2</sub> O, HOR neutral		
3	Carboxylic Acid		10 <sup>-5</sup>				
4	Ammonium Ion (Charged)	 Charged, but only weakly acidic!	10 <sup>-12</sup>		 Neutral, but basic!		
5	Water	HOH	10 <sup>-16</sup>		HO <sup>-</sup>		
6	Alcohol	ROH	10 <sup>-17</sup>		RO <sup>-</sup>		
7	Ketones and Aldehydes		10 <sup>-20</sup>				
8	Amine (N-H)	(iPr) <sub>2</sub> N-H	10 <sup>-33</sup>		(iPr) <sub>2</sub> N <sup>-</sup> Li <sup>+</sup>		
9	Alkane (C-H)	RCH <sub>3</sub>	10 <sup>-50</sup>		RCH <sub>2</sub> <sup>-</sup>		

**Quick Checklist of Acid/Base Factors**

- |                          |   |
|--------------------------|---|
| 1. Charge                | 1. Cations more acidic than neutrals; anions more basic than neutrals |
| 2. Electronegativity     | 2. Carbanions < nitrogen anions < oxyanion < halides in stability     |
| 3. Resonance/Conjugation | 3. resonance anions more stable than anions without resonance         |

▪ When neutral acids are involved, it's best to draw the conjugate anionic bases, and then think from the anion stability side.

- The above three factors will be needed this semester. The following three will also become important in Organic II.
- Hybridization
- Impact of Electron Donors/Withdrawers
- Amines/Ammoniums



Molecular Structure

1

## 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 zig-zagging. 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

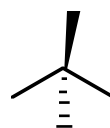
-if the two in plane are "up", the hash/wedge should be down.

-the hash/wedge should never point in same direction as the in-plane lines, or else the atom doesn't look tetrahedral

-for polyatomic molecules, it is strongly preferable to NOT have either of the in-plane atoms pointing straight up. Straight-up in-plane atoms do not lend themselves to extended 3-D structures.



Good! Look tetrahedral



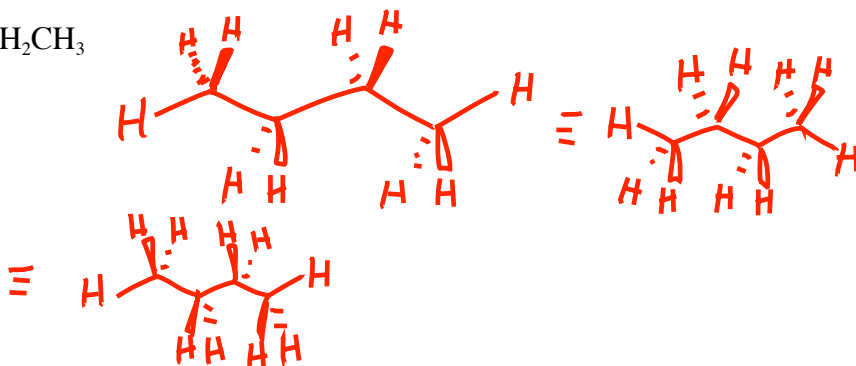
Bad! These don't look tetrahedral!

1. ALKANE. butane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

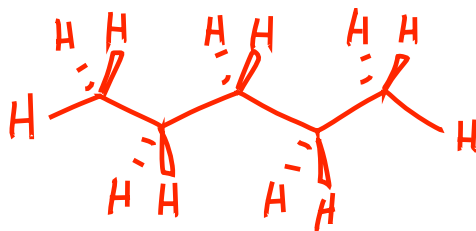
-take the chain and wiggle around all the single bonds.

-The most stable actual shape is the one with the carbons zig-zagged and co-planar.

-Notice the symmetry possible.



2. ALKANE. Pentane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

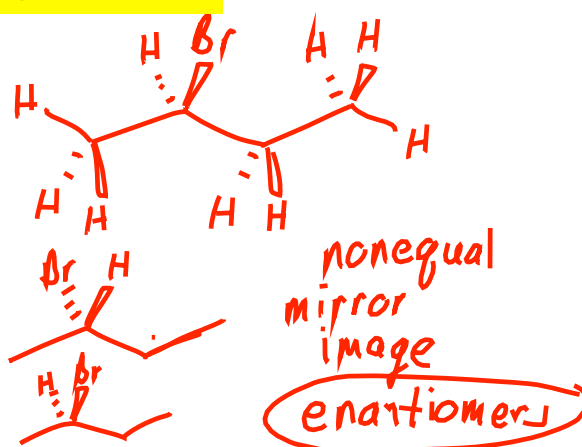


3. HALOALKANE. 2-bromobutane,  $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$ 

-notice that if the 4 carbons are co-planar zig-zagged, the attached Br can't be in the same plane.

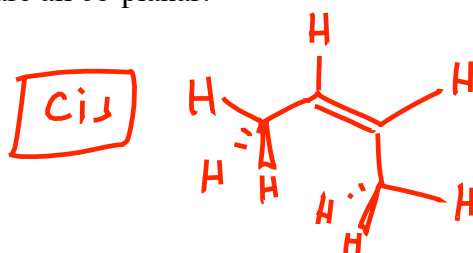
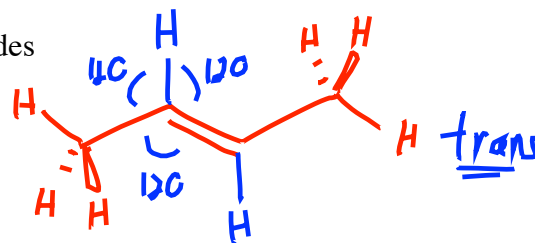
-try to compare with a partner 2 cases in which Br is in front versus behind. Are they the same molecule, or isomers?

Isomers, not same  
Stereoisomers

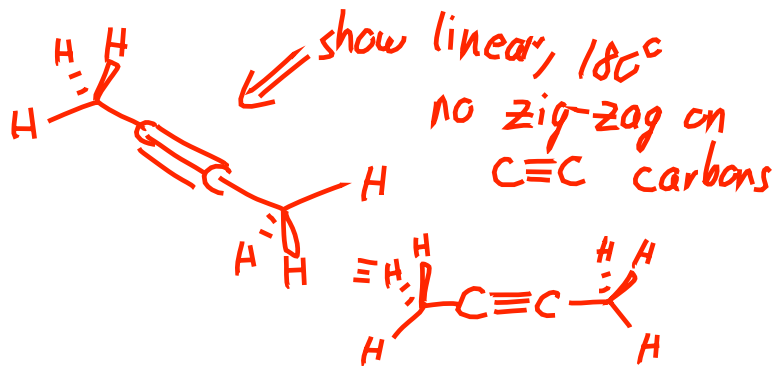
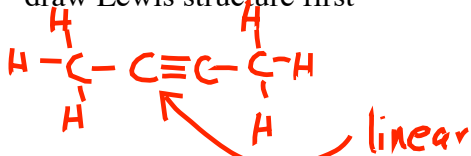
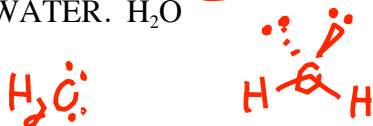
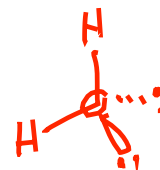
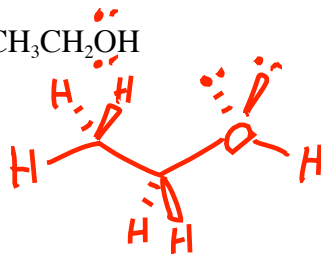
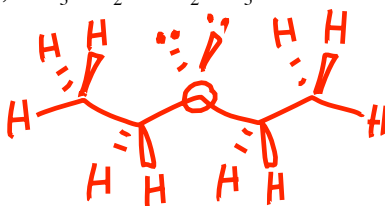
4. ALKENE. Draw both: a) trans-2-butene,  $\text{CH}_3\text{CH}=\text{CHCH}_3$  and b) cis-2-butene

(trans means the two  $\text{CH}_3$  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.

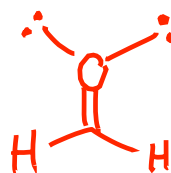
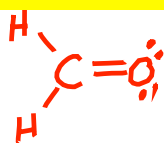
5. ALKYNE. 2-butyne,  $\text{CH}_3\text{CCCH}_3$ 

-draw Lewis structure first

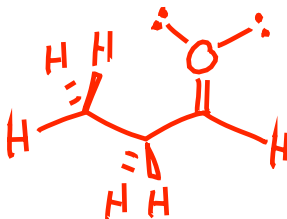
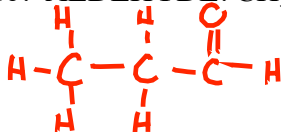
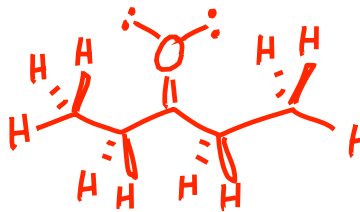
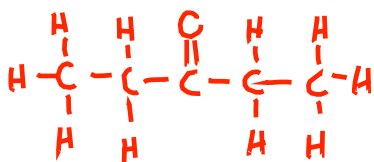
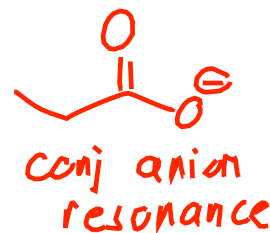
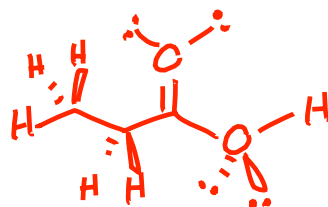
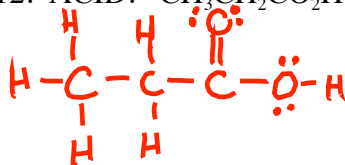
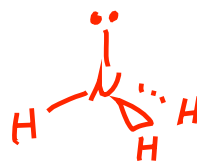
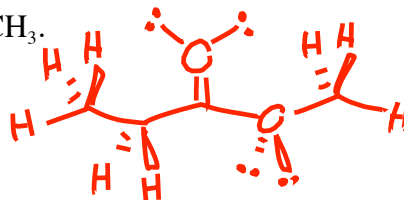
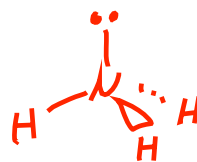
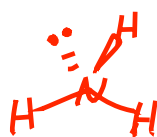
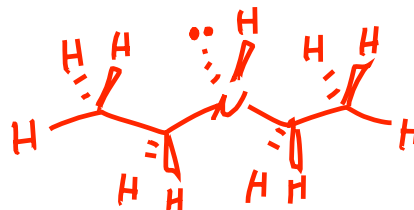
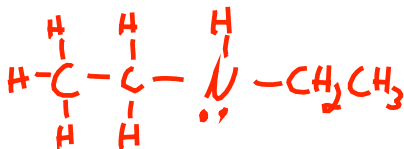
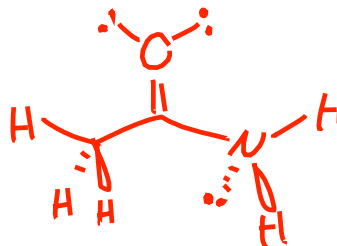
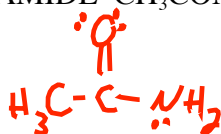
6. WATER.  $\text{H}_2\text{O}$ 7. ALCOHOL. Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ 8. ETHER. Diethyl ether,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ 

9. FORMALDEHYDE.  $\text{CH}_2\text{O}$ .

-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!



lone pairs  
in plane

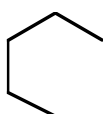
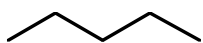
10. ALDEHYDE.  $\text{CH}_3\text{CH}_2\text{CHO}$ .11. KETONE.  $\text{CH}_3\text{CH}_2\text{C(O)CH}_2\text{CH}_3$ .12. ACID.  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ .13. ESTER.  $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ .14. AMMONIA.  $\text{NH}_3$ 15. AMINE.  $(\text{CH}_3\text{CH}_2)_2\text{NH}$ 16. AMIDE.  $\text{CH}_3\text{CONH}_2$ .

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

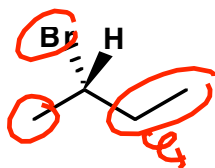
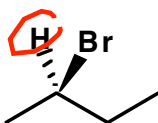
1. Structures which can be interchanged or made equivalent by rotations around single bonds are considered to be the same.
2. "Isomers" are things with the same formula that can't be made superimposable by simple rotations around single bonds.

(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.)

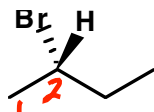
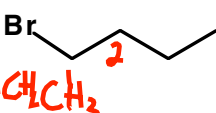
enantiomers (mirror image) vs diastereomers (cis/trans)



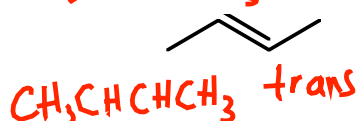
same



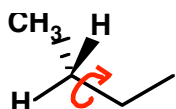
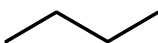
stereoisomers (enantiomers)  
mirror image



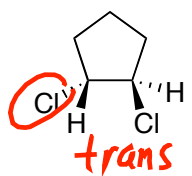
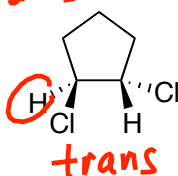
structural isomers (condensed formulas differ)



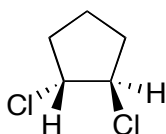
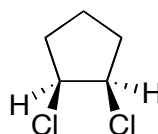
stereoisomers (diastereomers)



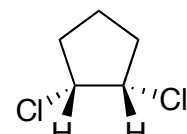
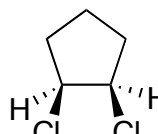
same



stereoisomers (mirror)



stereoisomers diastereomer



same

cis

cis

## Organic Chemistry I

## 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 completing dealing with Newman Projections and Cyclohexane Chair conformations.

Same name, condensed formula.

But atoms can't be superimposed, even by single bond rotation

Two families:

1. Unequal mirror images (enantiomers)
2. Cis/trans (diastereomers)

stereoisomers

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

- same compound

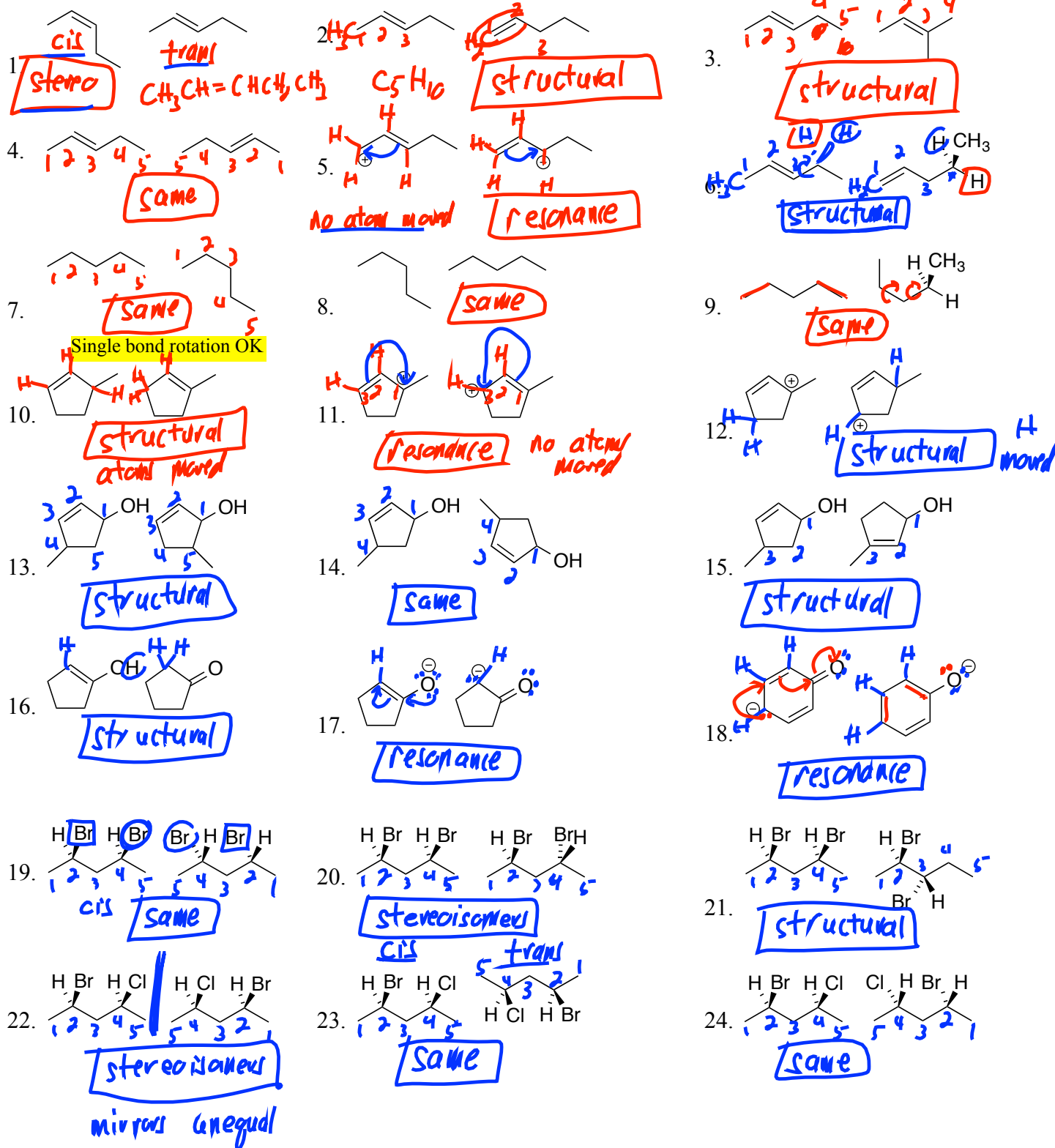
- structural isomers

- resonance structures

Remember, single bonds can rotate, but double bonds can't.

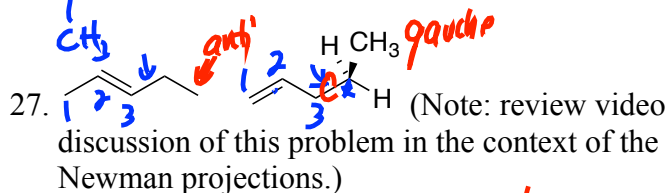
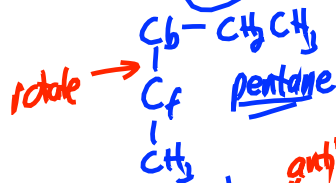
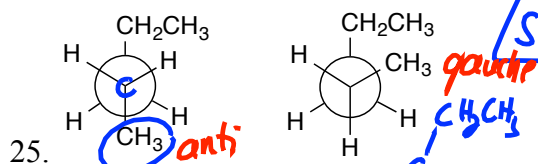
Different condensed formula,  
Different name

No atoms move, formal charge,  
double bonds, lone pairs may.

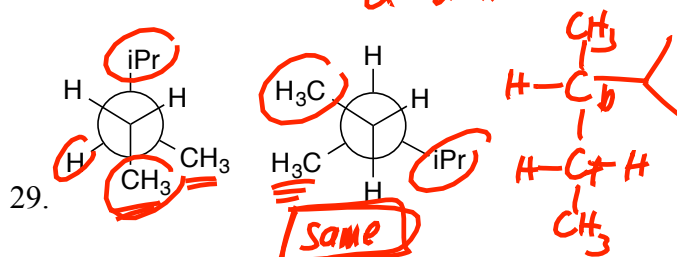


For the following pairs, classify the relationship between each pair as either:

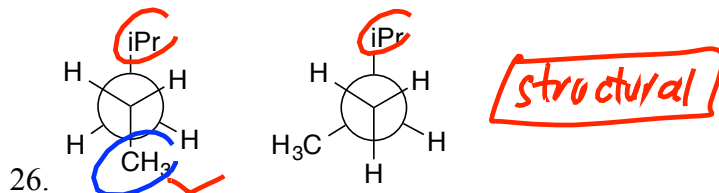
- same compound
- structural isomers
- resonance structures
- stereoisomers



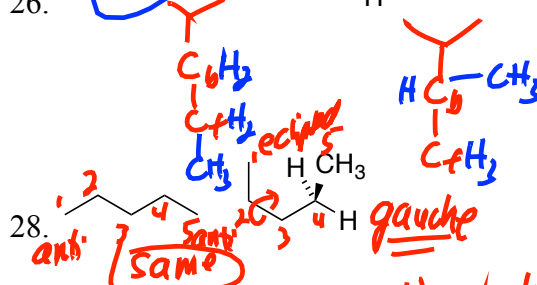
**structural** ⇒ on account of double bond



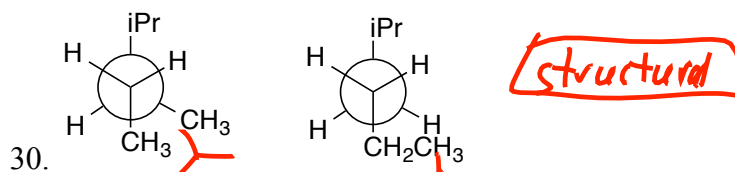
**same**



**structural**

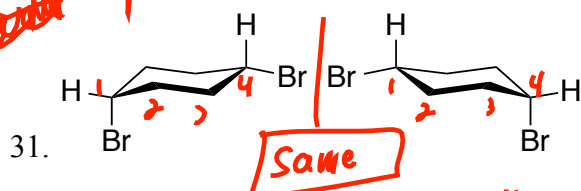


anti-gauche rotation  
anti-eclipsed rotation

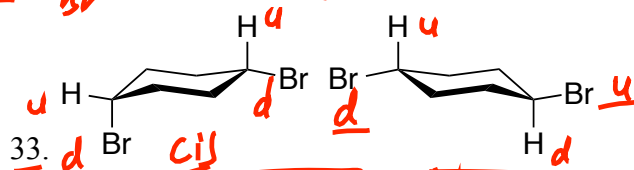
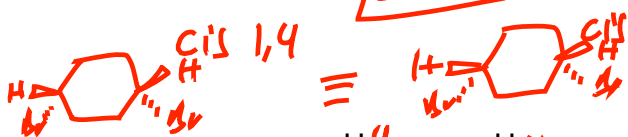


**structural**

~~Cyclohexane~~

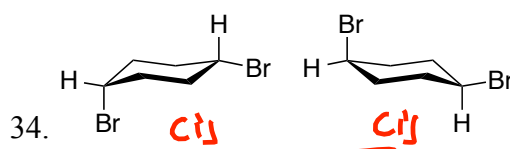


**same**

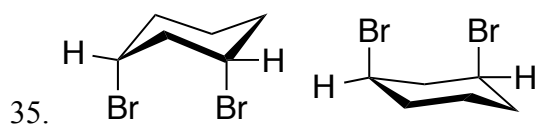


**stereo**

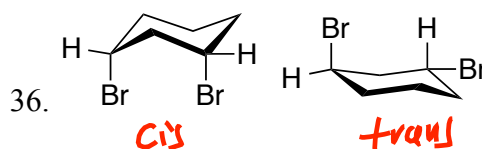
**trans**



**same**



**same**



**stereo**

## Newman Projection Practice

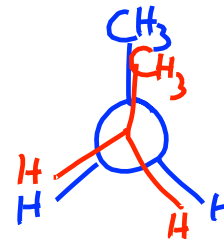
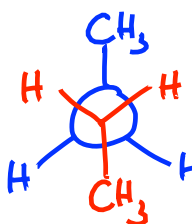
Organic Chemistry I – Jasperse Newman Projection Practice  
(See page 4 for some summary of operations/steps for handling Newman projections)

**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

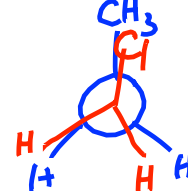
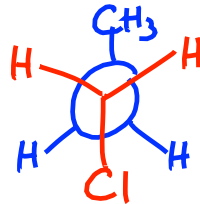
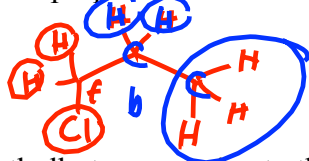


*best*  
anti

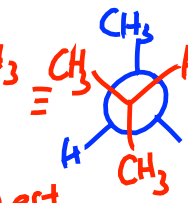
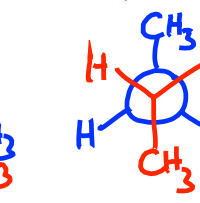
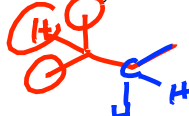


*worst*  
*totally eclipsed*

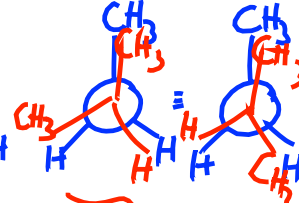
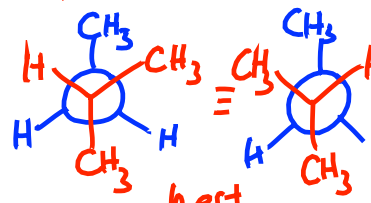
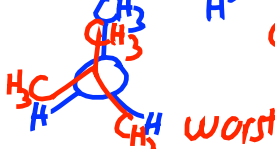
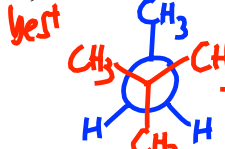
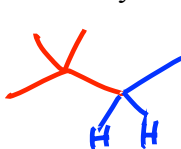
2. 1-chloropropane, relative to the C1-C2 bond



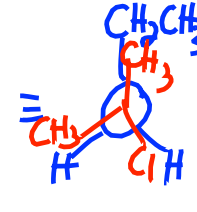
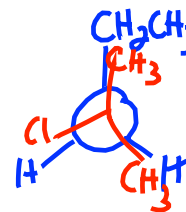
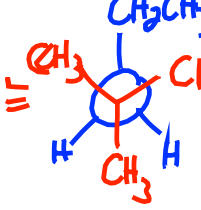
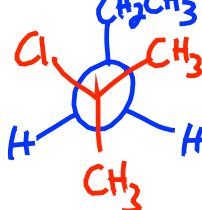
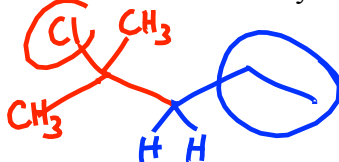
3. 2-methylbutane, relative to the C2-C3 bond



4. 2,2-dimethylbutane, relative to the C2-C3 bond



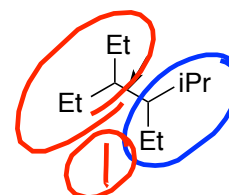
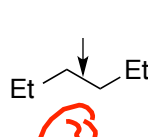
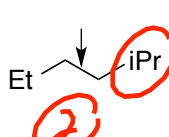
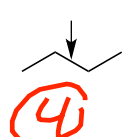
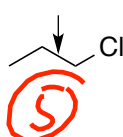
5. 2-chloro-2-methylpentane, relative to the C2-C3 bond  
Note: Cl is smaller than methyl



**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 NH<sub>2</sub> is smaller than a CH<sub>3</sub> or any other alkyl group.



Key:  
*worst*

*totally eclipsed conformation*

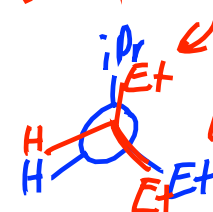
*What groups are totally eclipsing??*

*Larger ⇒ more steric strain ⇒ larger rotation barrier*

*Sizes:*

*iPr > Et > CH<sub>3</sub> > Cl > H*

*2 total eclipses*



**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.)**

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

7.		steric (1 gauche)
8.		torsional: one is eclipsed, one isn't
9.		<u>torsional</u> : same as in 8 plus <u>steric</u> (1 total eclipse of 2 nonhydrogens)
10.		<u>torsional</u>
11.		<u>steric</u> strain. Larger iPr makes gauche sterics worse
12.		methyl-methyl vs methyl-isopropyl <u>steric</u> larger
13.		1 gauche vs 2 gauche <u>steric</u>



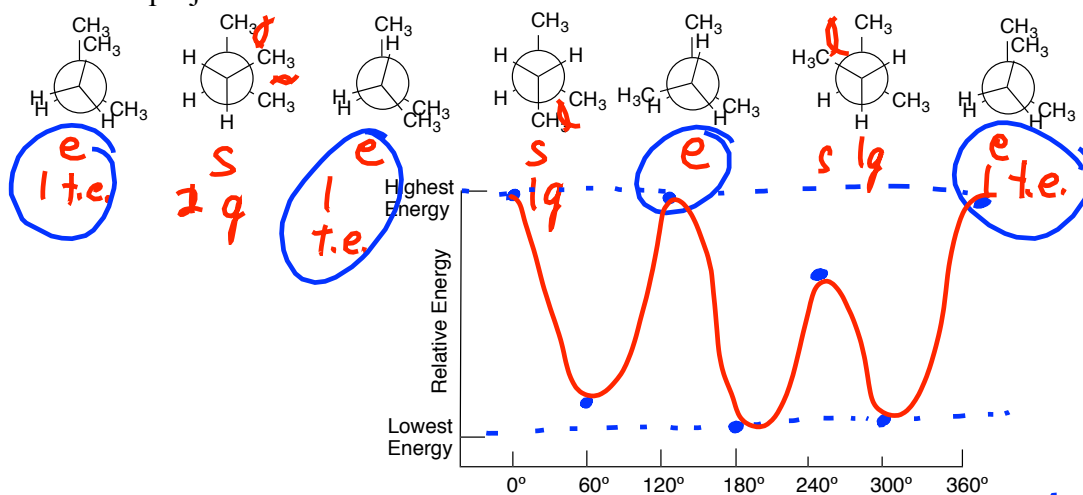
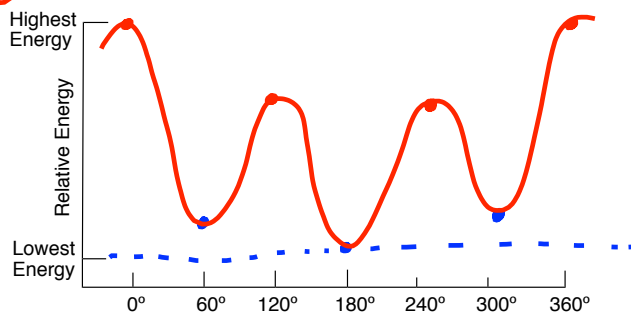
isopropyl  $\text{CH}(\text{CH}_3)_2$  group. Put S (for staggered) by any eclipsed) by an eclipsed conformation. **0 gauche 240** **1 gauche**

**0** **60** **120** **180** **240** **300**

**1 total eclipse** **1 gauche**

energy

Highest Energy



the  $\text{CH}_2$  and  $\text{CH}$  carbons. The Newman projections are drawn below, using  $\text{H}$  1 for the isopropyl  $\text{CH}(\text{CH}_3)_2$  group.

*Me-Me 9* *Me-iPr*

Relative Energy

Highest Energy

Lowest Energy

0° 60° 120° 180° 240° 300° 360°

*e* *s* *e* *s* *e* *s* *e*

**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
  - 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 relevant 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 compare 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

Cyclohexane Chair Practice  
Organic Chemistry I – Jasperse

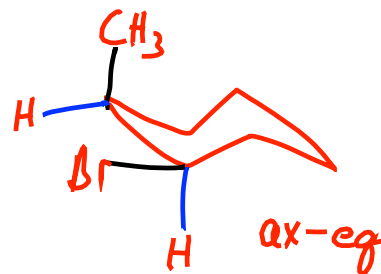
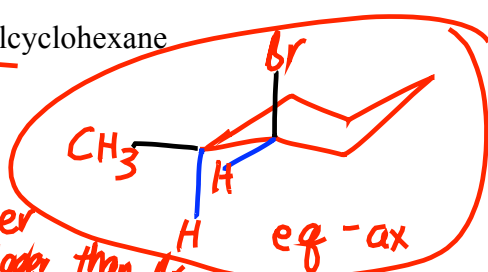
Cyclohexane Chair Practice

**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....)
- Assume that a halogen, OH, or NH<sub>2</sub> is smaller than a CH<sub>3</sub> or any other alkyl group.
- Remember to draw in the hydrogens on each of the “substituted” carbons

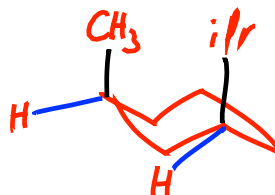
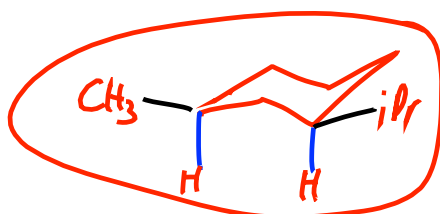
1. Cis-2-bromo-1-methylcyclohexane

blue downer  
black upper

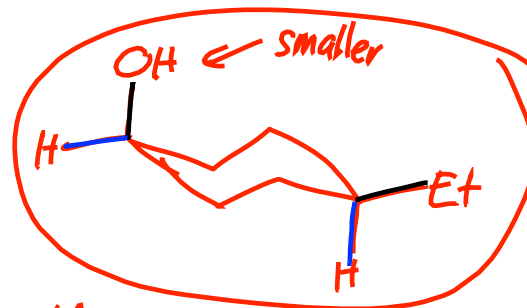
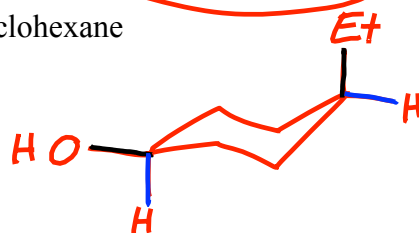


2. Cis-3-isopropyl-1-methylcyclohexane

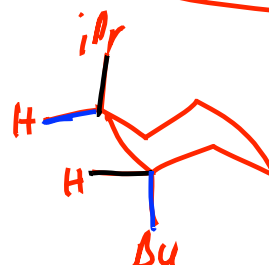
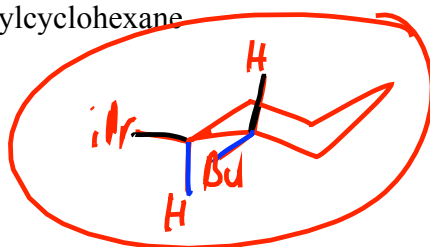
better  
methyl bigger than Br



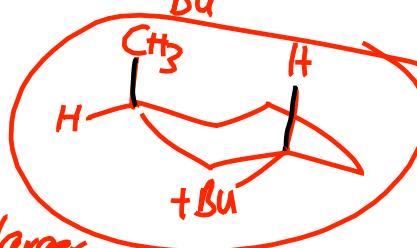
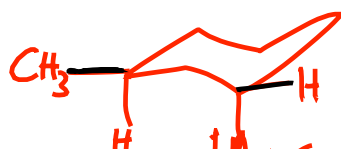
3. Cis-4-ethyl-1-hydroxycyclohexane



4. trans-2-butyl-1-isopropylcyclohexane



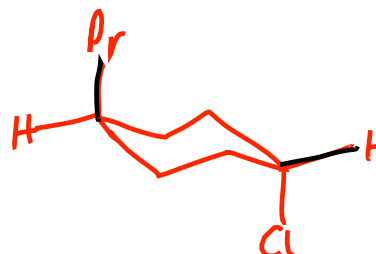
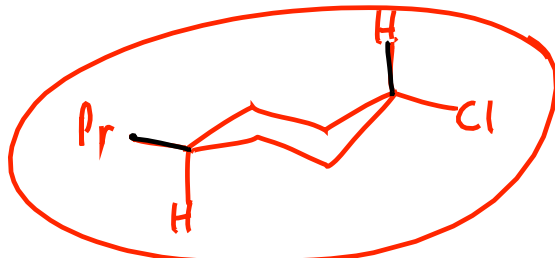
5. trans-3-t-butyl-1-methylcyclohexane



6. trans-4-chloro-1-propylcyclohexane

tBu - larger

disaster



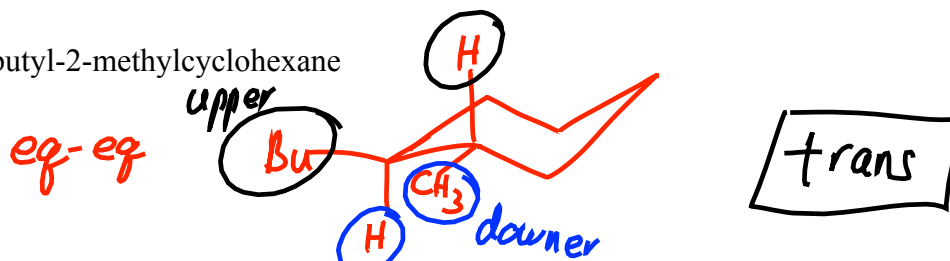
Cyclohexane Chair Practice

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

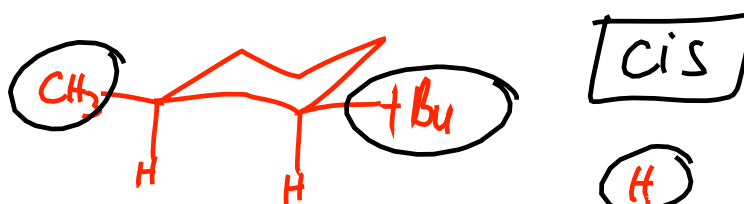
- A. draw the most stable chair form for the more stable stereoisomer for the molecule  
 B. identify whether the more stable stereoisomer is cis or trans.

*non-H's  $\Rightarrow$  equatorial*

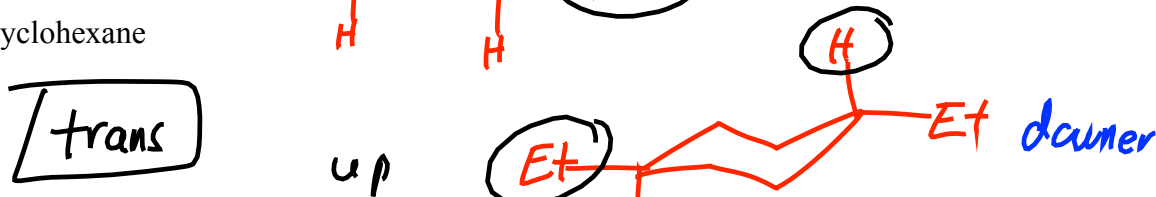
7. 1-butyl-2-methylcyclohexane



8. 3-t-butyl-1-methylcyclohexane



9. 1,4-diethylcyclohexane



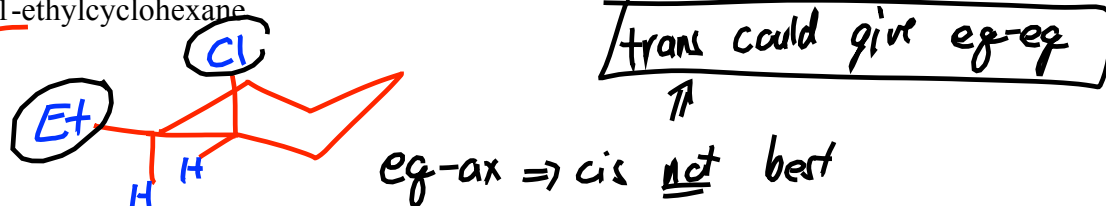
C. For each of the following, do two things:

- A. draw the most stable chair form  
 B. identify whether the more stable stereoisomer would be the cis or the trans stereoisomer

*put largest thing eg*

*smaller*  
*bigger*

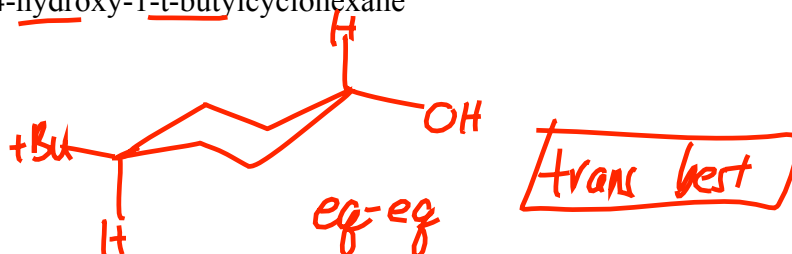
10. Cis-2-chloro-1-ethylcyclohexane



11. trans-3-butyl-1-isopropylcyclohexane



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



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

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### 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
  - 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 relevant 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

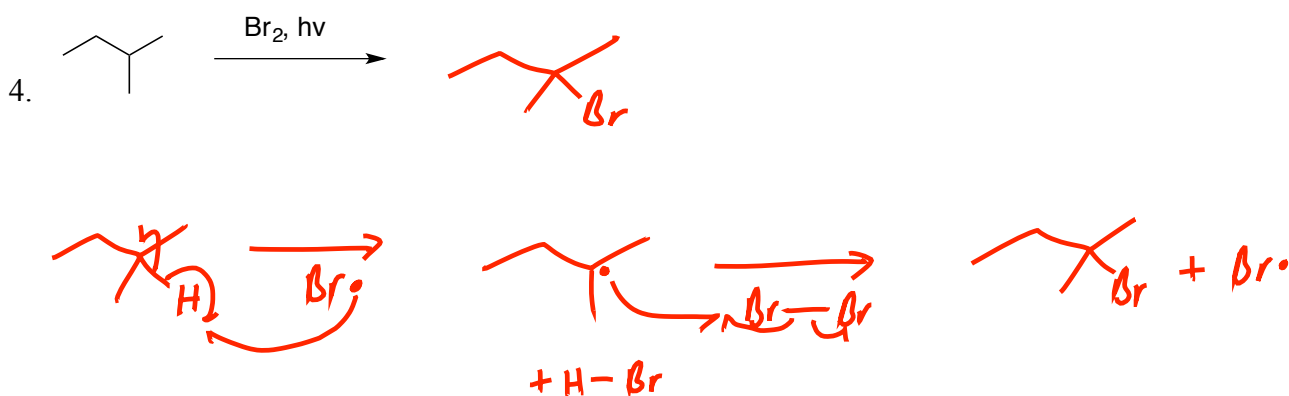
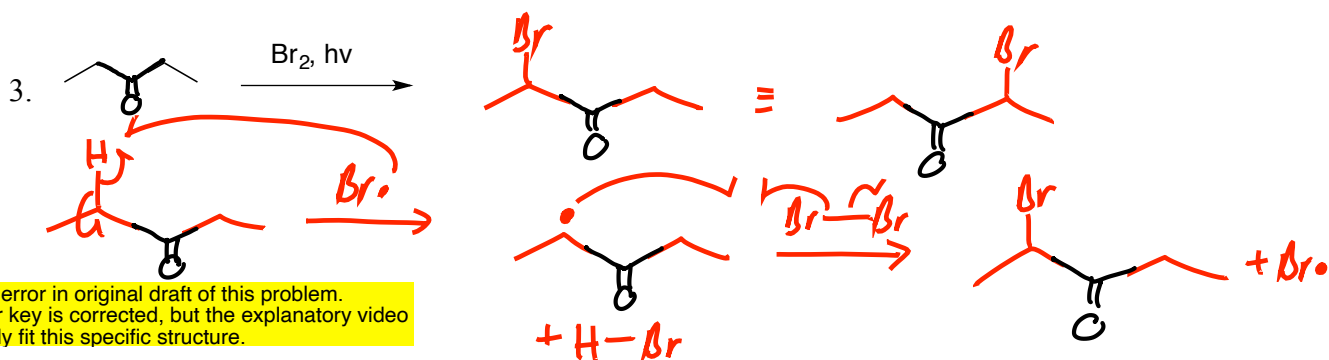
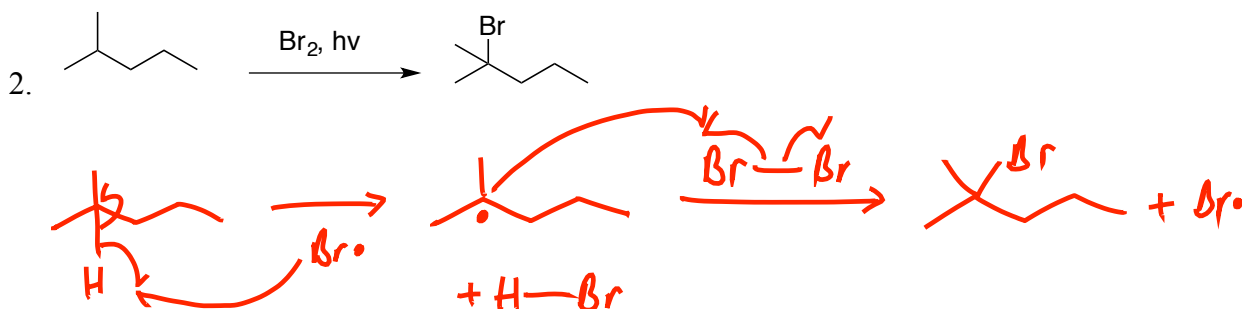
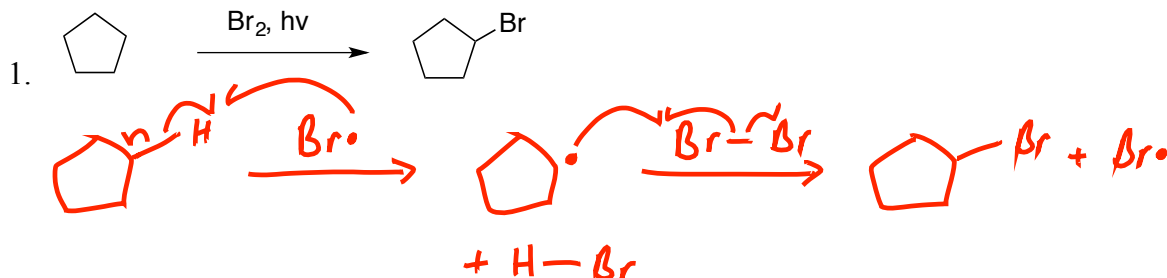
1. Use the "worst" (totally eclipsed version) as 0° and 360°.
2. 120° and 240° will be the other "eclipsed" conformations => energy crests.
3. 60°, 180°, and 300° will be the staggered conformations => energy valleys
4. 60° and 300° will be the other two staggered conformations (gauche) => energy valleys.
5. To compare 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

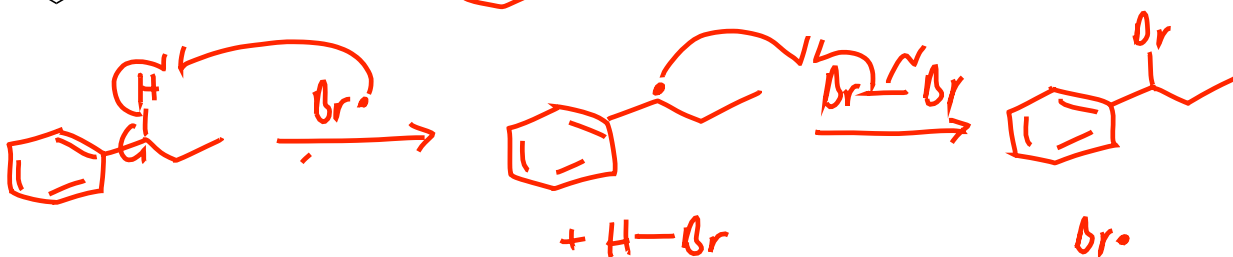
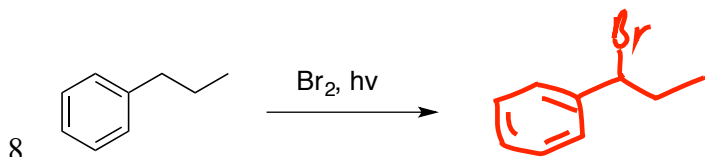
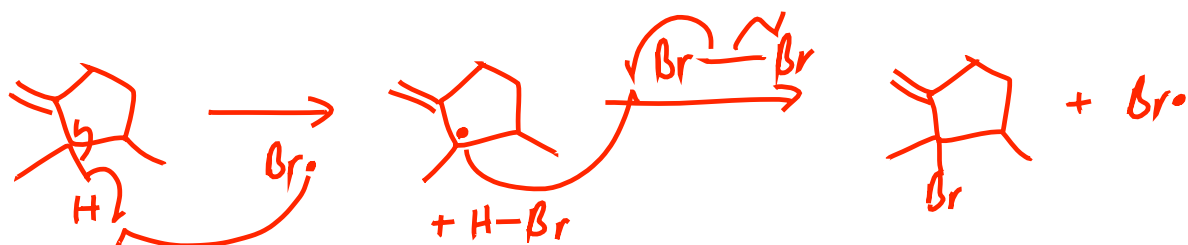
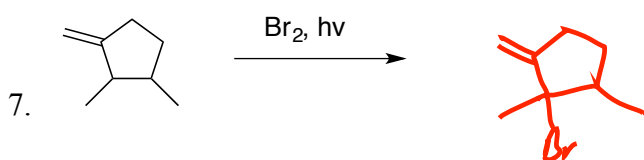
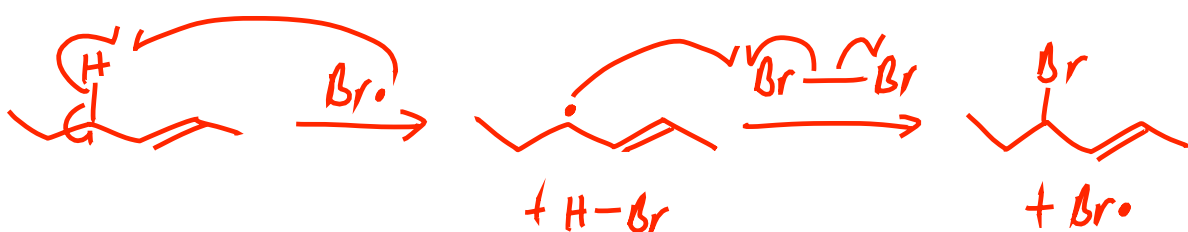
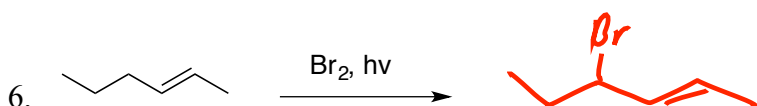
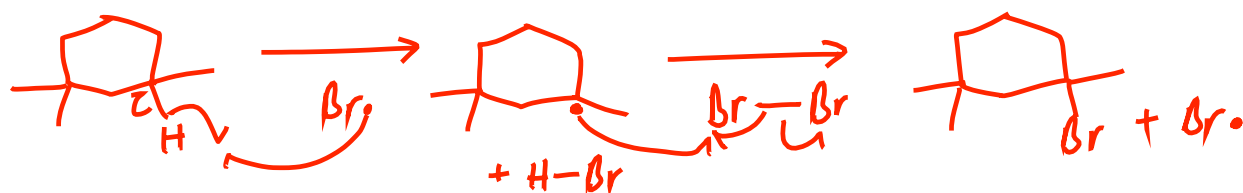
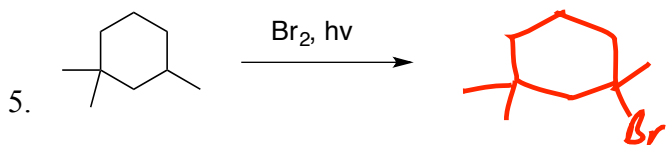
**Test 1 PS#6: Cyclohexane Chair Practice Set**

## 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.







**Test 2 PS#2: PS2:**  
**Stereochemistry Practice Set**

Priorities: 1. Heteroatom. 2. C-with-heteroatom.  
 3. C > CH > CH<sub>2</sub> > CH<sub>3</sub>.  
 4. Proceed down chain until point of difference.

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Organic Chemistry I

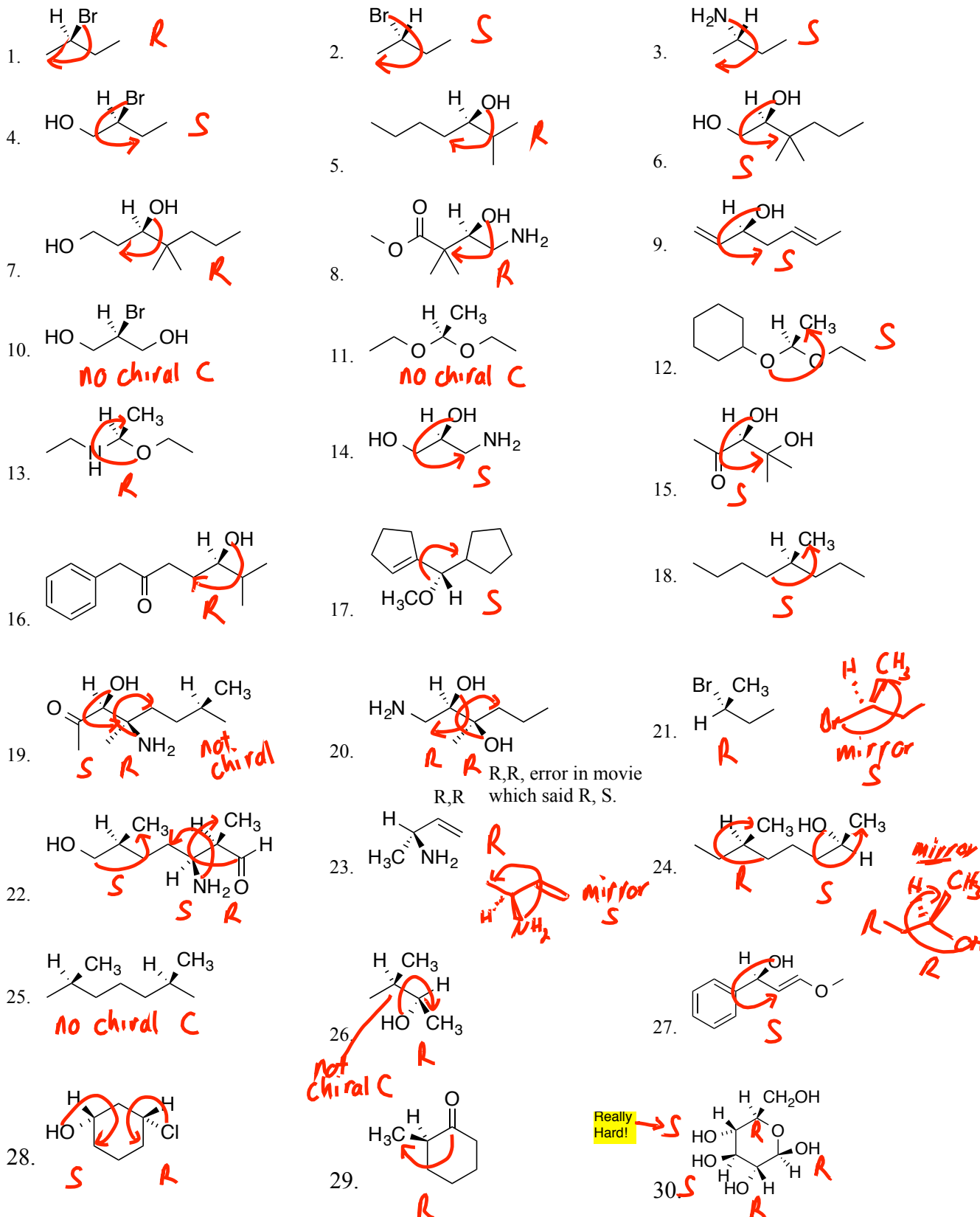
Test 2

Extra Stereochemistry Practice Problems

Page 1: Designate R/S Page 2: Chiral or Achiral?

Page 3: Same, Enantiomer, or Diastereomer?

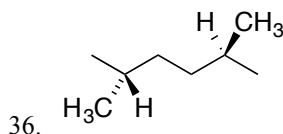
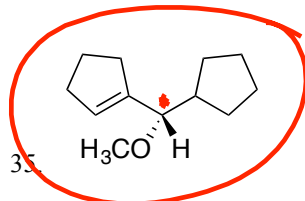
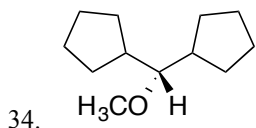
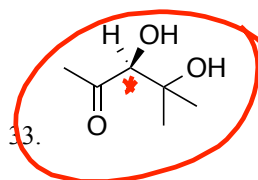
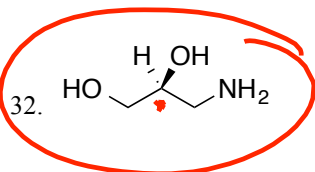
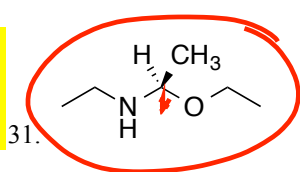
**A. Designate the R/S configuration for any chiral centers in the following molecules.**



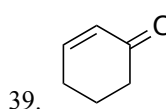
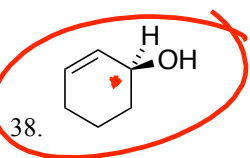
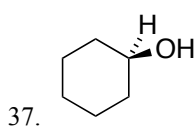
This one is very hard.  
 But for each of the 5 chiral C's, the tie-breaking processes do work.  
 The upper-left S is harder than the others.

**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).**

One chiral carbon  $\Rightarrow$  chiral molecule

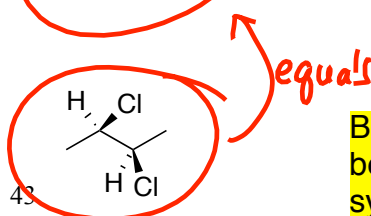
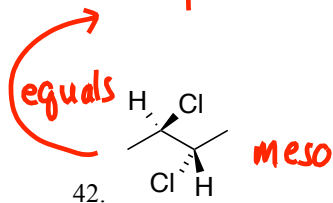
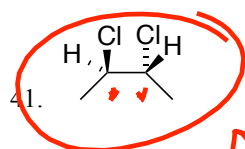
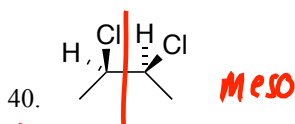


Two common attachments  $\Rightarrow$  achiral

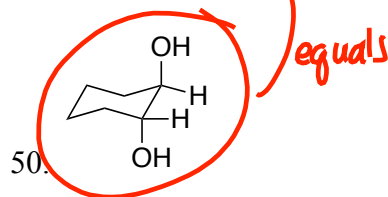
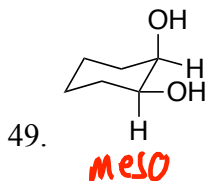
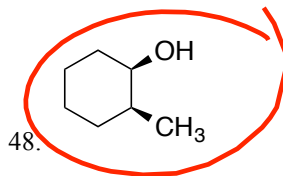
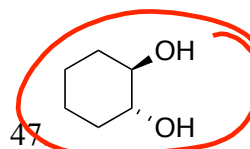
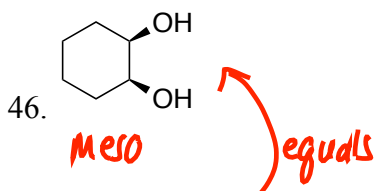
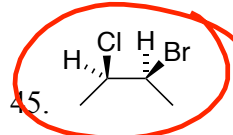
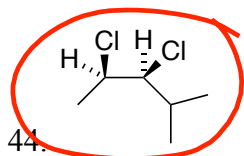


Plane of symmetry  $\Rightarrow$  achiral

Two common attachments  $\Rightarrow$  achiral



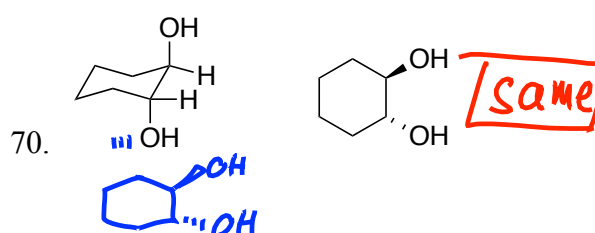
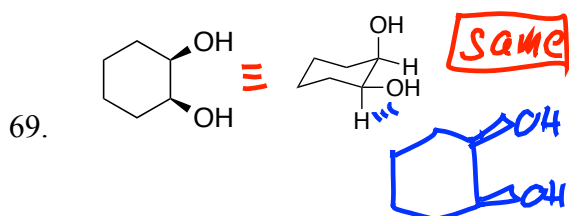
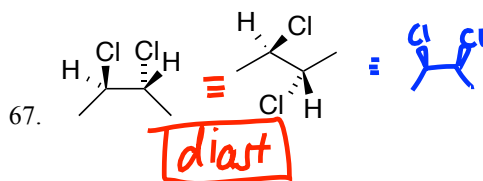
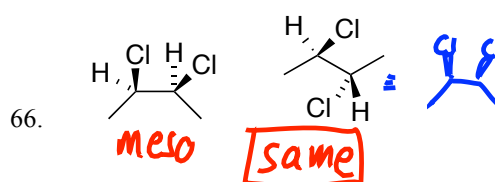
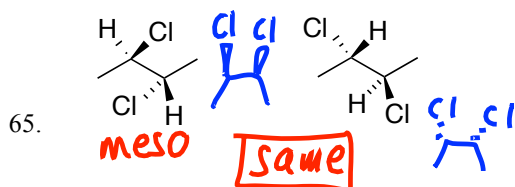
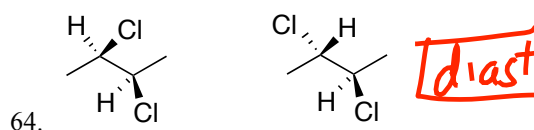
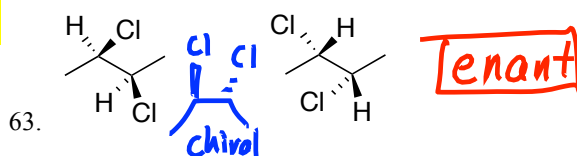
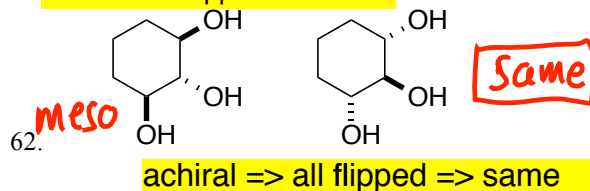
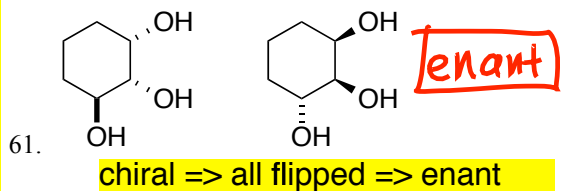
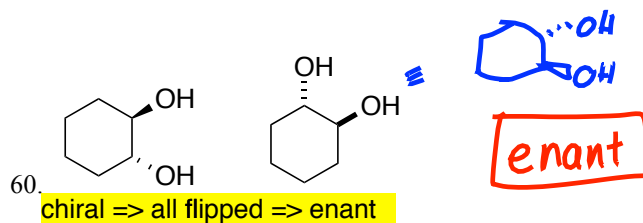
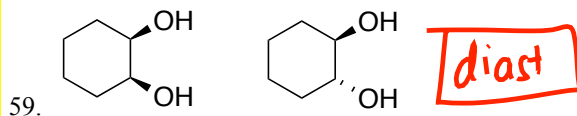
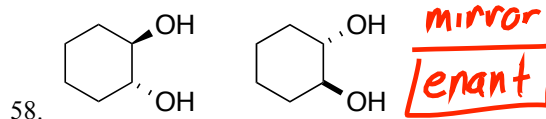
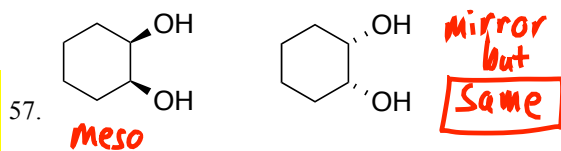
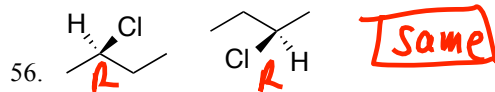
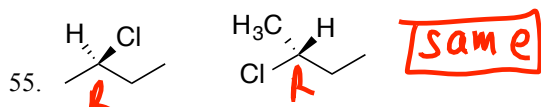
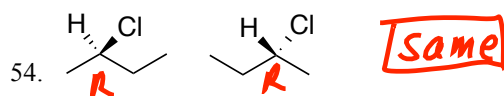
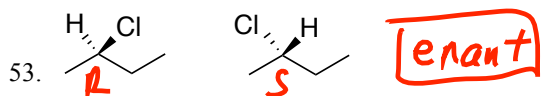
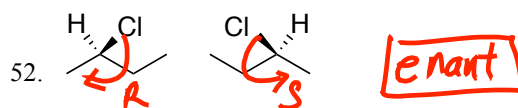
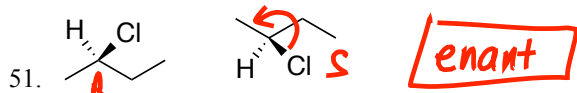
Be able to rotate in order to better visualize planes of symmetry or lack thereof



NT

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

With just one chiral C, if you can assign R/S for both, you can tell if same or different.



With two chiral C's:  
1. orient them the same;  
2. look for all flipped (mirror) vs some flipped (not mirror, diastereomer)  
3. If mirror, check for plane of symmetry (meso, achiral, mirror same) vs not (chiral, mirror is enantiomer)

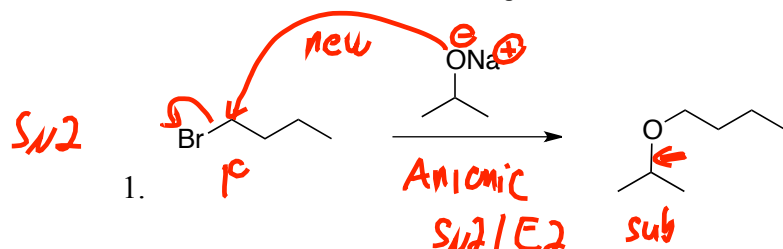


## Organic Chemistry I

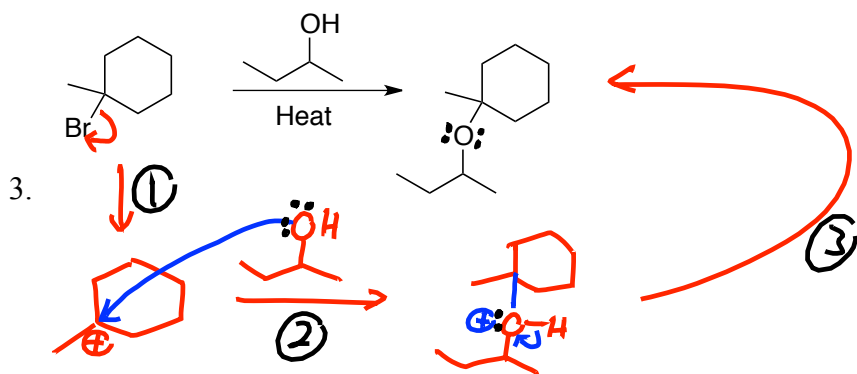
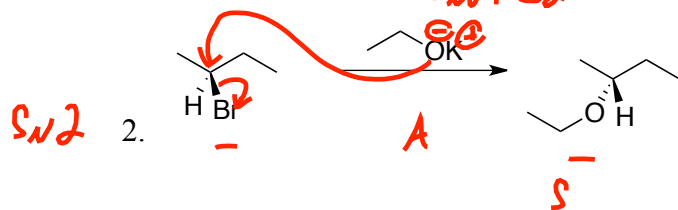
## Test 2 Extra Mechanism Practice Problems

## Answers

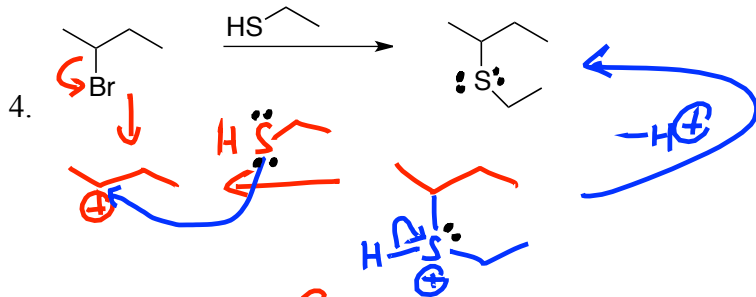
Note: In each of these cases, I am asking you to draw the mechanism for the product shown. In some cases where both elimination and substitution may occur, there may be another product in addition to the one shown. And in cases where elimination is happening, there may be an additional structural isomer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



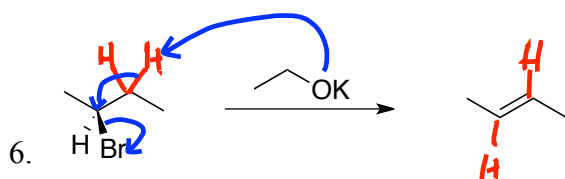
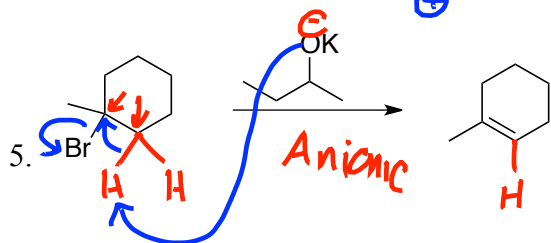
$\text{S}_{\text{N}}2$ : No intermediates

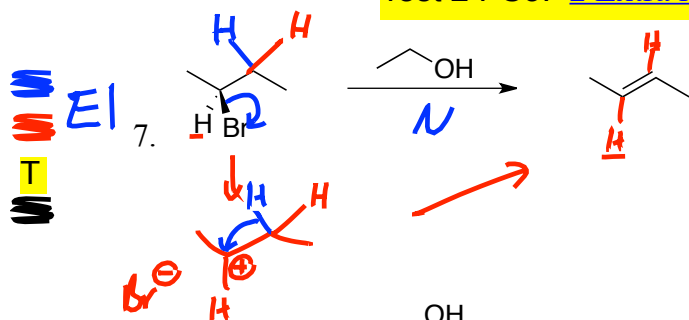


$\text{S}_{\text{N}}1$ : 3 steps  
1. Cation formation  
2. Cation Capture  
3. Loss of proton



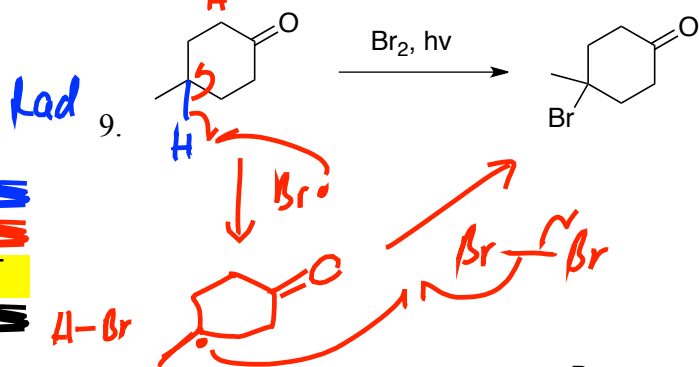
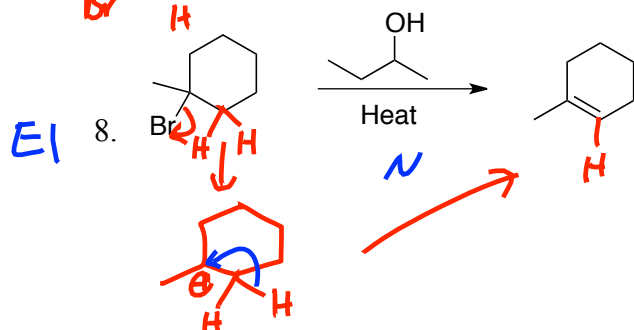
Mech explains changes in:  
1. Bonds  
2. Lone pairs  
3. Formal charges





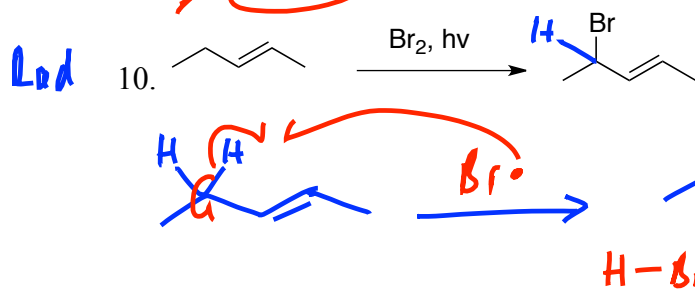
E1:

1. Cation formation
2. Loss of a neighbor H



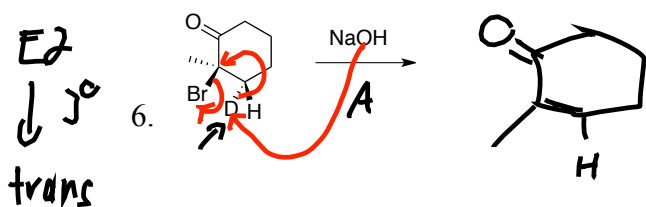
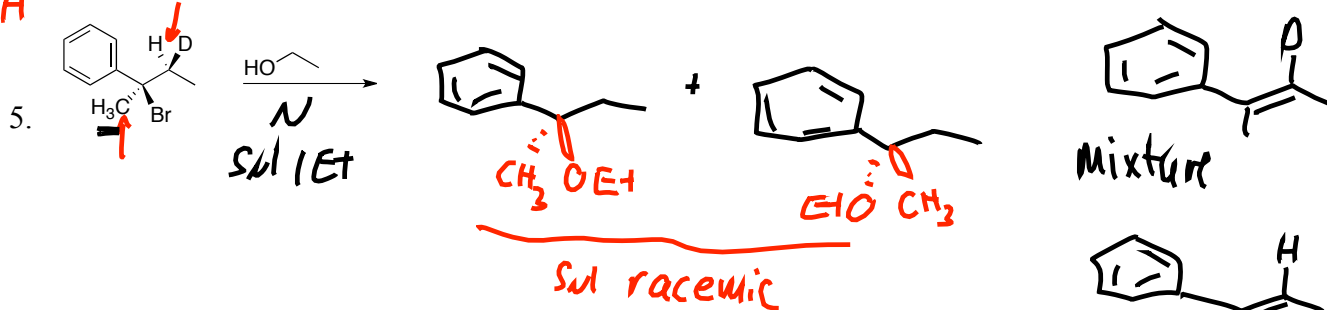
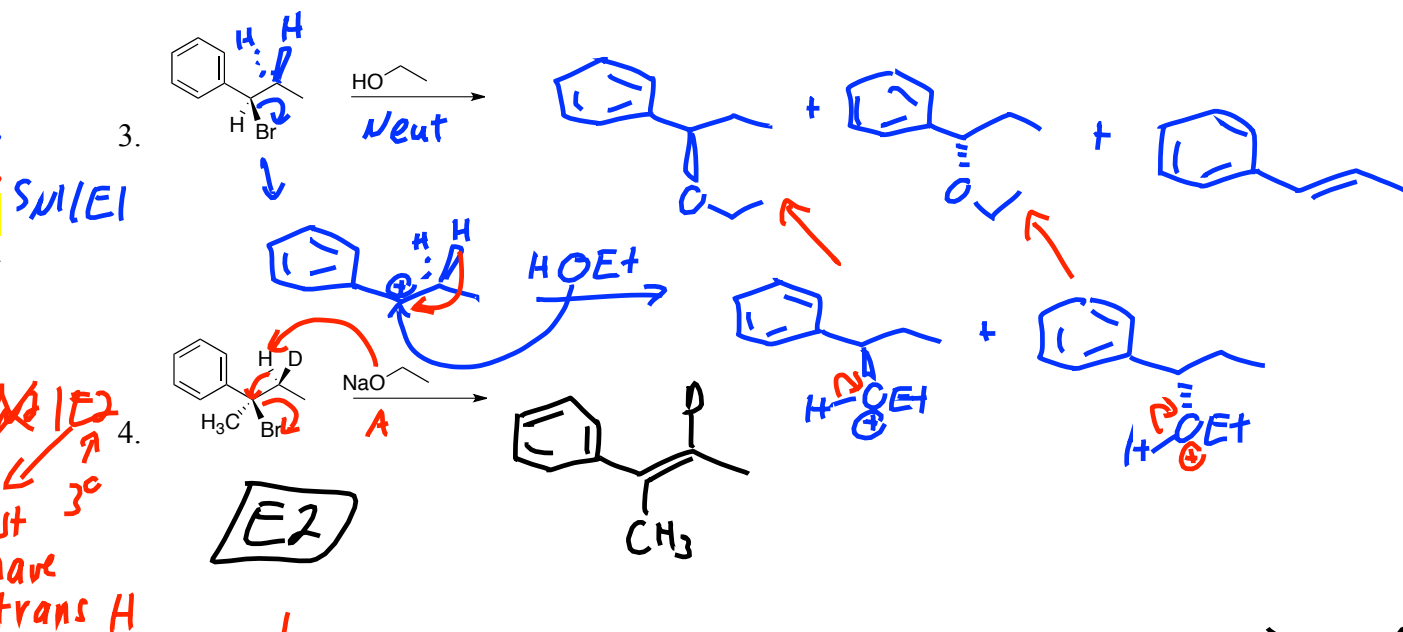
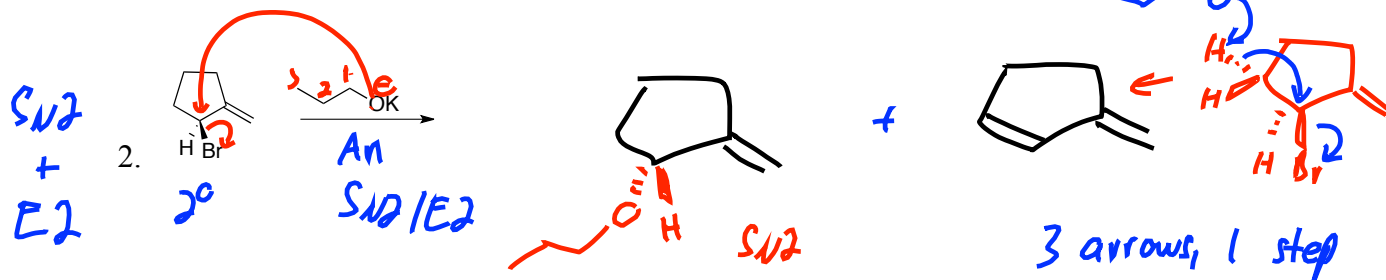
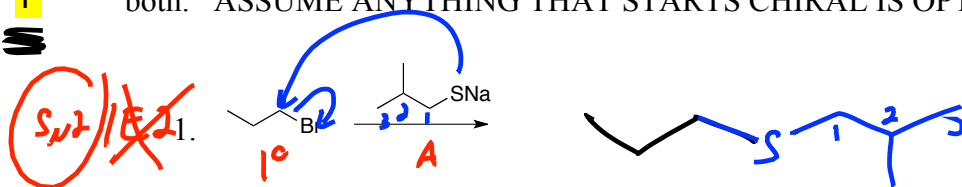
Radical Bromination:

1. Abstract H using Br radical
2. Attach Br to carbon radical

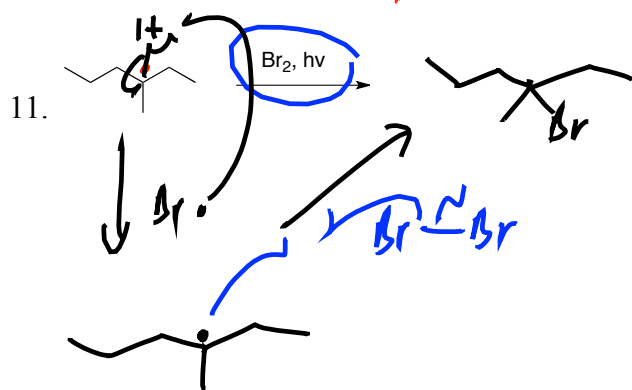
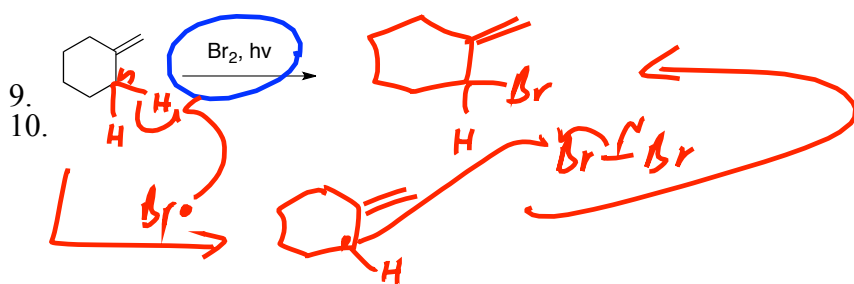
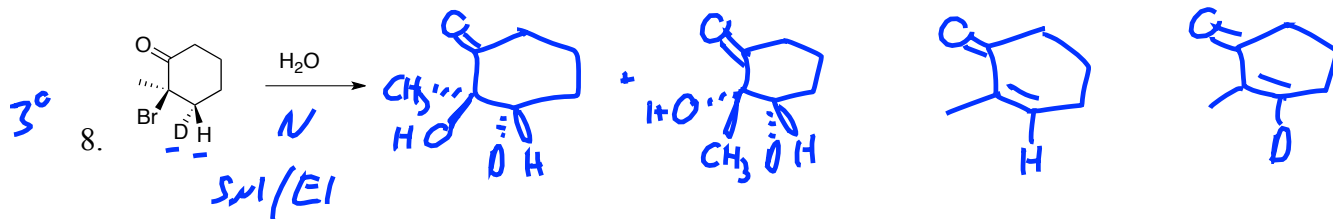
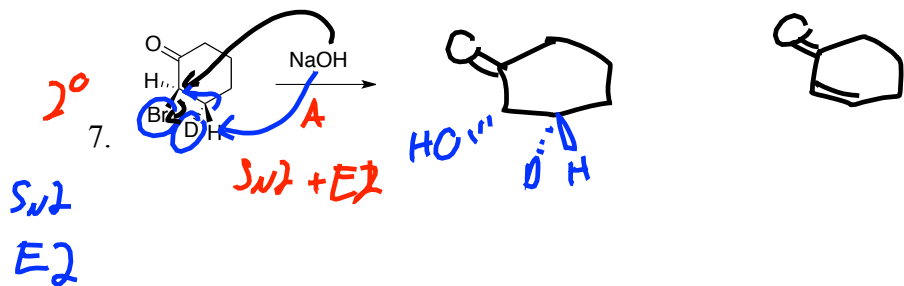


$\text{Br}^\bullet$

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.



W  
W  
T  
W



W  
W  
T  
W

W  
W  
T  
W



## Organic Chemistry I

Jasperse Some Chapter 7 Quiz-Like Practice, But NOT REQUIRED. Answer key available:

1. How many elements of unsaturation are present for a molecule with formula  $C_5H_5NO_2$ ?

- a. 0
- b. 1
- c. 2
- d. 3
- e. 4**
- f. 5

Theory:

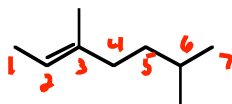
$$12 + 1 = 13$$

Actual

$$\frac{5}{2}$$

$$8H \text{ short} = 4 EU$$

2. Provide the proper IUPAC name for the alkene shown below.

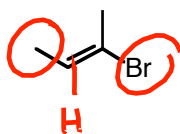
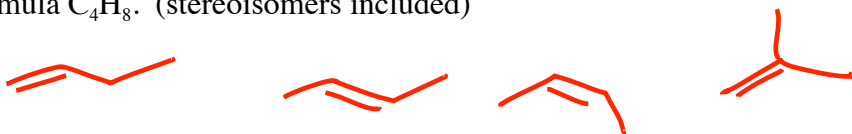
**(E)-3,6-dimethylhept-2-ene**

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 alkenes (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

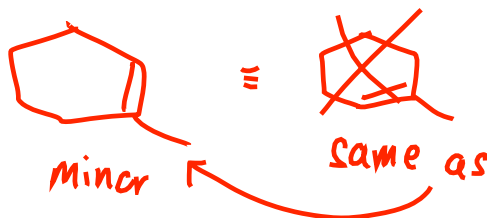
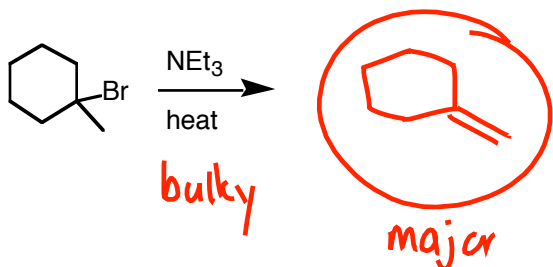
d. They are all of equal stability

tri-subbed  
alkene

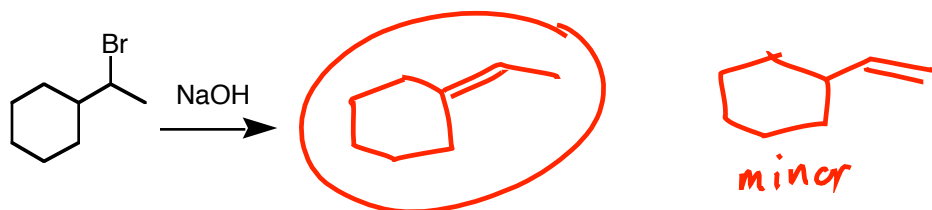
di-subbed

6. a) Draw and circle the major alkene product that would result from the following reaction.

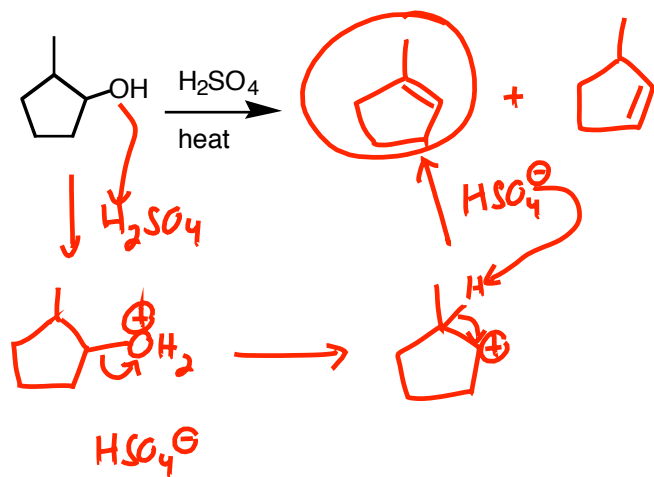
b) In addition, draw any other minor isomers that would form, but don't draw the same isomer twice.



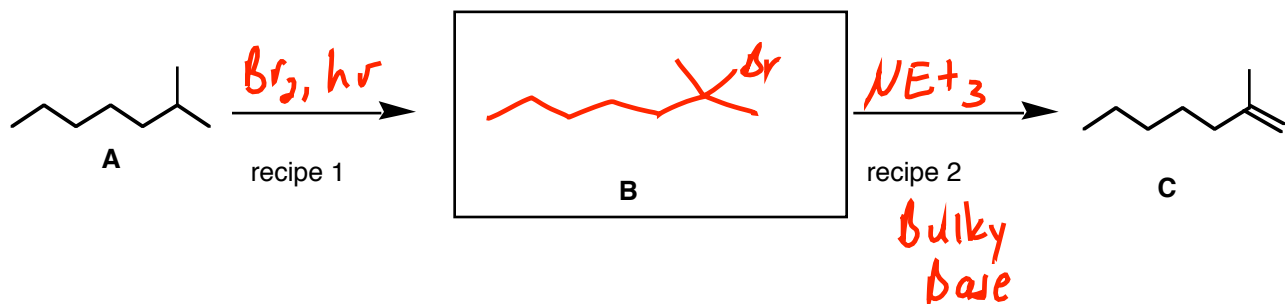
7. a) Draw and circle the major alkene product for the following reaction. (There may be a lot of  $S_N2$  product that forms as well, but you need not draw that.)  
b) In addition, draw any other minor isomers that would form, but don't draw the same isomer twice.



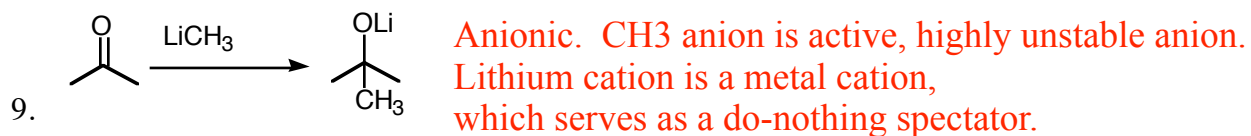
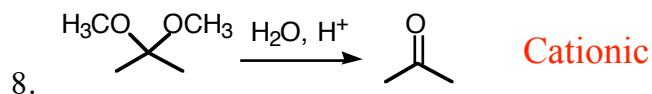
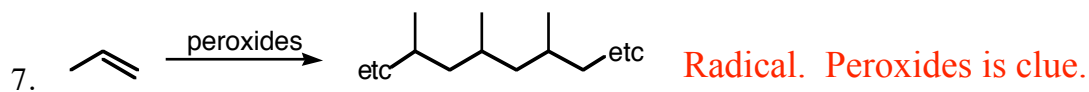
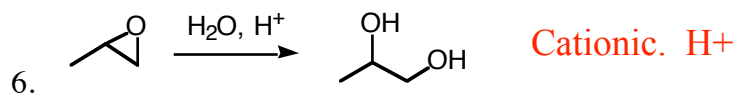
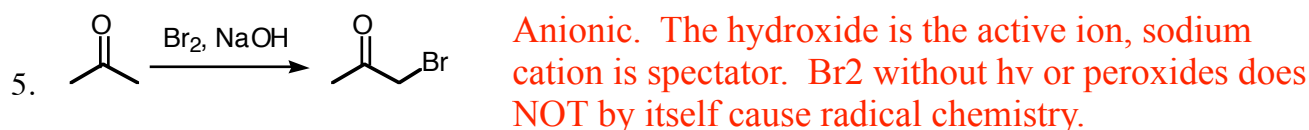
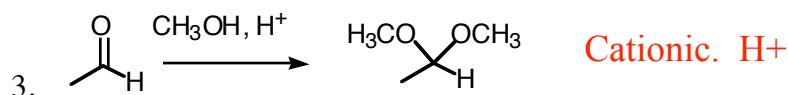
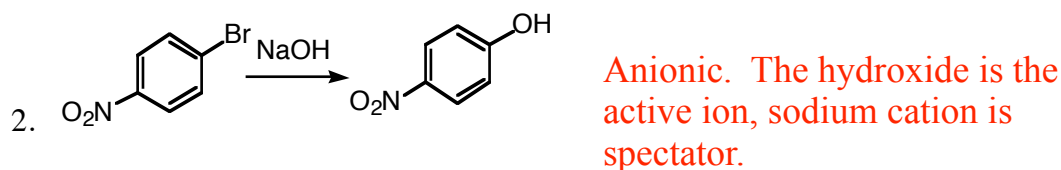
8. a) Draw and circle the major alkene product for the reaction shown. (There may be some  $S_N1$  product that forms as well, but you need not draw that.)  
b) In addition, draw any other minor isomers that would form, but don't draw the same isomer twice.  
c) Draw a detailed, step-by-step mechanism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



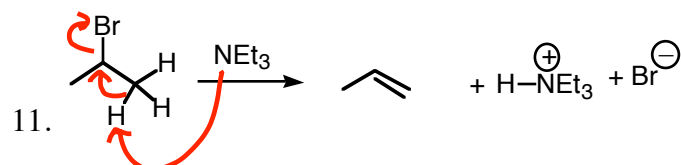
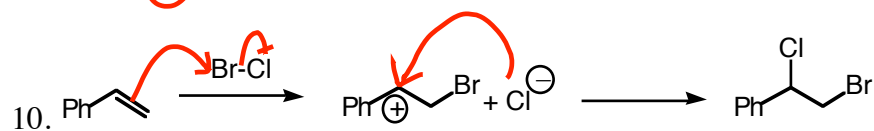
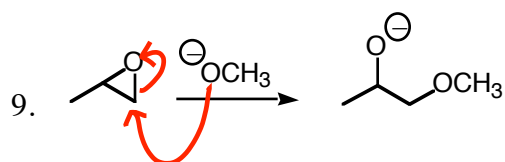
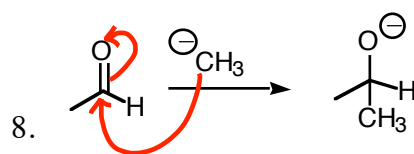
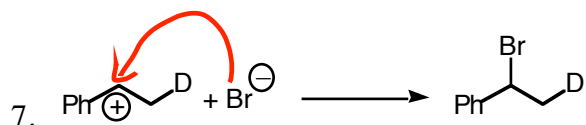
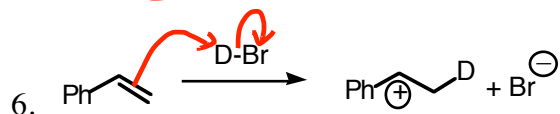
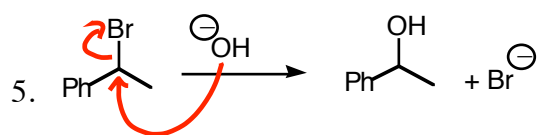
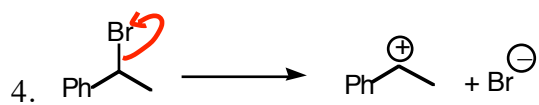
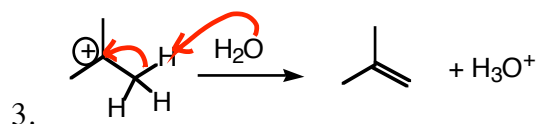
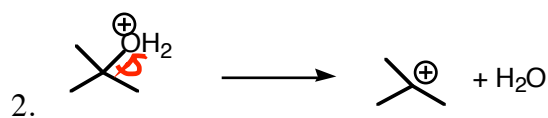
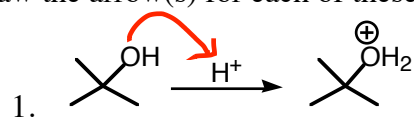
9. Provide the chemicals necessary for transforming 2-methylheptane (A) into 2-methyl-1-heptene (C), and draw the structure for the chemical B which you can make from A and which serves as a precursor to C. Above the arrows write in recipes for the  $A \rightarrow B$  transformation and for the  $B \rightarrow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



1.  Cationic (The H<sup>+</sup> is the active ion. Nitrate does nothing.)



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



## Organic Chemistry I

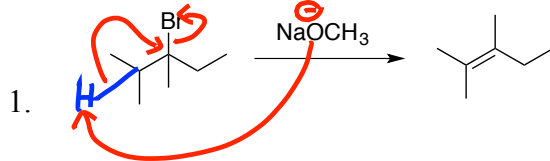
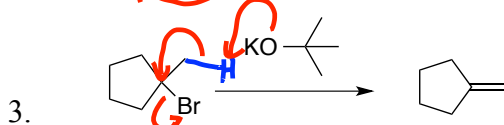
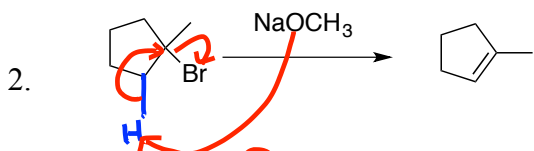
## Test 3 Extra Mechanism Practice Problems

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

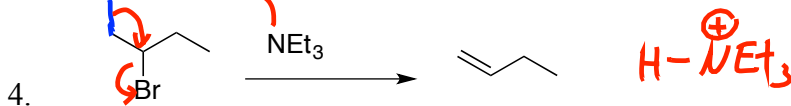
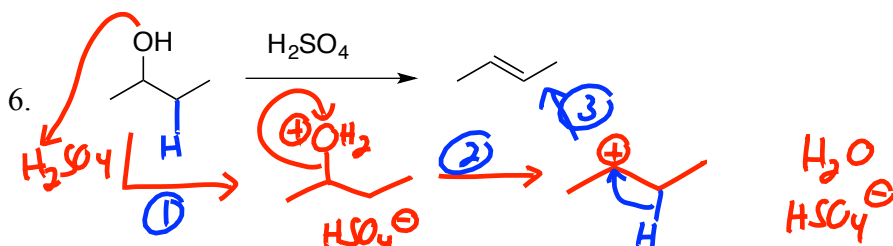
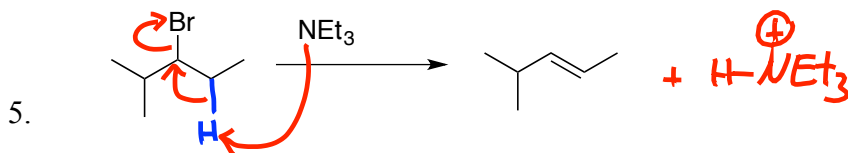
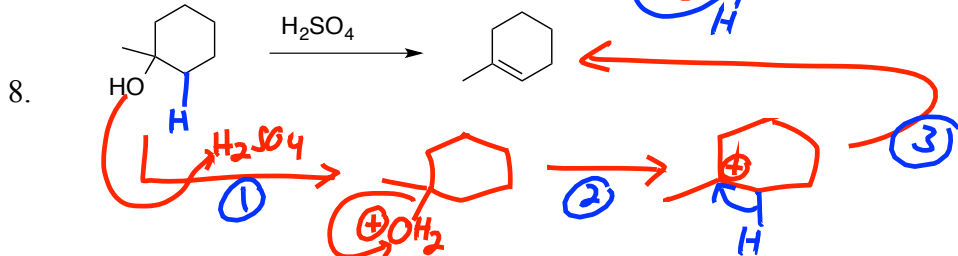
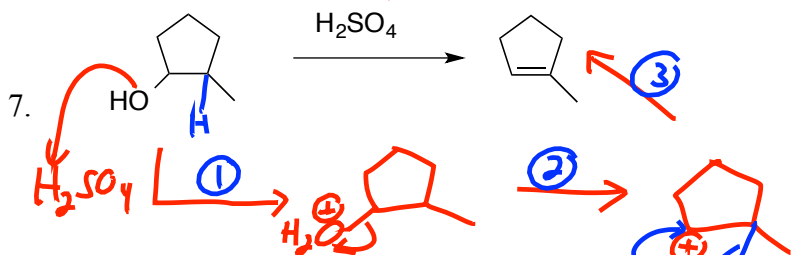
**Answers**

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! ☺

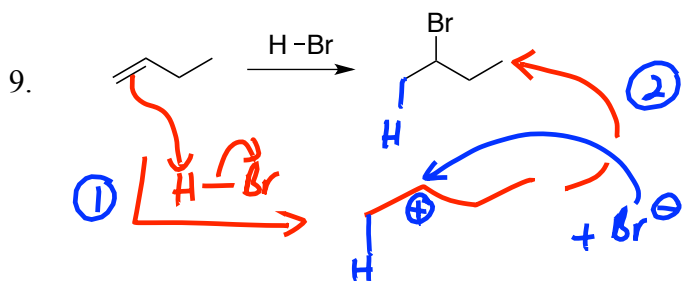
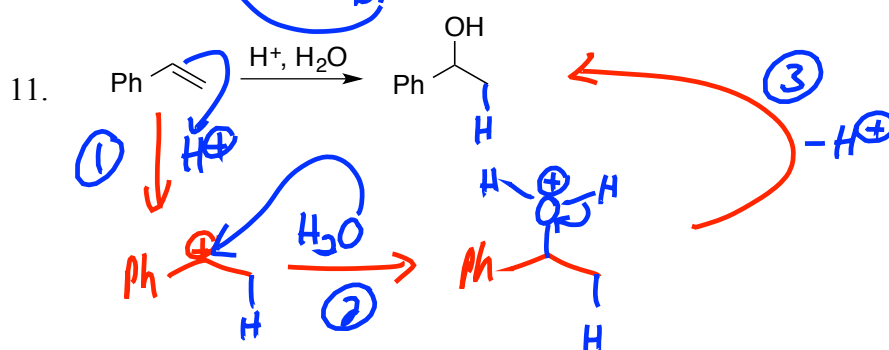
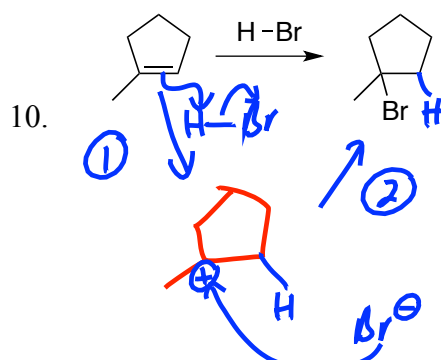
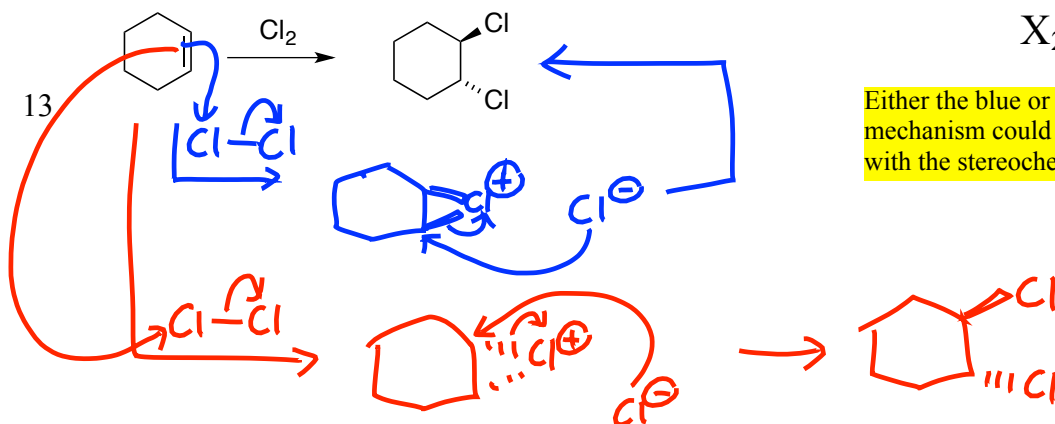
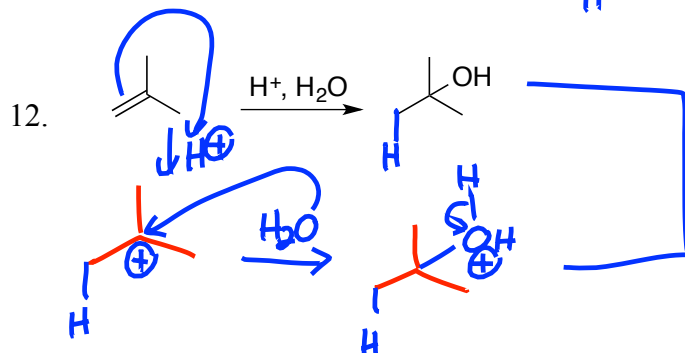
## Ch. 7 Elimination Reactions

E2,  
Small/Normal  
Base

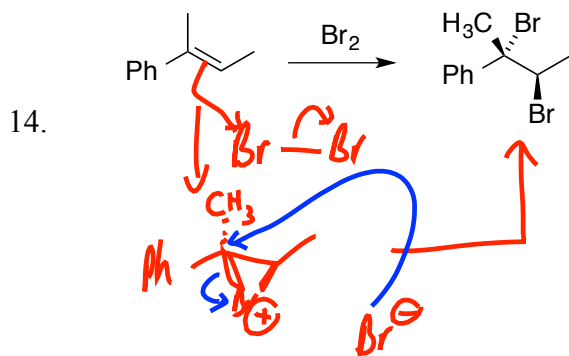
E2, Bulky Base

E2, Bulky Base  
using Neutral  
NEt<sub>3</sub>H<sup>+</sup>-Catalyzed  
Dehydration

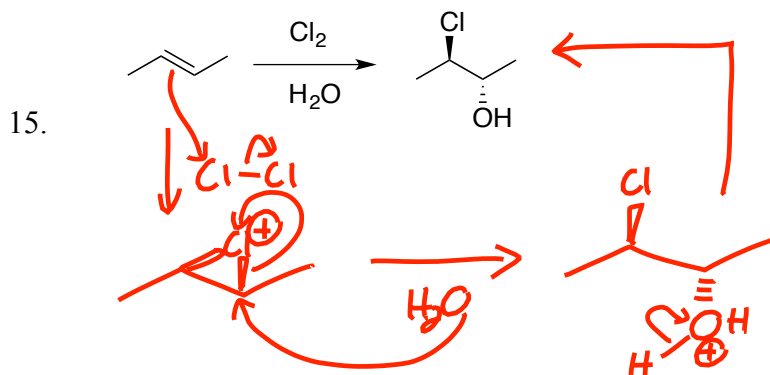
## Ch. 8 Reactions.

Ionic H-X  
Addition $H^+$  catalyzed  
 $H_2O$  Addition $X_2$  addition

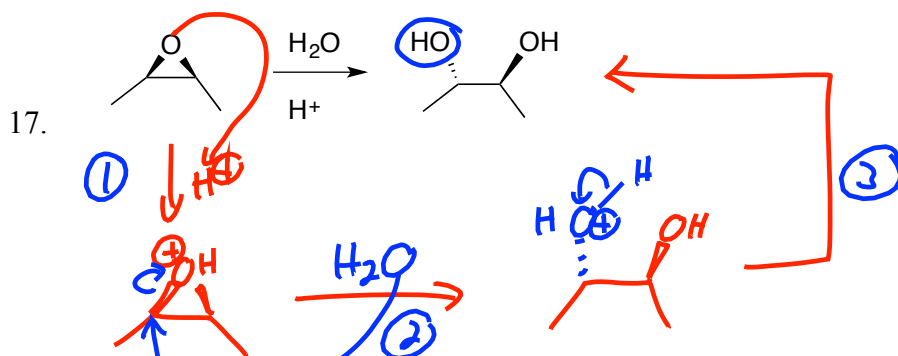
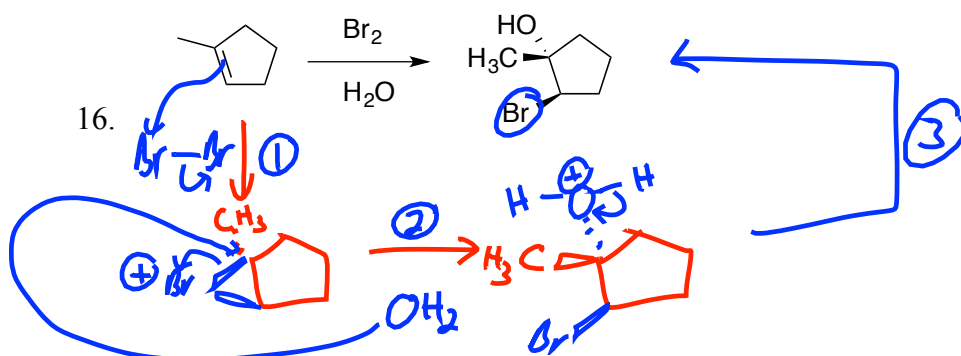
Either the blue or the red mechanism could explain the product with the stereochemistry illustrated.



X<sub>2</sub> addition

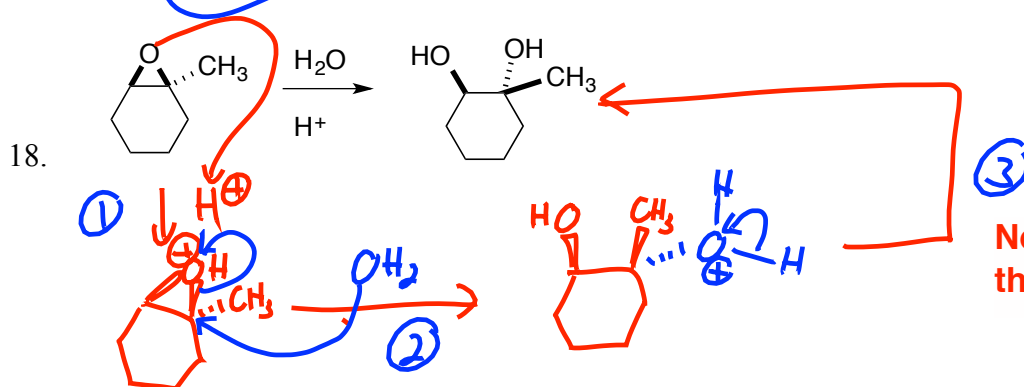


X<sub>2</sub>/H<sub>2</sub>O addition



H<sup>+</sup> catalyzed  
H<sub>2</sub>O addition

Not Responsible for  
this Year's Testing



Not Responsible for  
this Year's Testing

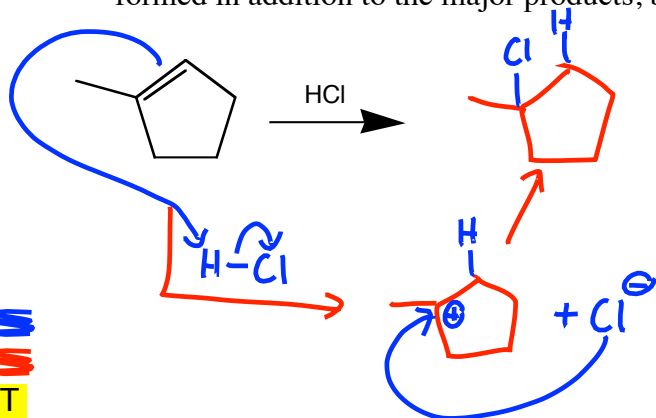




## Organic Chemistry I

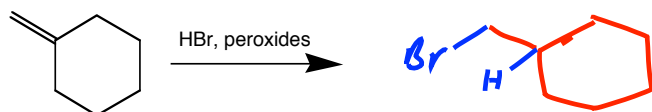
## Test 3 Extra Alkenes Reactions Practice Problems. (First half of the alkenes reactions only)

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.) Draw the mechanism.

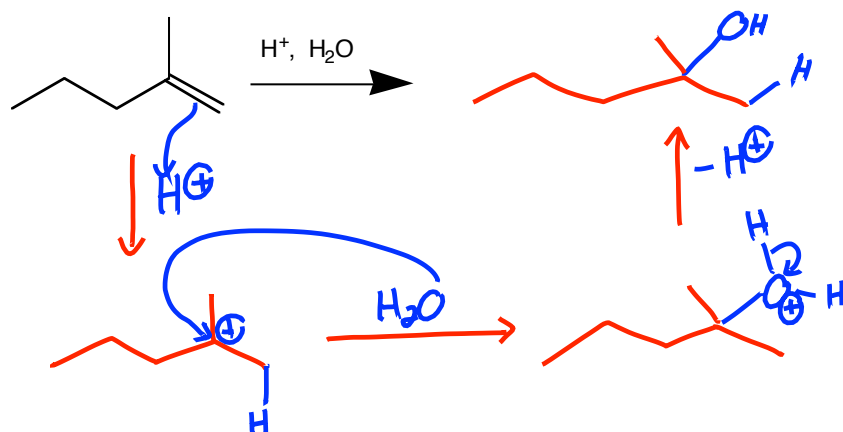


1. Protonate on less substituted end to make carbocation on more substituted end.
2. Capture the cation

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.

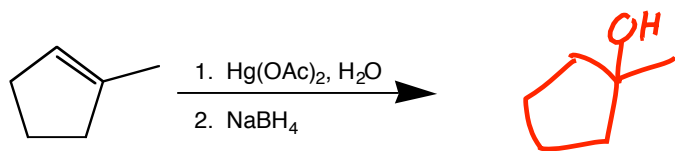


1. Protonate on less substituted end to make carbocation on more substituted end.
2. Capture the cation. Capture by neutral water results in cationic product.
3. Deprotonate to get back to neutral.

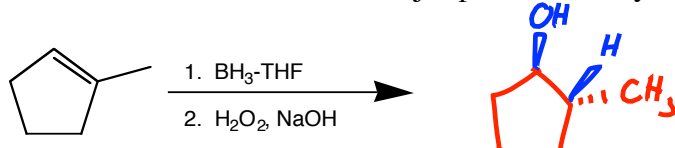
4. Draw the major product for the reaction shown. No mechanism required.



5. 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.

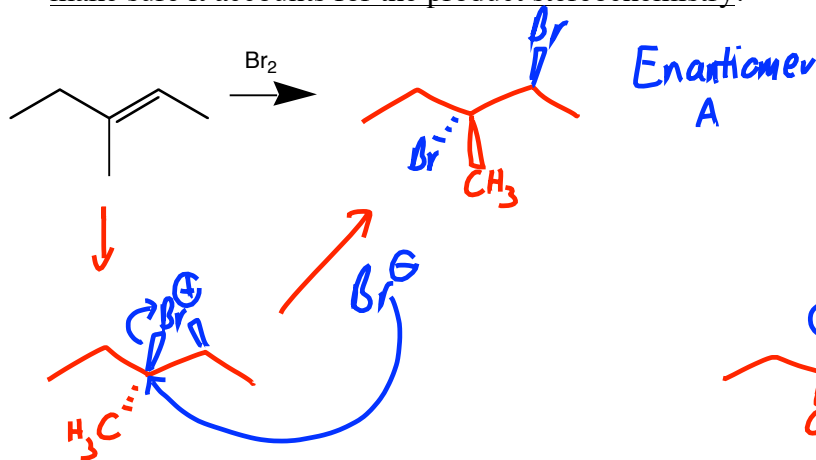


6. Draw the major product for the reaction shown. (There may be some side products or isomers formed in addition to the major products, but you don't need to draw them.)

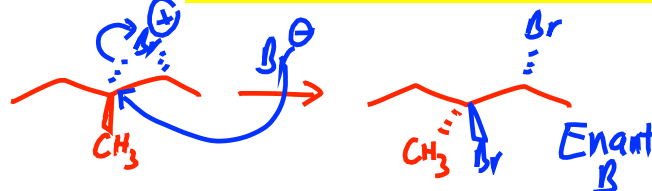


1. Stereochemistry must be designated
2. Either enantiomer is fine.

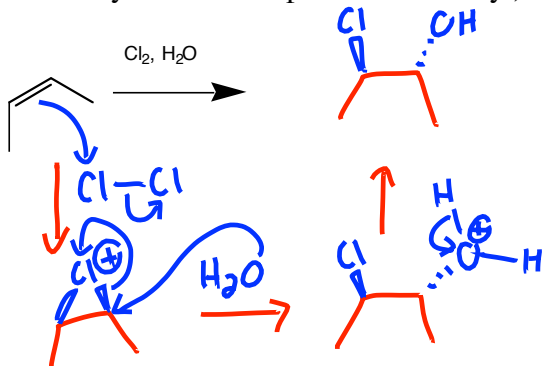
7. Draw the major product for the reaction shown. Include stereochemistry. Draw the mechanism, and make sure it accounts for the product stereochemistry.



1. Stereochemistry must be designated
2. Either enantiomer is fine.
3. Really ugly to draw the stereochem of the 3-membered ring. But for the enantiomer I drew, you'd need to show the bromide anion attacking the more substituted end, and you'd need the original bromine to be in front.



8. Draw the major product for the reaction shown. Include stereochemistry. Draw the mechanism, and make sure it accounts for the product stereochemistry. 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.)



1. Stereochemistry must be designated
2. Either enantiomer is fine.
3. For the enantiomer I drew, you'd need to show the chloride on the front, and have the water attack the right carbon. Your mechanism and product stereochemistry must be internally consistent.

Answers

## Organic Chemistry I

## 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.

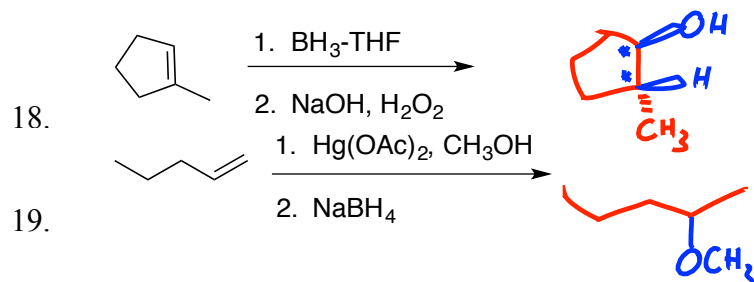
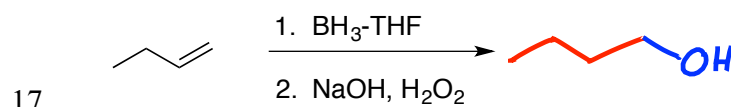
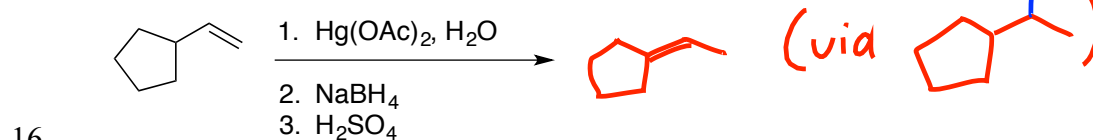
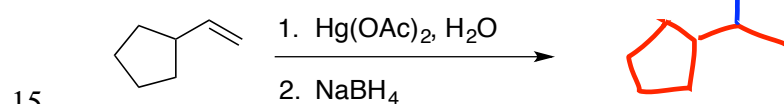
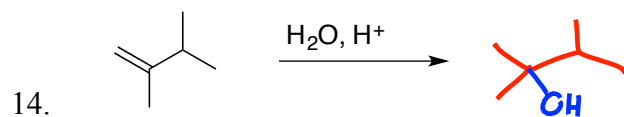
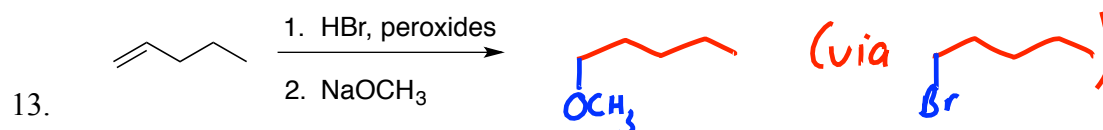
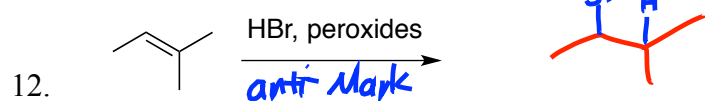
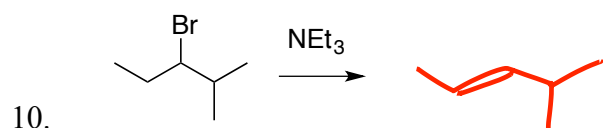
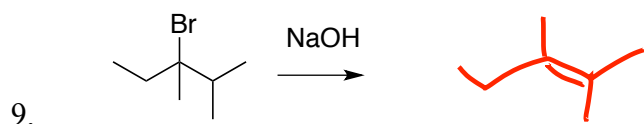
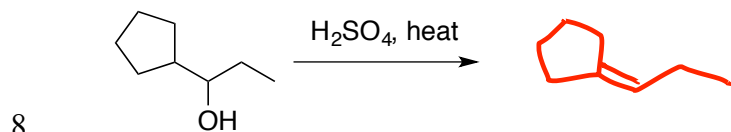
Page 5: Recognizing cationic/anionic/radical reactions, and reasonable intermediates/first steps

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

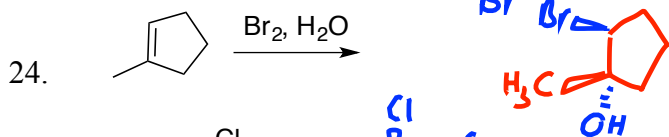
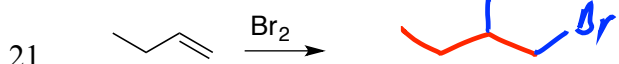
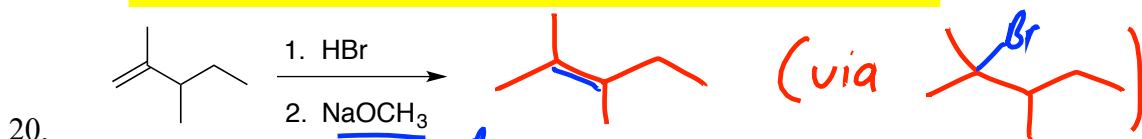
## A. Provide reagents for the following transformations.

1.  $\text{H}_2\text{SO}_4$   
2.  $\text{Br}_2$
1.  $\text{H}_2\text{SO}_4$   
2.  $\text{Hg}(\text{OAc})_2$   
3.  $\text{NaBH}_4$
1.  $\text{NEt}_3$  (bulky base) or  $\text{KOt}$   
2.  $\text{Cl}_2$ ,  $\text{H}_2\text{O}$
1.  $\text{NEt}_3$  (bulky base)  
2.  $\text{BH}_3 \cdot \text{THF}$   
3.  $\text{NaOH}$ ,  $\text{H}_2\text{O}_2$
1.  $\text{NEt}_3$   
2.  $\text{OsO}_4$ ,  $\text{H}_2\text{O}_2$
1.  $\text{Br}_2$ ,  $h\nu$   
2.  $\text{NaOH}$  (small base)  
3.  $\text{O}_3$   
4.  $\text{Me}_2\text{S}$
1.  $\text{Br}_2$ ,  $h\nu$   
2.  $\text{NaOH}$   
3.  $\text{CH}_3\text{CO}_3\text{H}$ ,  $\text{H}_2\text{O}$

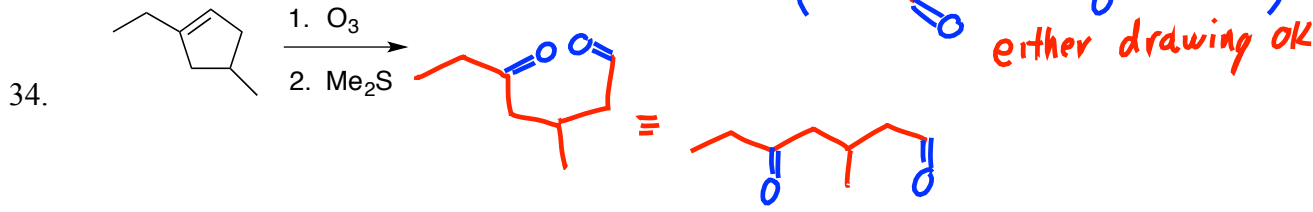
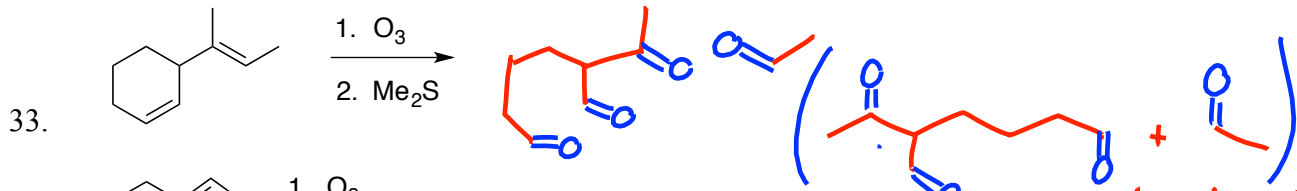
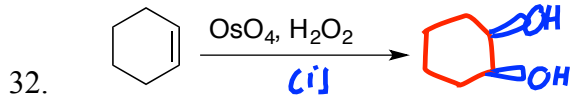
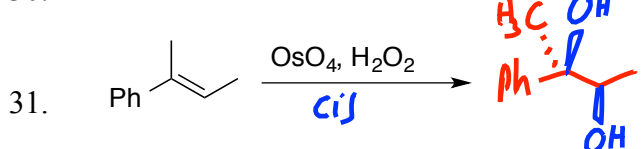
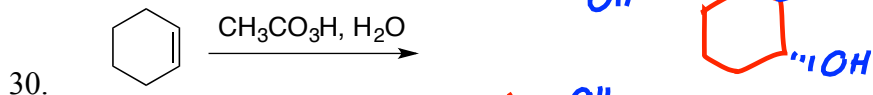
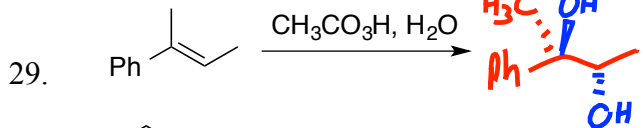
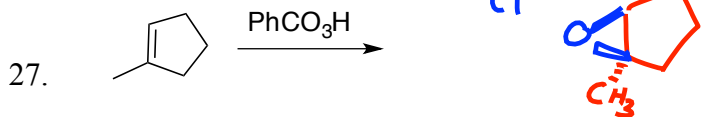
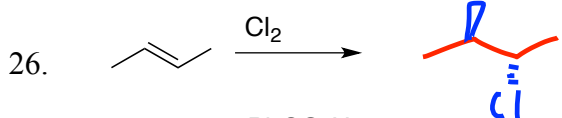
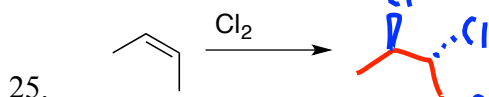
B. Draw the **major** product for each of the following reactions or reaction sequences. You needn't bother to show side products or minor products. For chiral molecules that are racemic, you needn't draw both enantiomers. BE CAREFUL TO SHOW THE CORRECT ORIENTATION, AND THE CORRECT STEREOCHEMISTRY IN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



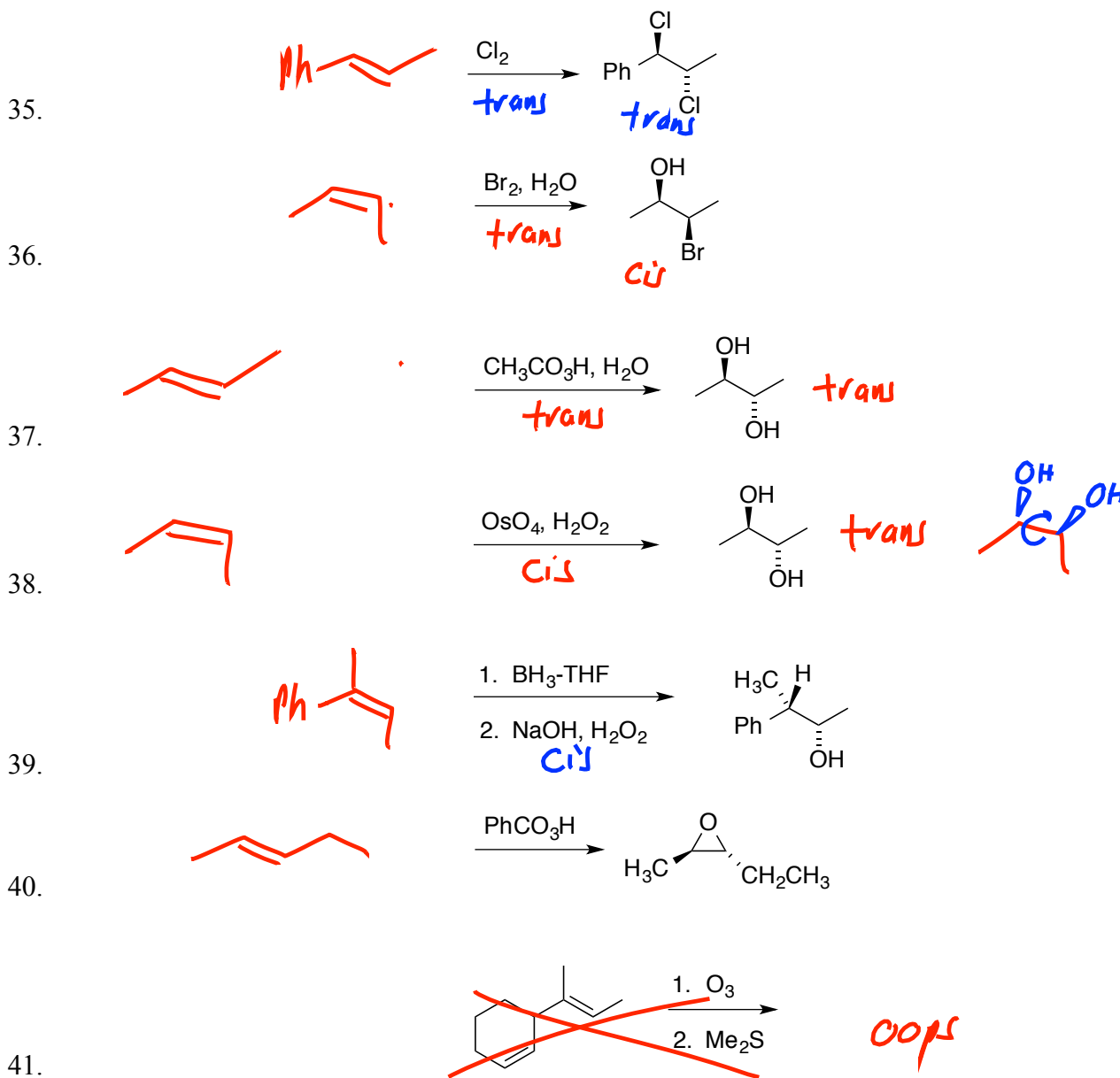
Note: explicit stereochemistry must be drawn. The enantiomer would have been equally acceptable.



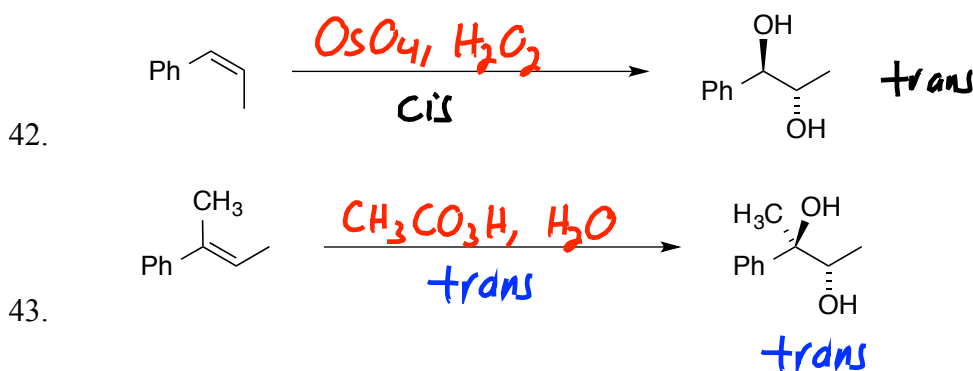
Note: explicit stereochemistry must be drawn. The enantiomer would have been equally acceptable. This principle will apply for any of the reactions producing two chiral centers. Problems 23-32



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

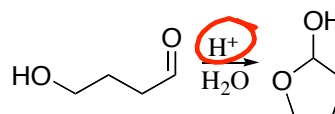


D. What reagent(s) would you use to conduct the following transformations?



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.

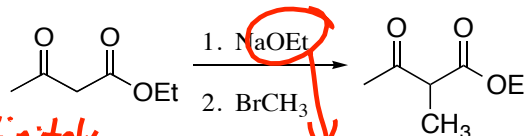
44. The transformation shown is common in many biological systems. Which of the following statements is definitely, absolutely **false**?



- a. The first step in the mechanism probably involves protonation of the carbonyl oxygen. **T**
- b. The overall reaction involves an addition reaction. **T**
- c. The mechanism is probably radical in nature. **Definitely false**

**Cationic**

45. For the transformation shown, which of the following statements is definitely, absolutely **false**?

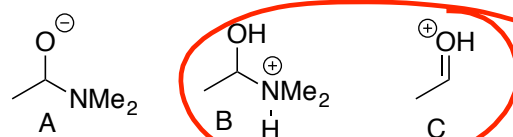
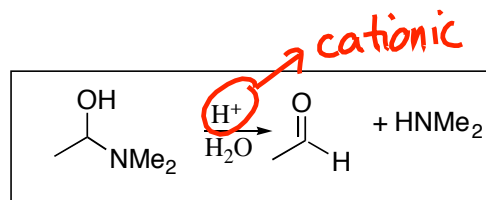


- a. The first step in the mechanism probably involves protonation of a carbonyl oxygen. **Definitely false**
- b. The overall reaction involves a substitution reaction. **T**
- c. The mechanism is probably anionic in nature. **T**
- d. The first step in the mechanism involves ethoxide anion grabbing a hydrogen. **T**

**Definitely false**

**anionic**

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?

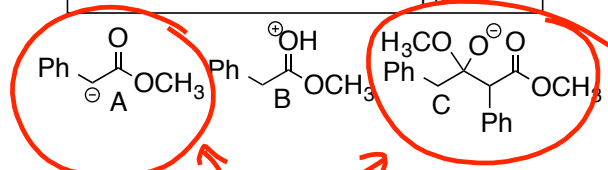
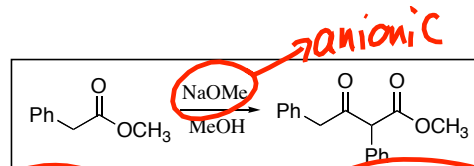


**anionic**

**cationic**

- 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 intermediate; structures **B** and **C** definitely aren't

47. Shown is a reaction, and some possible intermediates along the mechanistic pathway. Given the reaction conditions shown, which of the following statements is true?



**anionic**

- 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 intermediate; structures **B** and **C** definitely aren't

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  $C_5H_8$ , given that it reacts with excess  $H_2/Pt$  to give  $C_5H_{10}$ .

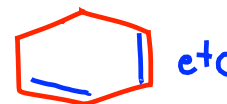
Answer must show one alkene and one ring. (Other structures also meet that requirement).  $H_2/Pt$  test proved 1 alkene. EU=2 originally. So the other EU must be ring.



etc

49. Provide a possible structure for a compound with formula  $C_6H_8$ , given that it reacts with excess  $H_2/Pt$  to give  $C_6H_{12}$ .

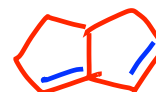
Answer must show two alkene and one ring. (Other structures also meet that requirement).  $H_2/Pt$  test proved 2 alkenes. EU=3 originally. So the other EU must be ring.



etc

50. Provide a possible structure for a compound with formula  $C_8H_{10}$ , given that it reacts with excess  $H_2/Pt$  to give  $C_8H_{14}$ .

Answer must show two alkenes and two rings. (Other structures also meet that requirement).  $H_2/Pt$  test proved 2 alkene. EU=4 originally. So the other two EU must be two rings.



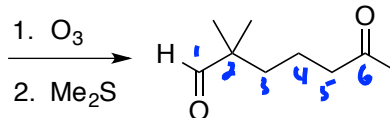
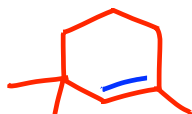
51. Provide a possible structure for a compound with formula  $C_6H_8$ , given that it reacts with excess  $H_2/Pt$  to give  $C_6H_{12}$ .

~~Answer must show two alkene and one ring. (Other structures also meet that requirement).  $H_2/Pt$  test proved 2 alkenes. EU=3 originally. So the other EU must be ring.~~

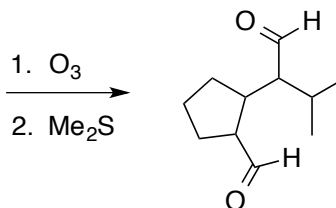
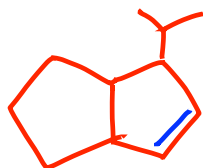
*Oops, same as #49*

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.

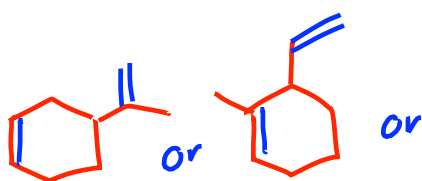
52.



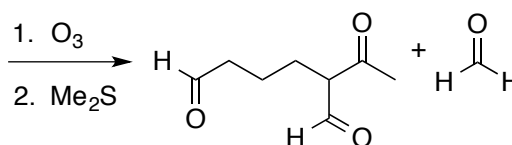
53.



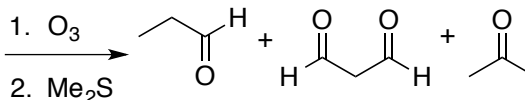
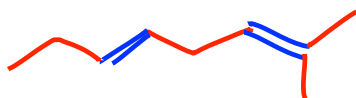
Any of three answers



54.



55.





Practice with HBr addition to Dienes.

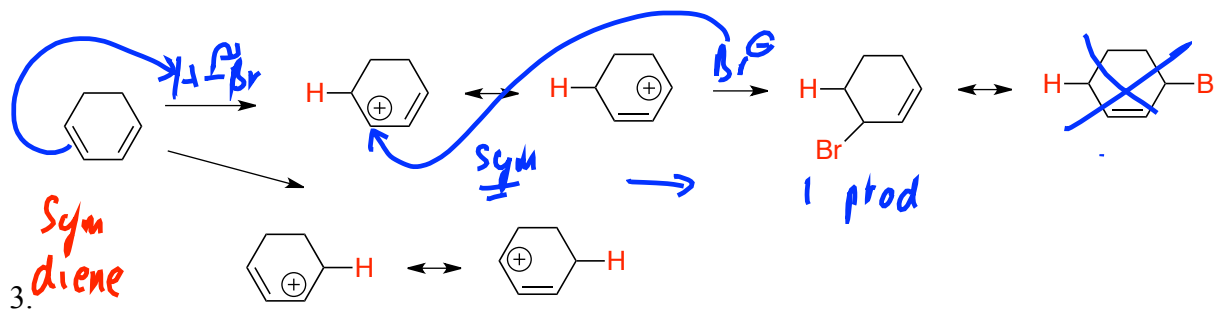
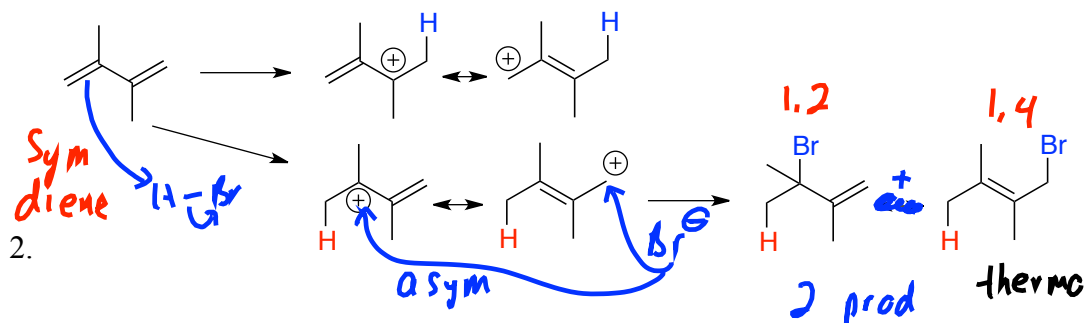
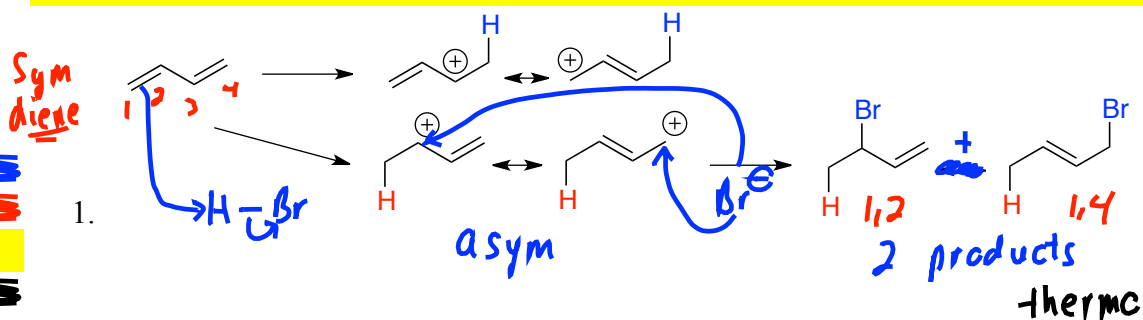
### Review on predicting products when H-X adds to a diene.

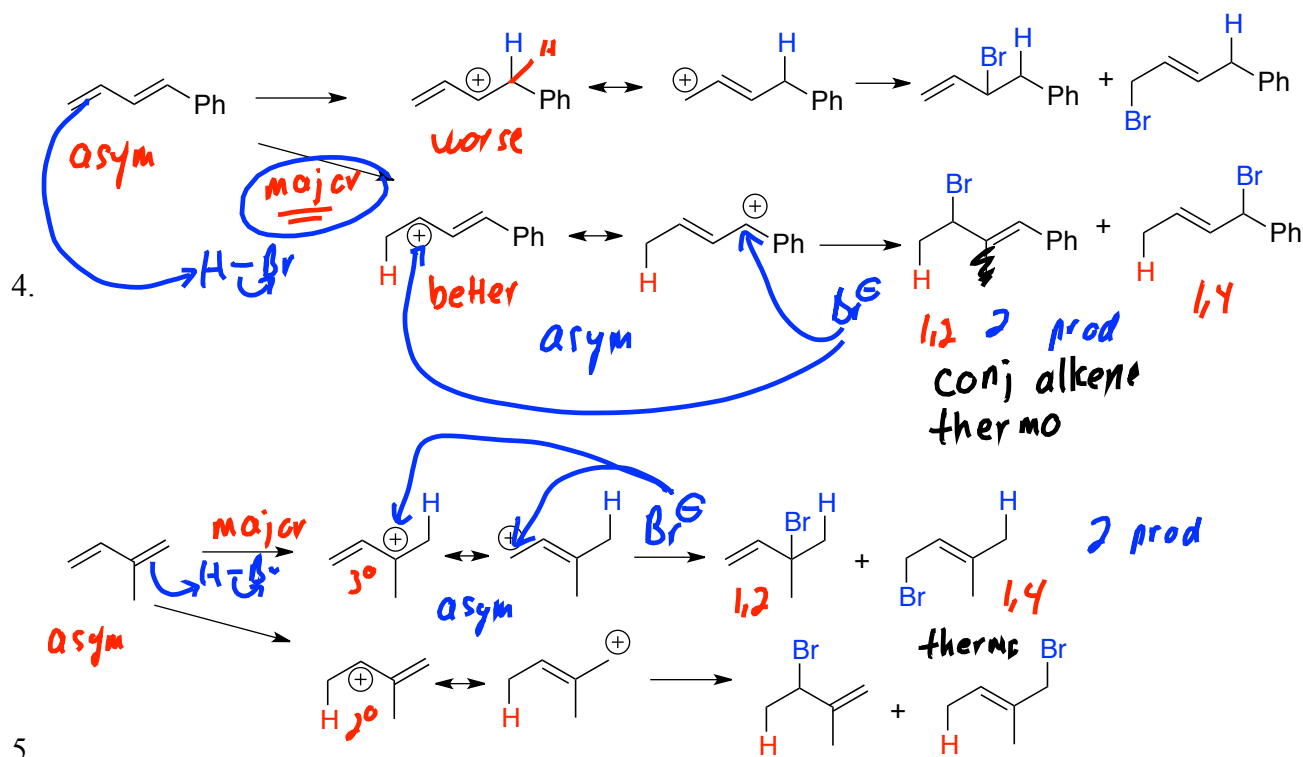
1. Always protonate first on an outside rather than inside carbon.
  - This will give an allylic rather than isolated cation
2. Is the diene symmetric or asymmetric?
  - If it's symmetric, it doesn't matter which outside carbon you add to first.
  - If it's asymmetric, then protonating at different ends 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?

\*Problems 1-3 involve symmetric dienes. I have drawn the allylic cations that would result from protonation on either end, but this is only for illustration sake only. On a real test question, either cation would be fine.

\*Problems 1 and 2 represent cases where the diene is symmetric, but the resulting allylic cation is not symmetric. Thus two structure isomers would be produced.

\*Problem 3 represents a case where not only is the diene symmetric, but so too is the allylic cation. Thus only one isomer will form.

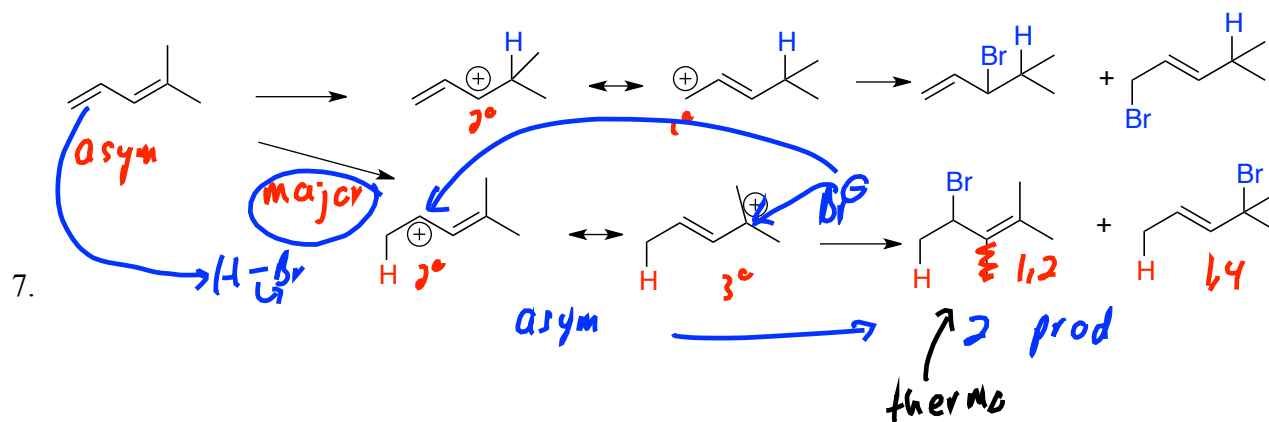
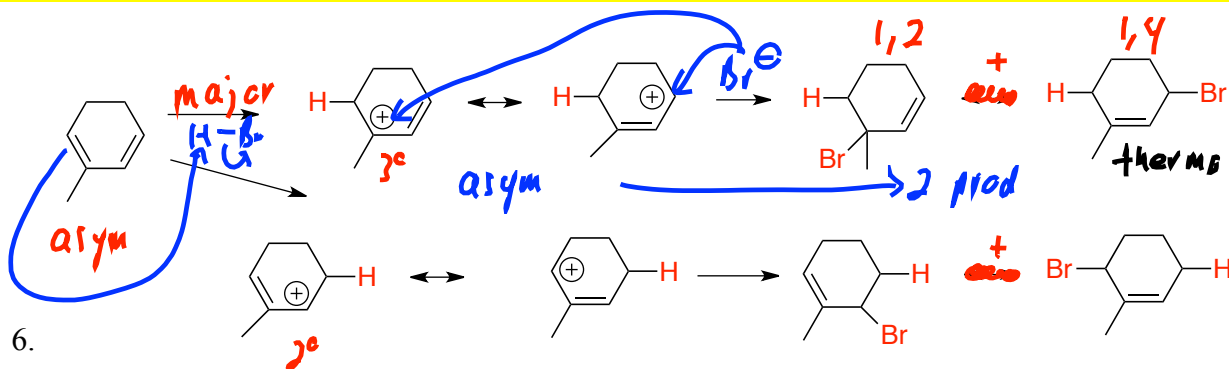




\*Problems 4-8 all involve asymmetric dienes. I have drawn the allylic cations that would result from protonation on either end, and have drawn the products that would result. But the yields of products resulting from the "minor" allylic cation may be low.

\*In each case the major allylic cation is asymmetric, leading to two structural isomers.

\*Problems 4 and 7 both illustrate cases where the 1,2 addition is the more stable "thermodynamic" product.

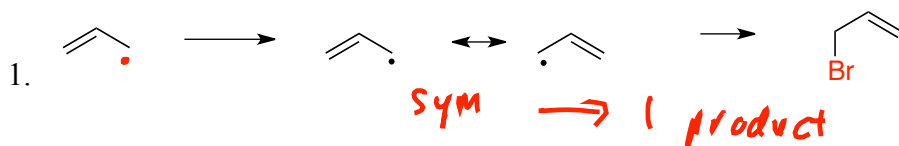


Practice with NBS bromination of Alkenes.

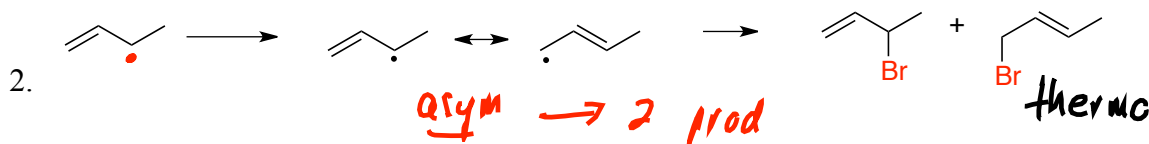
**Review on predicting products for NBS allylic radical bromination of an alkene.**

- Any allylic spot with an H could give up an H to product an allylic radical. How many allylic spots are there?
- 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.
- Once 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  $2 \times 2 = 4$  isomer products.

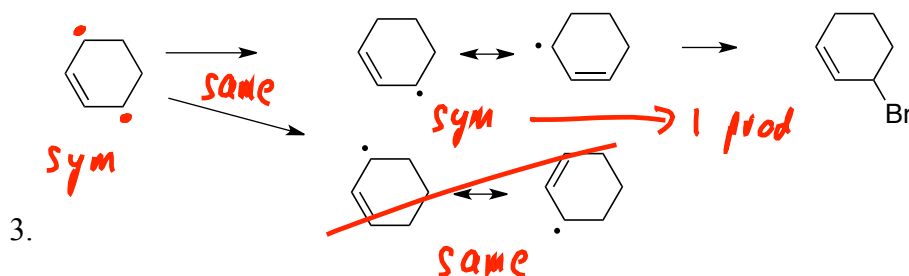
Draw products following NBS/peroxides bromination. Identify radicals, and draw all resonance structures for the radicals.



\*This illustrates the simplest case. There is only one allylic position, and the allylic radical is symmetric leading to a single product.



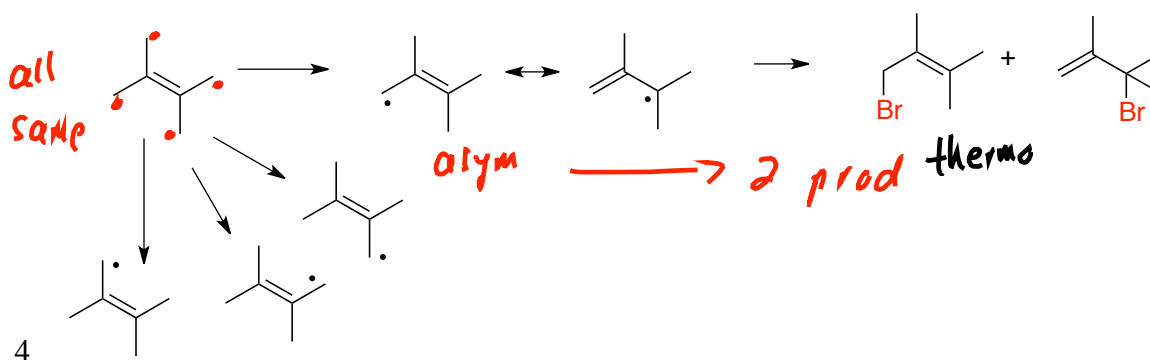
\*Problem 2 has only a single allylic position, but proceeds via an asymmetric radical which leads to two products.



\*Problem 3 represents a symmetric alkene.

It has two allylic positions, but due to symmetry they are both equivalent.

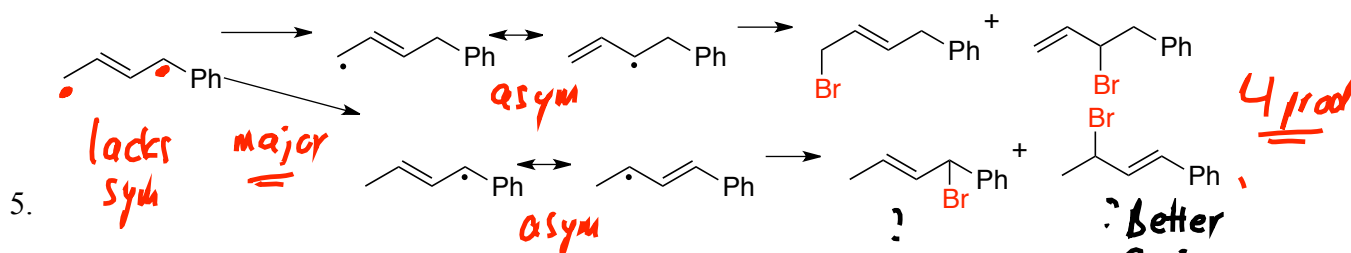
The allylic radical formed is symmetric, thus only a single isomer is produced.



\*Problem 4 represents a symmetric alkene.

It has four allylic positions, but due to symmetry they are all equivalent.

\*The allylic radical formed is asymmetric, thus two isomers are produced.



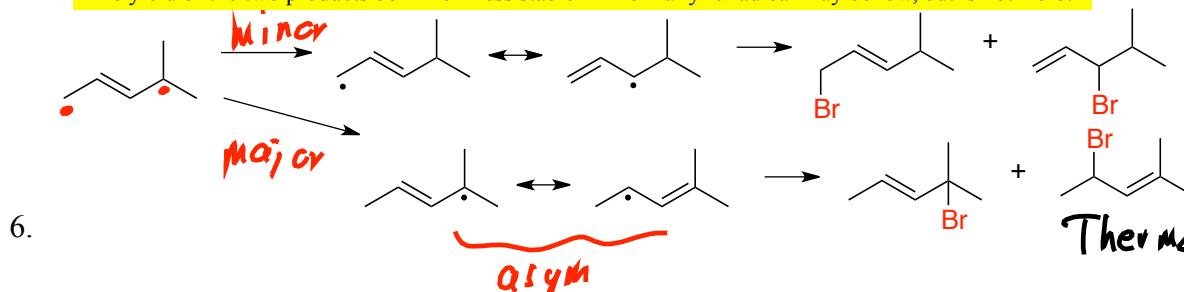
\*Problem 5 represents an asymmetric alkene.

It has two allylic positions, and they are not equivalent.

\*Each allylic radical formed is asymmetric, thus each produces two isomers.

\*2 isomers x 2 products from each => 4 isomeric products.

\*The yield of the two products born from less stable "minor" allylic radical may be low, but is not zero.

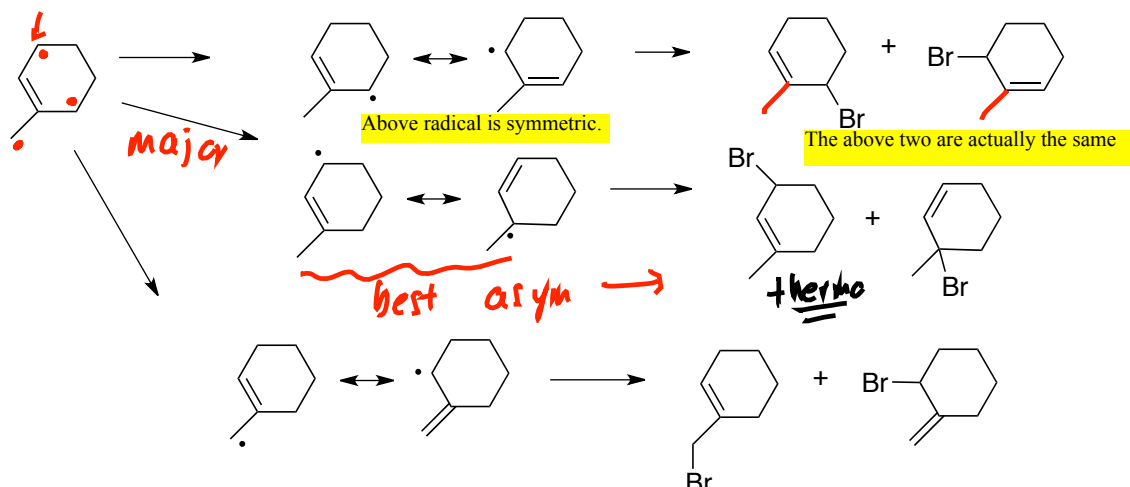


\*Problem 6 represents another asymmetric alkene. It has two allylic positions, and they are not equivalent.

\*Each allylic radical formed is asymmetric, thus each produces two isomers.

\*2 isomers x 2 products from each => 4 isomeric products.

\*The yield of the two products born from less stable "minor" allylic radical may be low, but is not zero.

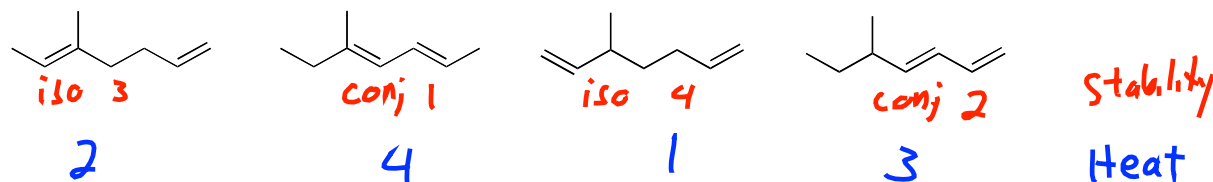


\*Problem 7 represents another asymmetric alkene, with 3 non-equivalent allylic positions

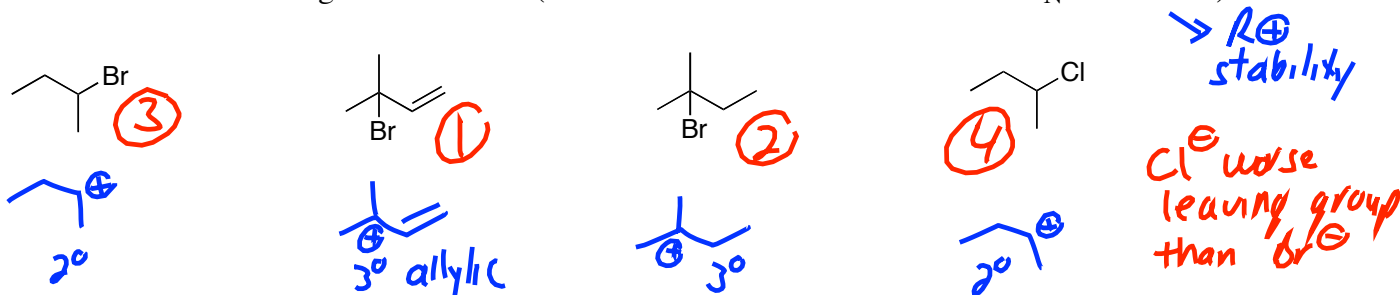
## Organic Chemistry I Jasperse

## 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 ( $AgNO_3/CH_3CH_2OH$ ), 1 being most reactive and 4 being least reactive. (Think: what determines the rates for  $S_N1$  reactions?)

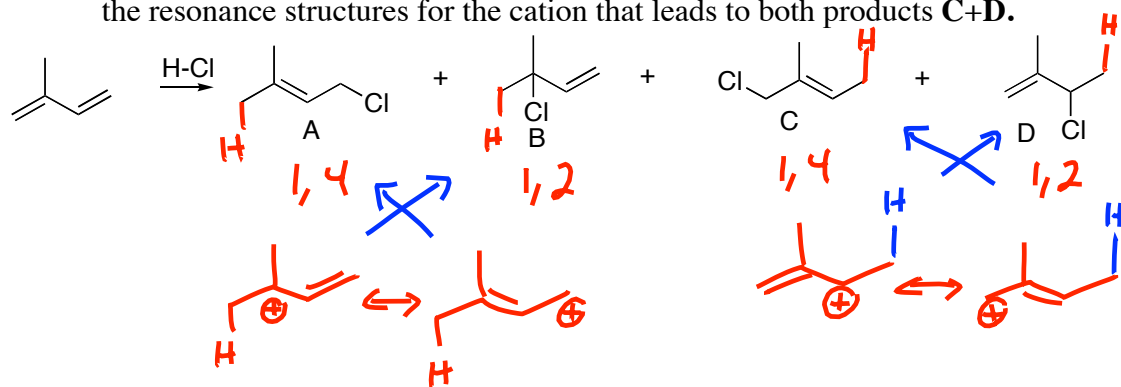


3. Products **A** and **B** combine to make up over 90% of the product mixture.

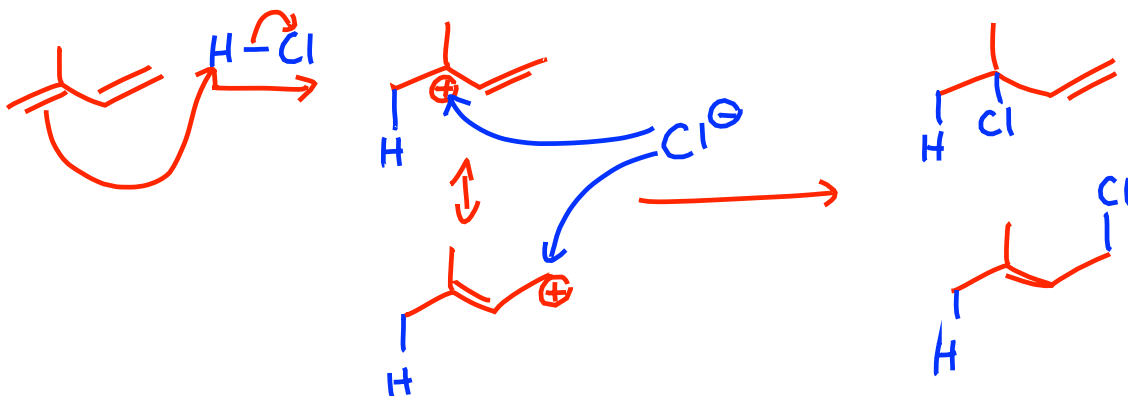
a. For each of the structures **A-D**, attach an H atom to the carbon that in fact added an H.

b. Classify each of the four structures as either a 1,2 or 1,4 addition product.

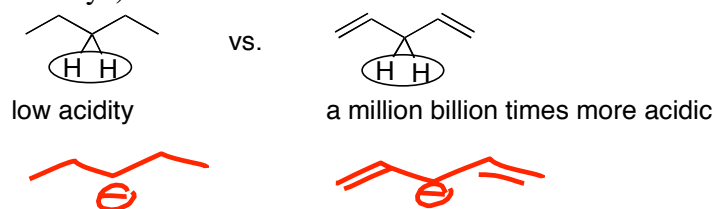
c. Draw the resonance structures for the cation that leads to both products **A + B**, and also draw the resonance structures for the cation that leads to both products **C+D**.



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



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

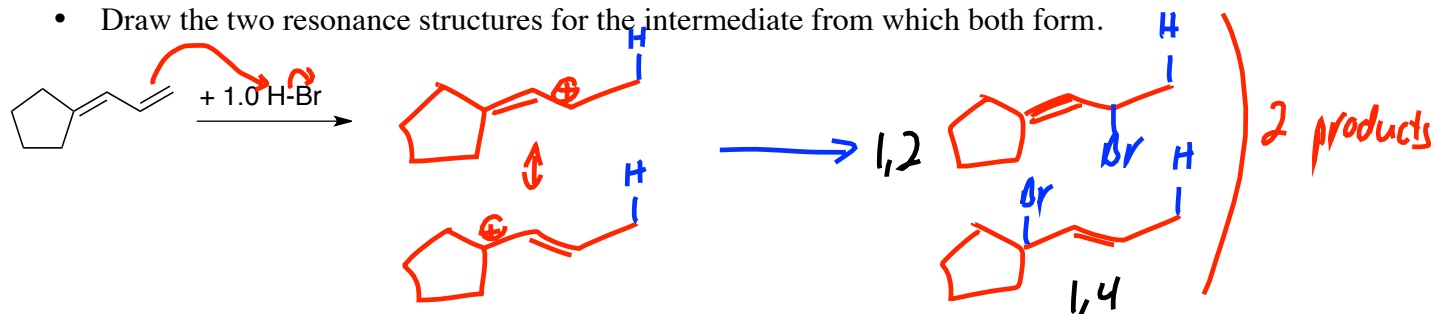


anion

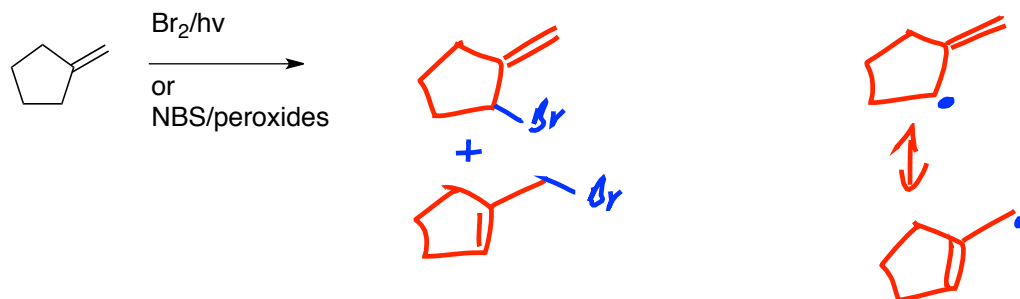
The diene produces a much more stable ANION

6. Draw the two major products for the following reaction.

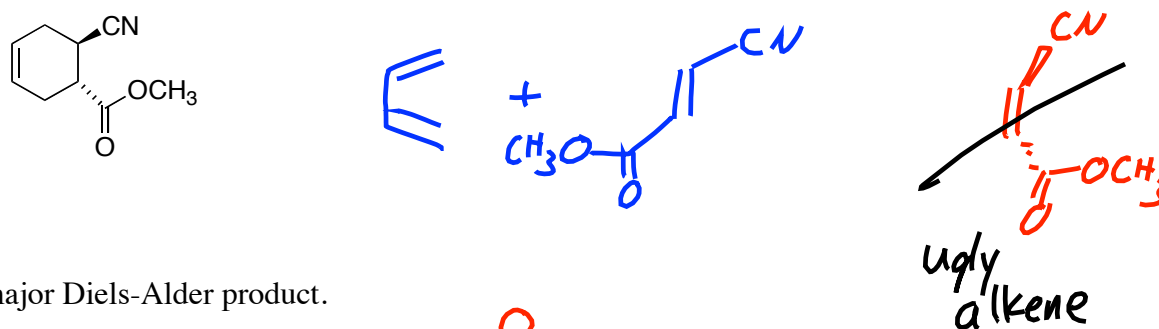
- Identify each as either a 1,2 or 1,4 addition product.
- Write either “thermodynamic” or “kinetic” underneath each one.
- Draw the two resonance structures for the intermediate from which both form.



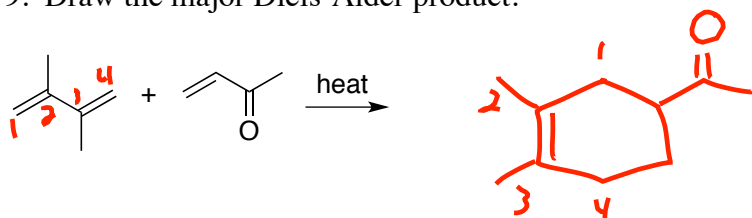
7. Draw the major product or products for the following reaction. Draw the resonance structures for the intermediate from which both form.



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

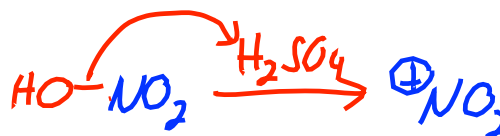
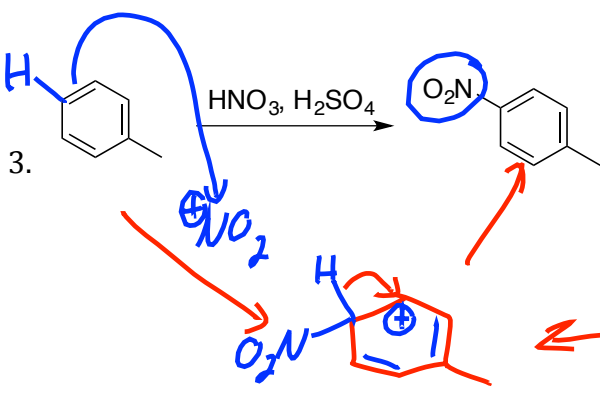
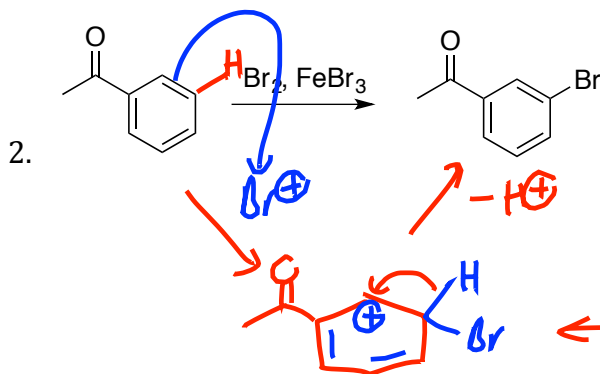
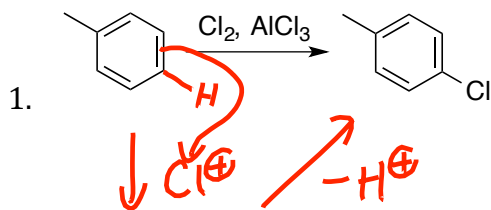
Test 4 Extra Practice: Drawing Mechanisms when the Reactants and Products are Given

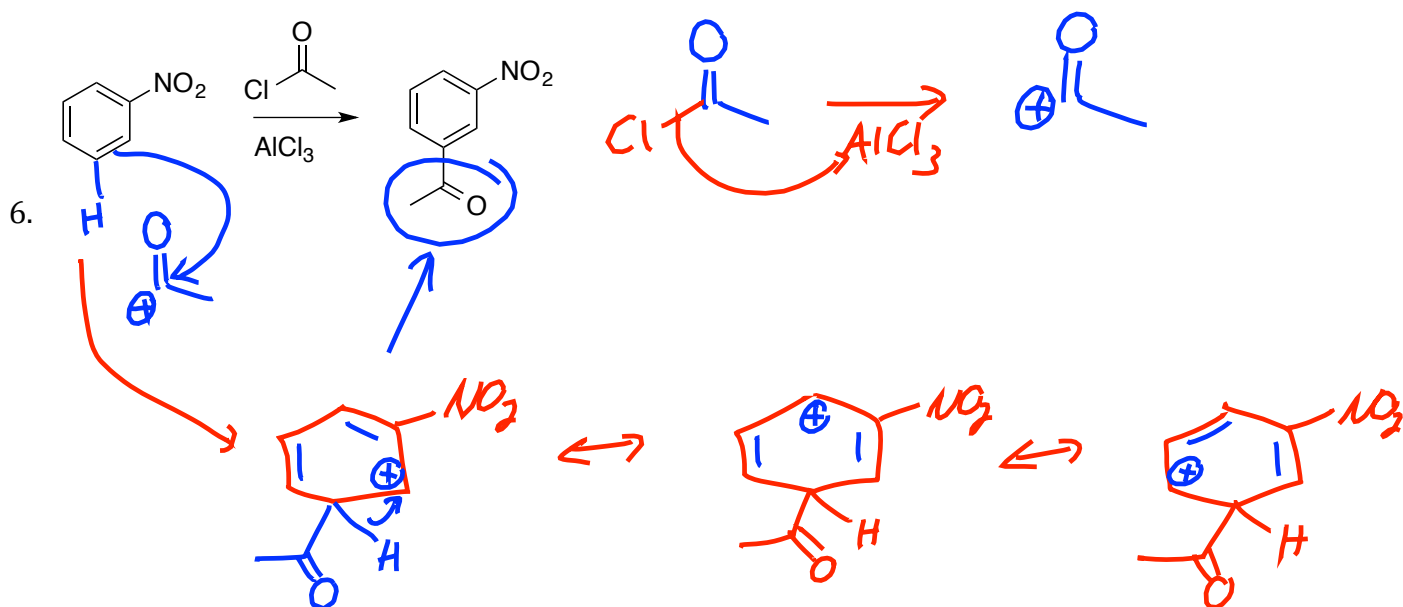
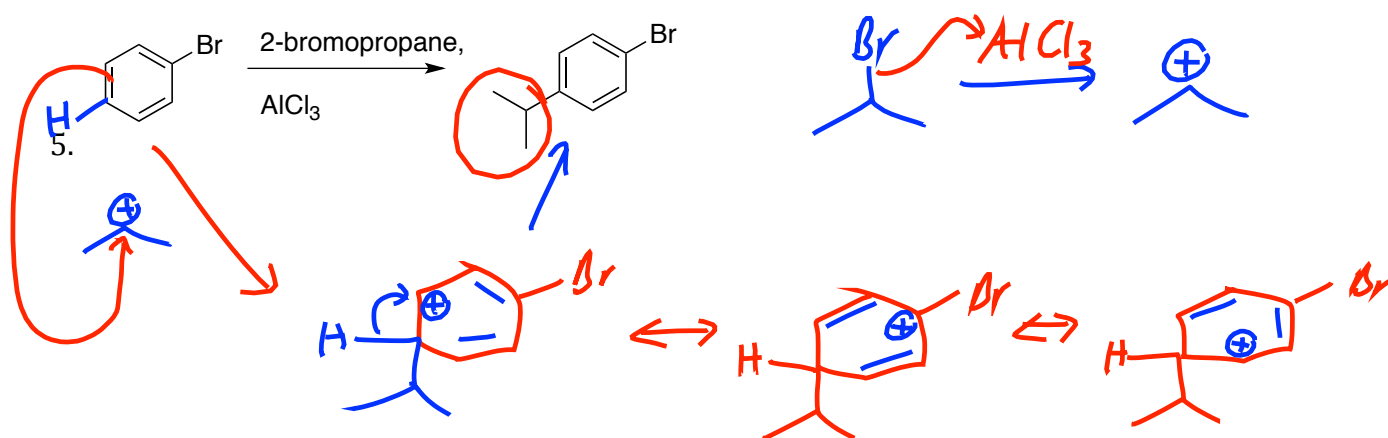
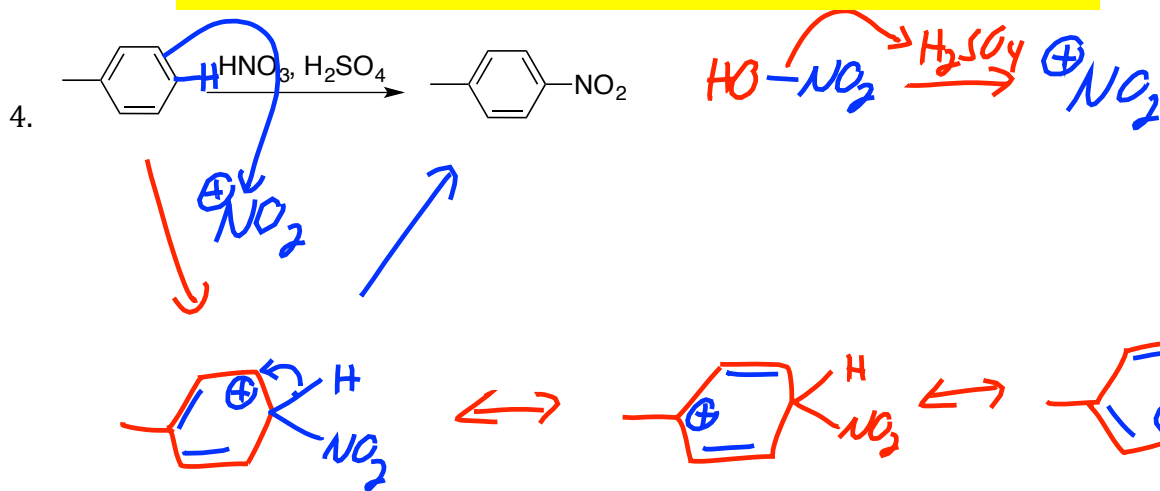
**Aromatic Substitution Mechanism Practice. Product given.**

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

Standard Mechanism:

1. Create cationic electrophile. Use the acid to enable this.
  2. Aromatic bonds to cation. Arrow from aromatic to cationic electrophile.
  3. Deprotonation. Two electrons in C-H bond go to cation.
- \*At least 3 resonance structures always available for the cation.





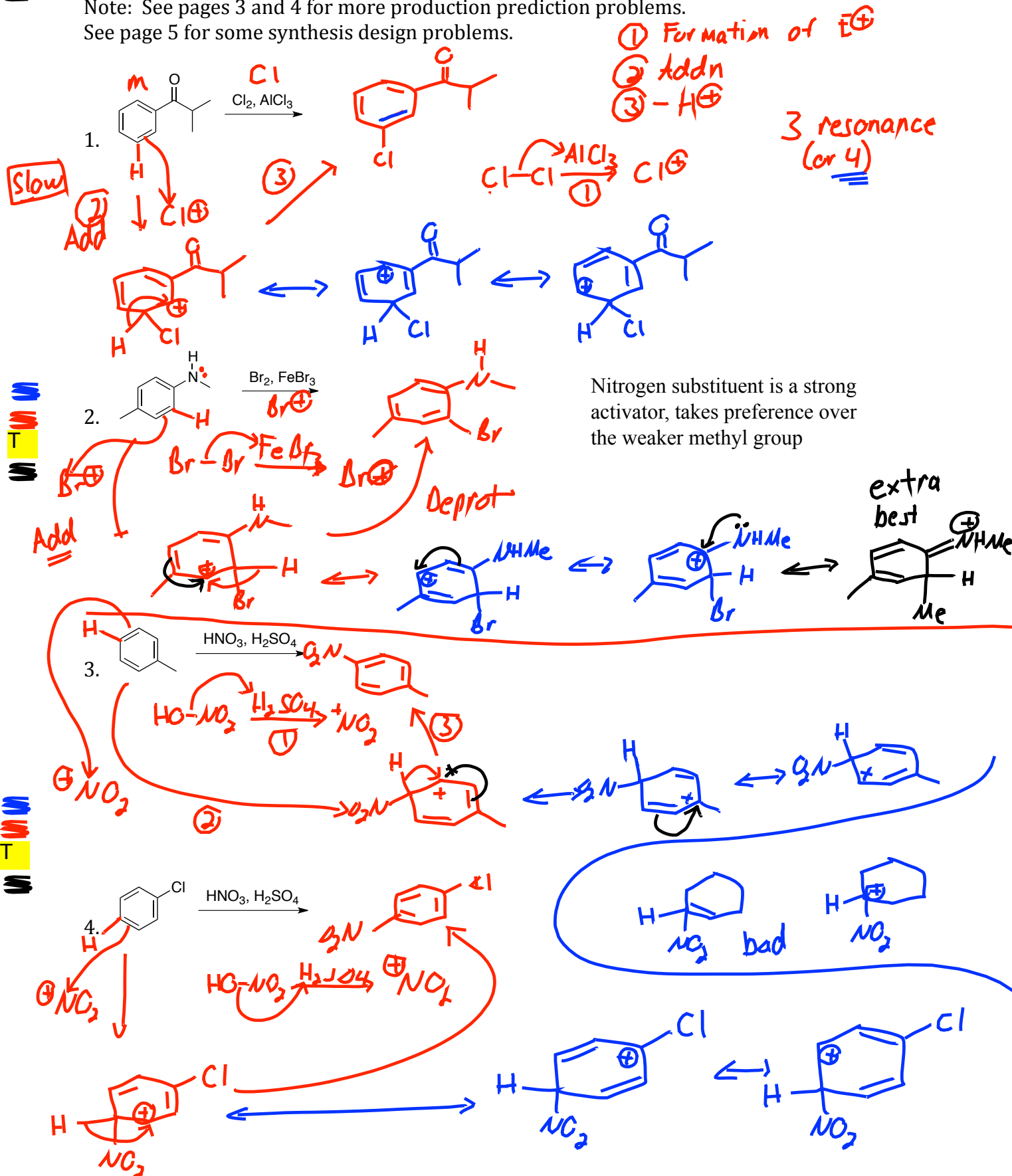


**Aromatic Substitution Reaction Mechanisms**

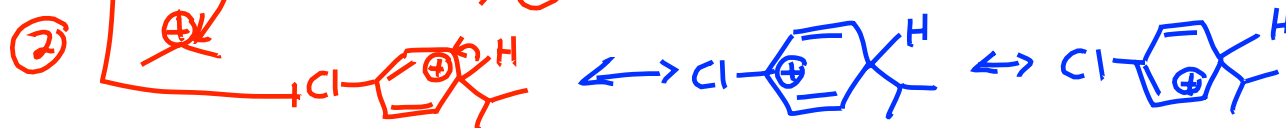
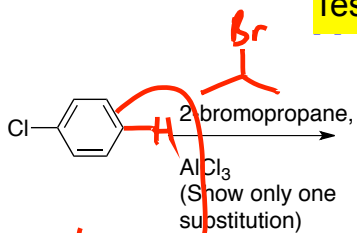
- Draw the major product and the mechanism for each of the following reactions, using detailed arrow-pushing.
- Draw the resonance structures for carbocationic intermediate.

Note: See pages 3 and 4 for more production prediction problems.

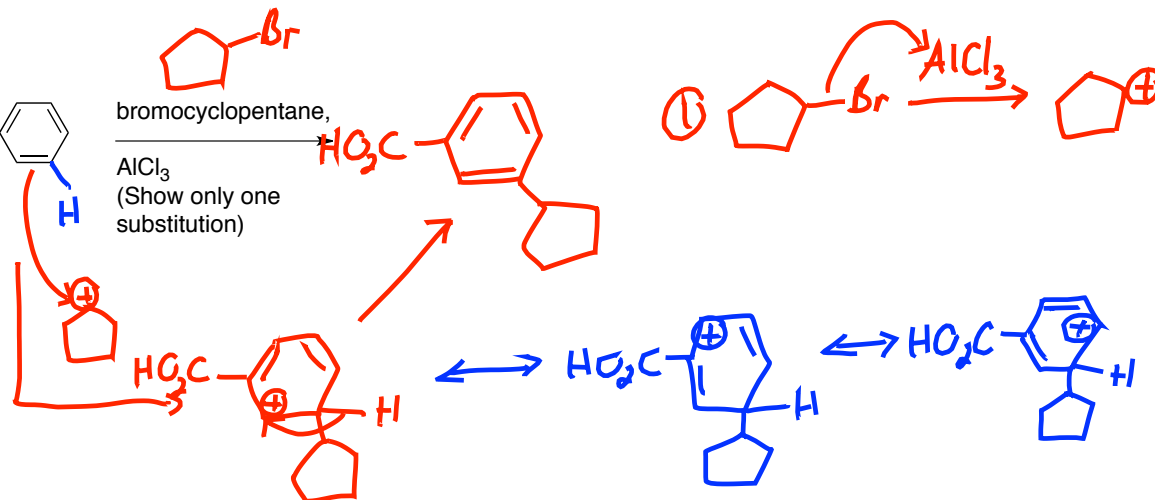
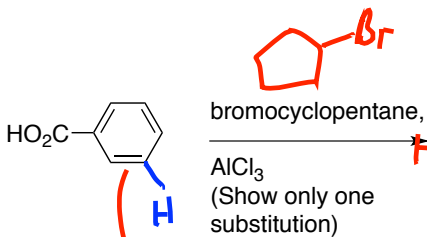
See page 5 for some synthesis design problems.



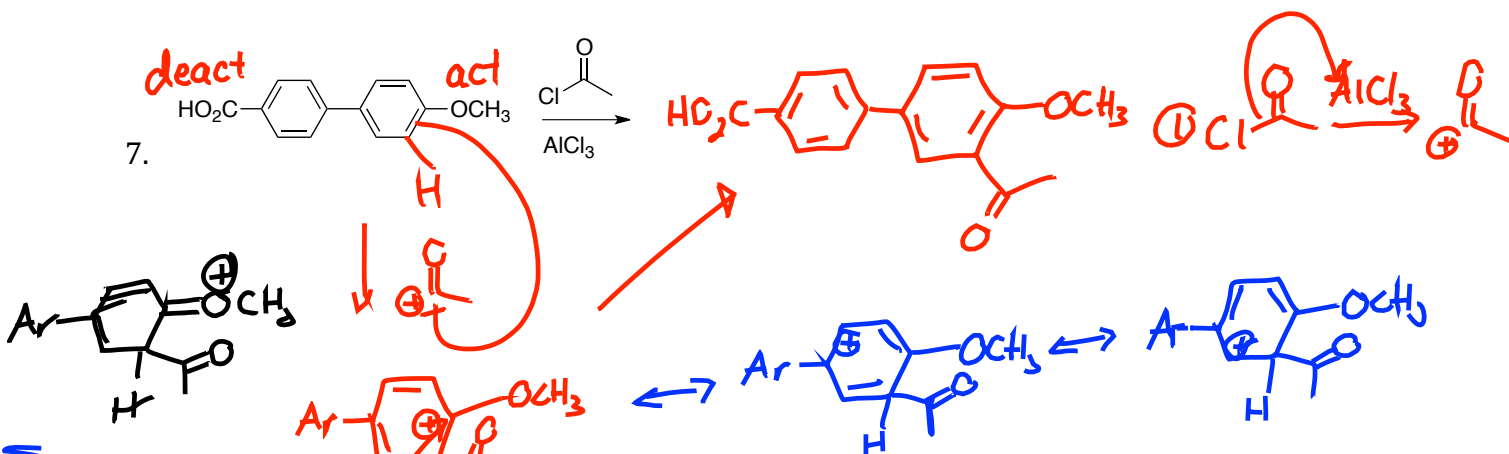
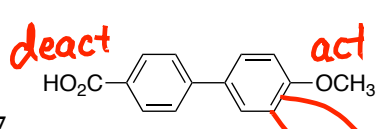
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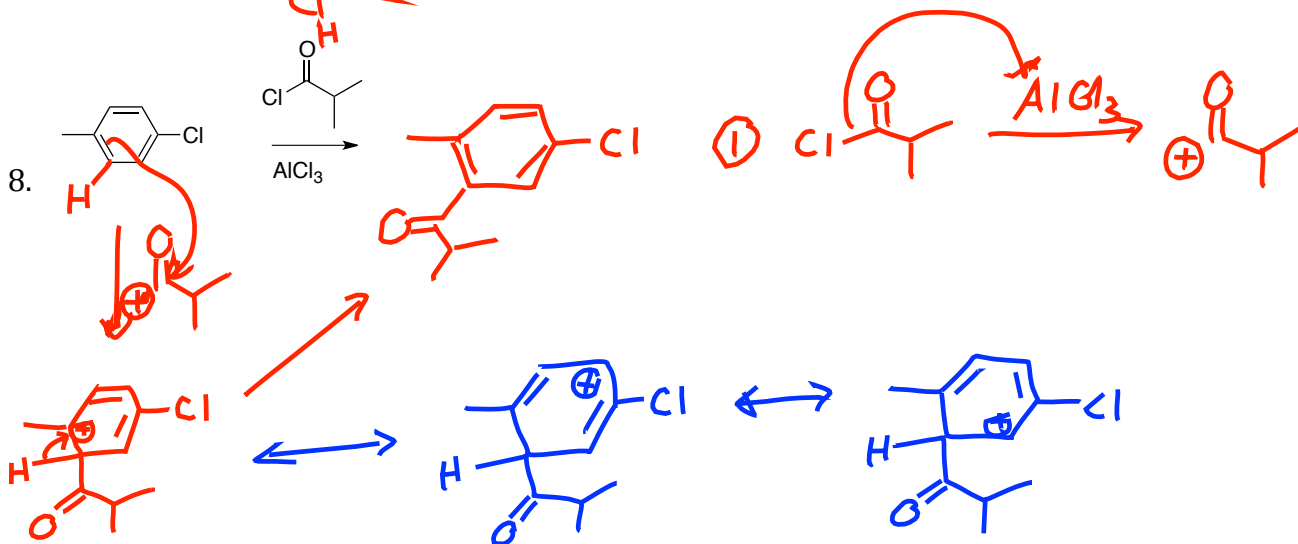
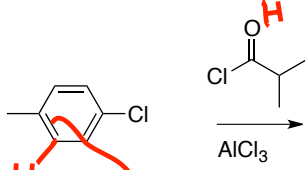
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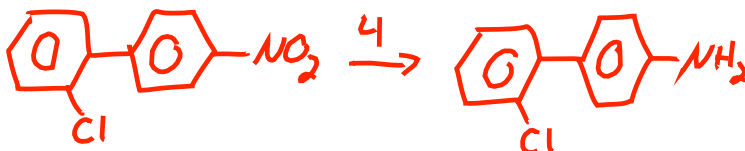
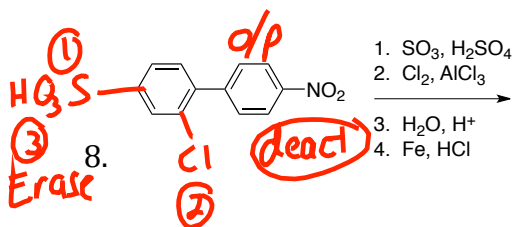
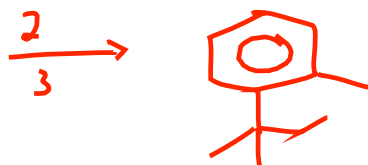
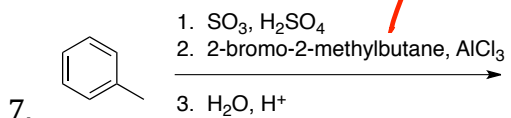
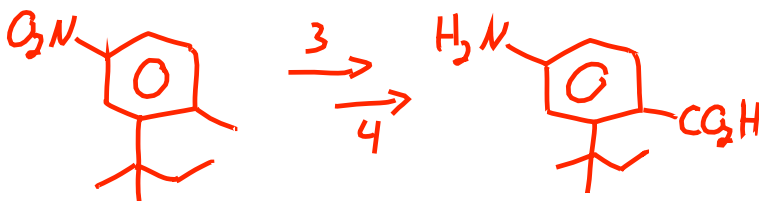
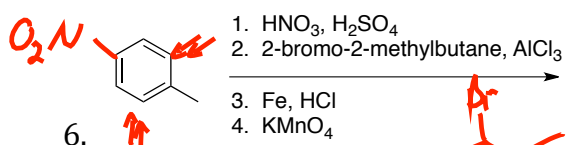
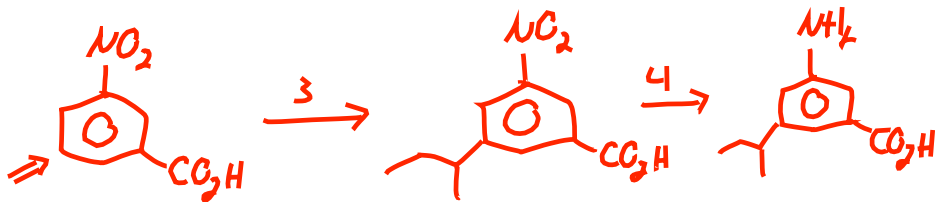
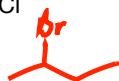
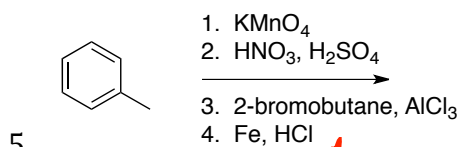
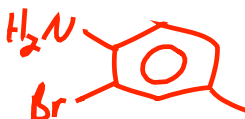
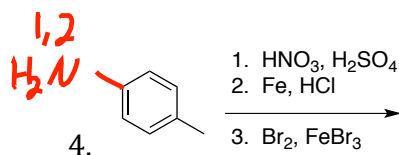
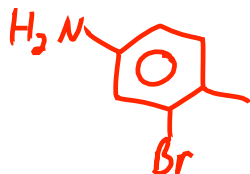
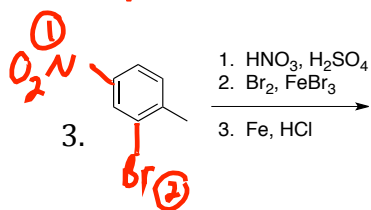
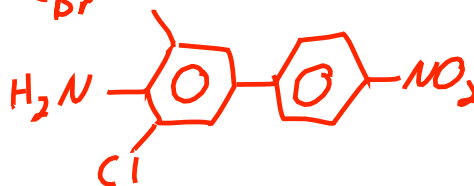
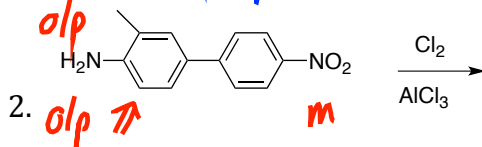
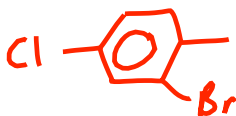
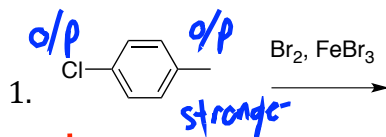
7.



8.



Draw the major product for the following reactions.



9. c1ccc(cc1)-c2ccc(OC)cc2  $\xrightarrow[\text{AlCl}_3]{\text{bromocyclopentane}}$  COc1ccc(cc1)-c2ccc(cc2)C3CCCC3  
*act* *Br-*
10. O=[N+]([O-])c1ccccc1  $\xrightarrow[3. \text{Zn(Hg), HCl}]{1. \text{AlCl}_3, \text{Cl-C(=O)-CH}_2\text{CH}_2\text{CH}_3; 2. \text{AlCl}_3, \text{2-bromopropane}}$  CC(C)C(=O)c1ccc([N+](=O)[O-])cc1  $\xrightarrow{2}$  CC(C)C(=O)c1ccc([N+](=O)[O-])cc1C(C)C  $\xrightarrow{3}$  CC(C)C(=O)c1ccc([N+](=O)[O-])cc1C(C)CC(C)C  
*m* *Ar*
11. Clc1ccccc1  $\xrightarrow[3. \text{AlCl}_3, \text{2-bromopropane}]{1. \text{AlCl}_3, \text{Cl-C(=O)-CH}_2\text{CH}_2\text{CH}_3; 2. \text{Zn(Hg), HCl}}$  CC(C)C(c1ccccc1Cl)C(C)C  $\rightarrow$  CC(C)C(c1ccccc1Cl)C(C)CC(C)C  
*o/p*
12. Clc1ccccc1  $\xrightarrow[3. \text{Zn(Hg), HCl}]{1. \text{AlCl}_3, \text{Cl-C(=O)-CH}_2\text{CH}_2\text{CH}_3; 2. \text{AlCl}_3, \text{2-bromopropane}}$  CC(C)C(c1ccccc1Cl)C(C)C
13. Clc1ccccc1  $\xrightarrow[4. \text{Zn(Hg), HCl}]{1. \text{SO}_3, \text{H}_2\text{SO}_4; 2. \text{AlCl}_3, \text{Cl-C(=O)-CH}_2\text{CH}_3; 3. \text{H}_2\text{O, H}^+}$  CC(c1ccccc1Cl)C(C)C
14. CCc1ccccc1  $\xrightarrow[2. \text{NaOCH}_3]{1. \text{NBS, peroxides (or Br}_2, \text{hv)}}$  CCOC(c1ccccc1)C(C)C  
*small radical* *2°* *SN2* *2°*
15. CCc1ccccc1  $\xrightarrow[2. \text{NEt}_3]{1. \text{NBS, peroxides (or Br}_2, \text{hv)}}$  CC=Cc1ccccc1  
*Bulky* *E2*
16. CC(C)c1ccccc1  $\xrightarrow[2. \text{NEt}_3]{1. \text{NBS, peroxides (or Br}_2, \text{hv)}}$  CC(C)=Cc1ccccc1  
*Hoffman*
17. CC(C)c1ccccc1  $\xrightarrow[2. \text{NaOCH}_3]{1. \text{NBS, peroxides (or Br}_2, \text{hv)}}$  CC=Cc1ccccc1  
*small/normal* *3°  $\Rightarrow$  E2* *Zaitsev*

**Design Syntheses for the following transformation:**

