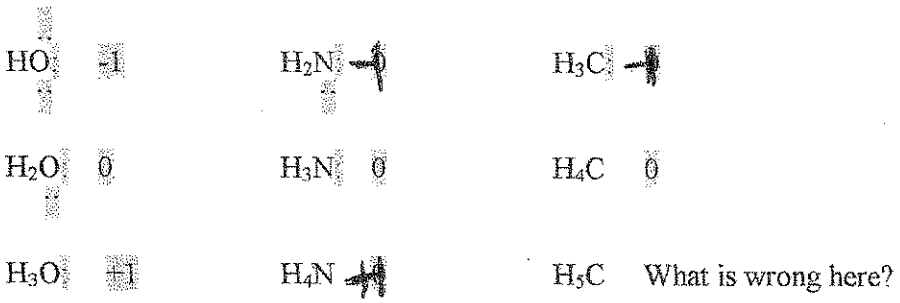
Chapter 1. Formal Charges Problem Set. Answer Key

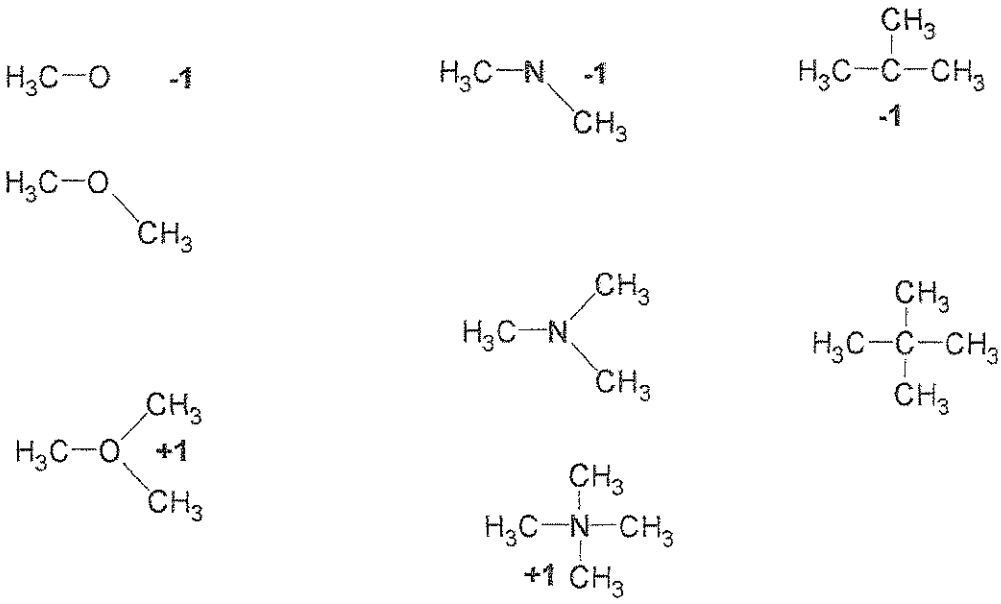
1. The following structures are drawn incorrectly. None of the lone pair electrons have been drawn. Use the octet rule to figure out how many lone pair electrons should be drawn about each central atom. (Fill in the electrons in the drawings below.)



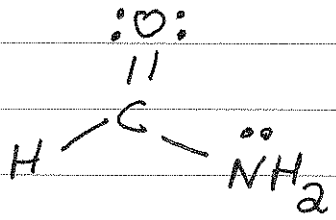
2. Calculate the formal change on each O, N and C shown above.

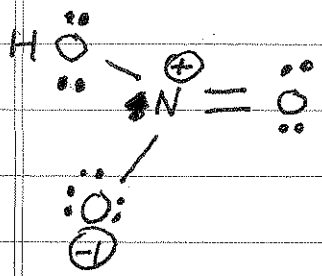
3. Use the results from question #2 to come up with general trends for O, N and C. For example, when oxygen is bonded to 2 other atoms, what is its formal change? What is oxygen's formal charge when it is bonded to 3 other atoms?

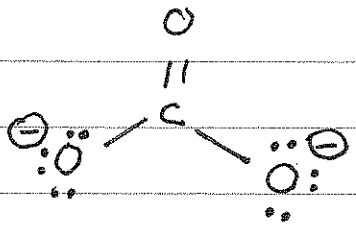
4. Use the trends you have determined in question #3 to *quickly* select the appropriate formal charge for each of the molecules show below. (Again, lone pair electrons have not been drawn, but this should not be important in your determination.)

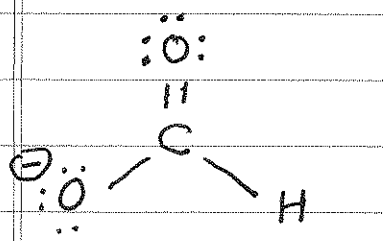


Lewis Structures / Minger









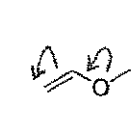
5/7 b

Answer key

CHM 235
Dr. Minger

Resonance practice problems

For each of the molecules shown, draw mechanistic arrows and provide at least one additional reasonable resonance structure. (Some will have only one.) **Not all lone pairs are shown, but all non-zero formal charges are included.**



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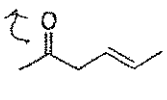

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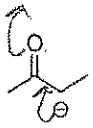

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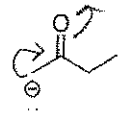
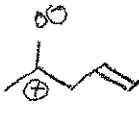


4

(How many hydrogens are on the carbon with the negative charge in structure 3? in structure 4?)

5



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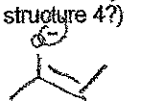

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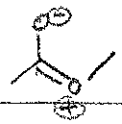

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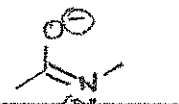

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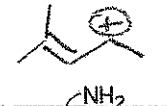

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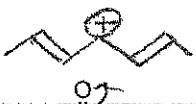

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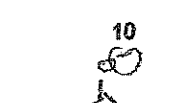

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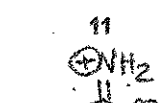

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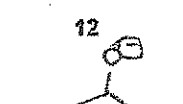

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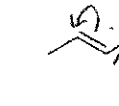

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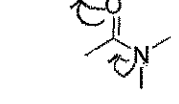

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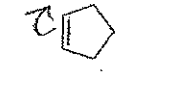
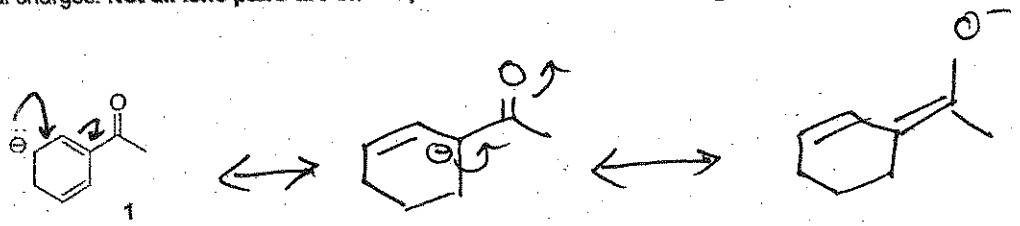


20

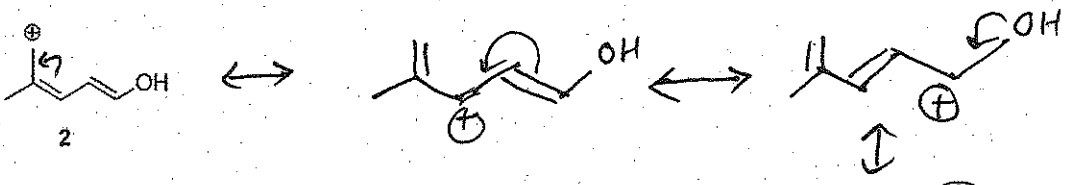
8/26/10

Resonance practice problems 2

For each of the chemical species shown, provide at least two additional resonance contributors. Show the conversion of each structure to the next using curved arrow notation. Include all lone pairs and formal charges. **Not all lone pairs are shown, but all non-zero formal charges are included.**



1



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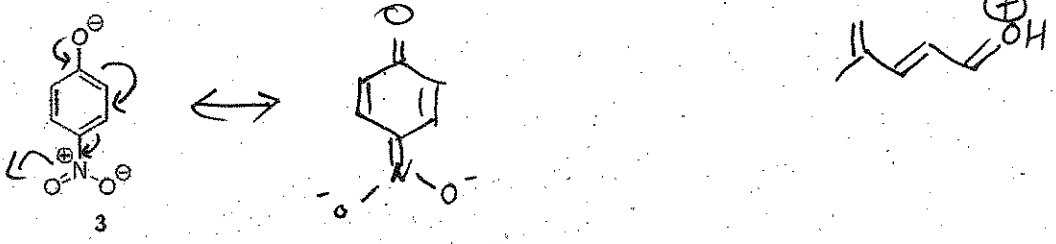

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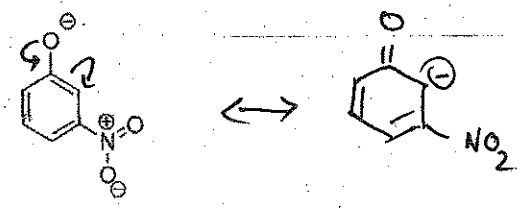

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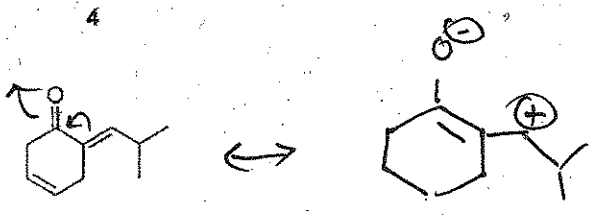

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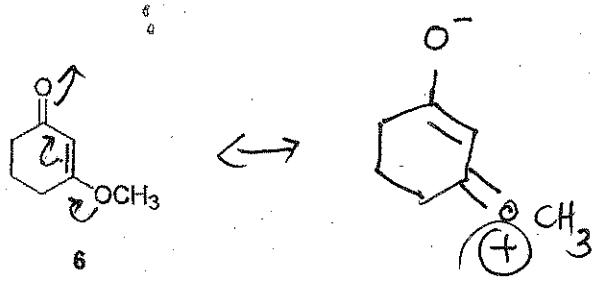

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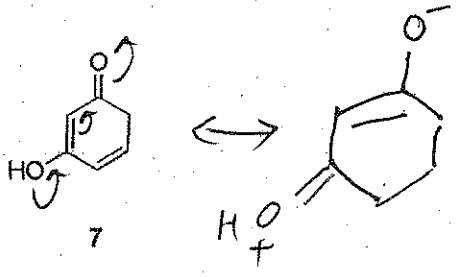

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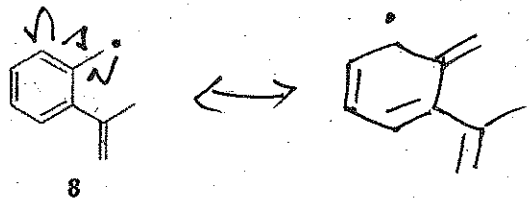

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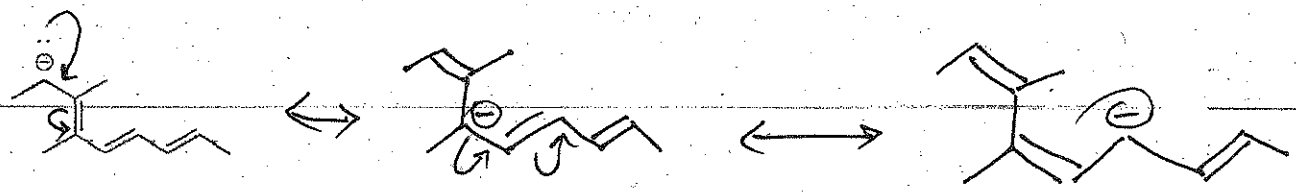

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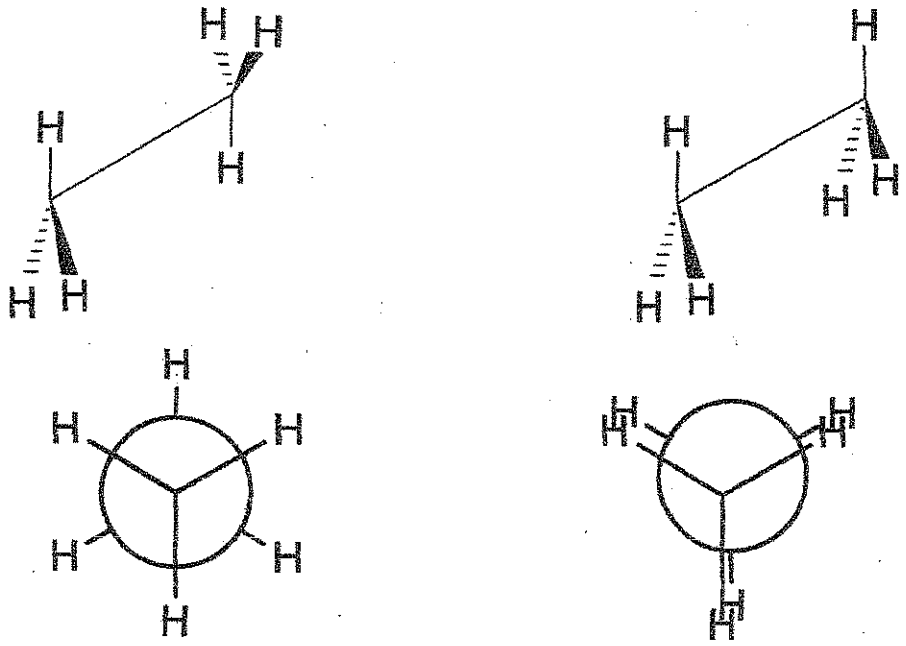
Chapter 2. Newman Projections Problem Set . Answer key

1. The following are diagrams of the staggered and eclipsed conformations of ethane.

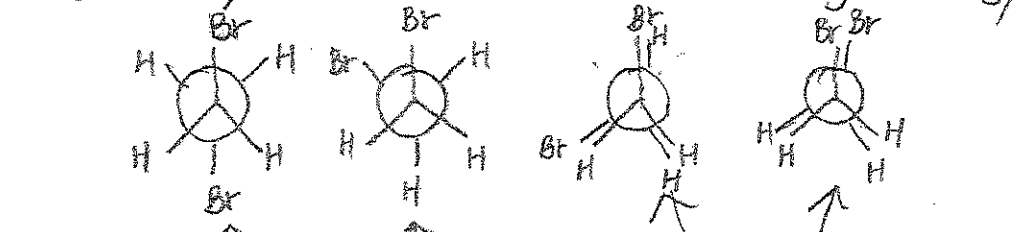
Staggered **Eclipsed**



Using the models provided, figure out how many unique staggered and eclipsed conformations 1,2-dibromoethane has.

2. Draw a Newman projection for each conformation (imagine you are looking straight down the carbon carbon bond).

lowest energy ⟶ highest energy



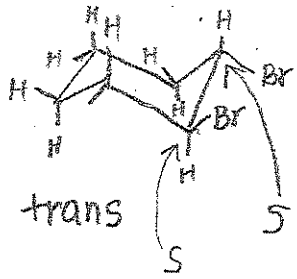
3. Rank the conformations from highest to lowest energy and justify your ranking system.

anti (staggered) gauche (staggered) eclipsed

Chapters 2-3. Cyclohexane & StereoChem Problem Set. Answer Key

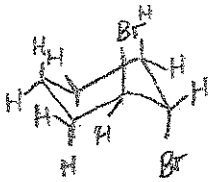
1. You have been given a model of 1,2-dibromocyclohexane.
   a. Draw this compound in its proper chair conformation. Accurately depict all axial and equatorial groups.
   b. Determine if your compound is cis or trans.
   c. Flip the ring and redraw the chair.
   d. Draw a Newman projection along the C1-C2 bond for this new chair conformation. Label all gauche interactions.
   e. Determine the stereochemistry (R or S) of the C1 and C2 carbons of your molecule.
   f. Is your molecule chiral? How do you know?

a.

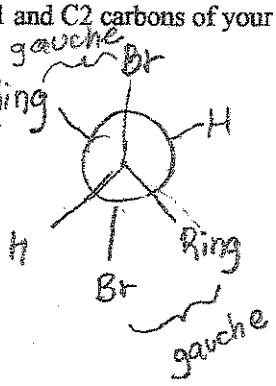


b. trans

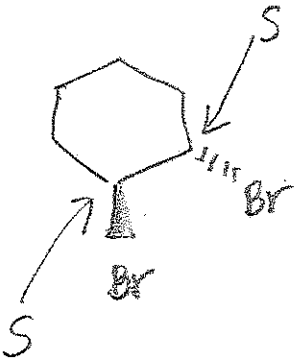
c.



d.

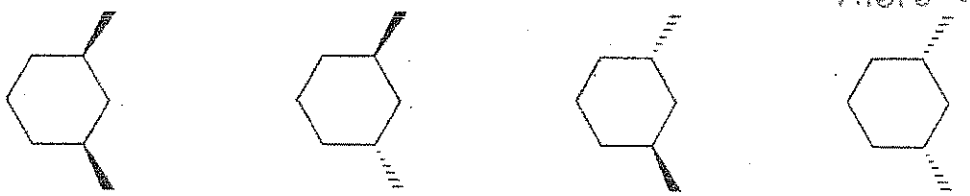


e.



f. no plane of symmetry therefore chiral

2.

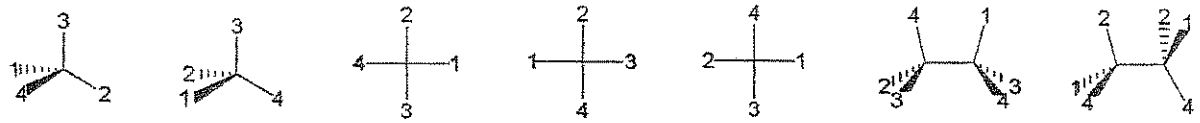


A B C D

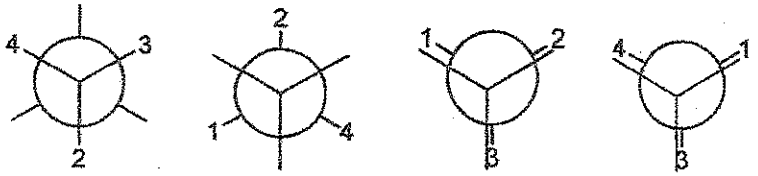
a. Which of the above stereoisomers are chiral? B, C
b. Which are enantiomers? B & C
c. Which are diasteriomers? A & B, A & C
d. Which isomer has the lowest energy chair conformation? A (and D)

Chapter 3. StereoChem Problem Set. Answer Key

1. Determine the R or S configuration of each of the following molecules:

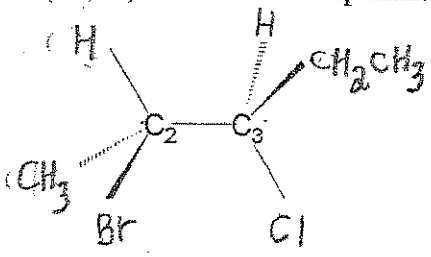


R R R R S RR SS

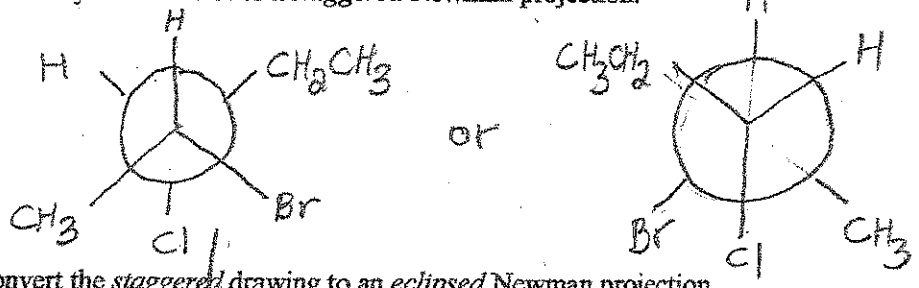


R R S S

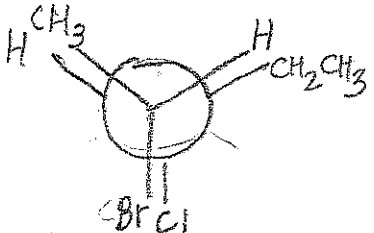
2a. Draw a sawhorse representation of (2R,3R)-2-bromo-3-chloropentane depicting the chirality about carbons 2 and 3.

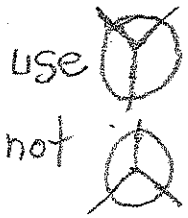


2b. Convert your sawhorse to a *staggered* Newman projection.

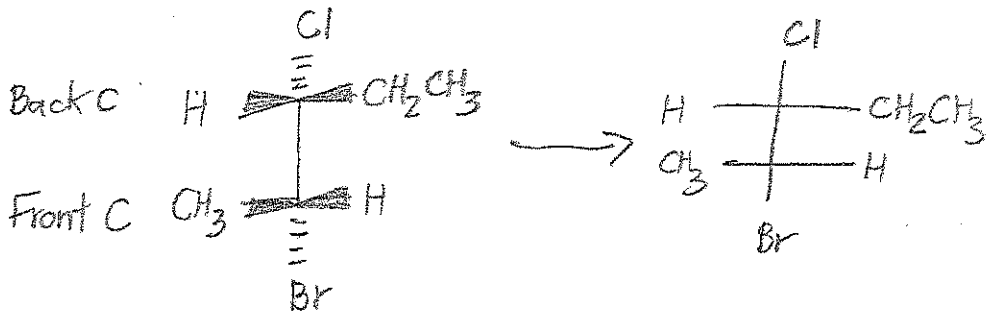


2c. Convert the *staggered* drawing to an *eclipsed* Newman projection.





2d. Convert the eclipsed Newman projection to a Fisher projection.



Chapter 4. Acid Base Problem Set. Answer Key

a. $H\text{-}I + Br^- \; <\!\!-\!\!?\!\!-\!\!> \; H\text{-}Br + I^-$

ACID BASE → ACID BASE

(WEAKER, LARGER)

b. $NH_3 + OH^- \; <\!\!-\!\!?\!\!-\!\!> \; NH_2^- + H\text{-}O\text{-}H$

ACID BASE ← BASE ACID

(WEAKER, MORE ELECTRONEGATIVE)

c. $CH_4 + NH_2^- \; <\!\!-\!\!?\!\!-\!\!> \; CH_3^- +$ 

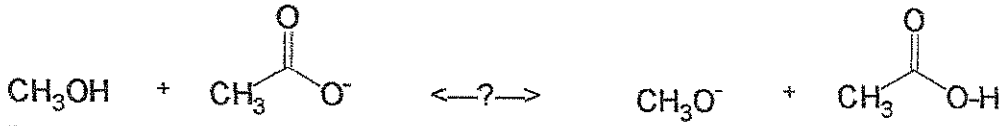
ACID BASE ← BASE ACID

(WEAKER, MORE ELECTRONEGATIVE)

d.  $+ CH_3^- \; <\!\!-\!\!?\!\!-\!\!> \; H_2C{=}CH^- + CH_4$

ACID BASE → BASE ACID

(WEAKER, MORE S CHARACTER)

e. 

ACID BASE ← BASE ACID

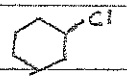
(WEAKER, RESONANCE STABILIZED)

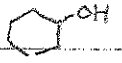
f. $CF_3CH_2O^- + CH_3CH_2OH \; <\!\!-\!\!?\!\!-\!\!> \; CF_3CH_2O\text{-}H + CH_3CH_2O^-$

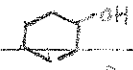
BASE ACID ← ACID BASE

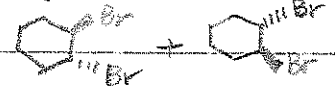
(WEAKER, INDUCTIVE EFFECT)

Chapter 6. Alkenes Problem Set. Answer key

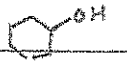
1a.  achiral

1b.  achiral

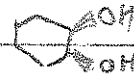
1c.  achiral

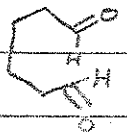
1d.  racemic

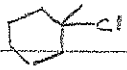
1e.  racemic

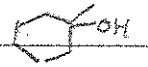
1f.  achiral

1g. 

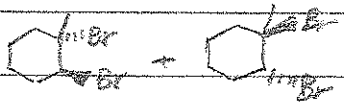
1h.  meso

1i. 

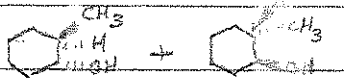
2a.  achiral

2b.  achiral

2c.  achiral

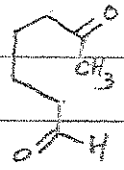
2d.  racemic

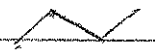
2e.  racemic

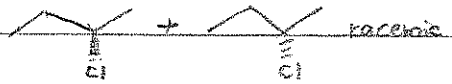
2f.  racemic

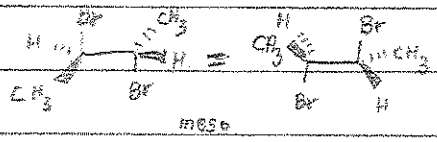
2g. 

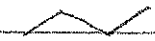
2h.  racemic

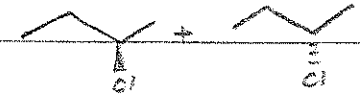
2i. 

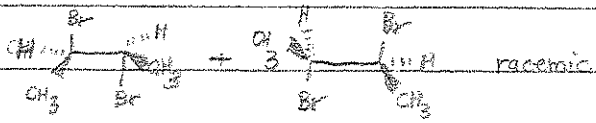
3a.  achiral

3b.  racemic

3c.  meso

4a.  achiral

4b.  racemic

4c.  racemic

Preparation for Exam I, Answer key

1a. $NH_3 > OH_2 > FH$ ← weakest base, most electronegative

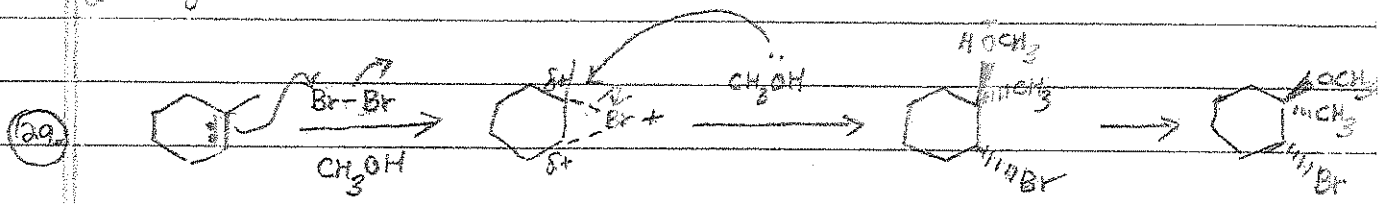
↑ strongest base, least electronegative

CH_4 cannot act as a base (violates octet rule)

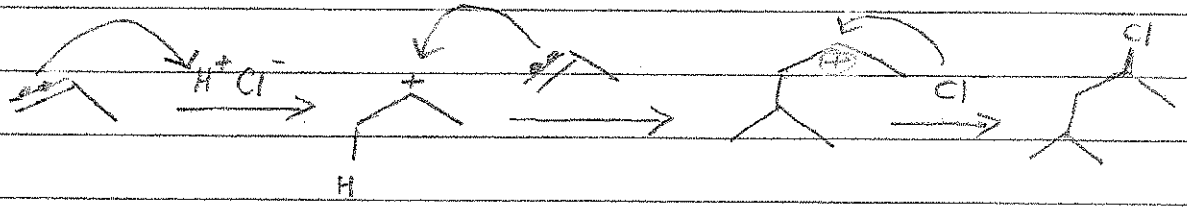
1b. $CH_3^{\ominus} > NH_2^{\ominus} > OH^{\ominus} > F^{\ominus}$

↑ strongest base, least electronegative

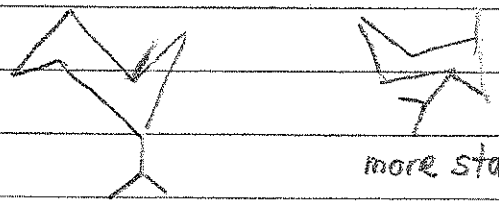
↑ weakest base, most electronegative



1a. b.



2.



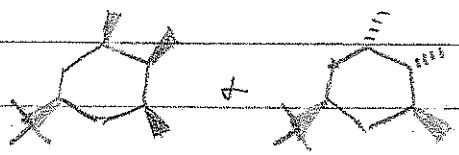
more stable

5. Always explain acidity in terms of stability of base.

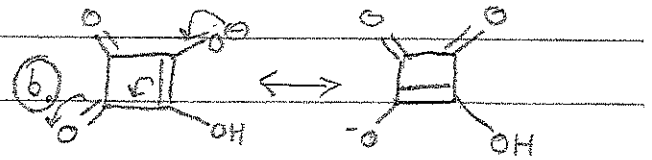
a. $^{\ominus}CH_2-N^{+}=O \longleftrightarrow CH_2=N^{+}-O^{-}$

both compounds ~~have resonance stabilized~~

4a.



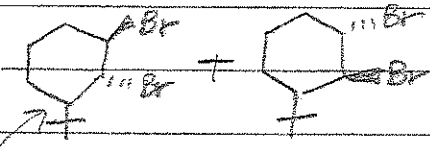
b.



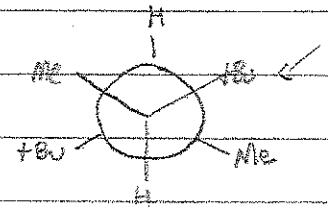
4b.

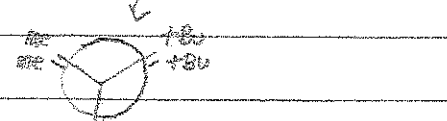
6.

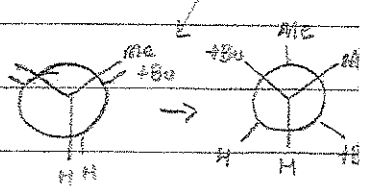
4c.



Stereochem not specified for tBu







Alkynes

a. H_2 / metal catalyst e.g. Pd, Pt

b. H_2 / lindlar catalyst only (metal + PbO_2)

c. Na / NH_3

d. $HgSO_4$, H_2SO_4

e. a. Sia_2BH b. H_2O_2, OH^-

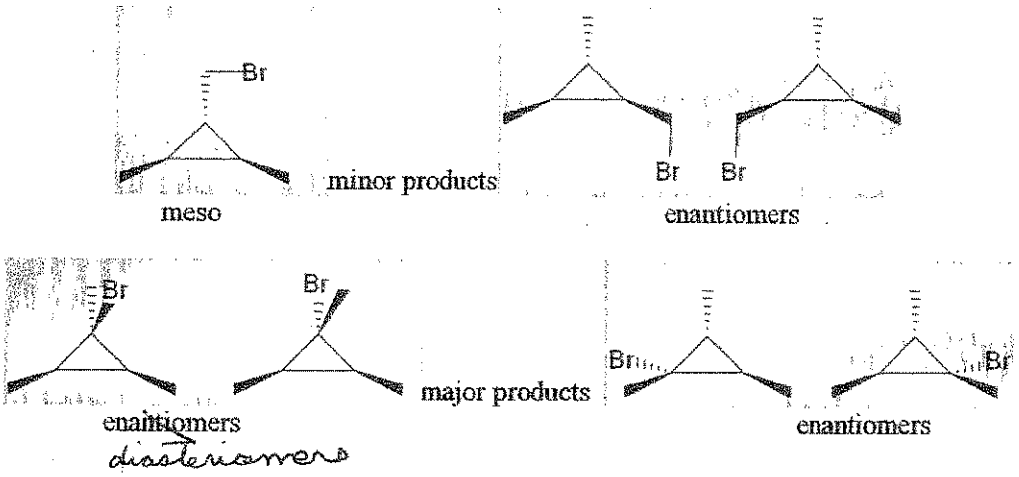
f. excess HCl

g. Cl_2

Chapter 8. Free Radical Halogenation Problem Set. Answer Key

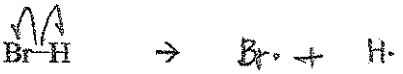
1a. Assume that the following compound undergoes monobromination. Draw all possible products that will be produced (including all enantiomers and diasteriomers).

1b. Which products will predominate?



2a. Use single headed mechanistic arrows to illustrate the reaction that takes place when a C-H bond breaks homolytically.

2b. Use single headed mechanistic arrows to show the reaction that takes place when a Br-H bond breaks homolytically.



3. Is homolytic bond breaking an exothermic or endothermic process? How do you know?

endothermic (see chart #4 breaking bonds always requires energy input)

4. Using the data provided below, calculate the enthalpy change for each of the following reactions and determine whether each reaction is exothermic or endothermic:

a) $Br\cdot + CH_3{-}H \rightarrow Br{-}H + CH_3\cdot$ $-368 + 414 = +46$ endothermic

b) $Cl\cdot + CH_3{-}H \rightarrow Cl{-}H + CH_3\cdot$ $-431 + 414 = -17$ exothermic

Bond Dissociation Energies

H_3C-H	+ 414 kJ/mol
Cl-H	+ 431 kJ/mol
Br-H	+ 368 kJ/mol

5. Draw an energy diagram for each of the reactions shown in question 4. Your diagram should show the relative energies of the starting materials, products and transition states.

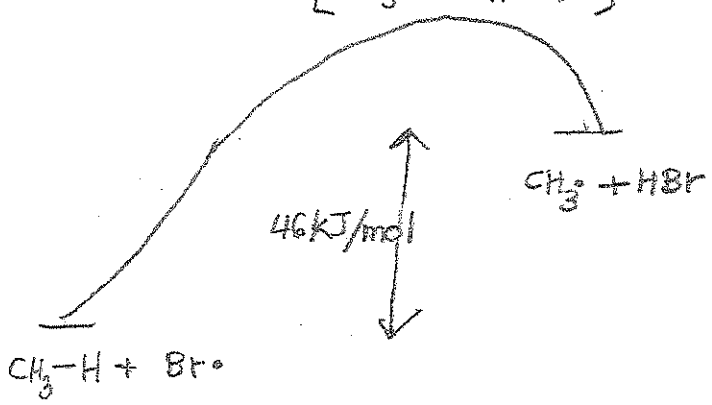
6. Draw a picture of what the transition state for each reaction looks like.

7a. How does the transition state for the bromine reaction look different from the transition state for the chlorine reaction?
7b. Why do these two transition states look different?
7c. How does this difference effect the types of products produced in chlorination versus bromination reactions?

5, 6, 7a, b

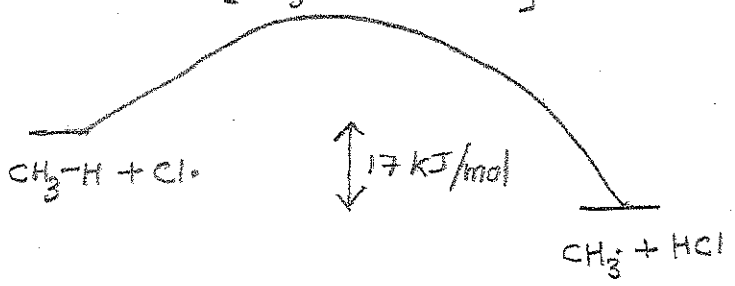
late transition state
looks like products ($CH_3\cdot$)

$[CH_3 ---- H -- Br]$



early transition state
looks like starting material (CH_3-H)

$[CH_3 -- H ---- Cl]$



7c. In the case of Cl, there is not much difference in activation energy between reacting a 1°, 2° or 3° position.

In the case of Br, the stability of the transition state depends on which radical is being formed (1°, 2°, 3°).

Chapter 9. Substitution Rxns Part 1 Problem Set, Answer key

1. Secondary alkyl halides can react via S_N2 or S_N1 mechanisms. The following is an example:

$(CH_3)_2CH\text{-}Br \quad + \quad I^- \quad \longrightarrow \quad (CH_3)_2CH\text{-}I$

Your choice of nucleophile and solvent will impact which mechanism will take place.

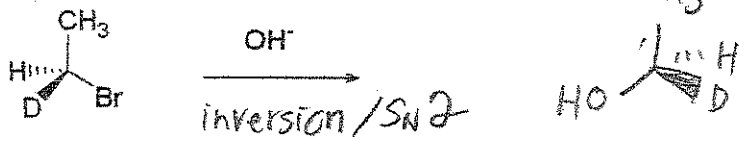
a. In order to favor S_N2, should you use a strong nucleophile or a weak nucleophile? Why?

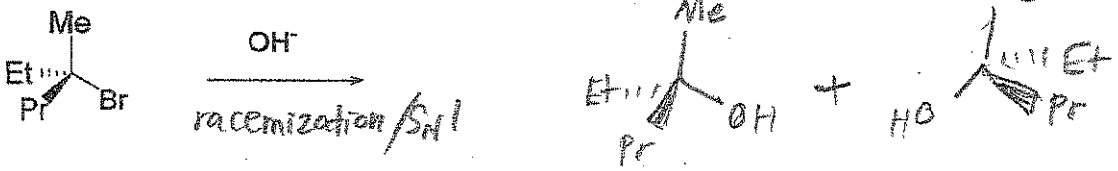
b. In order to favor S_N1, should you use a strong nucleophile or a weak nucleophile? Why? irrelevant

c. In order to favor S_N2, should you use a polar aprotic solvent or a polar protic solvent? Why? ← stabilizes Nuc too much
What is polar aprotic? What is polar protic? → capable of H bonding (ROH, RCO_2H, H_2O)
↳ cannot H bond

d. In order to favor S_N1, should you use a polar aprotic solvent or a polar protic solvent? Why?
stronger dipole stabilizes carbocation

2. What is the product of each of the following reactions? Make sure to show stereochemistry.

a. 

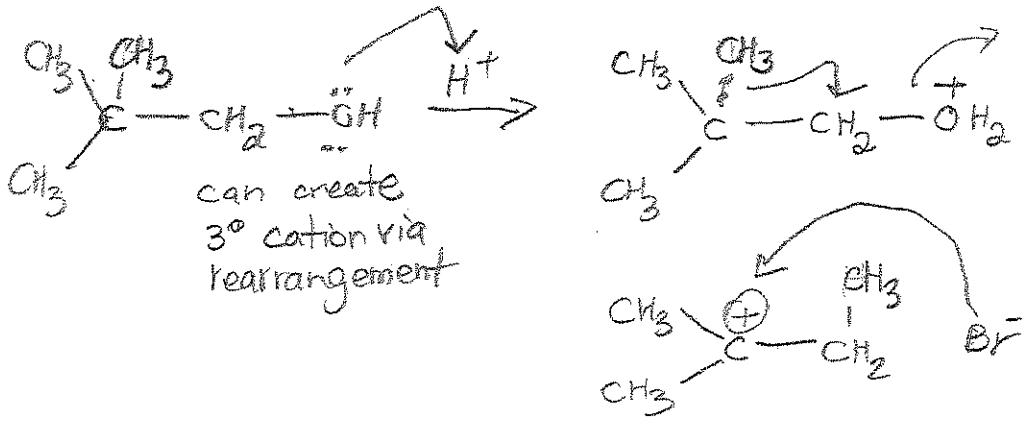
b. 

3. The following compound reacts via an S_N1 mechanism and undergoes rearrangement.

$(CH_3)_3C\text{-}CH_2\text{-}OH \quad + \quad HBr \quad \longrightarrow$

a. Draw the mechanism for the reaction and explain why the mechanism is S_N1 and why the compound undergoes rearrangement.

b. Why is H^+ (acid) required for this reaction? OH^- bad LG

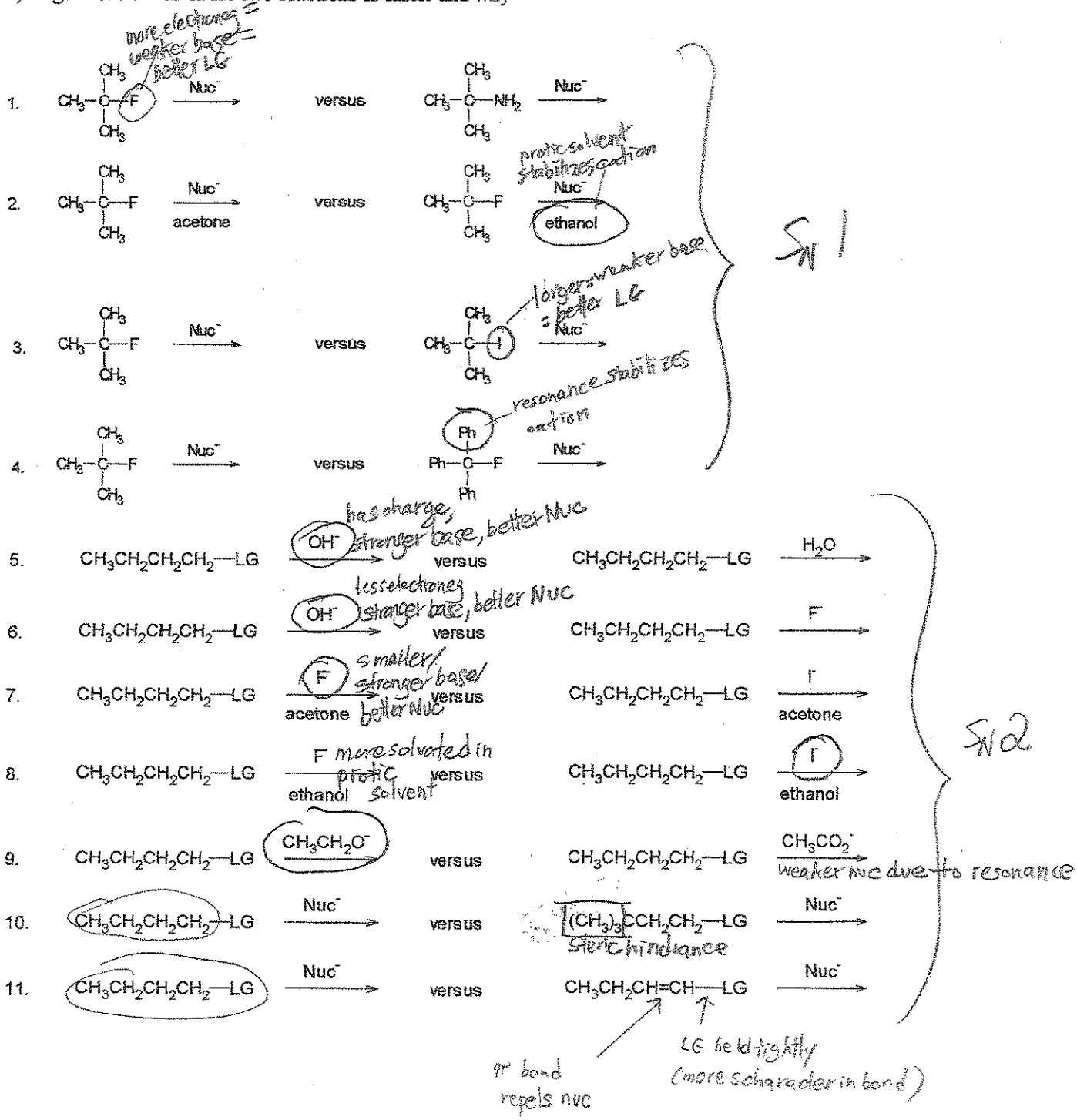


Chapter 9. Substitution Rxns Part 2 Problem Set. Answer key

For each of the following pairs of reactions:

a) determine if the mechanism is S_N2 or S_N1

b) figure out which of the two reactions is faster and why



Chapter 9. Elimination Rxns and Wrapup Problem Set. Answer Key

1a. Circle all the hydrogens in the following molecule that are *beta* to the leaving group:

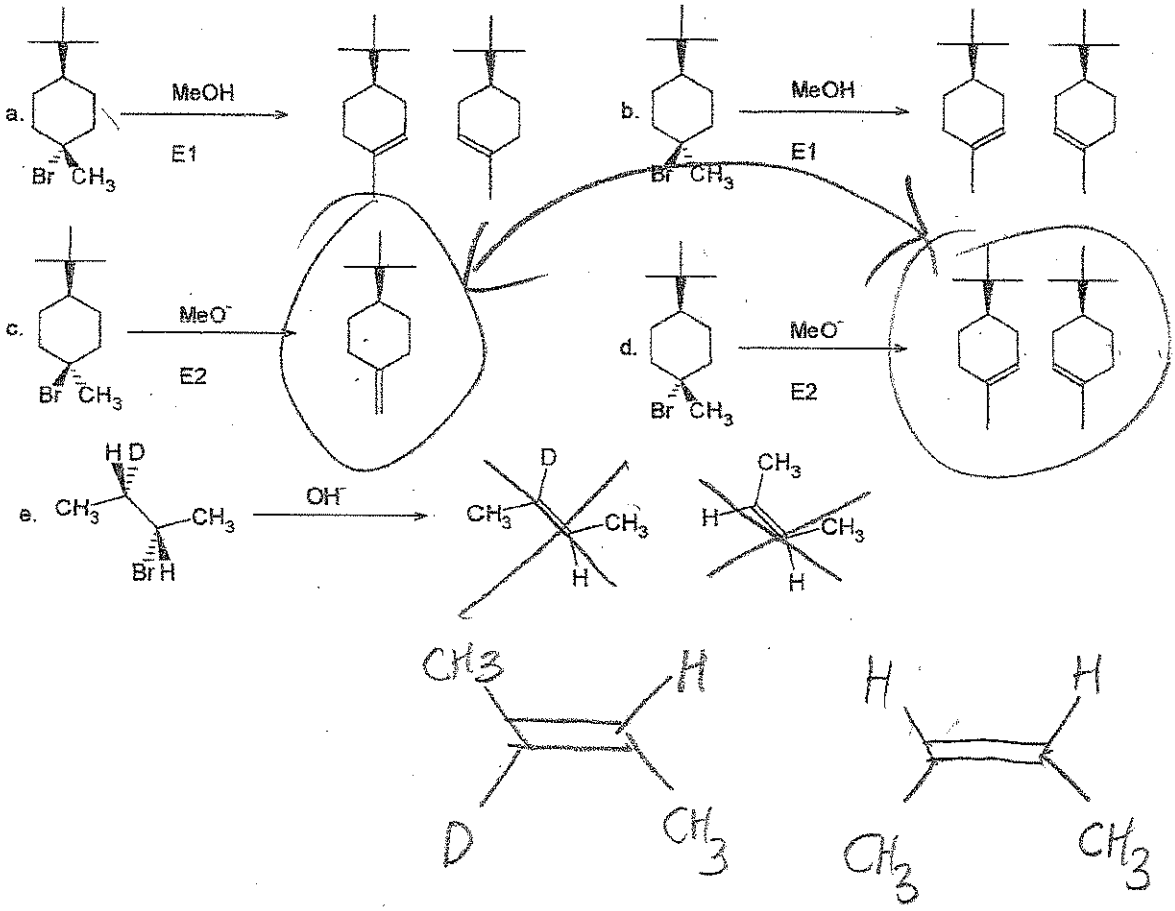
CH_3-CH_2-CHBr-CH_3

1b. For each hydrogen that you have circled, draw the product that would form if that hydrogen were removed in an elimination reaction. (Note: there are three possible products.)

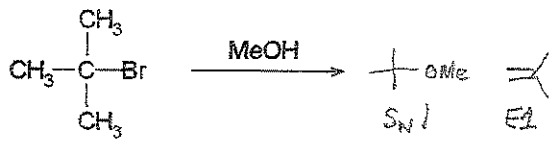
Cis CH_3-CH=CHBr-CH_3 Trans CH_3-CH=CHBr-CH_3 CH_3-CH_2-CHBr=CH_2

1c. Which of the three products will predominate? Why? Trans CH_3-CH=CHBr-CH_3

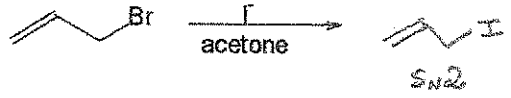
2. For each of the following reactions, determine whether the elimination will be E2 or E1.
2b. Draw the product(s) that forms in each case:

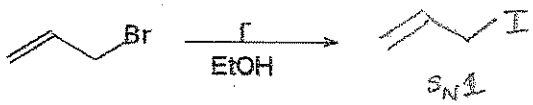


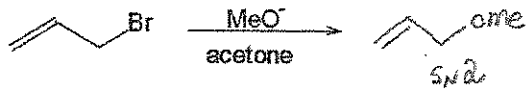
3. For each of the following reactions, determine which mechanism(s) predominate and what product(s) form:

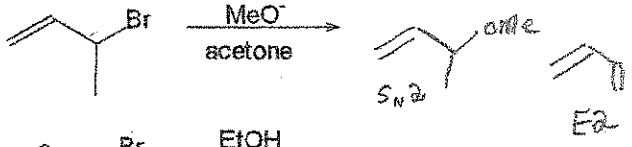
a. 

b. 

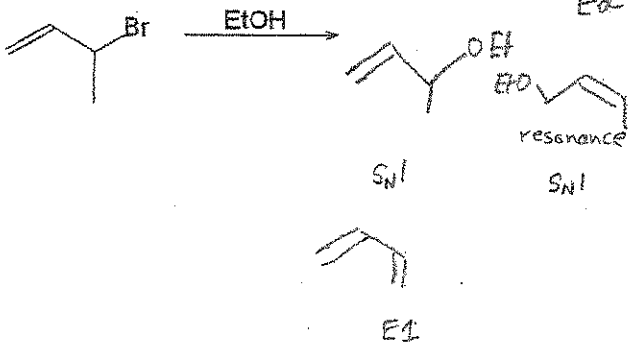
c. 

d. 

e. 

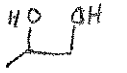
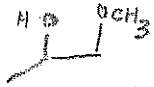
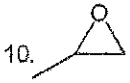
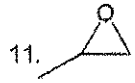
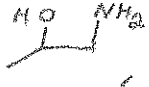
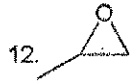
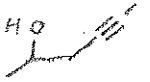
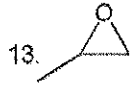
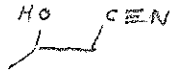
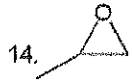
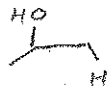
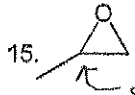
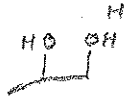
f. 

g. 

h. 

Chapters 10 & 11. Alcohol Ether Problem Set . Answer key

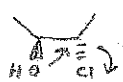
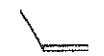
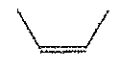
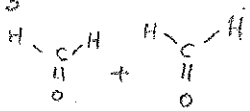
For each of the following substitution reactions, determine whether the mechanism is S_N2 or S_N1 and draw the structure of the products: Assume acidic workup.

1. $CH_3CH_2CH_2CH_2O^- \xrightarrow{CH_3-Br}$ $CH_3CH_2CH_2CH_2OCH_3$ S_N2
2. $CH_3CH_2CH_2CH_2S^- \xrightarrow{CH_3-Br}$ $CH_3CH_2CH_2CH_2SCH_3$ S_N2
3. $CH_3CH_2OH \xrightarrow{H^+/CH_3CH_2OH}$ $CH_3CH_2OCH_2CH_3$ S_N2
4. $CH_3CH_2CH_2CH_2-I \xrightarrow{HS^-}$ $CH_3CH_2CH_2CH_2SH$ S_N2
5. $CH_3CH_2CH_2CH_2OH \xrightarrow{HBr}$ $CH_3CH_2CH_2CH_2Br$ S_N2
6. $(CH_3)_3C\text{-}OH \xrightarrow{HBr}$ $(CH_3)_3C\text{-}Br$ S_N1
7. $(CH_3)_3C\text{-}O\text{-}CH_3 \xrightarrow{HBr}$ $(CH_3)_3C\text{-}Br + CH_3Br$ S_N2 & S_N1
8.  $\xrightarrow{HO^-}$  S_N2
9.  $\xrightarrow{CH_3O^-}$  S_N2
10.  $\xrightarrow{HS^-}$  S_N2
11.  $\xrightarrow{NH_3}$  S_N2
12.  $\xrightarrow{CH_3C\equiv C^-}$  S_N2
13.  $\xrightarrow{N\equiv C^-}$  S_N2
14.  $\xrightarrow{LiAlH_4\ (Hydride\ Ion)}$  NA
15.  $\xrightarrow{H_3O^+}$  cross between S_N1 & S_N2

attack here but with inversion

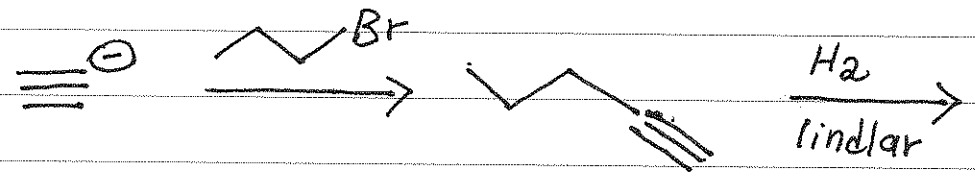
Determine the product (and intermediate) in each of the following reactions:

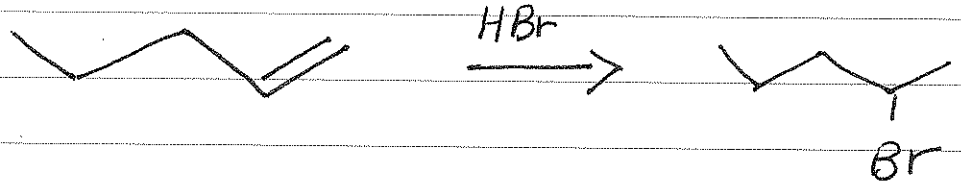
note: mechanisms below are more complicated than simple S_N2

1. $CH_3CH_2\text{—}OH \xrightarrow[\text{substitution}]{(CH_3)_3Si\text{-}Cl}$ $CH_3CH_2O\text{—}Si(CH_3)_3$
2. $CH_3CH_2\text{—}O\text{—}Si(CH_3)_3 \xrightarrow[\text{substitution}]{F^-}$ $CH_3CH_2\text{—}OH$
3. $CH_3CH_2\text{—}OH \xrightarrow{Cl\text{—}S(=O)\text{—}CH_3}$ (substitution) $CH_3CH_2O\text{—}S(=O)\text{—}CH_3$
4. $CH_3CH_2\text{—}OH \xrightarrow{Cl\text{—}S(=O)\text{—}C_6H_4\text{—}CH_3}$ (substitution) $CH_3CH_2O\text{—}S(=O)\text{—}C_6H_4\text{—}CH_3$
5. $CH_3CH_2\text{—}OH \xrightarrow{PBr_3}$ (substitution x 2) $CH_3CH_2\text{—}O\text{—}PBr_2$ $\xrightarrow{Br^-}$ CH_3CH_2Br
6. $CH_3CH_2\text{—}OH \xrightarrow{Cl\text{—}S(=O)\text{—}Cl}$ (substitution x 2) $CH_3CH_2O\text{—}S(=O)\text{—}Cl$ $\xrightarrow{Cl^-}$ CH_3CH_2Cl
7. $CH_3CH_2\text{—}OH \xrightarrow[\text{elimination}]{H_2SO_4}$ $CH_2=CH_2$
8. $CH_3CH(OH)\text{-}CH(OH)CH_3 \xrightarrow[\text{pinacol rearrangement}]{H^+}$ $CH_3\text{—}C(=O)\text{—}CH_2\text{—}CH_3$
9.  $\xrightarrow[\text{addition}]{Cl_2/H_2O}$  $\xrightarrow{\text{substitution}}$ 
10.  $\xrightarrow[\text{addition}]{H^+/CH_3OH}$ 
11.  $\xrightarrow[\text{oxidation}]{RCO_3H}$ 
12. $(CH_3)_2CH\text{—}OH \xrightarrow[\text{oxidation}]{H_2CrO_4}$ $(CH_3)_2C=O$
13. $CH_3CH_2\text{—}OH \xrightarrow[\text{oxidation}]{H_2CrO_4}$ $CH_3\text{—}C(=O)\text{—}OH$
14. $CH_3CH_2\text{—}OH \xrightarrow[\text{oxidation}]{PCC}$ $CH_3\text{—}C(=O)\text{—}H$
15. $HO\text{-}CH_2CH_2\text{—}OH \xrightarrow[\text{oxidation}]{HIO_4}$ 

Synthesis, chapters 7, 8, 9

1.





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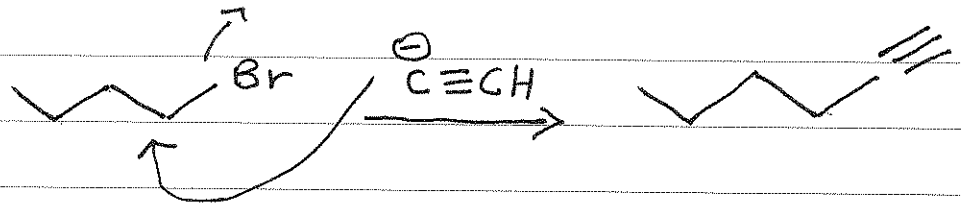
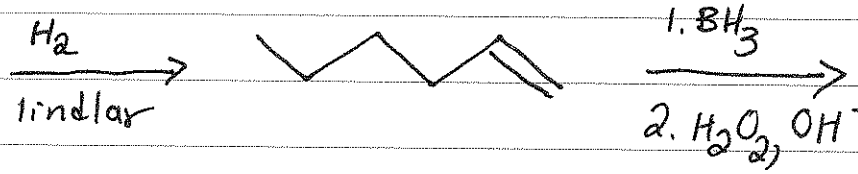
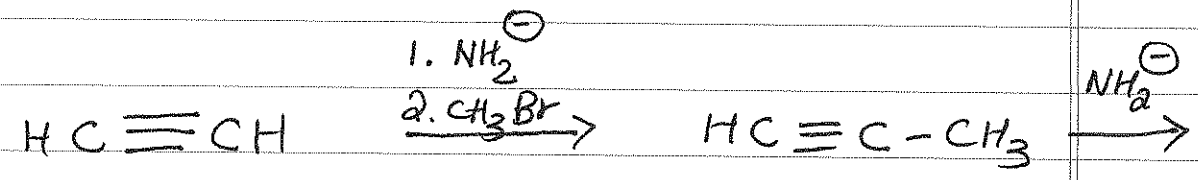
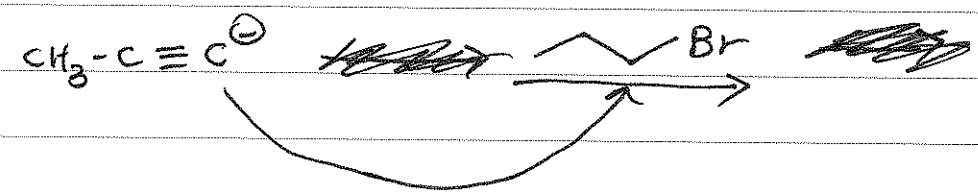


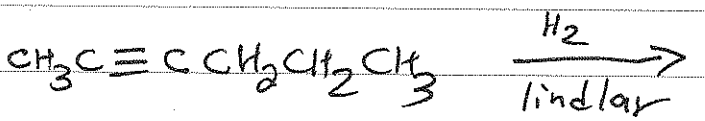


3. see #1 above

4.

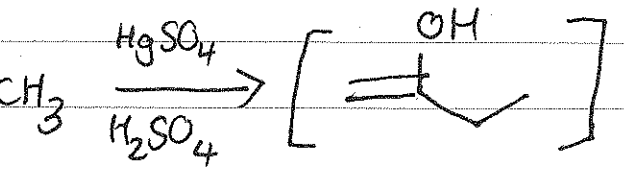


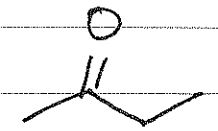




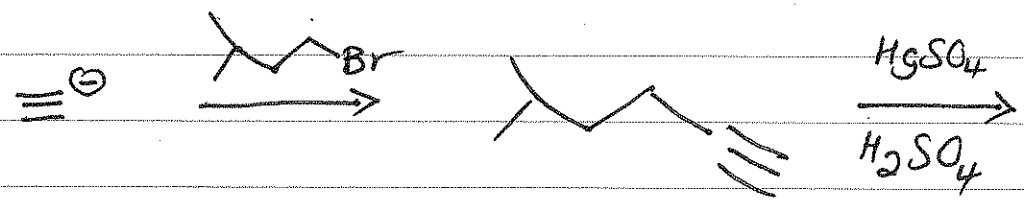
Synthesis, chapters 7, 8, 9 cont

5. $HC\equiv CH \xrightarrow{H^{\ominus}} HC\equiv C^{\ominus} \xrightarrow{CH_3CH_2Br}$

$HC\equiv C-CH_2CH_3 \xrightarrow[H_2SO_4]{HgSO_4}$  $\longrightarrow$

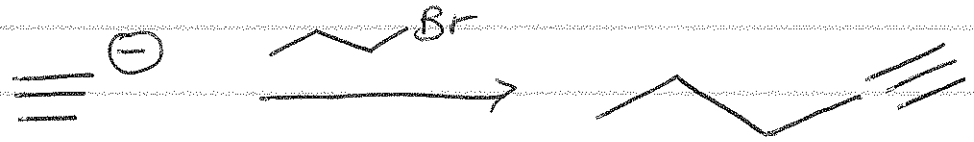


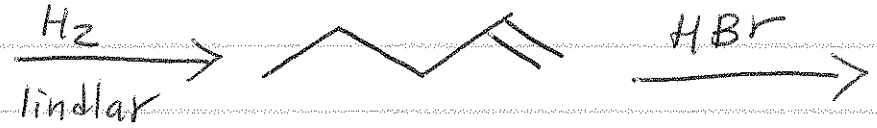
6. take $HC\equiv C-CH_2CH_3$ from # 5
& add Sia_2BH & then H_2O_2, OH^-

7. 

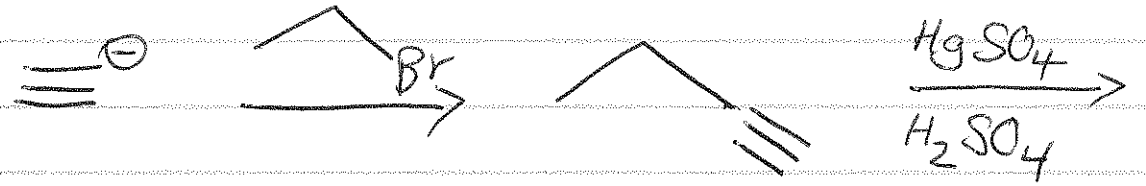
Synthesis chapters 9, 10, 11

1.



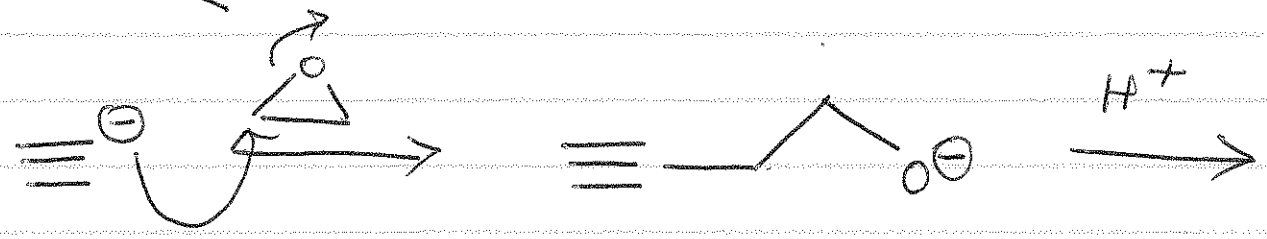


2.

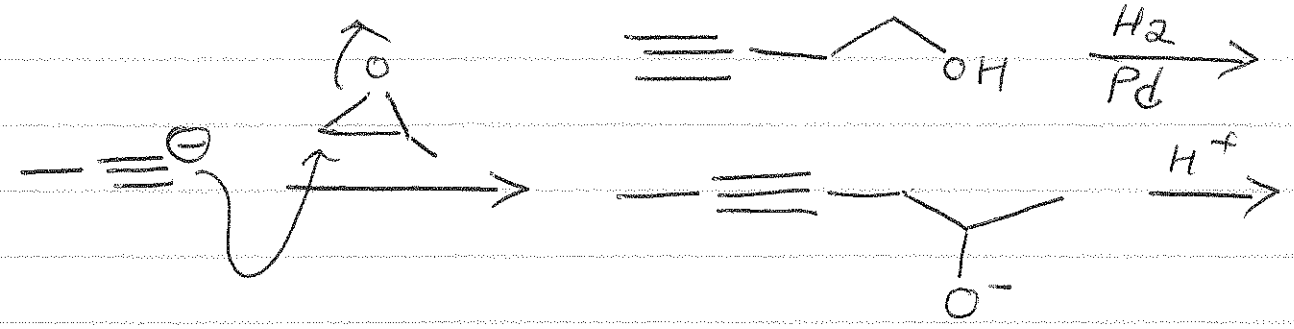


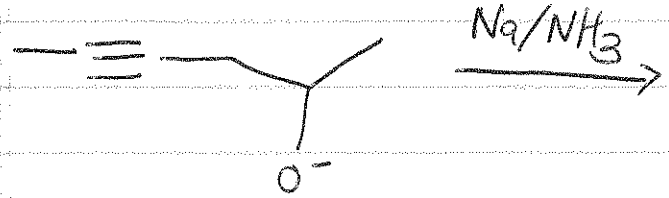
~~3.~~ from #

3.



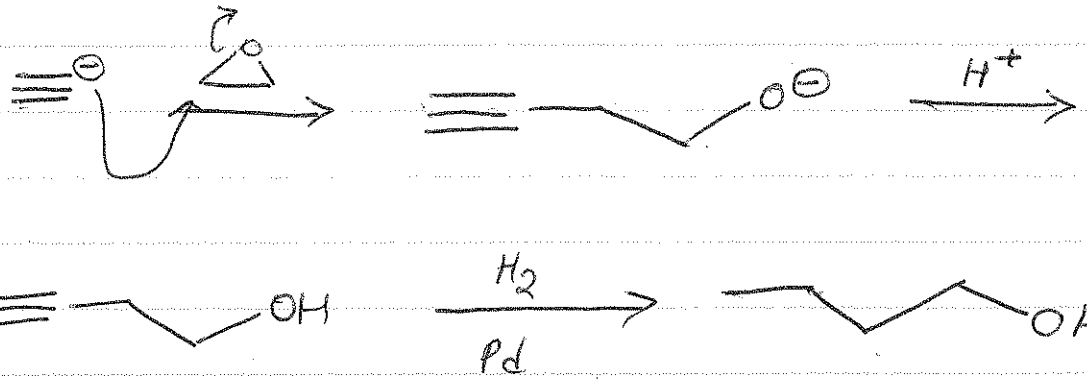
4.





Synthesis chapter 9, 10, 11 cont

5.



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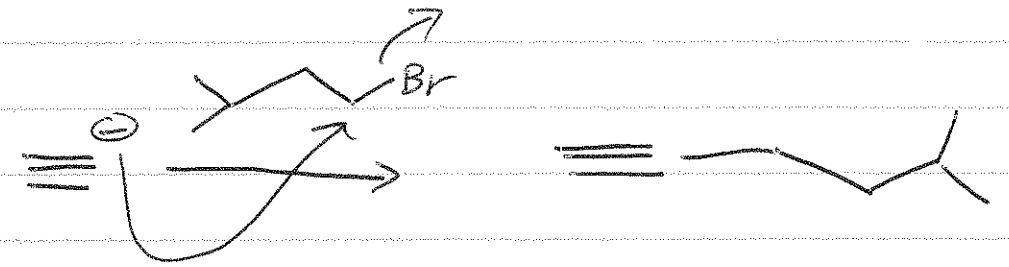
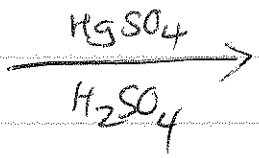
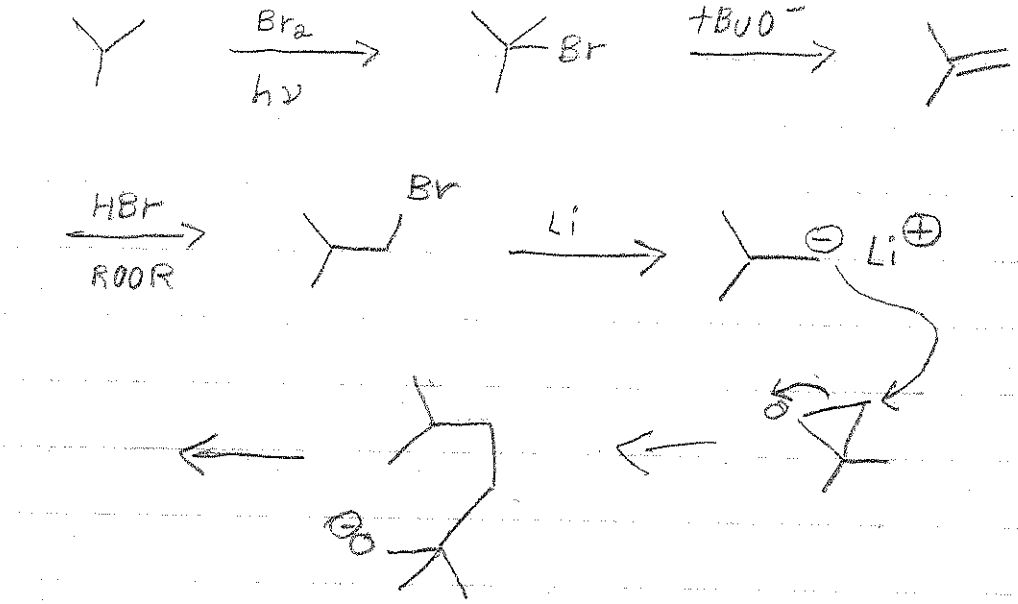




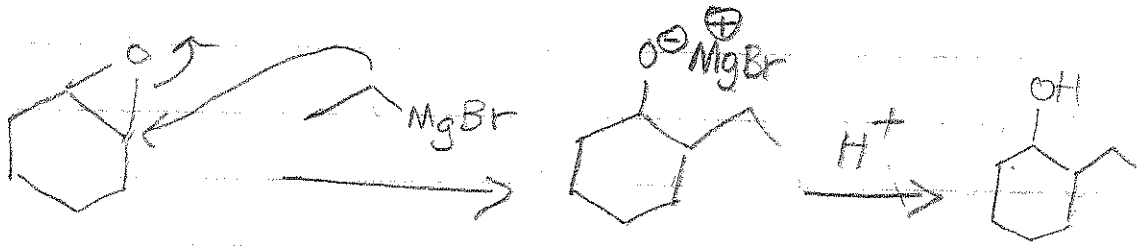
Chapter 15 - Synthesis Practice

~~Key~~

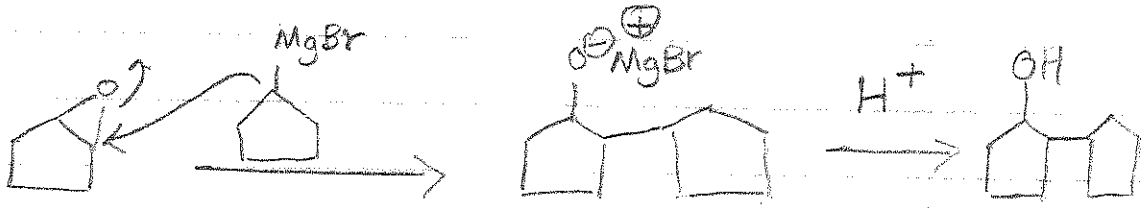
a.



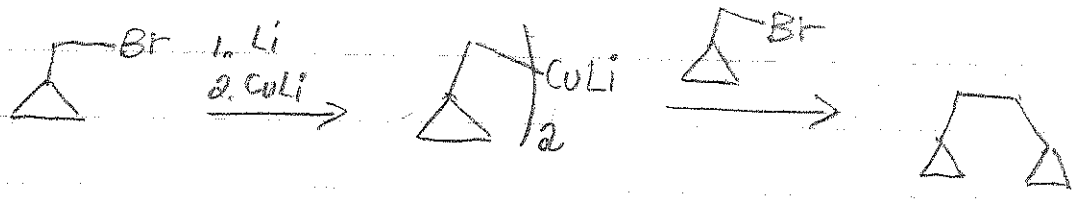
b.



c.



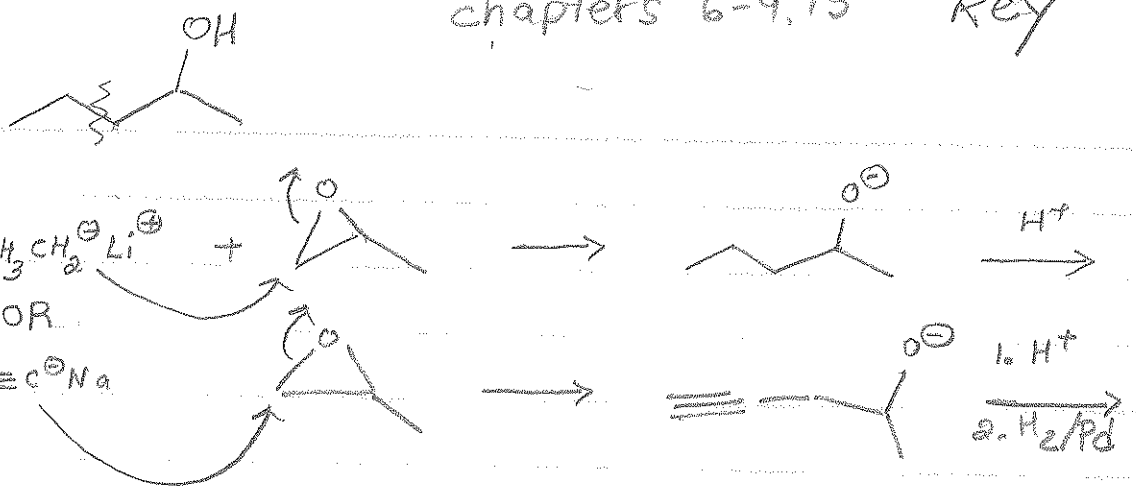
d.



Synthesis

chapters 6-9.15 key

1.



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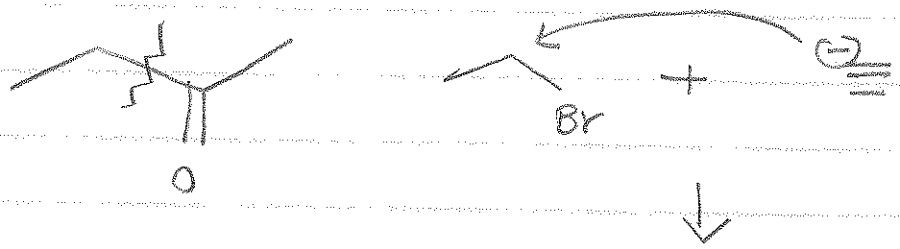

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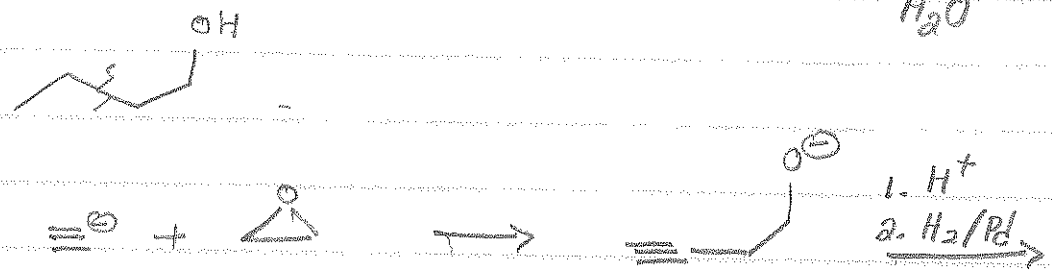

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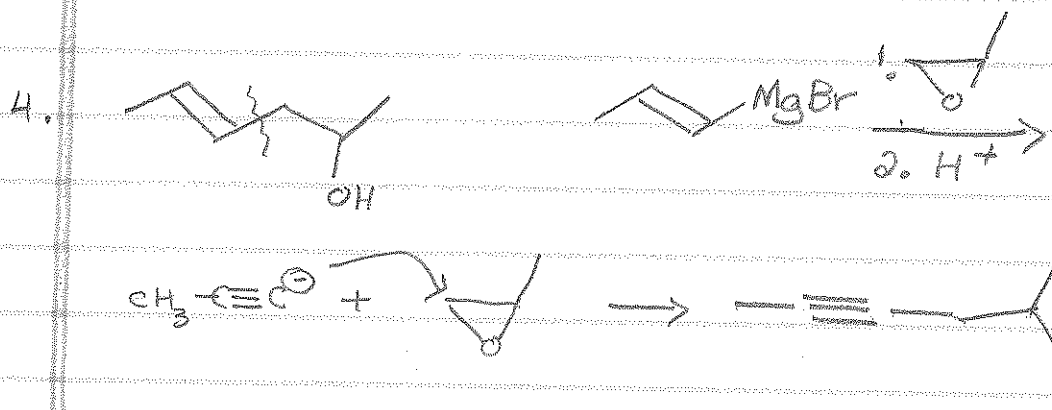
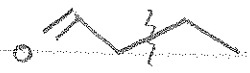
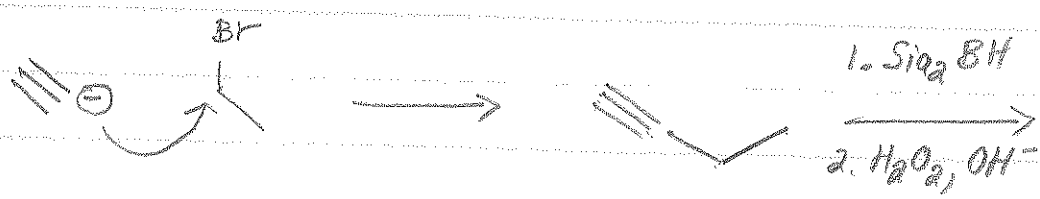


Synthesis key cont

5.





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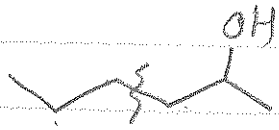
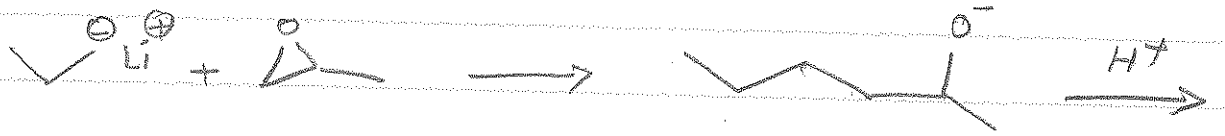
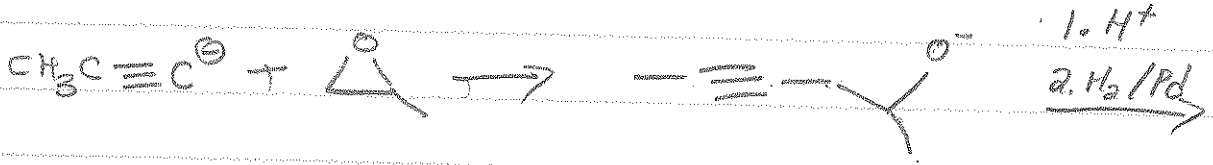




OR



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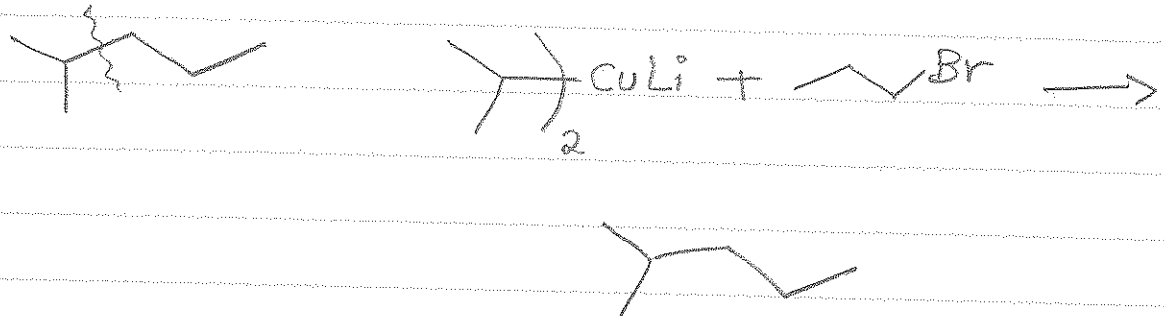
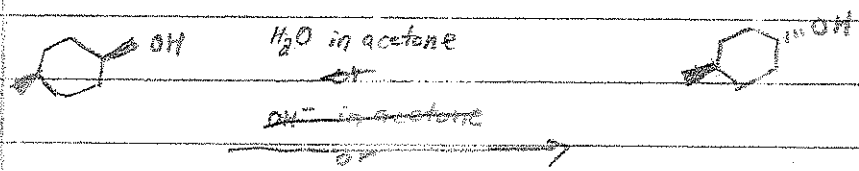
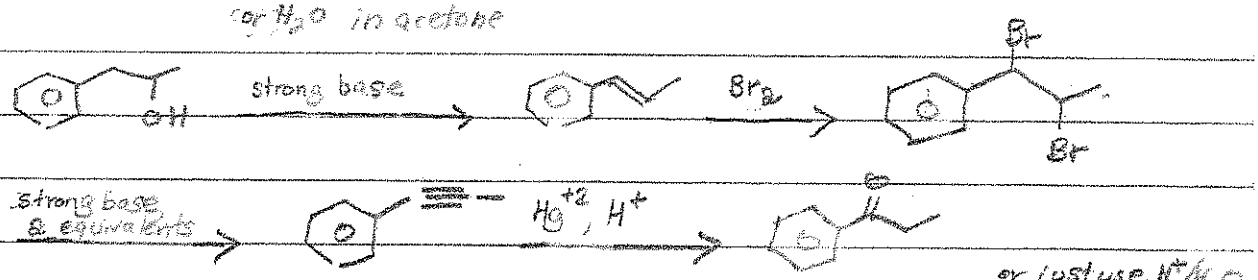
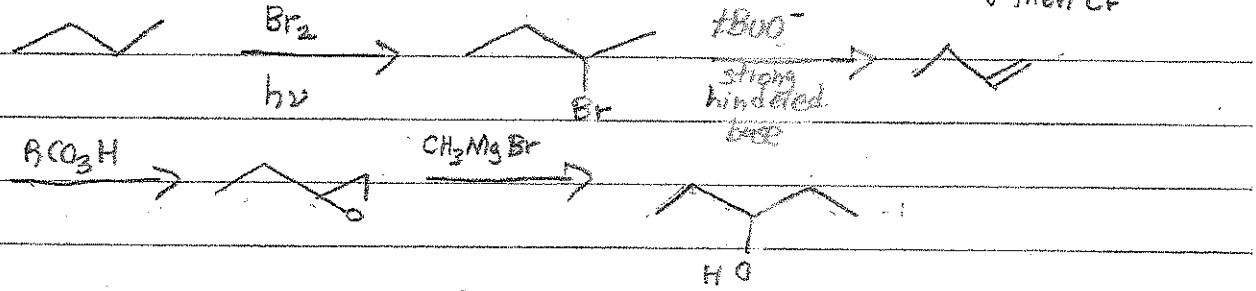
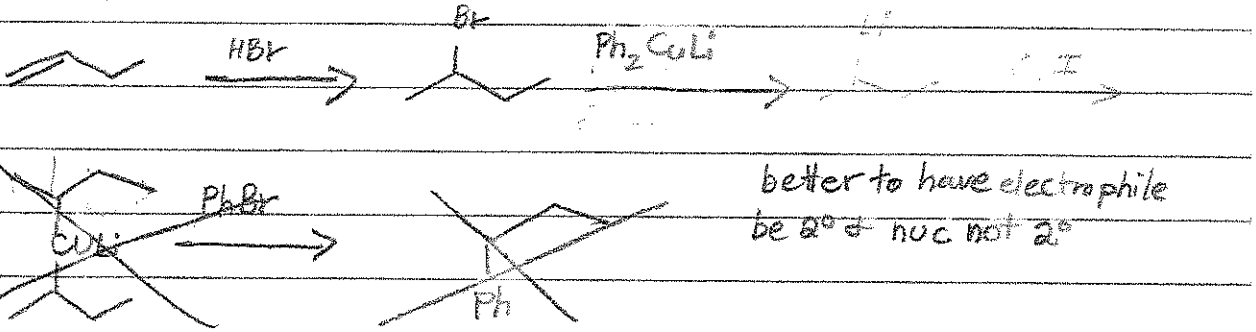


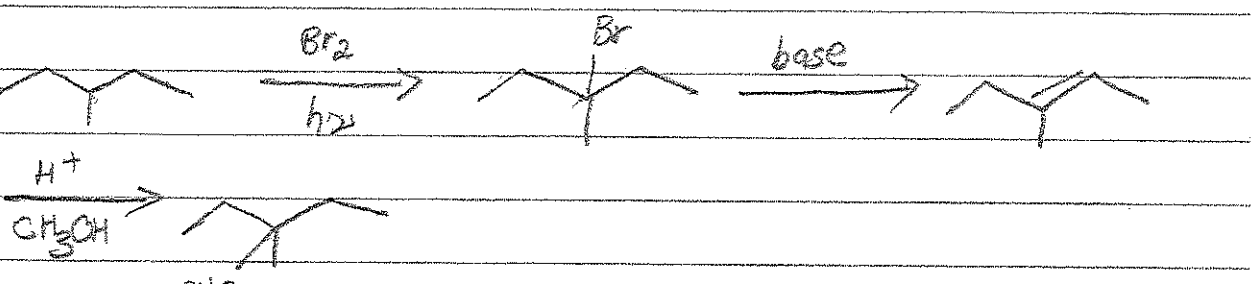
Chapter 15. Organometallics & Synthesis Problem Set. Answer key

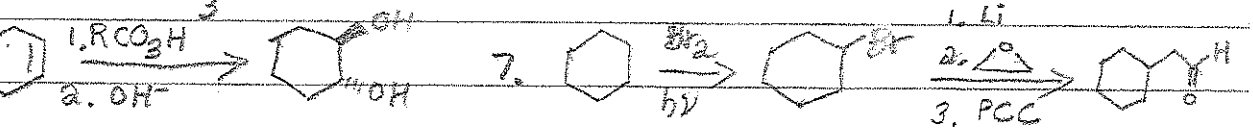
1. 

2. 

3. 

4. 

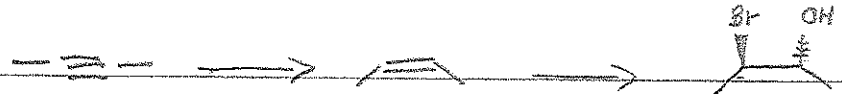
5. 

6. 

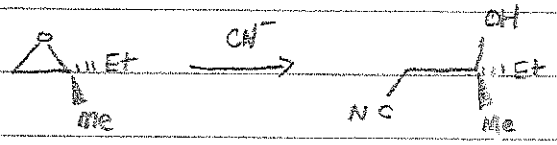
7.

Preparation for Exam II. Answer key

1a.



b.



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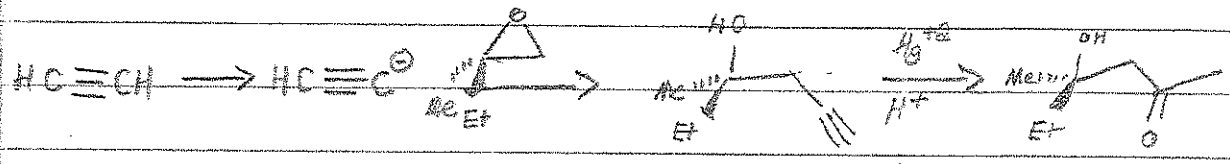

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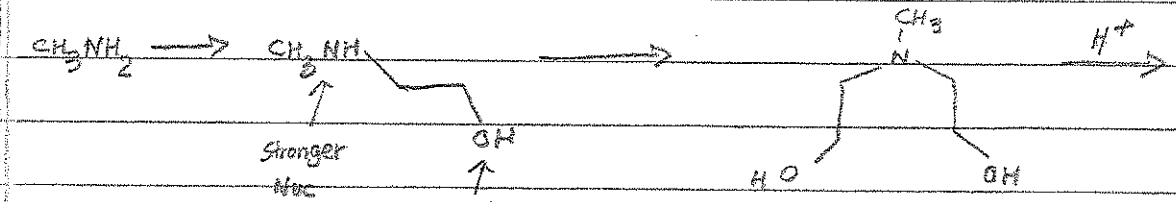
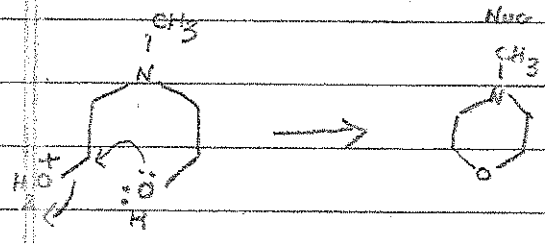
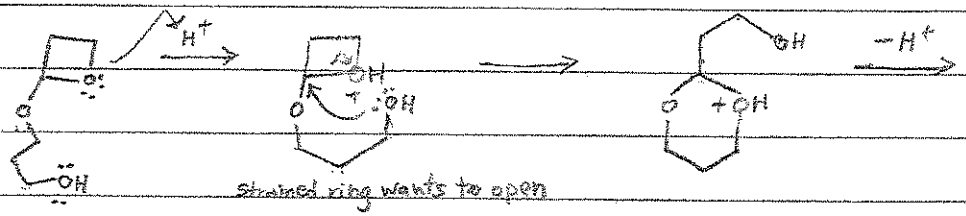




2a.



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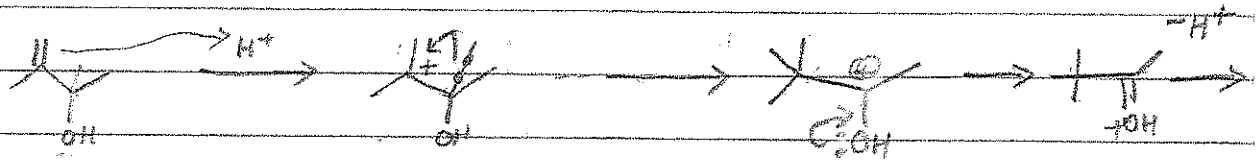
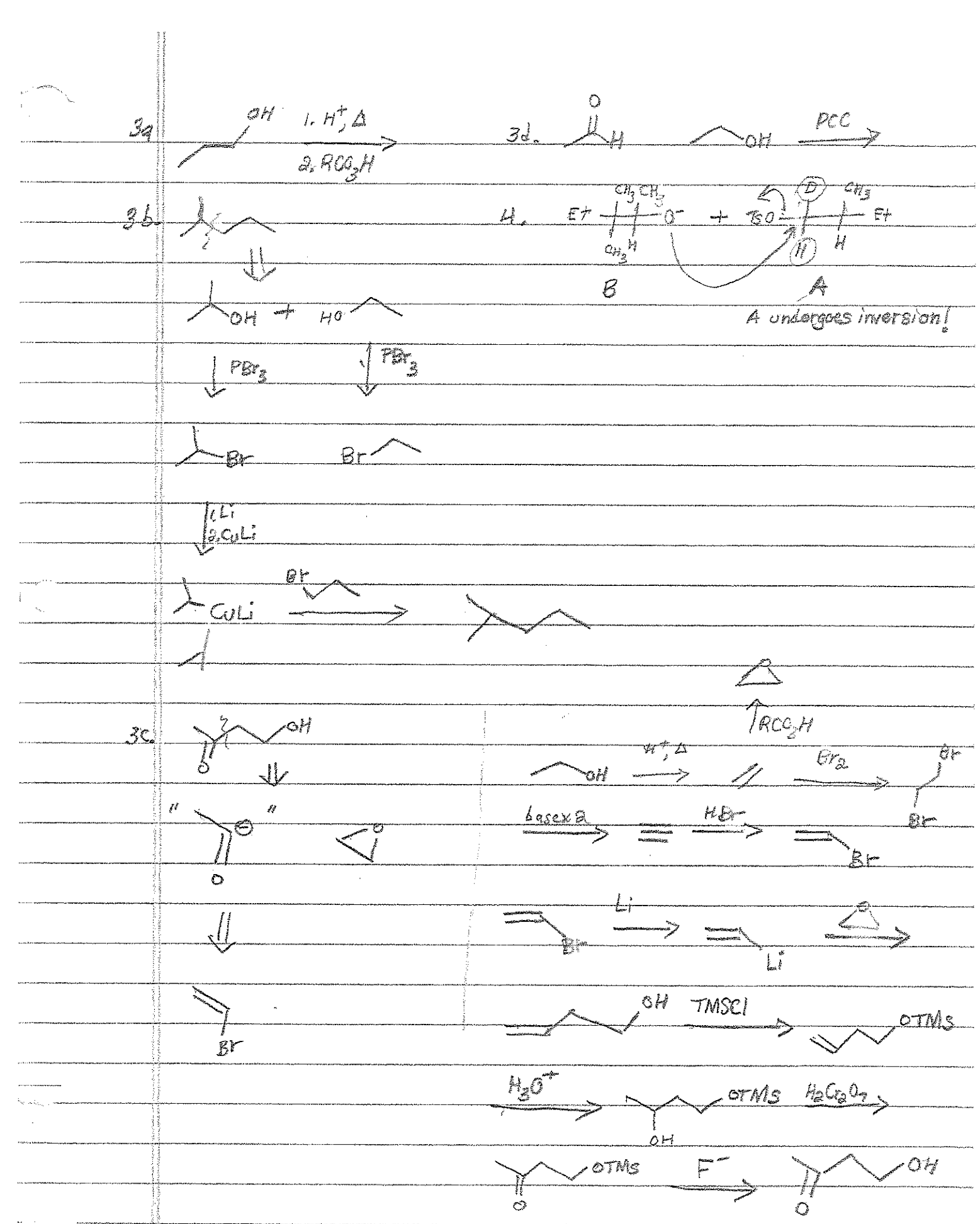
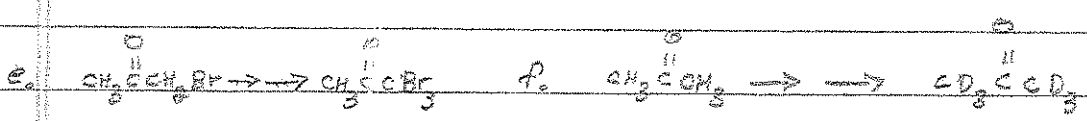
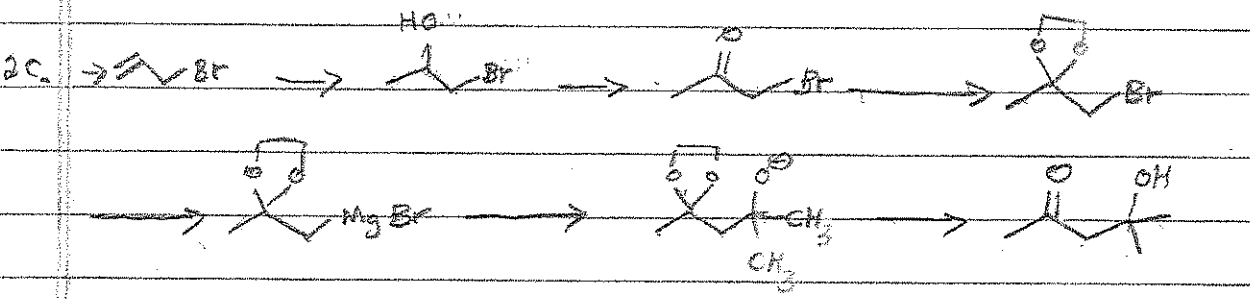


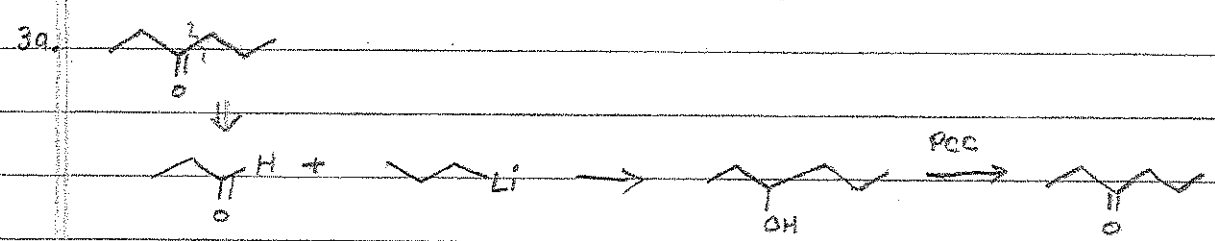

3a.
1. H+, Δ
2. RCO3H
3d.
PCC
3b.
4.
A undergoes inversion!
PBr3
PBr3
1. Li
2. CuLi
3c.
RCO3H
H+, Δ
Br2
base x 2
HBr
Li
TMSCl
H3O+
H2Cr2O7
F-

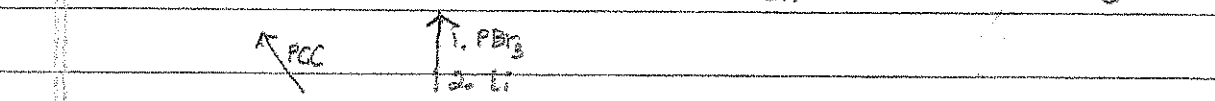
Chapter 16, Aldehydes + Ketones Problem Set. Answer key

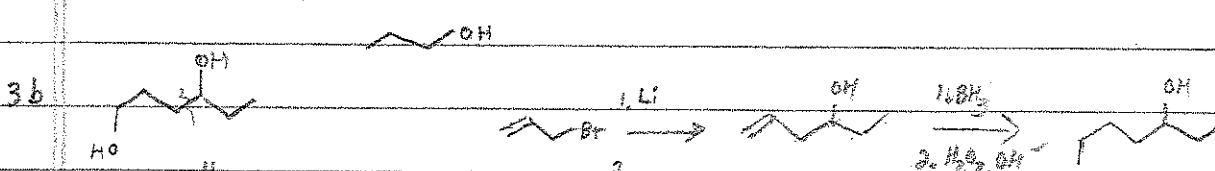
1. Mechanisms are not shown here.

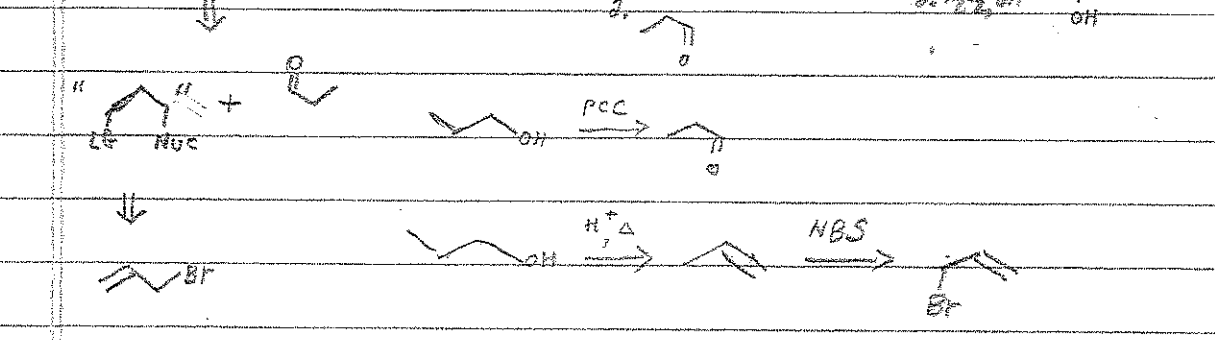




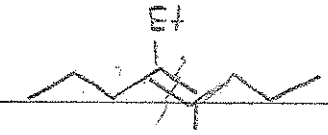


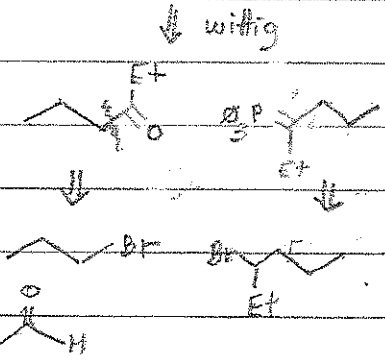


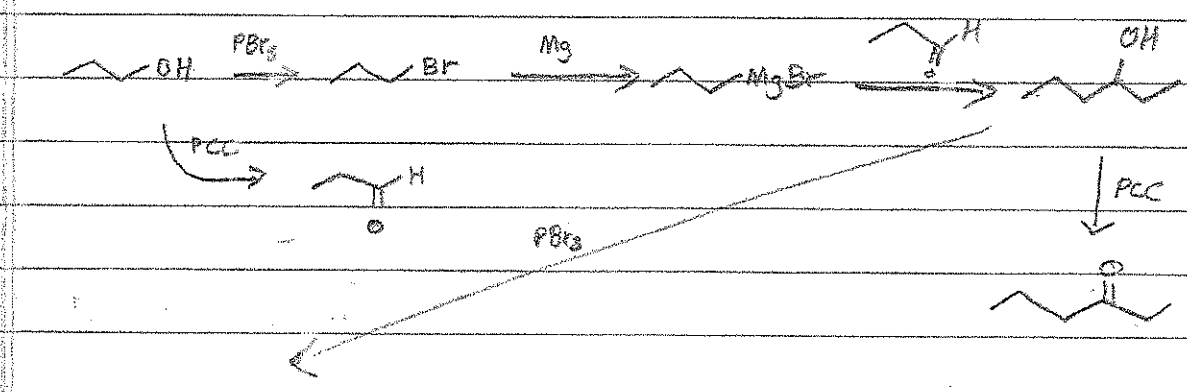


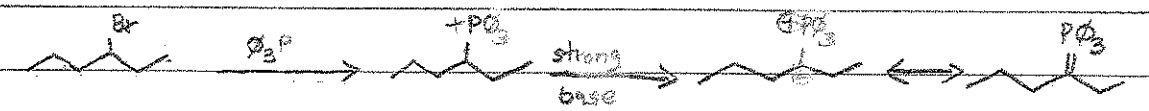


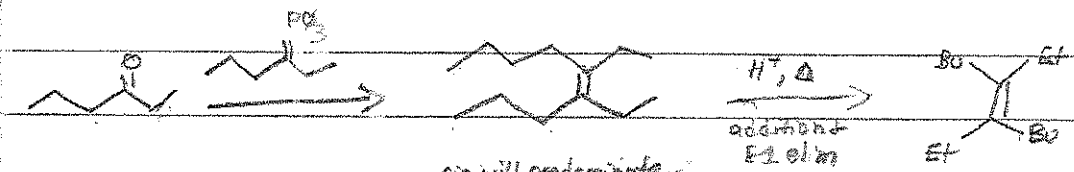
3c.





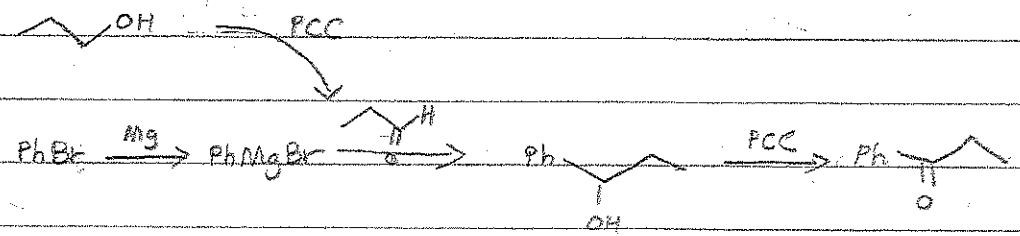






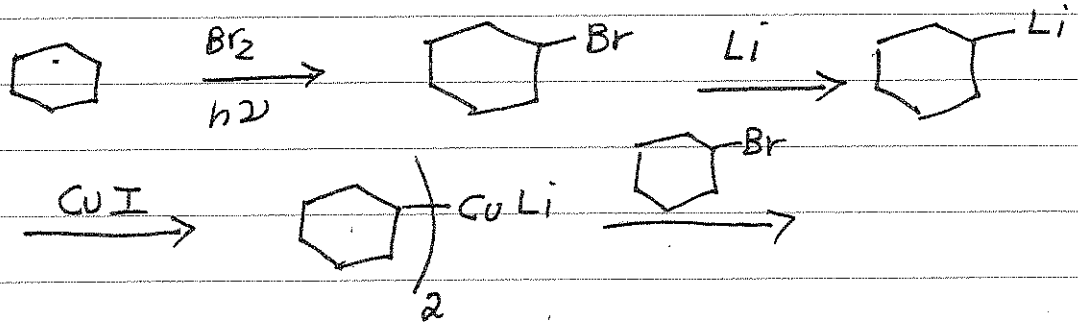
cis will predominate

3d.



Synthesis (chapters 15 & 16)

1.



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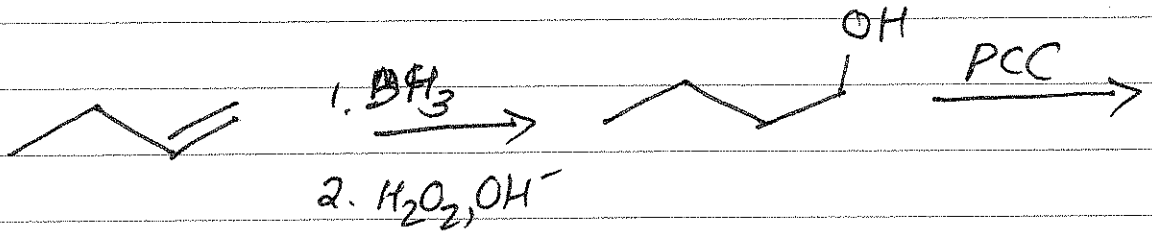
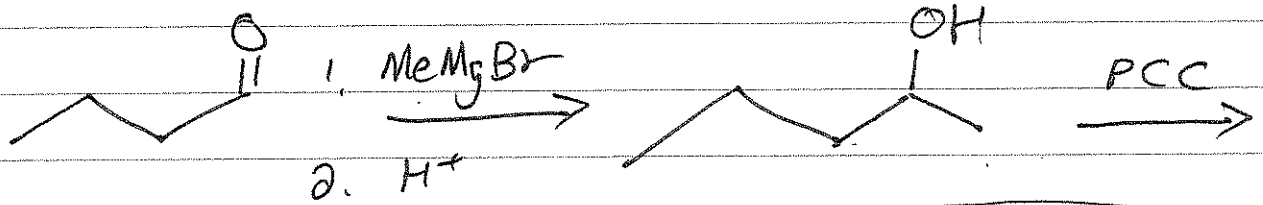
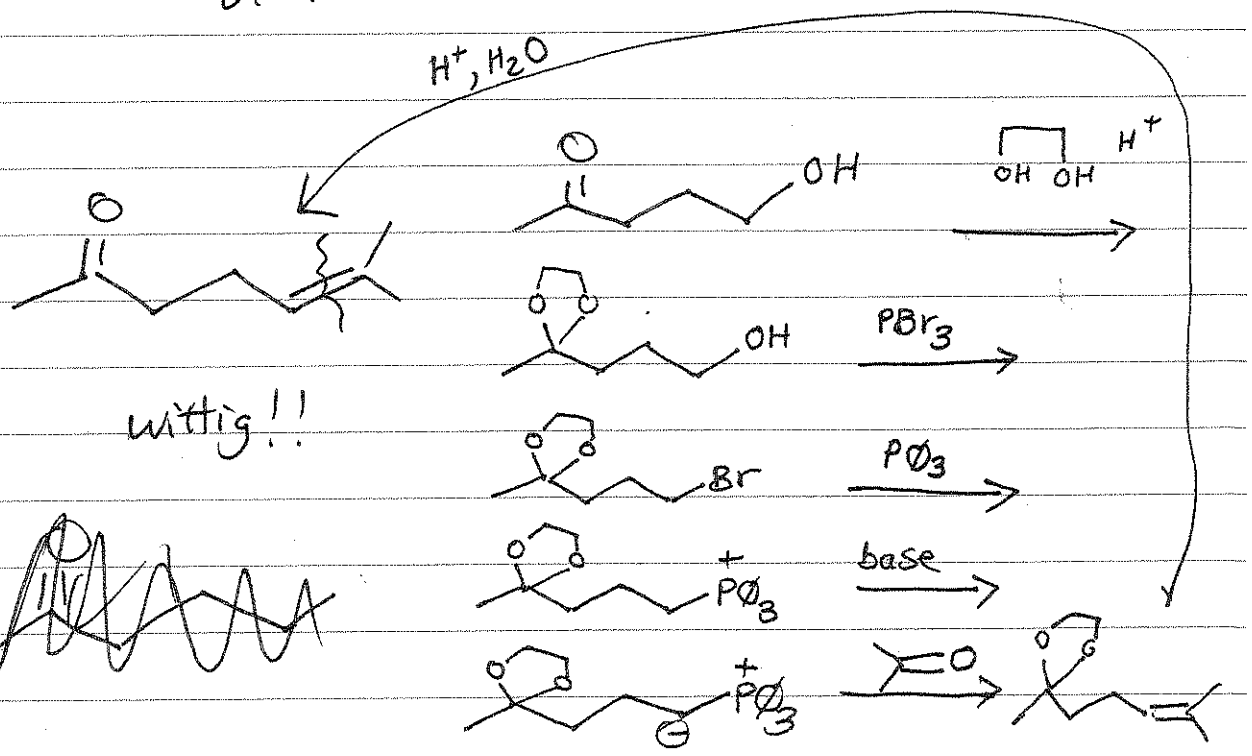




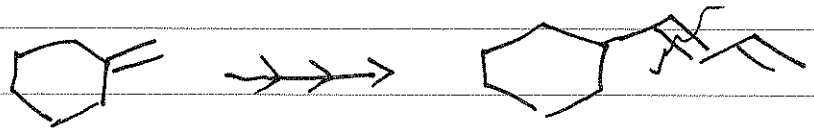
3.



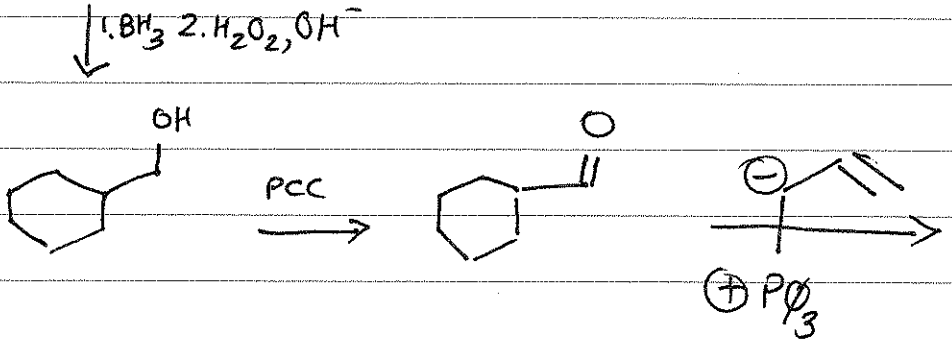
wittig!!

Synthesis cont

4.



with g!



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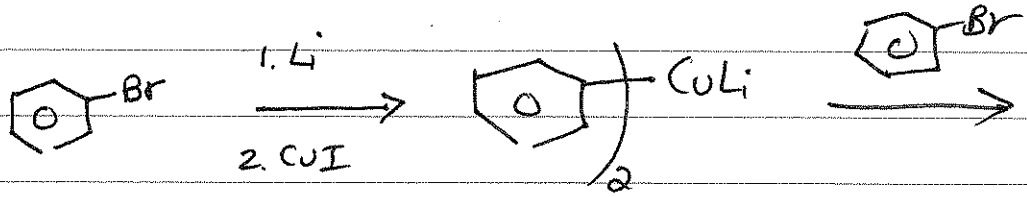
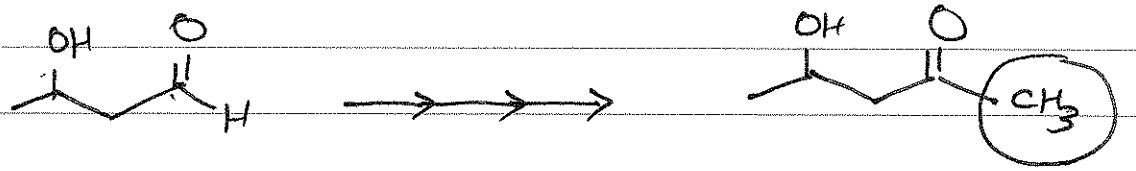
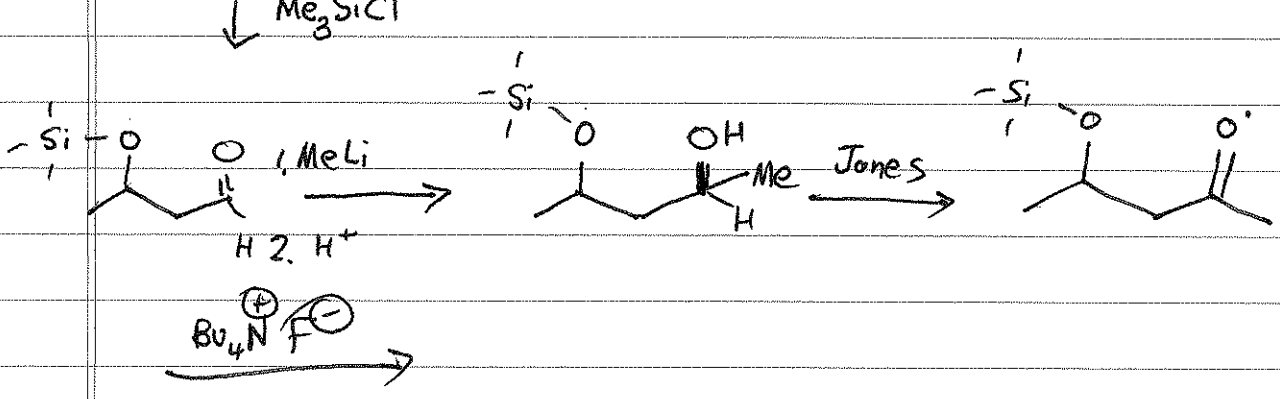


6.

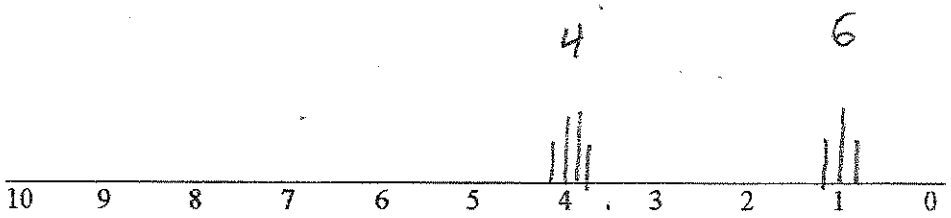




Chapter 13. Proton NMR Problem Set. Answer Key

1. Answer the following series of questions regarding the molecule diethyl ether ($CH_3CH_2OCH_2CH_3$).

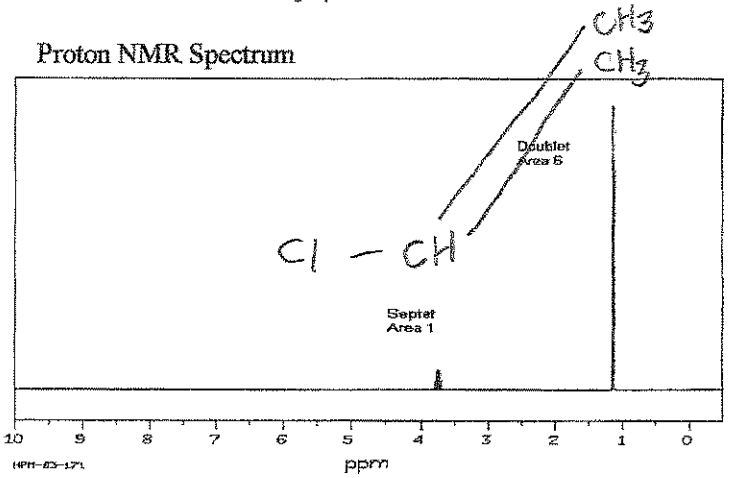
   a. Looking at the symmetry of the ether molecule, how many different types of hydrogens are present? 2
   b. Based on your answer to a, how many peaks should the proton NMR spectrum of diethyl ether have? 2
   c. What should the position or chemical shift of each peak be? (Consult the attached chart.) 1.0, 4.0
   d. Draw a preliminary/approximate drawing of what the proton NMR spectrum of diethyl ether should look like on the graph below. USE A PENCIL, NOT A PEN.
   e. What should the area under each peak be, given the number of hydrogens of each type present in the molecule? Modify your drawing so that your areas look approximately correct.
   f. What about splitting? How many H neighbors are next door to the methyl (CH_3) group? How many H neighbors are next door to the methylene (CH_2) group? Use the n+1 rule (# of lines = # of next door neighbors +1) to determine how many lines each peak should have due to the influence of its next door neighbors. Modify your drawing below accordingly.



2. Solve the following NMR puzzle using the step by step instructions below. This is a general NMR puzzle solving strategy that I want you to use/learn/master!

Molecular Formula: C_3H_7Cl

Proton NMR Spectrum

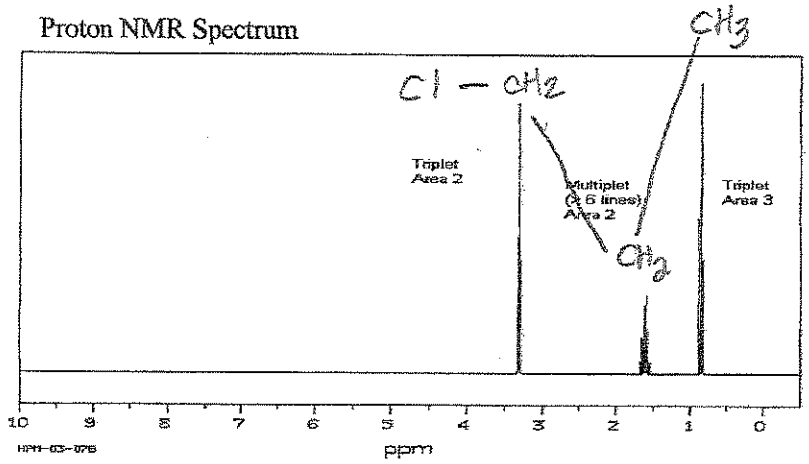


a. How many UNITS OF UNSATURATION does this molecule have? (You can use a formula to figure this out or you can just draw out a hypothetical molecule.) 0
b. Based on your answer to a, how many double bonds or rings does this molecule have? 0
c. Based on the NUMBER OF PEAKS in the spectrum, how many different types of hydrogens are present in this molecule? 2
d. Given the number of carbons present, what does your answer to question c tell you about the symmetry of the molecule? 2 identical carbons
e. Based on the AREA under each peak (listed above), how many hydrogens are represented by each peak?
f. Based on your answer to e, what group (methyl CH_3, methylene CH_2 or methyne CH) is represented by each peak? How many methyl (CH_3) groups must be present in this molecule?
g. Draw what you know so far (all the methyl, methylene and methyne groups present) next to each peak above.
h. What else is present in the molecule (based on the molecular formula)? Cl
i. What electronegative atom has caused the CHEMICAL SHIFT of one of the peaks to appear at ~ 3.8? What atom is directly attached to the group that appears at 3.8? Draw the attachment above. Cl
j. Now it is time to look at SPLITTING. Why is the group at 1.2 split into two lines? How many next door neighbor hydrogens does it have? What carbon group is it attached to?
k. Why is the group at 3.8 split into 7 lines? How many next door neighbor hydrogens does it have? What carbon groups is it attached to?
l. What is the structure of the compound?

3. Solve the following slightly more difficult NMR puzzle using the step by step instructions below.

Molecular Formula: C_3H_7Cl

Proton NMR Spectrum

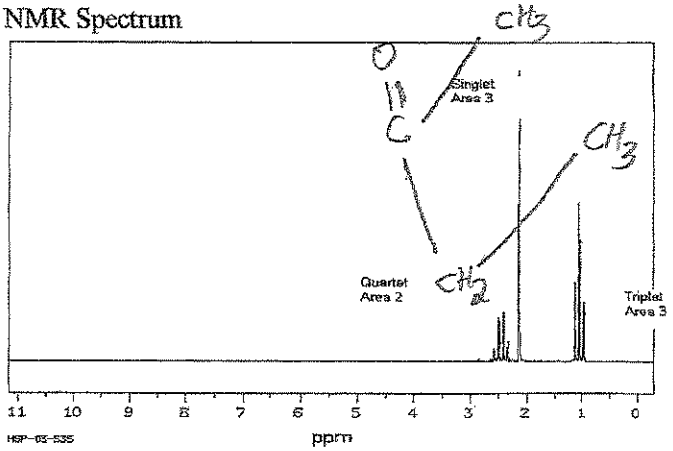


a. How many UNITS OF UNSATURATION does this molecule have? 0
b. How many double bonds or rings does this molecule have? 0
c. Based on the NUMBER OF PEAKS in the spectrum, how many different types of hydrogens are present in this molecule? 3
d. Given the number of carbons present, what does your answer to question c tell you about the symmetry of the molecule? not s
e. Based on the AREA under each peak (listed above), how many hydrogens are represented by each peak?
f. Based on your answer to e, what group (methyl CH_3, methylene CH_2 or methyne CH) is represented by each peak?
g. Draw what you know so far (all the methyl, methylene and methyne groups present) next to each peak above.
h. What else is present in the molecule (based on the molecular formula)? Cl
i. What electronegative atom has caused the CHEMICAL SHIFT of one of the peaks to appear at ~ 3.4? What atom is directly attached to the group that appears at 3.4? Draw this attachment above. Cl
j. Now it is time to look at SPLITTING, starting with the simpler splitting patterns, saving the most complex one for last. Why is the group at 3.4 split into three lines? How many next door neighbor hydrogens does it have? What carbon group is it attached to? Draw this attachment above.
k. Why is the group at 0.9 split into 3 lines? How many next door neighbor hydrogens does it have? What carbon group is it attached to? Draw this attachment above.
l. Explain why the group at 1.6 is split into so many lines.
m. Draw the final structure of the compound.

4. Solve the following NMR puzzle using the step by step instructions below.

Molecular Formula: C_4H_8O

Proton NMR Spectrum

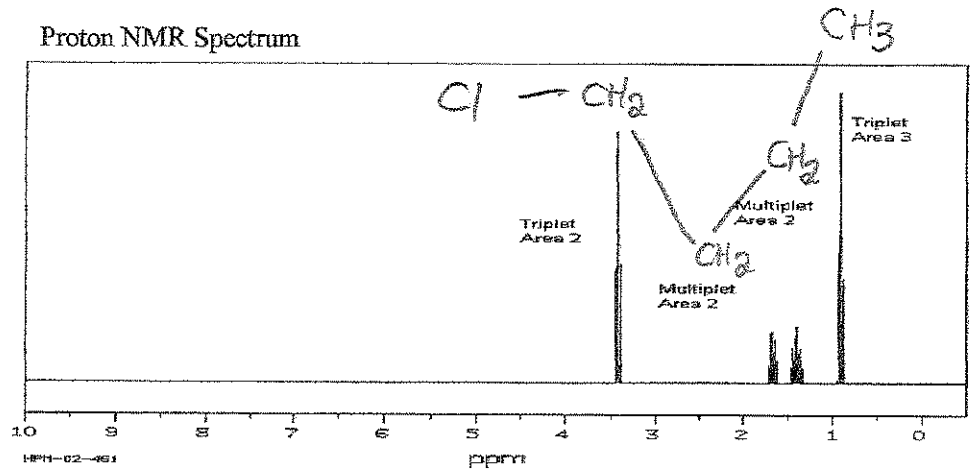


a. How many UNITS OF UNSATURATION does this molecule have? 1
b. How many double bonds or rings does this molecule have? 1
c. Based on the NUMBER OF PEAKS in the spectrum, how many different types of hydrogens are present in this molecule? 3
d. Given the number of carbons present, what does your answer to question c tell you about the structure or symmetry of the molecule? 2 identical carbons, 1 C with no H
e. Based on the AREA under each peak (listed above), how many hydrogens are represented by each peak?
f. Based on your answer to e, what group (methyl CH_3, methylene CH_2 or methyne CH) is represented by each peak?
g. Draw what you know so far (all the methyl, methylene and methyne groups present) next to each peak.
h. What else is present in the molecule (based on the molecular formula)?
i. What electronegative species has caused the chemical shift of one of the peaks to appear at ~ 2.1? Don't forget about the units of unsaturation! Draw this attachment above.
j. What electronegative species has caused the CHEMICAL SHIFT of one of the peaks to appear at ~ 2.5? Draw this attachment above.
k. Now it is time to look at SPLITTING, starting with the simpler splitting patterns, saving the most complex one for last. Why is the group at 2.1 a singlet? How many next door neighbor hydrogens does it have? What carbon group is it attached to?
l. Why is the group at 1.0 split into 3 lines? How many next door neighbor hydrogens does it have? What carbon group is it attached to? Draw this attachment above.
m. Why is the group at 2.5 split into 4 lines? How many next door neighbor hydrogens does it have? What carbon group is it attached to? Draw this attachment above.
n. Draw the structure of the product.

5. Solve the following NMR puzzle.

Molecular Formula: C_4H_9Cl

Proton NMR Spectrum



a. UNITS OF UNSATURATION
How many double bonds or rings does this molecule have? 0

b. NUMBER OF PEAKS
How many different types of hydrogen are present in this molecule? 4

c. AREA
Which group (methyl, methylene or methyne) is represented by each peak?

d. CHEMICAL SHIFT
What electronegative species has caused of one of the peaks to appear at ~ 3.5? Cl

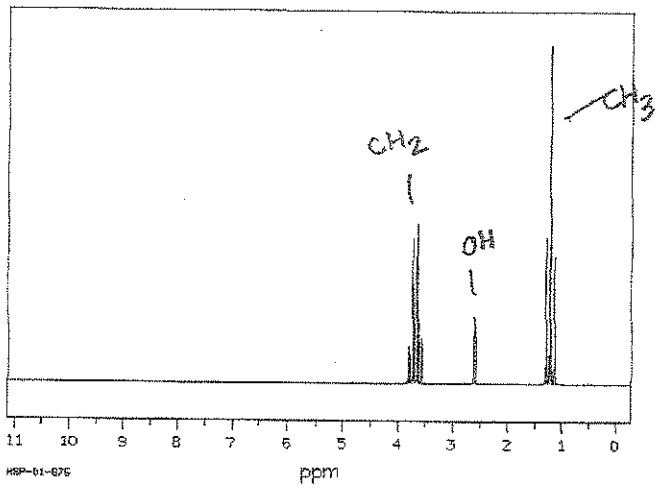
e. SPLITTING
Why is the peak at 3.5 a triplet? What must it be attached to?
Why is the peak at 0.9 a triplet? What must it be attached to?

f. PUTTING IT ALL TOGETHER
Where are the missing bonds (each carbon needs 4 bonds)? How can you attach everything together so that each carbon will be happy.

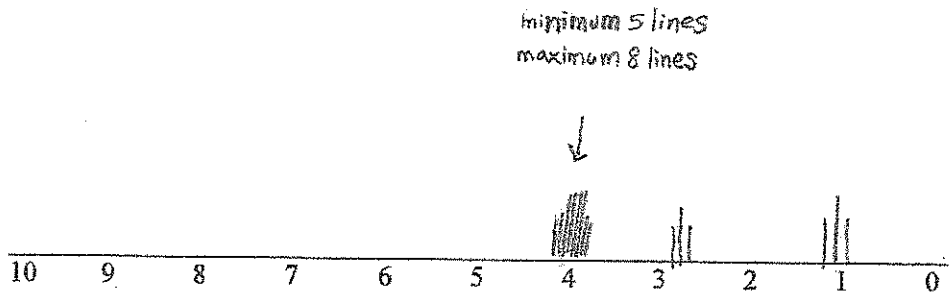
Chapter 13. Proton and Carbon NMR Problem Set. Answer key

1. The following is the proton NMR spectrum of a WET sample of ethanol (CH_3CH_2OH).

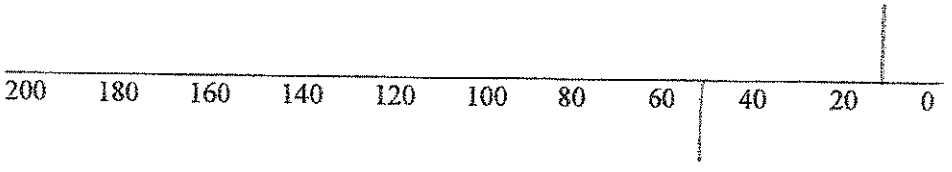
   a. Label each peak to indicate which H's it represents.



   b. On the axis provided below draw what the proton NMR spectrum of an ANHYDROUS sample of ethanol would look like. Note: the alcohol H will NOT undergo exchange here and splitting WILL be observed.

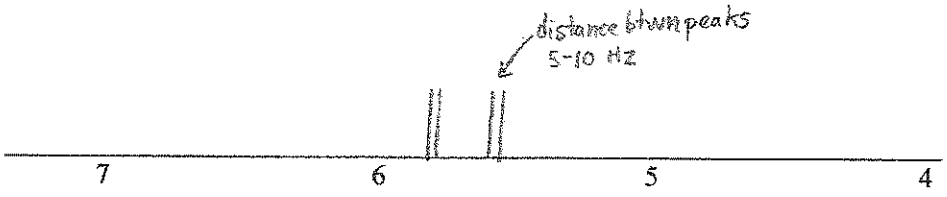


   c. Draw the carbon 13 DEPT spectrum of ethanol on the axis below.

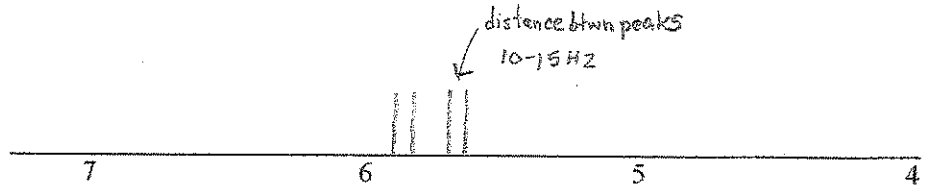


2. Draw the proton NMR spectra of cis and trans 1-bromo-2-chloroethene (BrCH=CHCl). Be sure to indicate how these two spectra would differ from one another.

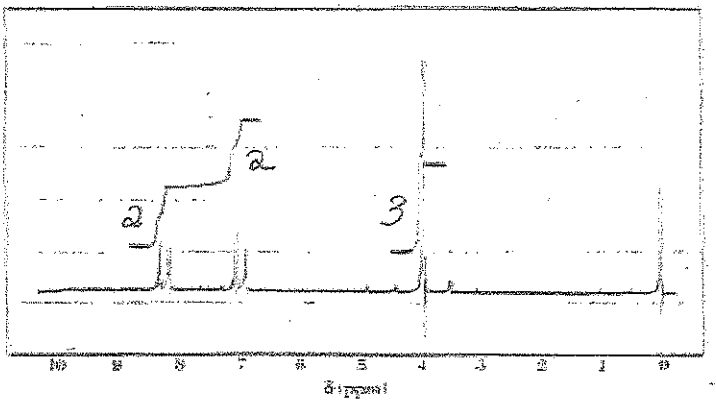
Cis compound

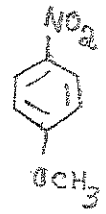


Trans compound

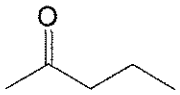


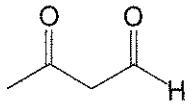
3. Determine the structure of $C_7H_7NO_3$ whose NMR spectrum is shown below:

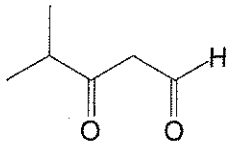


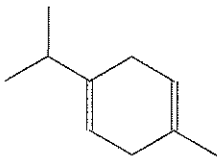
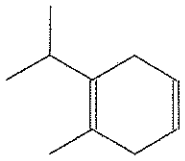


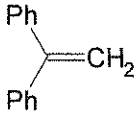
Chapters 12, 13 & 14. Spectroscopy Problem Set. Answer Key

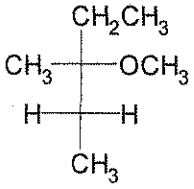
1. 

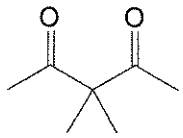
2A. 

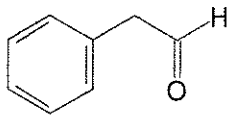
2B. 

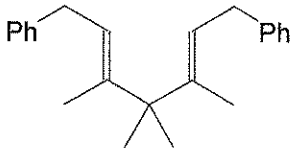
2X.  or 

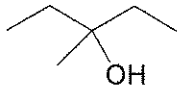
3. 

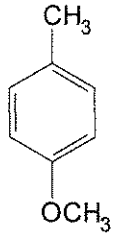
4. 

5A. 

5B.  X 2

5X. 

6. 

7. 

always # your carbons— it helps

Mechanism Practice

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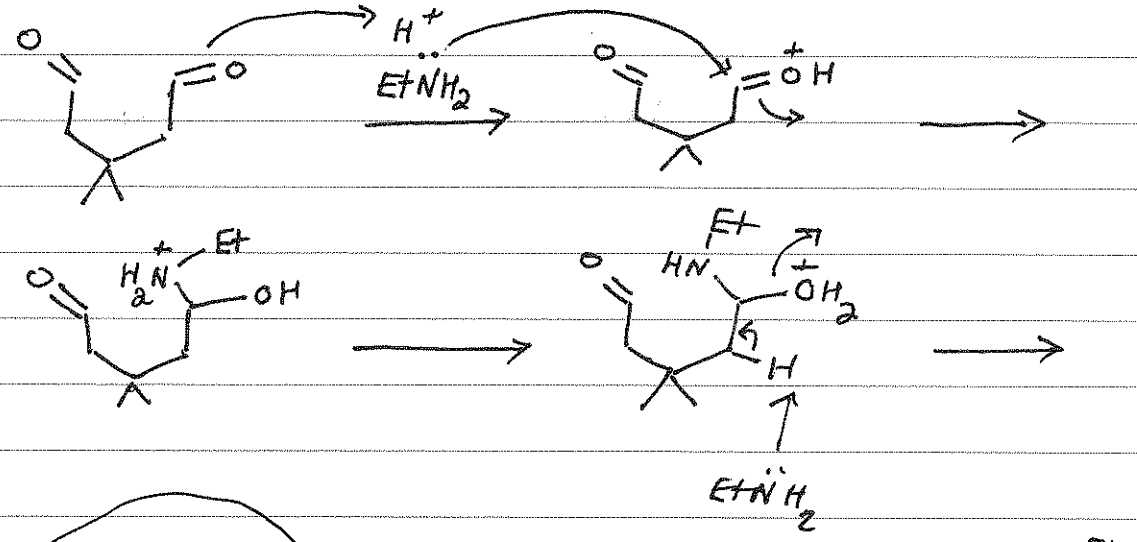

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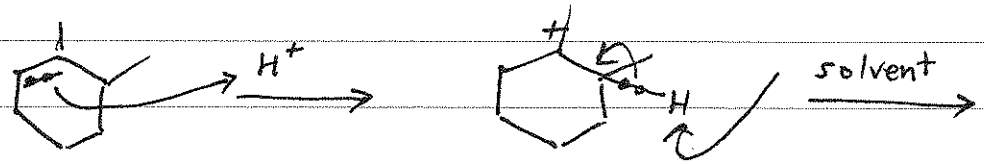

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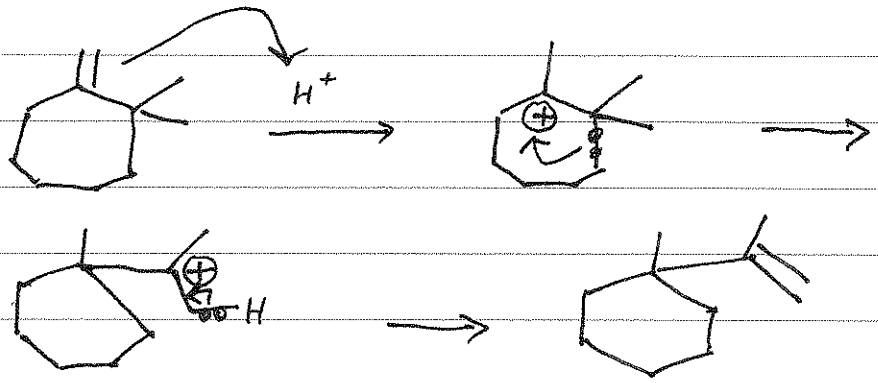
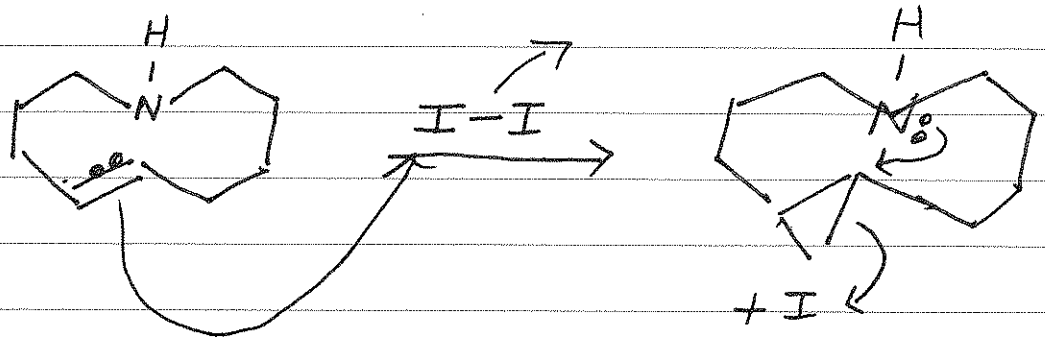


number your carbons to make things easier

mechanism Practice cont

4.



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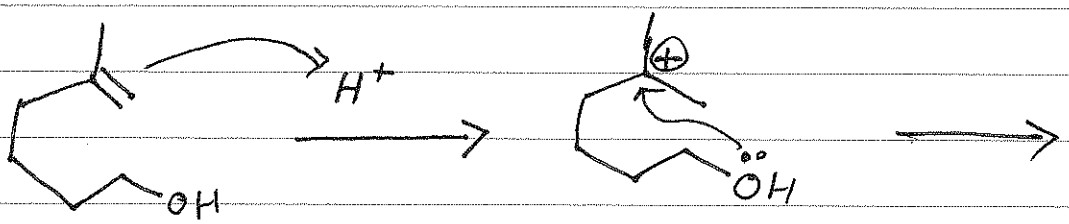

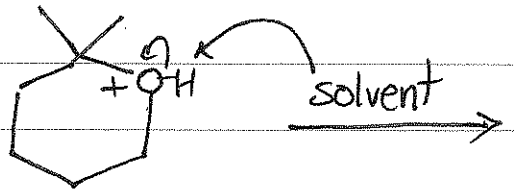

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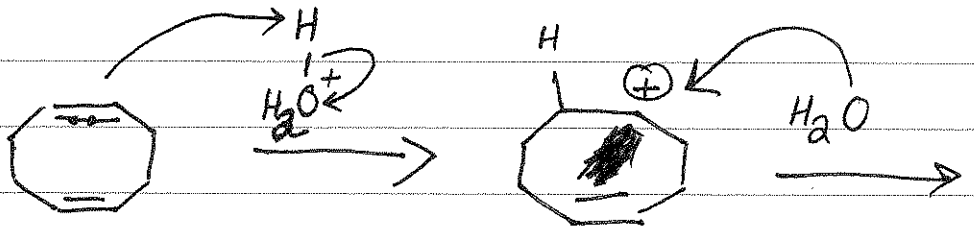

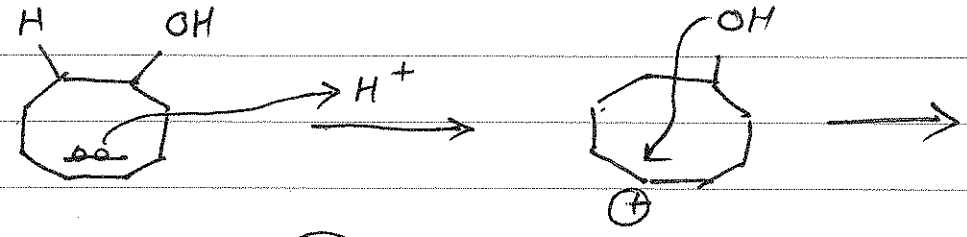

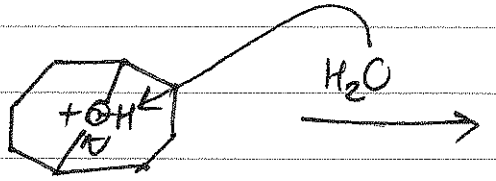

mechanism Practice cont

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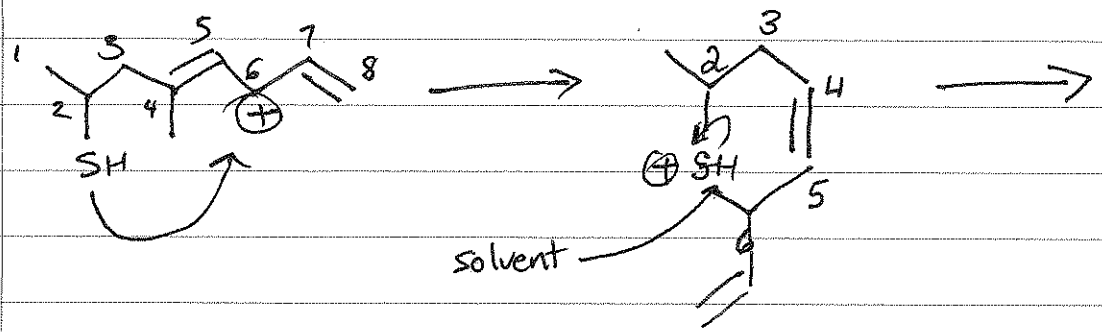

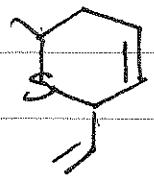

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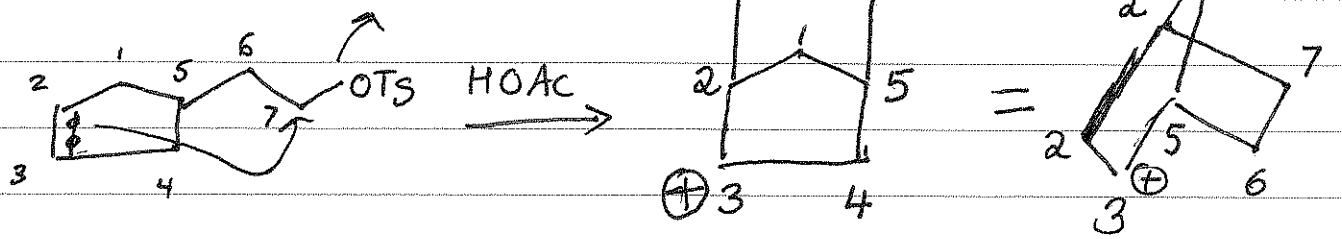

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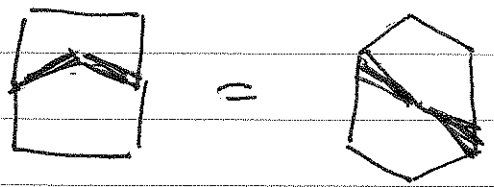

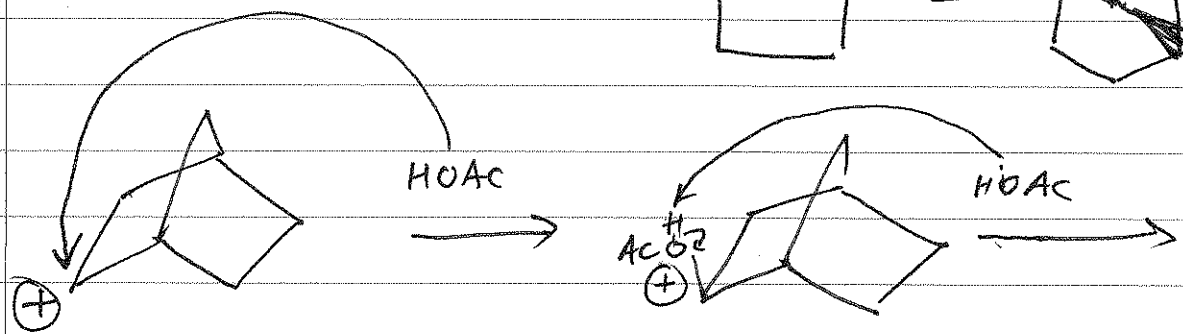

mech Pract cont

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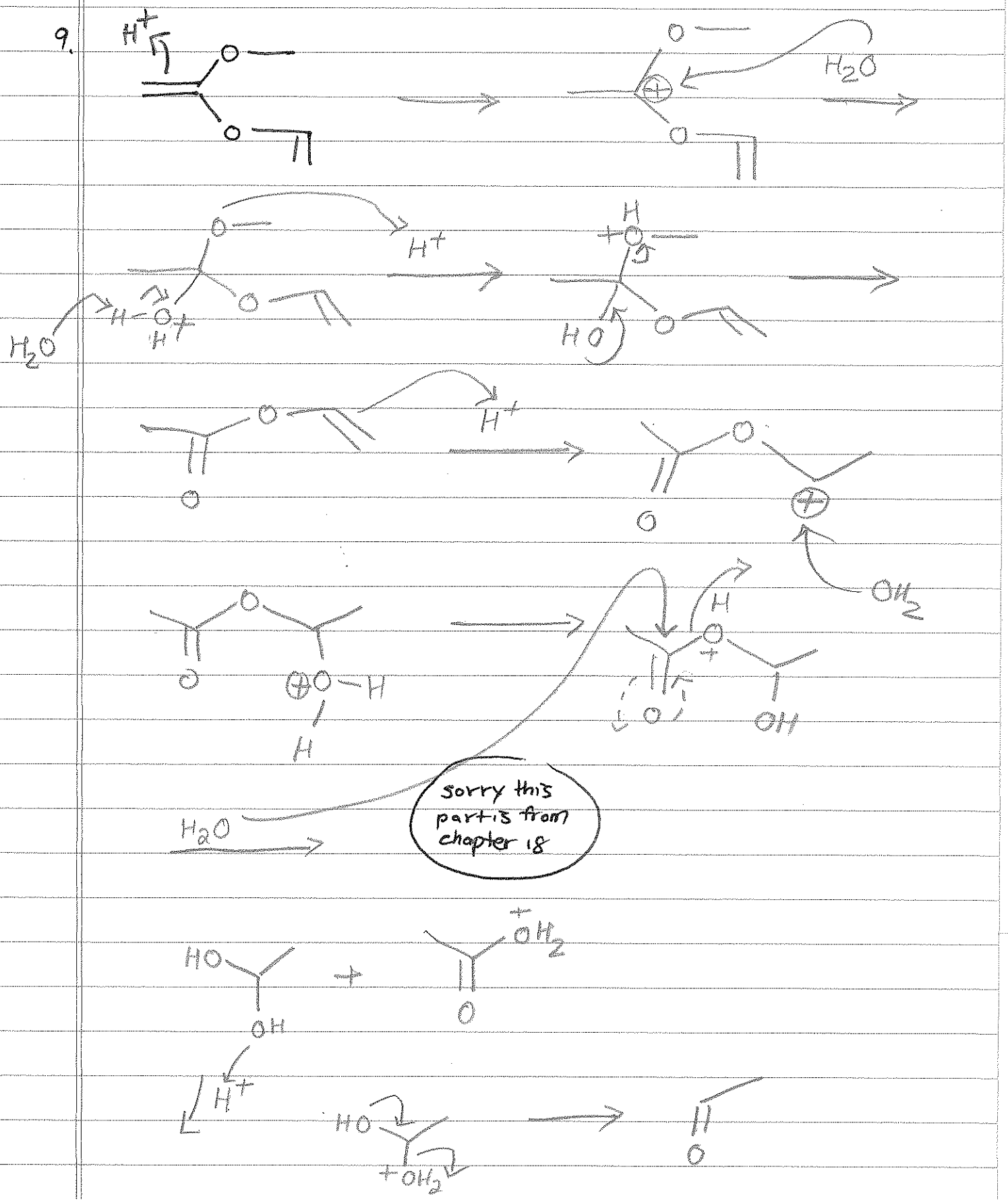

mech Practice cont

10.