ALKENES AND ALKYNES – REACTIONS

IN WEEK 1, A STUDENT SHOULD BE ABLE TO:

1. Predict the products of the following reactions of alkenes and alkynes, when given the starting materials and reaction conditions:

   Regioselective Markovnikov addition of acids to alkenes and alkynes, including the acid-catalyzed addition of water (hydration). Rearrangement is possible in the additions to alkenes; tautomerization occurs in the hydration of alkynes.
   Oxymercuration-Demercuration of alkenes (regioselective, Markovnikov).
   Hydroboration-Oxidation of alkenes (regioselective, anti-Markovnikov; stereospecific *syn*) and alkynes (involving tautomerization).
   Addition of halogens and halohydrin formation *via* halonium ion (stereospecific *anti*). In the case of halohydrin formation, the reaction is also regioselective Markovnikov.

2. Using any of the above reactions, propose syntheses of compounds that can be made using alkenes or alkynes as starting materials or intermediates. As always, synthesis problems may require any reaction that you have studied in the course so far.

3. Propose complete mechanisms, and predict and explain experimental results using your knowledge of mechanisms. Important reactions include:

   Markovnikov additions (*via* protonation of the alkene to give a carbocation which can rearrange).
   Addition of halogens and halohydrin formation (*via* formation of the halonium ion).

4. Understand the terms “regioselectivity”, “stereospecificity” “*syn*”, “*anti*”, and identify corresponding reactions.

   Also distinguish the terms “nucleophile” and “base” and be able to identify and give examples of nucleophiles and electrophiles.

IN WEEK 2, A STUDENT SHOULD BE ABLE TO:

5. Perform the objectives 1 - 4 detailed above for these additional reactions:

   Catalytic hydrogenation of alkenes (stereoselective *syn*)
   Epoxidation of alkenes, and the hydrolysis of the resulting epoxides to glycols (stereospecific *anti* addition; mechanism is important to know).
   Glycol formation using either $KMnO_4$ (cold) or OsO_4 (stereospecific *syn* additions).
   Oxidative cleavage of alkenes and alkynes using ozonolysis; predict products as well as identify starting alkenes/alkynes from the products given.
   Stereospecific catalytic hydrogenation of alkynes to produce *cis*-alkenes and dissolving metal reduction of alkynes to produce *trans*-alkenes.

To best prepare for this module, please work Chapter 9 and Chapter 10 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

Problems 1 - 4 should be mastered for the first week of this drill.

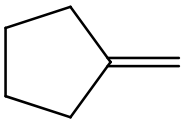
1. Predict the major organic product or products of each of the following reactions.

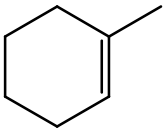
a) $(CH_3)_2CHCH{=}CH_2 \xrightarrow[H_2O]{H_2SO_4}$

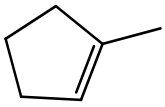
b) $(CH_3)_2CHCH{=}CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4}$

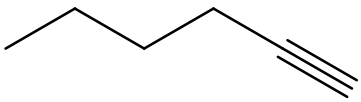
c) $(CH_3)_2CHCH{=}CH_2 \xrightarrow{BH_3:\ THF} \xrightarrow{H_2O_2,\ NaOH}$

d) $CH_3C{\equiv}CH \xrightarrow[HgSO_4]{H_2SO_4,\ H_2O}$

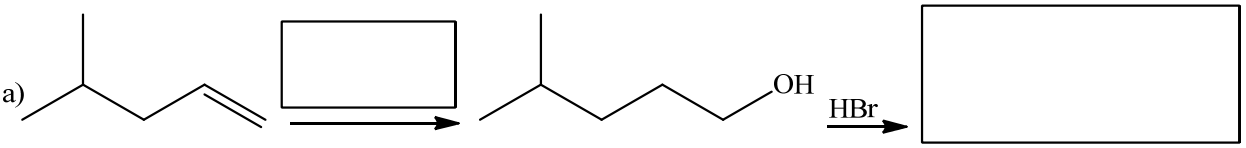
e)  $\xrightarrow{HCl}$

f)  $\xrightarrow[CCl_4]{Br_2}$

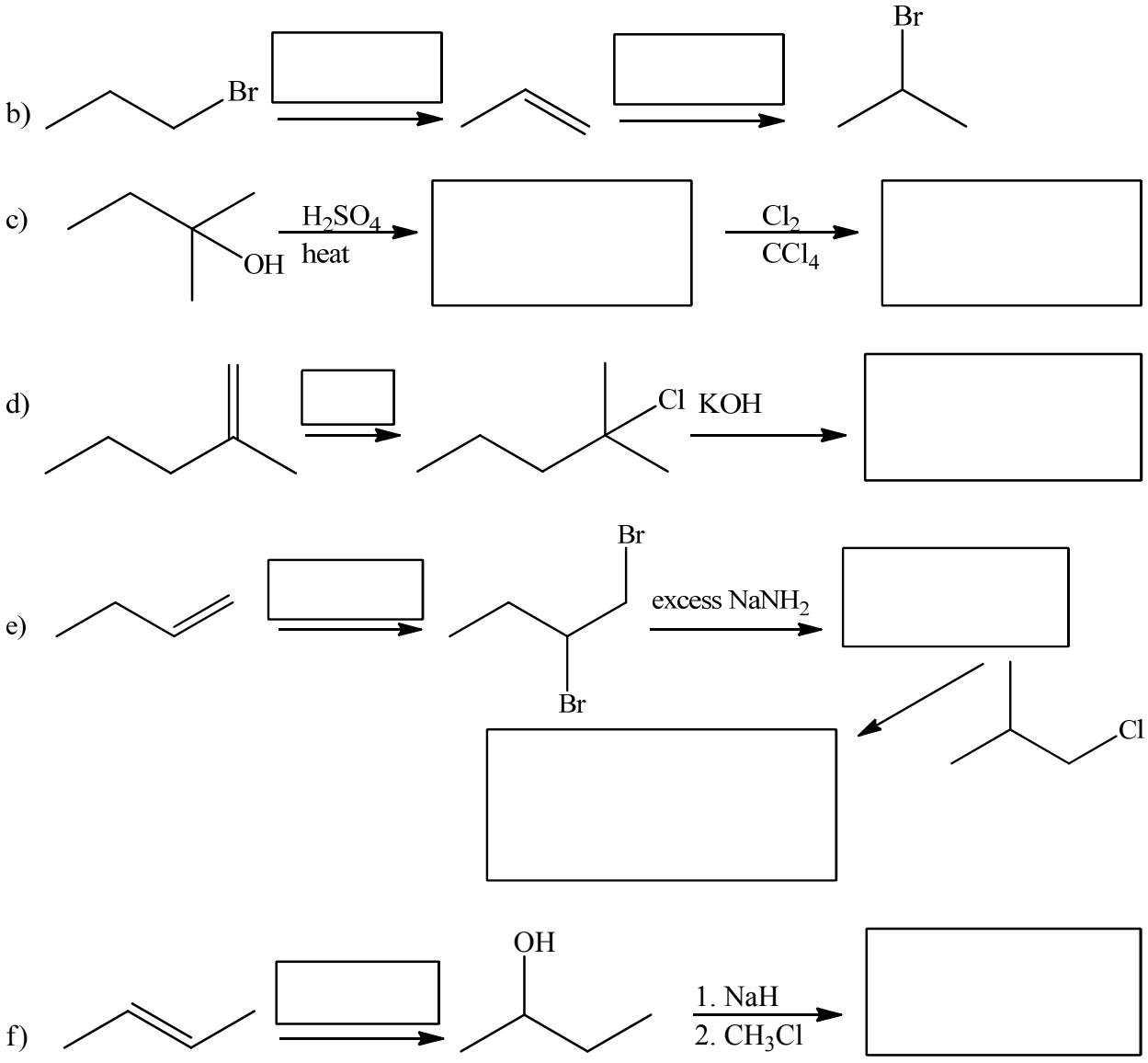
g)  $+ Cl_2 + H_2O \longrightarrow$

h)  $\xrightarrow{2\ HBr}$

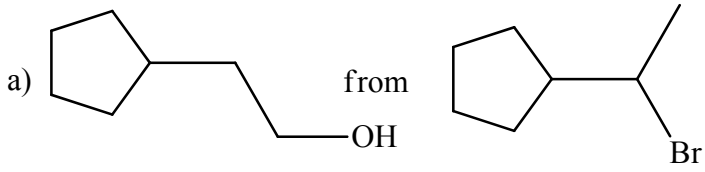
2.1 Fill in the missing reagent(s), intermediate(s), and product(s) for these reactions.

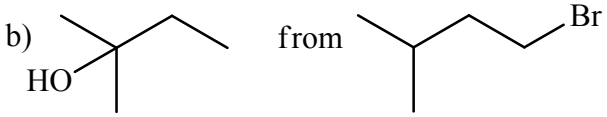
a) 

2.1

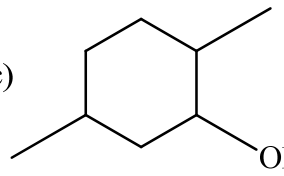
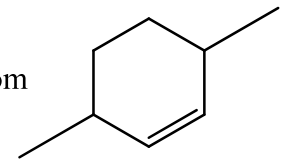


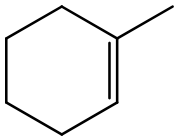
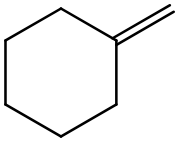
2.2 Propose a synthesis of each of these compounds, from the given starting material and any other needed reagent(s) and/or solvent.

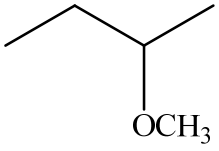
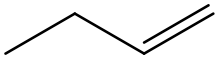


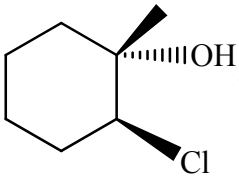
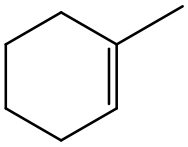


2.2

c)  from 

d)  from 

e)  from 

f)  from 

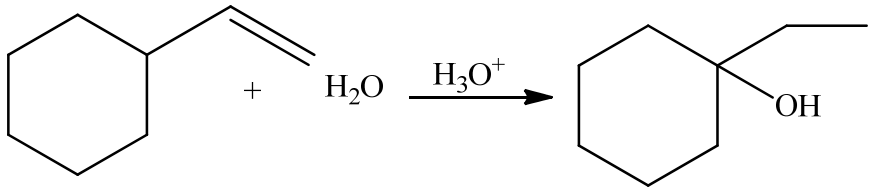
g) $(CH_3)_3CBr$ from $(CH_3)_2CHCH_2OH$

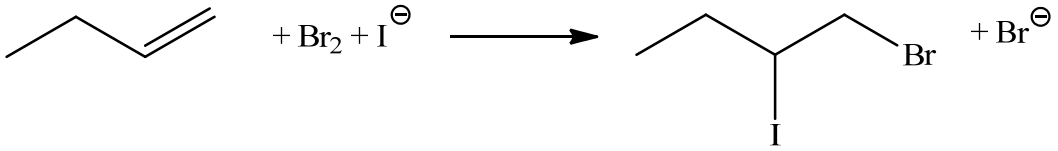
h) 3-octyne from 1-butene

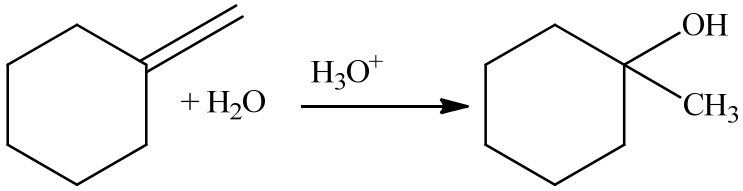
3. Propose a mechanism for each of the reactions shown.

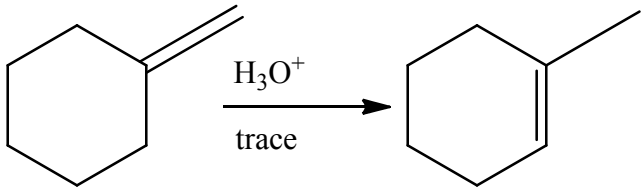
a) $(CH_3)_2CHCH{=}CH_2 + HCl \longrightarrow (CH_3)_2CClCH_2CH_3$

3.

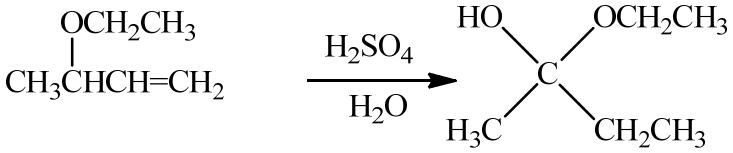
b) 

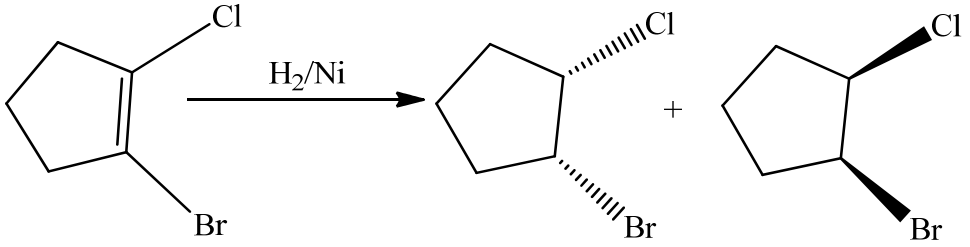
c) 

d) 

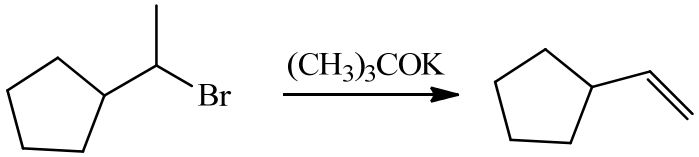
e) 

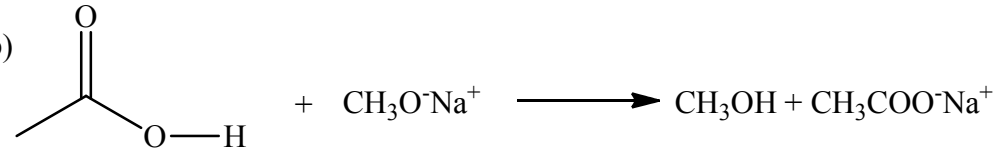
4.1 Which of the following reactions is stereoselective? Explain.

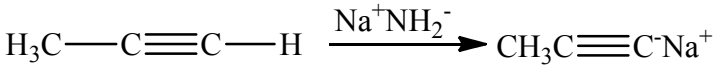
a) 

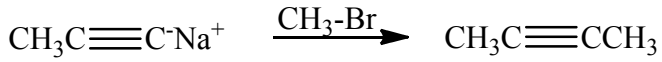
b) 

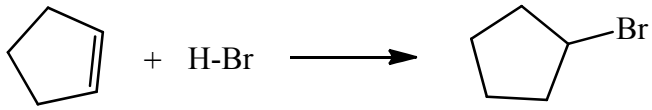
4.2 Find and label nucleophiles, electrophiles and bases in the following reactions. Note that all of the nucleophiles are Lewis bases, so put the label "base" only for Bronsted bases.

a) 

b) 

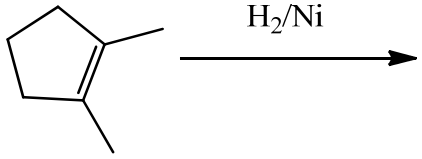
c) 

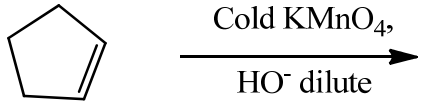
d) 

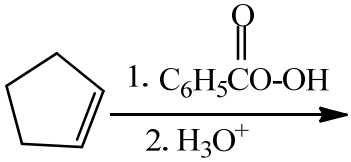
e) 

The following problems should also be mastered for the second week of this drill.

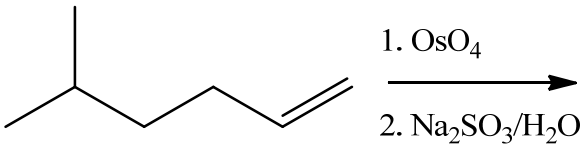
5.1

a) 

b) 

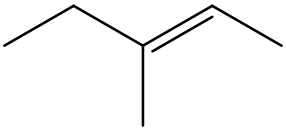
c) 

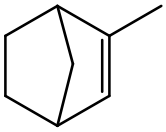
5.1

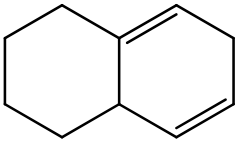
d) 

e) $CH_3C{\equiv}CCH_3$ $\xrightarrow[\text{Lindlar's catalyst}]{H_2}$

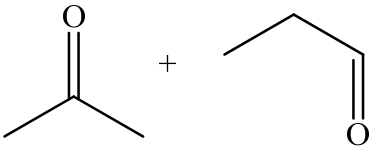
f) $CH_3C{\equiv}CCH_3$ $\xrightarrow[NH_3(\text{liquid})]{Li}$

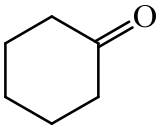
g) 

h) 

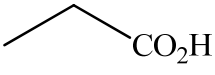
i) 

5.2 Identify each of these unknowns from the information given.

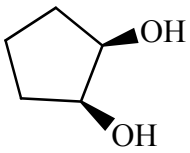
a) C_6H_{12} $\xrightarrow{O_3}$ $\xrightarrow[H_2O]{Zn}$ 

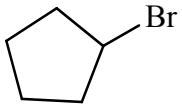
b) C_9H_{16} $\xrightarrow{O_3}$ $\xrightarrow{DMS}$ 

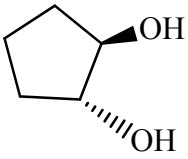
+ CH_3CH_2CHO

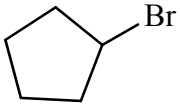
c) C_6H_{10} $\xrightarrow{O_3}$ $\xrightarrow[H_2O]{Zn}$ 2 

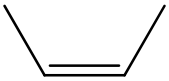
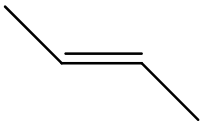
5.3 Propose a synthesis of each of these compounds, from the given starting material and any other needed reagent(s) and/or solvent.

a) 

from 

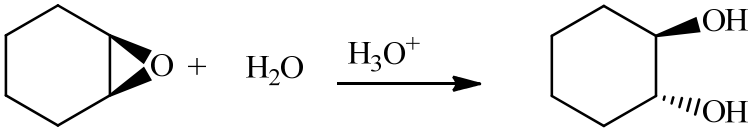
b) 

from 

c) 
from 

d) $CH_3CH_2CH{=}O$ from 2-chloropentane

5.4 Propose a mechanism for this reaction.



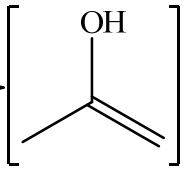
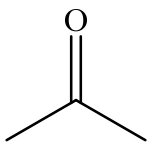
SOLUTIONS TO SAMPLE PROBLEMS:

1. Predict the major organic product or products of each of the following reactions.

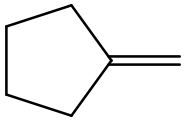
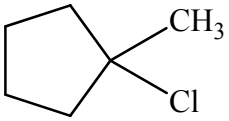
a) $(CH_3)_2CHCH{=}CH_2 \xrightarrow[H_2O]{H_2SO_4} (CH_3)_2C(OH)CH_2CH_3$ regioselective Markovnikov w/RAR

b) $(CH_3)_2CHCH{=}CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4} (CH_3)_2CHCH(OH)CH_3$ regioselective, Markovnikov, no RAR

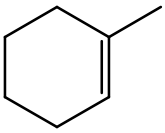
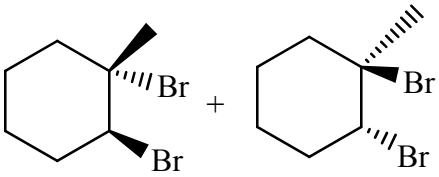
c) $(CH_3)_2CHCH{=}CH_2 \xrightarrow{BH_3:\,THF} \xrightarrow{H_2O_2,\,NaOH} (CH_3)_2CHCH_2CH_2OH$ regioselective, anti-Markovnikov

d) $CH_3C{\equiv}CH \xrightarrow[HgSO_4]{H_2SO_4,\,H_2O}$  $\xrightarrow{H_3O^+}$ 

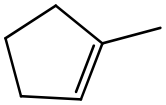
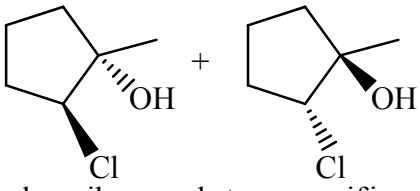
unstable enol tautomerizes to ketone

e)  $\xrightarrow{HCl}$ 

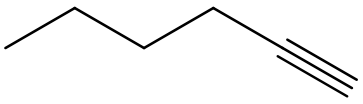
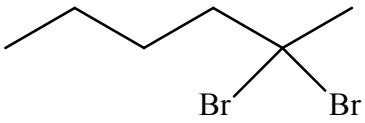
regioselective, Markovnikov

f)  $\xrightarrow[CCl_4]{Br_2}$ 

stereospecific, *anti*

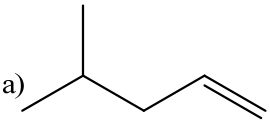
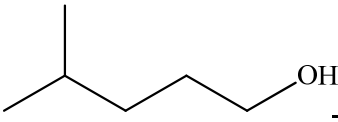
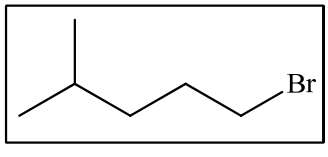
g)  $+ Cl_2 + H_2O \longrightarrow$ 

regioselective, Markovnikov, and stereospecific, *anti*

h)  $\xrightarrow{2\ HBr}$ 

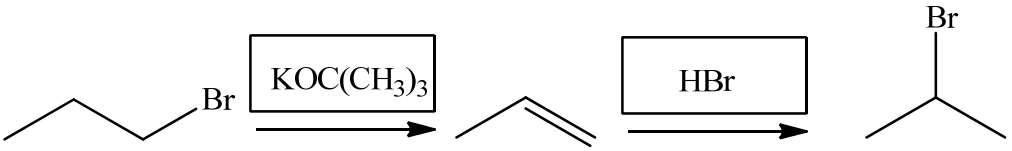
regioselective, Markovnikov

2.1 Fill in the missing reagent(s), intermediate(s), and product(s) for these reactions.

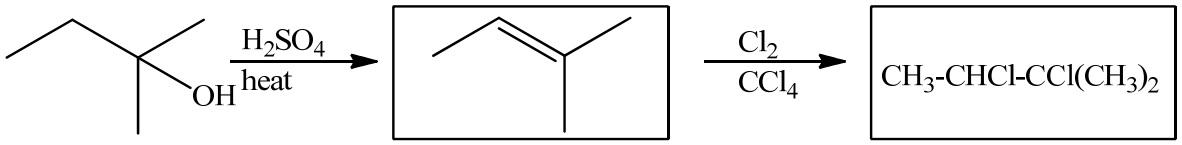
a)  $\xrightarrow{\text{1. } BH_3\text{-THF}\ \text{2. } H_2O_2,\,HO^-}$  $\xrightarrow{HBr}$ 

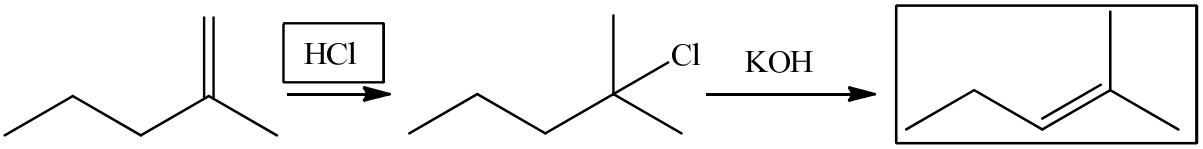
need anti-Markovnikov hydration

2.1

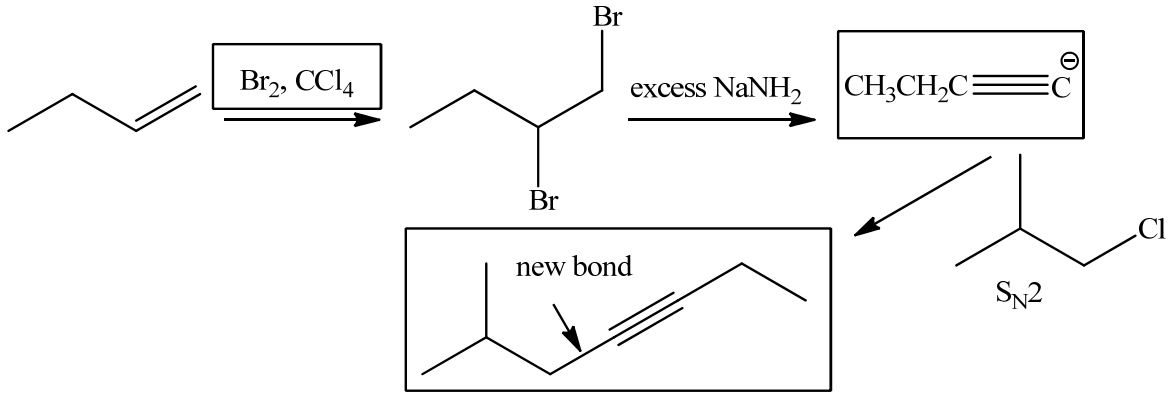
b) 

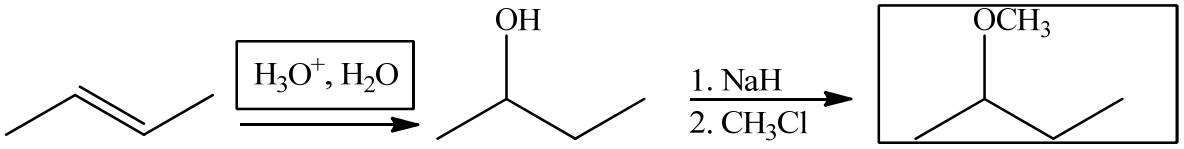
notice how the functional group is changed from one position to the next, via alkene

c) 

d) 

notice how the alkene is isomerized, via RX

e) 

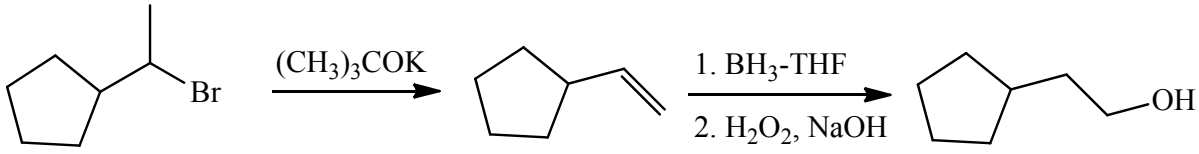
f) 

or 1. $Hg(OAc)_2$, H_2O; 2. $NaBH_4$

acid-base, then S_N2

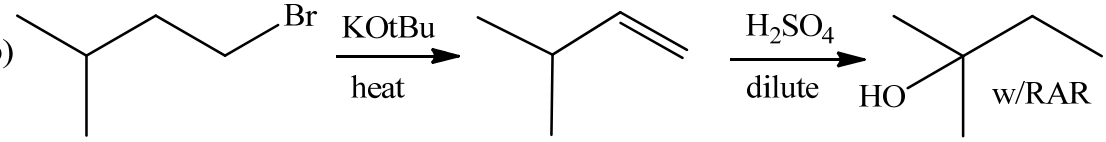
This is a Williamson ether synthesis, a very good way to make ethers.

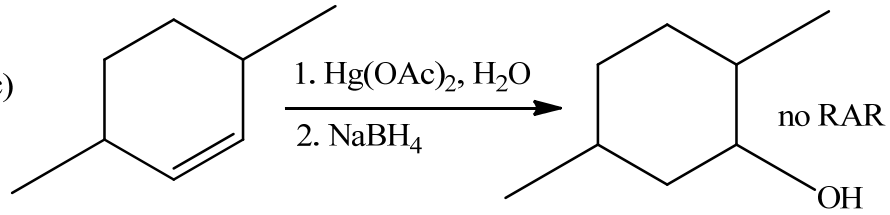
2.2 Propose a synthesis of each of these compounds, from the given starting material and any needed reagent(s) and/or solvent.

a) 

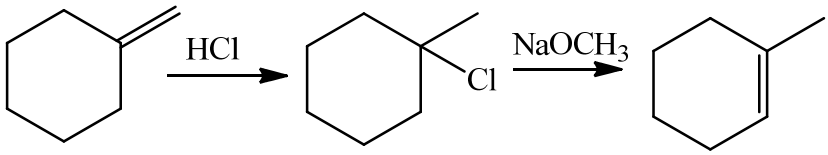
less substituted alkene is favored with bulky base

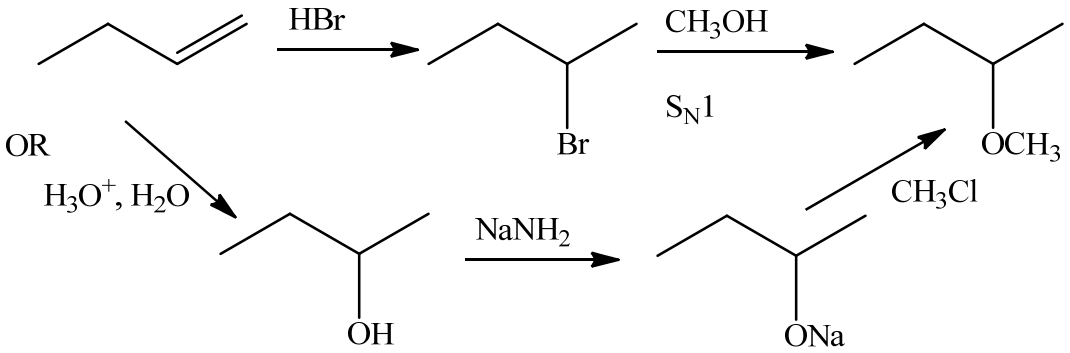
2.2

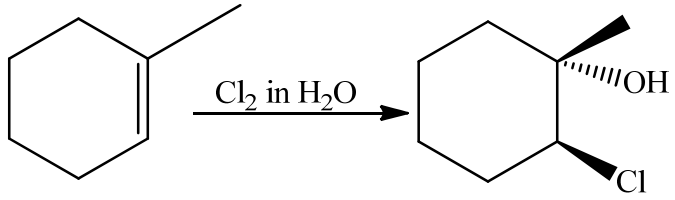
b) 

c) 

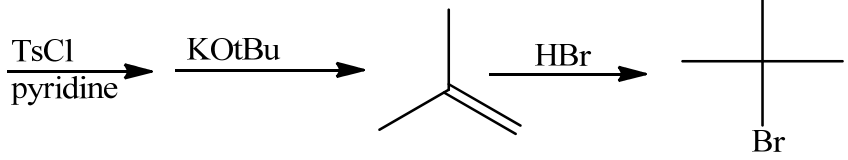
OR, this could be accomplished using BH_3-THF, then H_2O_2, OH^- (no RAR).

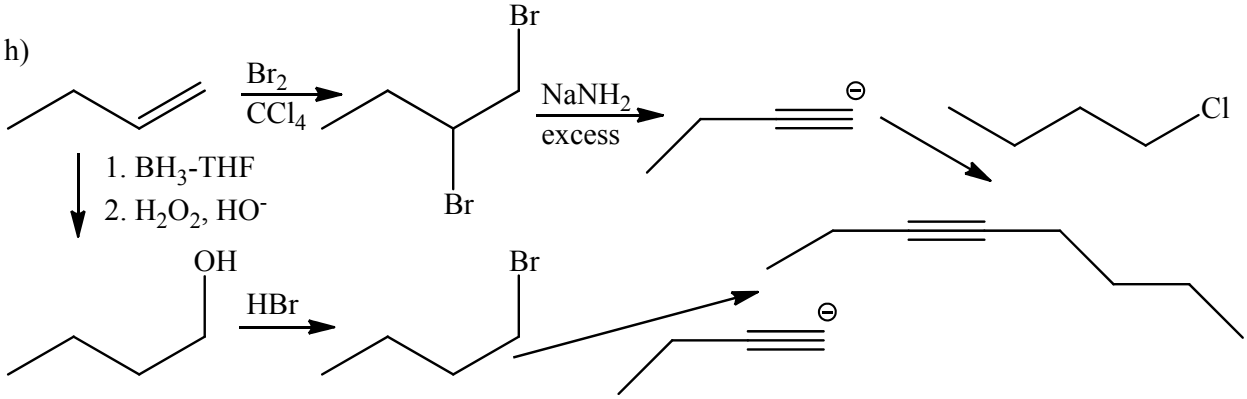
d) 

e) 

f) 

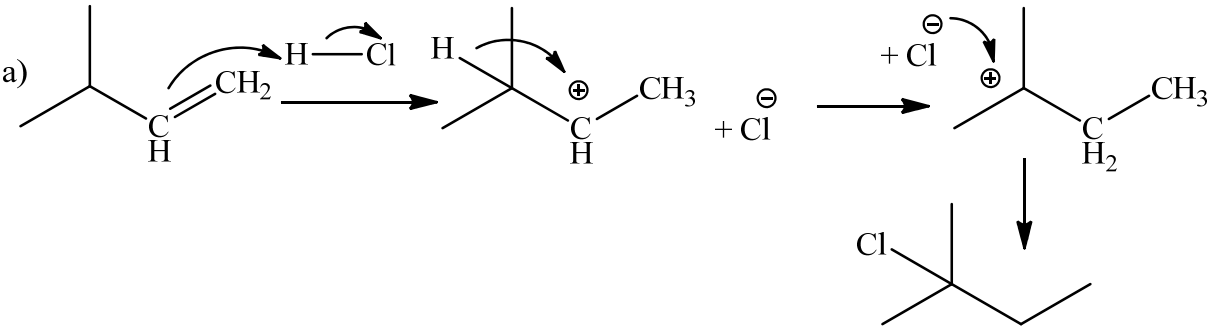
chlorohydrin

g) $(CH_3)_2CHCH_2OH$ 

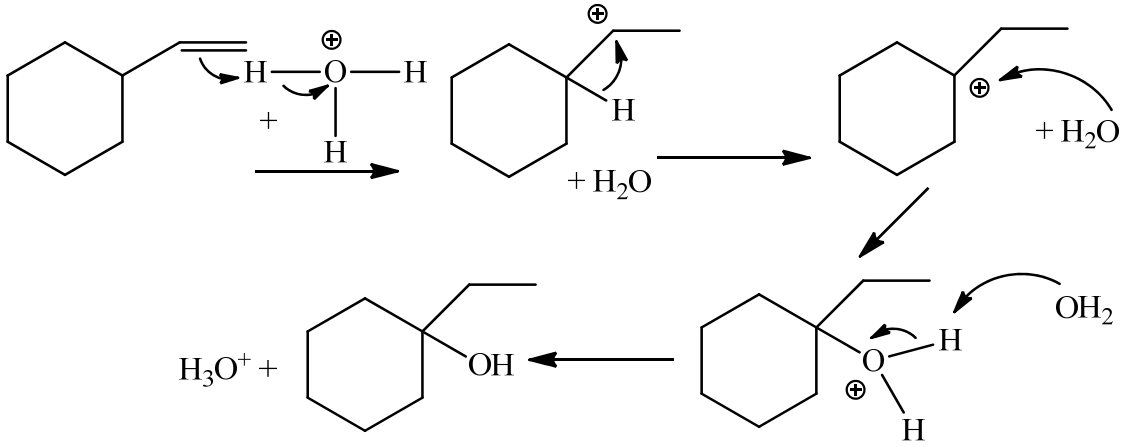
h) 

3. Mechanisms.

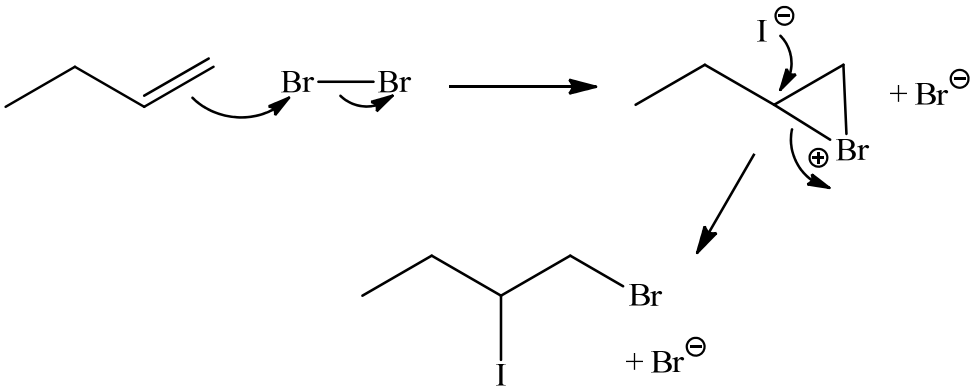
a)



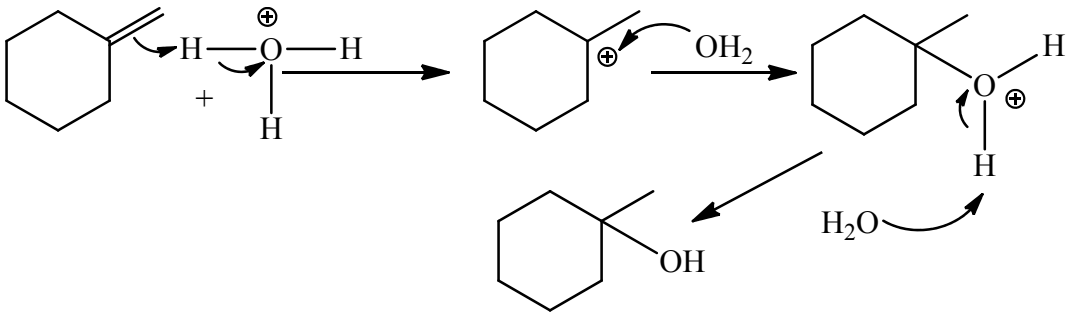
b)



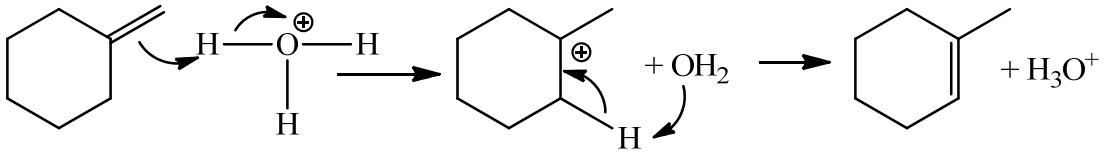
c)



d)

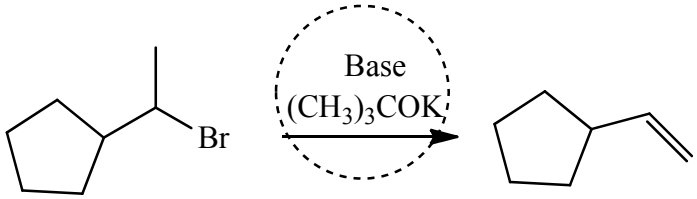


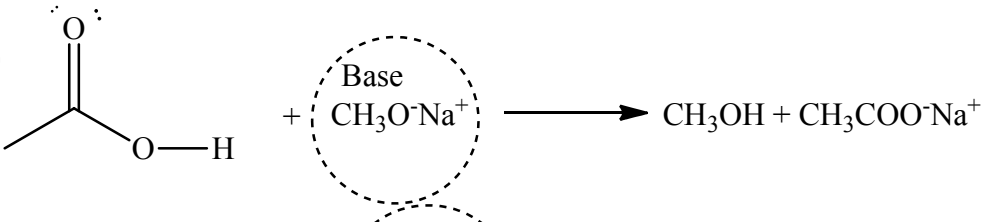
3.

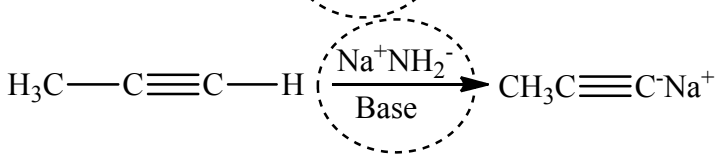
e) 

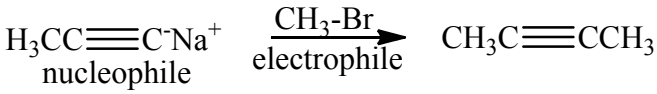
4.1. Reaction b) is stereoselective because the two hydrogens are added to the same face of the alkene in so-called *syn* fashion. As a result, the *cis* pair of enantiomers of the product forms as the major product, with minor amounts of the diastereomeric *trans* enantiomers. Reaction a) is not stereospecific because the carbocation that forms and then rearranges is trigonal planar (note sp^2-hybridization of the carbon) and can be attacked from either side. As a result, both possible enantiomers will form in approximately equal amounts, so the product will be racemic.

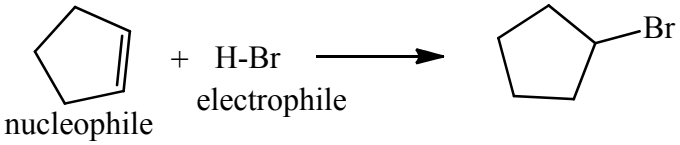
4.2.

a) 

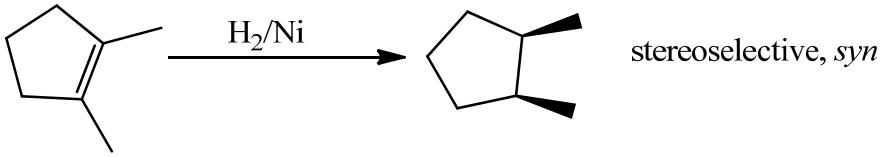
b) 

c) 

d) 

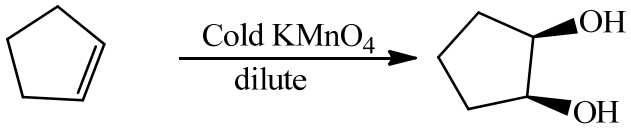
e) 

5.1

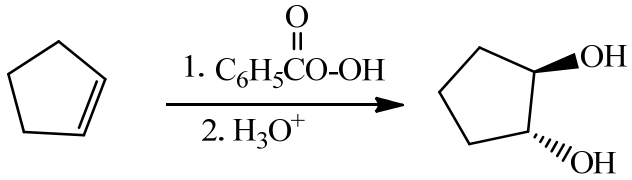
a) 

stereoselective, *syn*

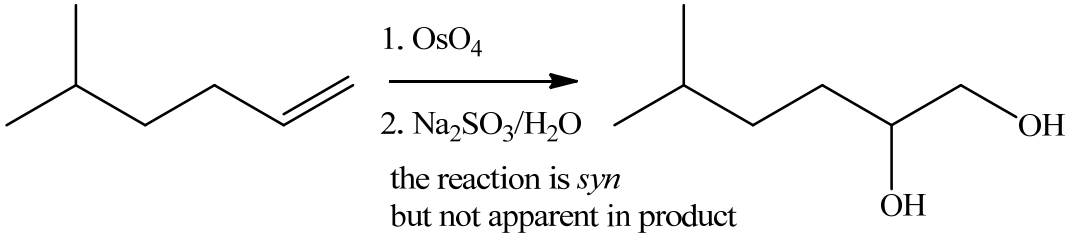
5.1

b) 

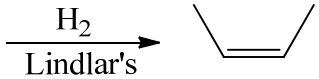
stereospecific, *syn*

c) 

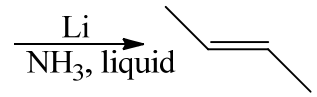
stereospecific, *anti*

d) 

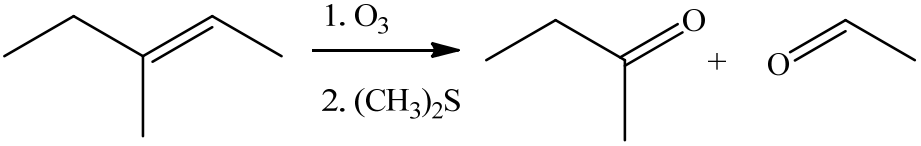
the reaction is *syn*
but not apparent in product

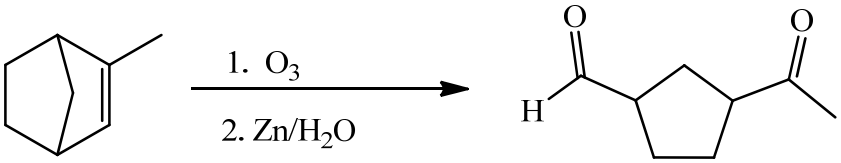
e) $CH_3C{\equiv}CCH_3$ 

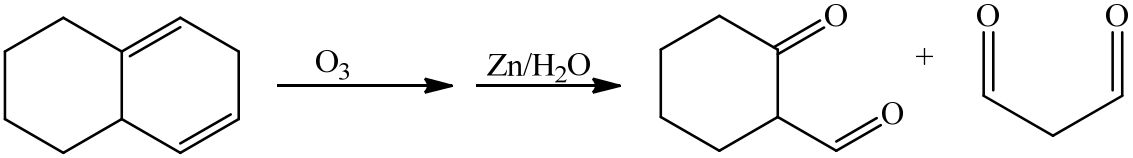
stereoselective, *cis*

f) $CH_3C{\equiv}CCH_3$ 

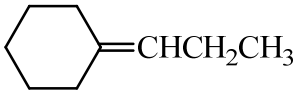
stereoselective, *anti*

g) 

h) 

i) 

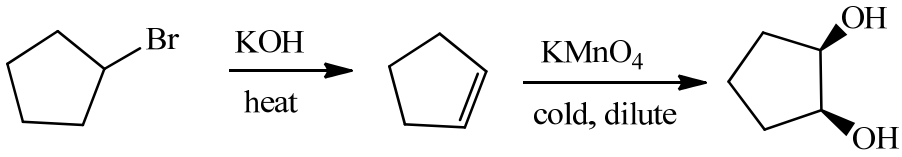
5.2 The unknowns are:

a) $CH_3CH_2CH{=}C(CH_3)_2$ b) 

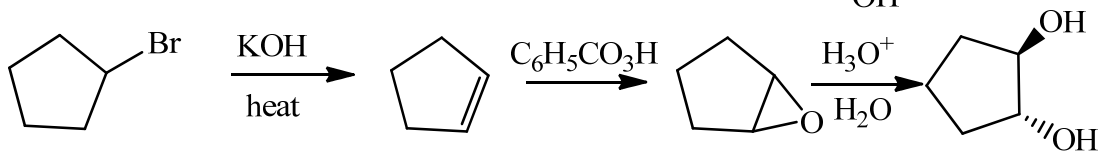
c) $CH_3CH_2{-}C{\equiv}C{-}CH_2CH_3$

5.3

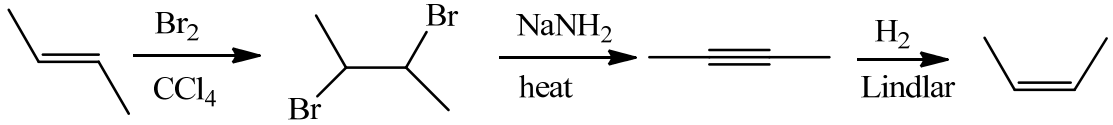
a)


Br
KOH
heat
KMnO4
cold, dilute
OH
OH

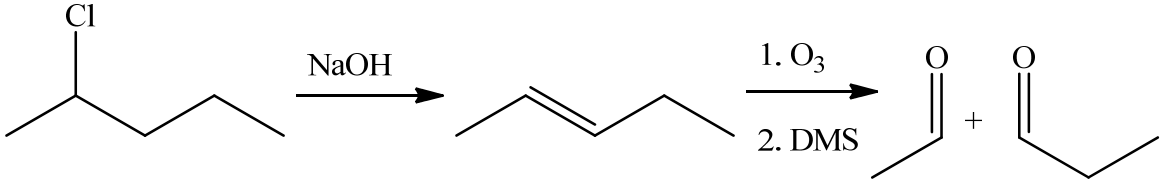
b)


Br
KOH
heat
C6H5CO3H
H3O+
H2O
O
OH
OH

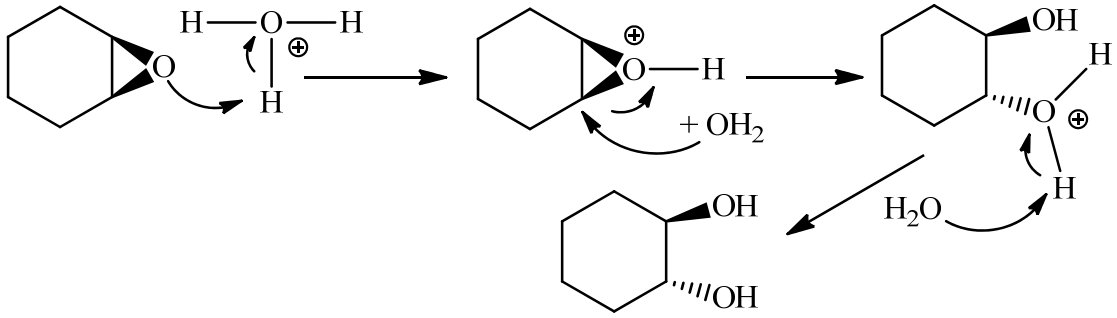
c)


Br2
CCl4
Br
Br
NaNH2
heat
H2
Lindlar

d)


Cl
NaOH
1. O3
2. DMS
O
O
+

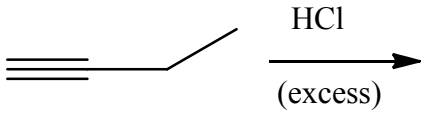
5.4

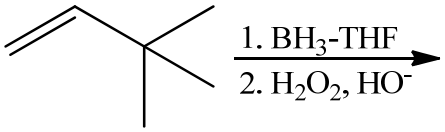

H
O
H
O
H
+ OH2
O
H
OH
H
O
H
H2O
OH
OH

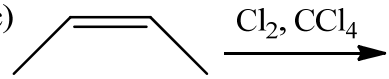
Name _____ Ninth Drill Test (Sample A)

Organic Chemistry 2210D Answer All Questions

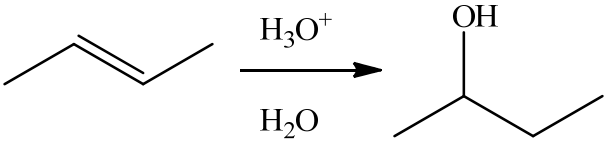
1. Predict the products. Show stereochemistry as appropriate.

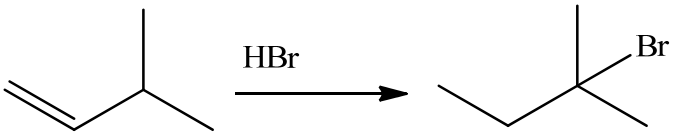
a) 

b) 

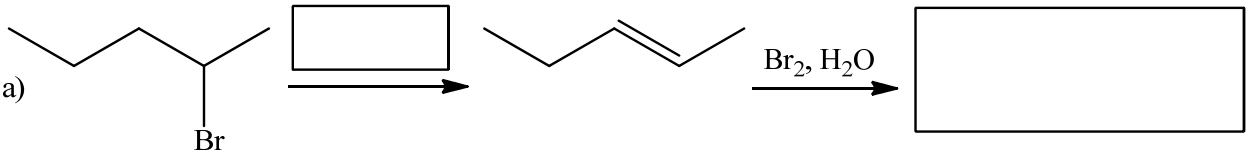
c) 

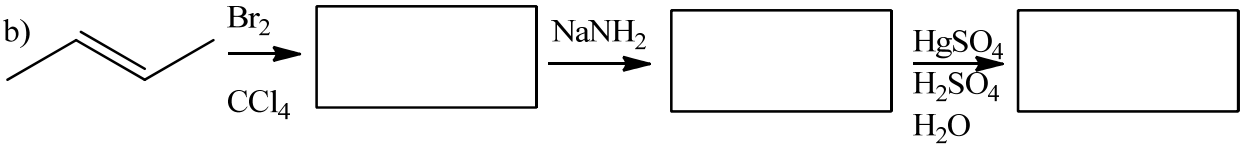
2. Propose mechanisms for these reactions:

a) 

b) 

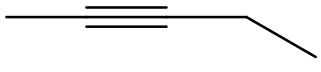
3. Complete these reactions:

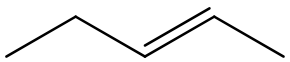
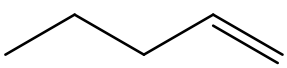
a) 

b) 

4. Propose a synthesis for the following compounds from the starting material given and any other necessary reagents.

a) $(CH_3)_3CCH(OH)CH_3$ from 3,3-dimethyl-1-butene

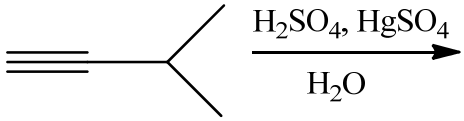
b)  from

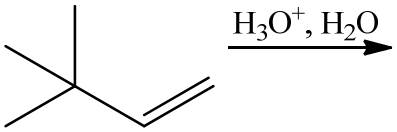
c)  from 

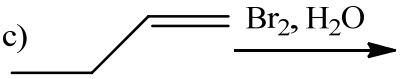
Name _____ Ninth Drill Test (Sample B)

Organic Chemistry 2210D Answer All Questions

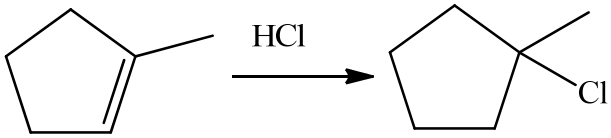
1. Predict the products. Show stereochemistry as appropriate.

a) 

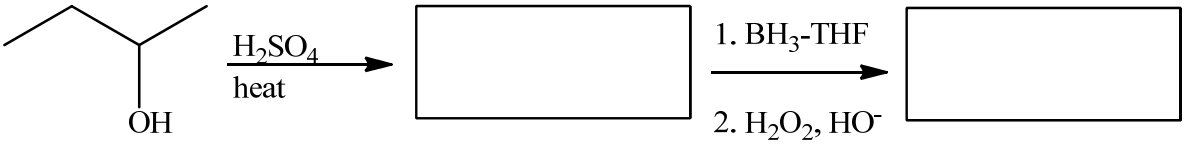
b) 

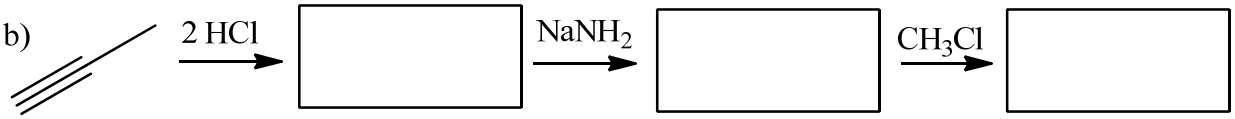
c) 

2. Propose a mechanism for this reaction:



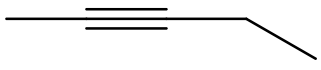
3. Complete these reactions:

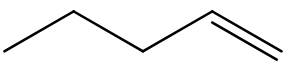
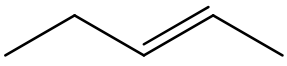
a) 

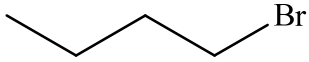
b) 

4. Propose a synthesis for the following compounds from the starting material given and any other necessary reagents.

a) 3-methyl-1,2-dibromopentane from 3-methyl-1-pentene

b)  from CH_3CH_2Cl

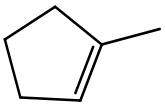
c)  from 

d) $CH_3CH_2CHClCH_3$ from 

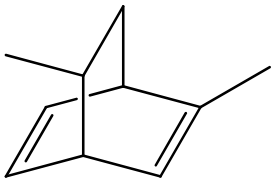
Name _____ Tenth Drill Test (Sample A)

Organic Chemistry 2210D Answer All Questions

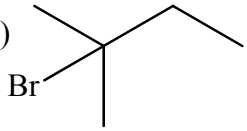
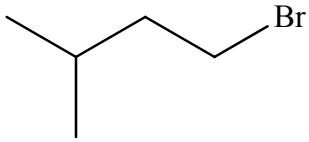
1. Predict the major organic product or products of the following reactions. Show correct stereochemistry where appropriate. Also label regioselective and stereospecific reactions.

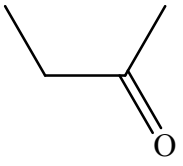
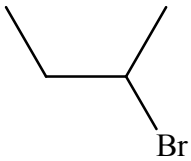
a)  BH_3-THF H_2O_2, NaOH

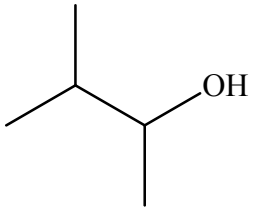
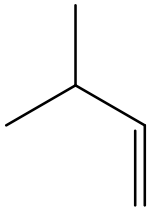
b) $(CH_3)_2CH\ CH{=}CH_2 + Cl_2 + H_2O$ ⟶

c)  1. O_3 ⟶ 2. Zn/H_2O

2. Propose a synthesis of each of the following compounds from the given starting material and any needed inorganic reagents or solvents.

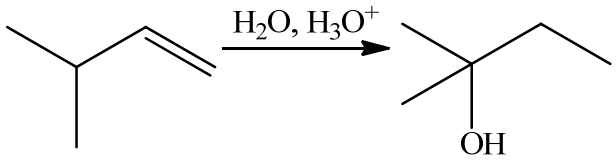
a)  from 

b)  from 

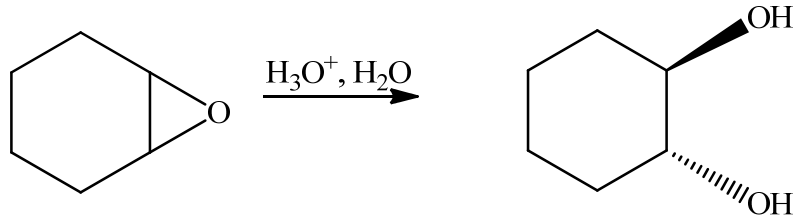
c)  from 

3. Propose a mechanism for each of the reactions shown.

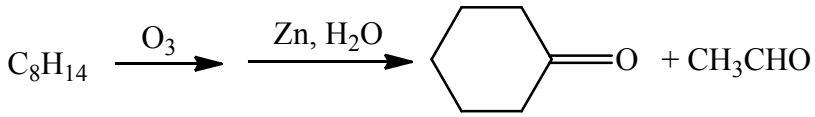
a)



b)



4. Give the structure of the unknown from the information given.

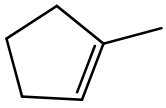


Name _____ Tenth Drill Test (Sample B)

Organic Chemistry 2210D Answer All Questions

1. Predict the major organic product of each of the following reactions.

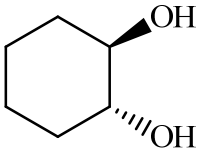
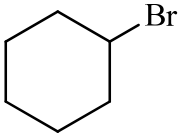
a) $H_3C—C\equiv C—CH_3 \xrightarrow[H_2SO_4,\ H_2O]{HgSO_4}$

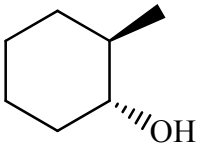
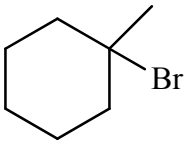
b)  $\xrightarrow[\text{cold, dilute}]{KMnO_4}$

c) $(CH_3)_2CHCH{=}CH_2 \xrightarrow{HCl}$

2. Propose a synthesis of each. You may use any needed inorganic reagents and solvents.

a) $(CH_3)_3CCl$ from $(CH_3)_3COH$

b)  from 

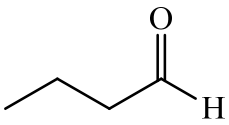
c)  from 

3. Propose a mechanism for each of the reactions shown. For problem a), first complete the equation by predicting the product.

a) $(CH_3)_2CHCH{=}CH_2 \xrightarrow{H_2SO_4,\ H_2O}$

b) $(CH_3)_2CHCH{=}CH_2 + Br_2 + NaCl \xrightarrow{H_2O} (CH_3)_2CHCHClCH_2Br + NaBr$

4. Give the structure of the unknown from the information given.

$C_7H_{14} \xrightarrow{O_3} \xrightarrow{Zn,\ H_2O}$  +