

ALKENES AND ALKYNES – REACTIONS

A STUDENT SHOULD BE ABLE TO:

1. Given the starting materials and reaction conditions, predict the products of the following reactions of alkenes and alkynes.

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).

Catalytic hydrogenation of alkenes (stereospecific *syn*)

Addition of halogens and halohydrin formation *via* halonium ion (stereospecific *anti*). In the case of halohydrin formation, the reaction is also regioselective Markovnikov.

Epoxidation of alkenes, and the hydrolysis of the resulting epoxides to glycols (stereospecific *anti* addition).

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 from the products given.

Stereospecific catalytic hydrogenation of alkynes to produce *cis*-alkenes and dissolving metal reduction of alkynes to produce *trans*-alkenes.

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 (which proceed by protonation of the alkene to give a carbocation which can rearrange).

Addition of halogens and halohydrin formation (*via* formation of the halonium ion).

Hydrolysis of epoxides (under acid conditions the oxygen is protonated first).

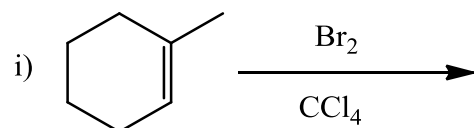
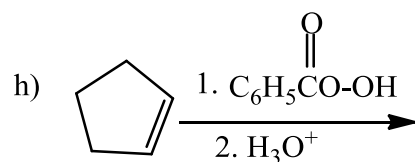
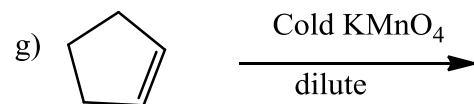
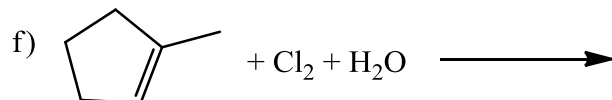
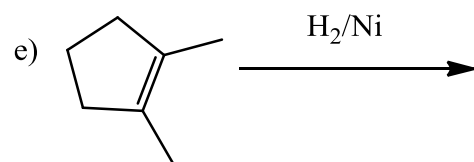
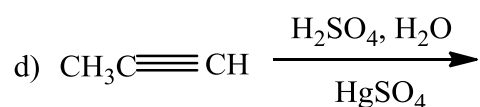
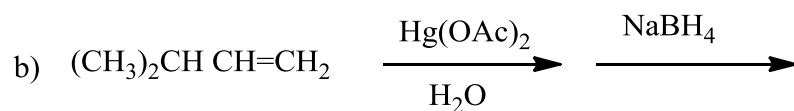
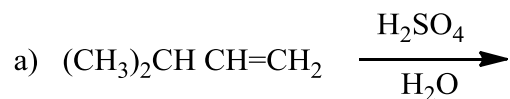
4. Understand the terms “regioselectivity”, “stereospecificity” “*syn*”, “*anti*”, and identify corresponding reactions. Pay attention to these issues in all of the reactions listed in 1. Be able to give examples of regioselective and stereospecific reactions.

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

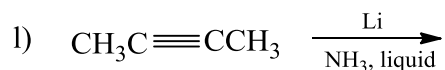
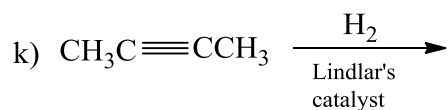
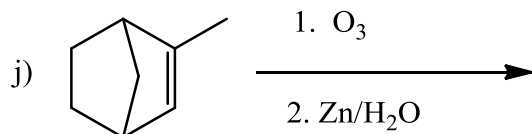
To best prepare for this module, please work Chapter 9 and Chapter 10 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

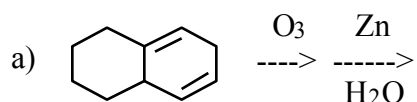
1.1 Predict the major organic product or products of each of the following reactions.



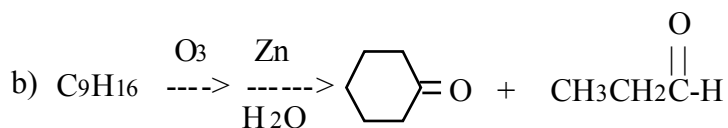
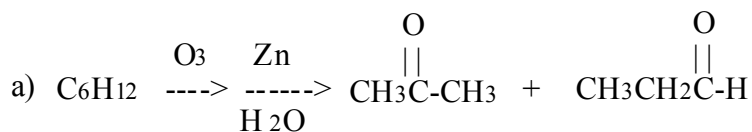
1.1



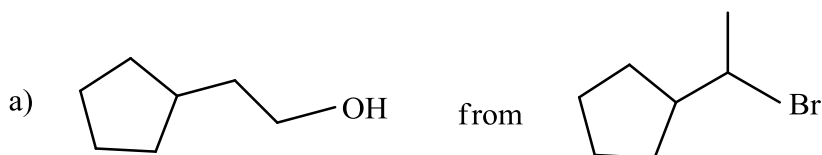
1.2 Predict the products of the following reaction.



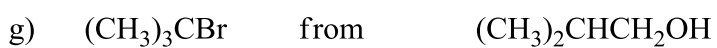
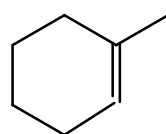
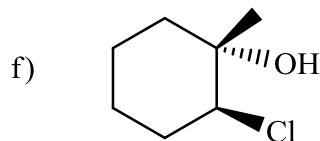
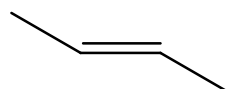
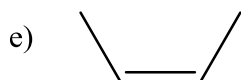
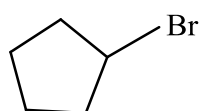
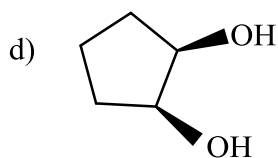
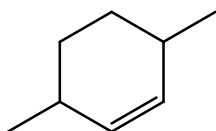
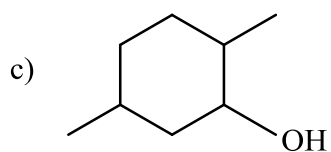
1.3 Identify each of these unknowns from the information given.



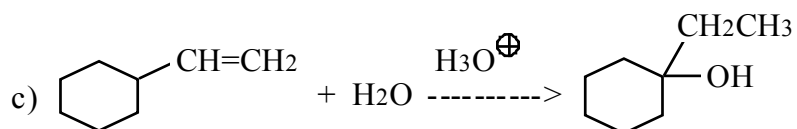
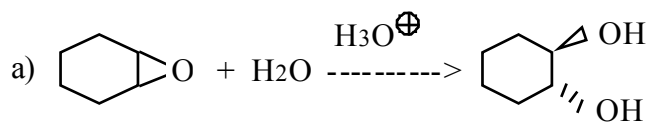
2. Propose a synthesis of each of these compounds, from the given starting material and any needed inorganic reagent and/or solvent.

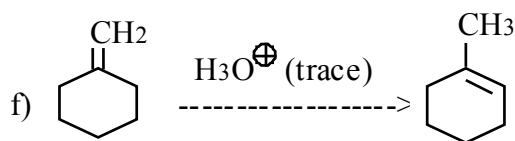
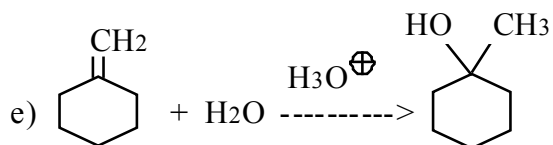
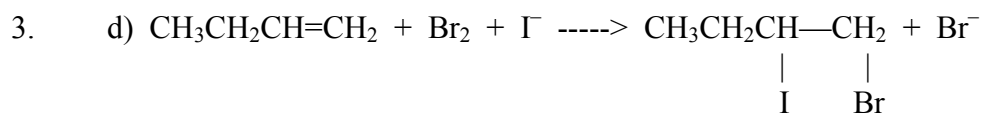


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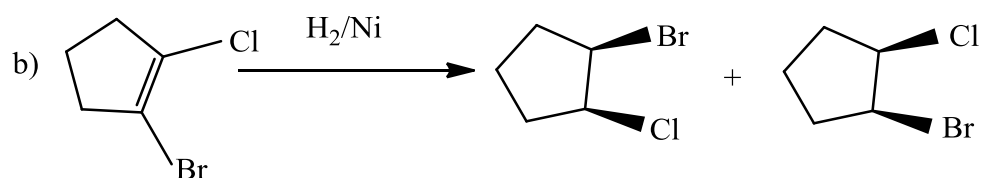
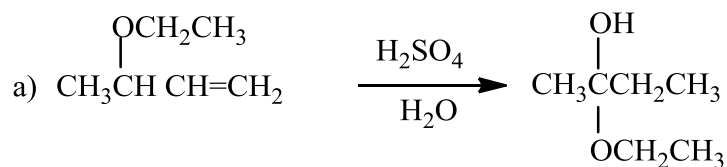


3. Propose a mechanism for each of the reactions shown.

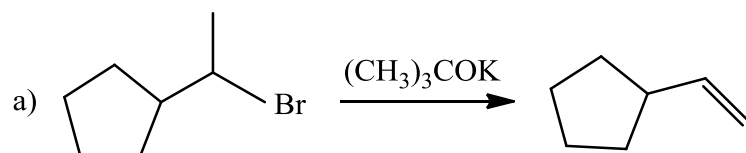




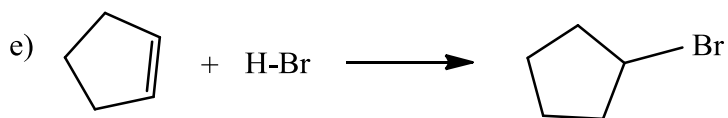
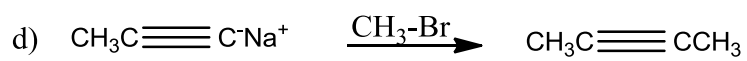
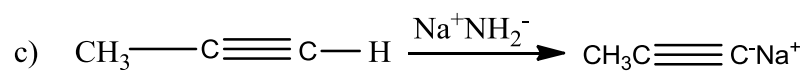
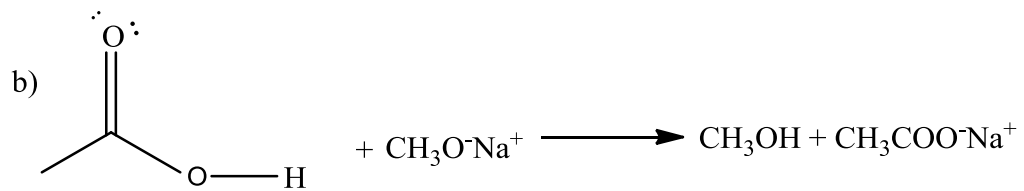
4.1 Which of the following reactions is stereospecific? Explain.



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 if the base does not perform the nucleophilic function.

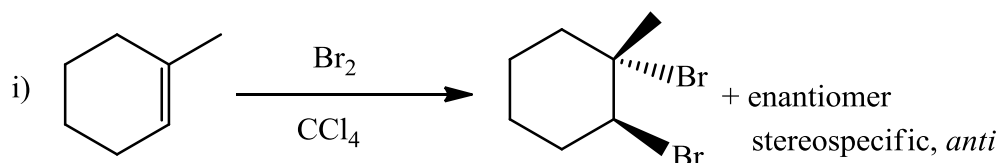
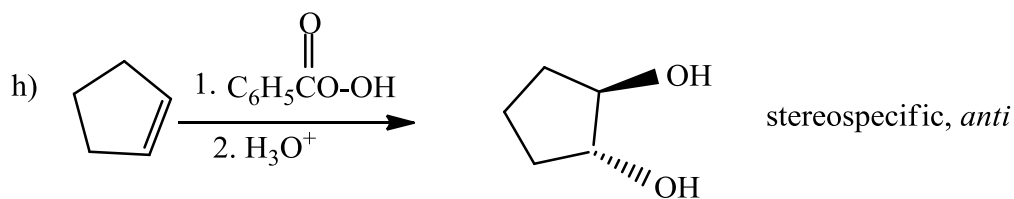
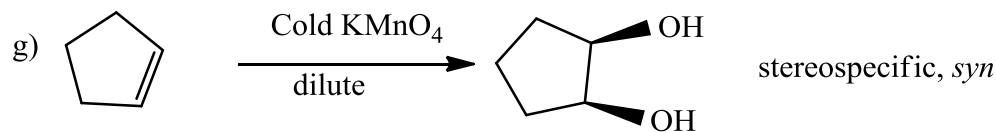
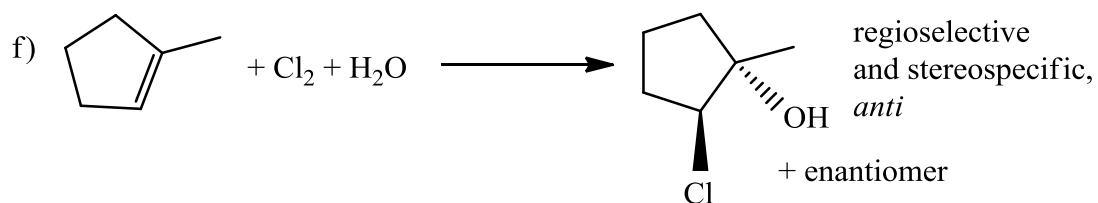
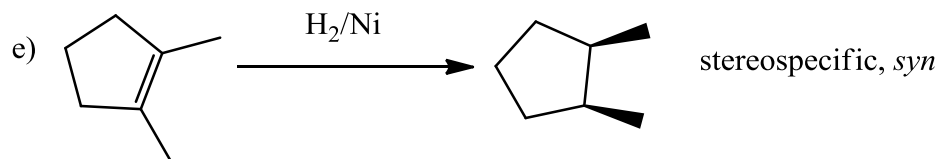
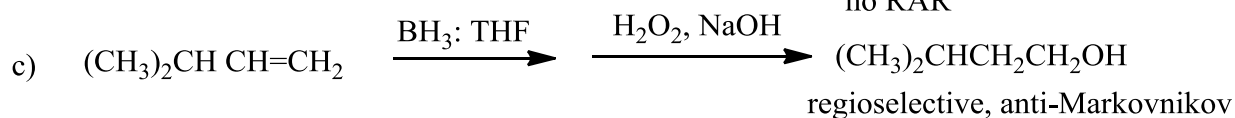
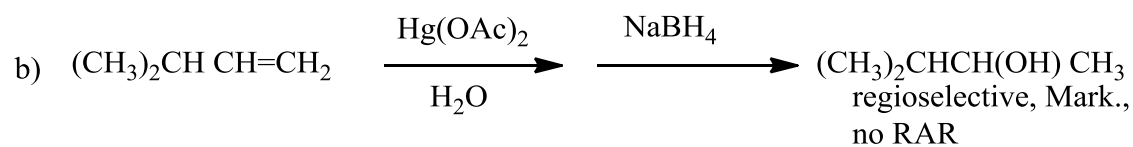
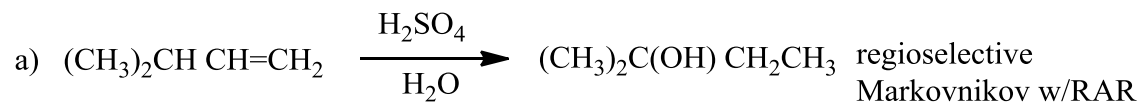


4.2

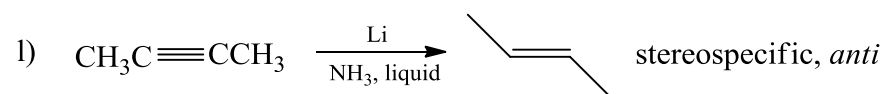
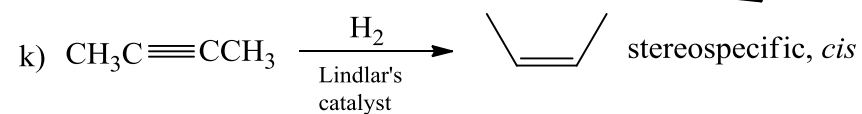
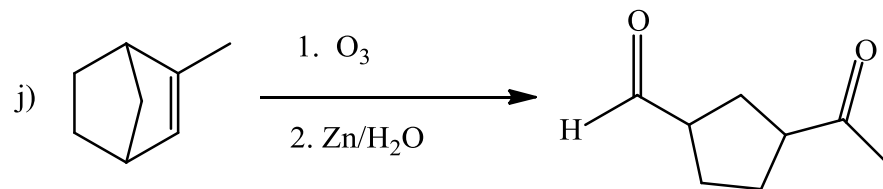


SOLUTIONS TO SAMPLE PROBLEMS:

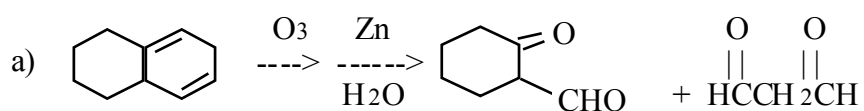
1.1 Predict the major organic product or products of each of the following reactions.



1.1



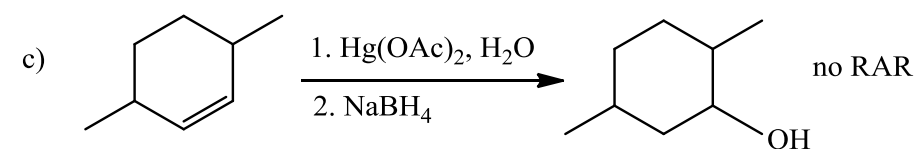
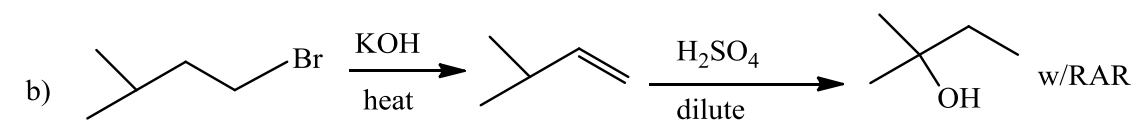
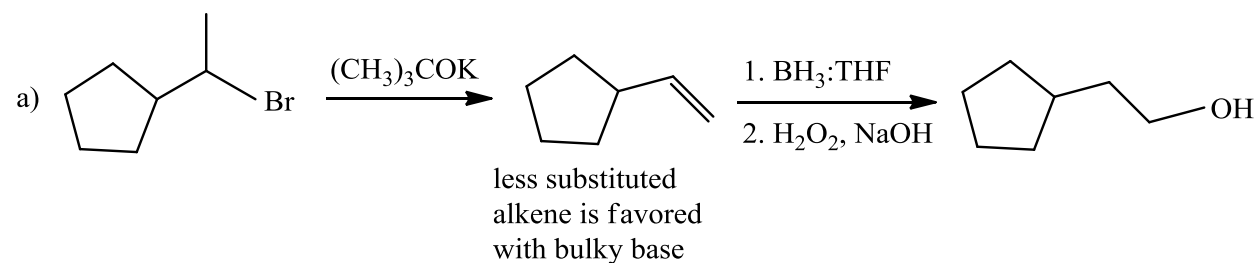
1.2 The products are:



1.3 The unknowns are:

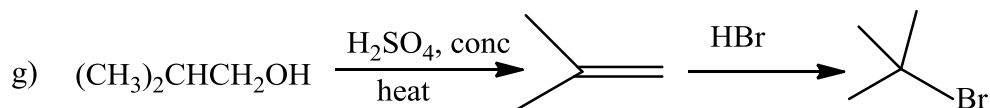
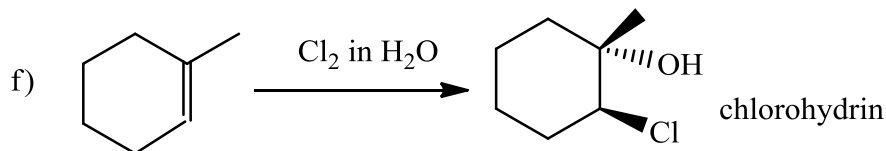
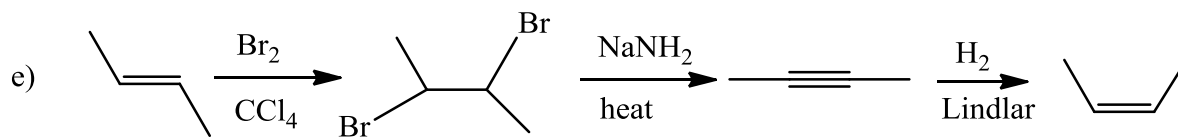
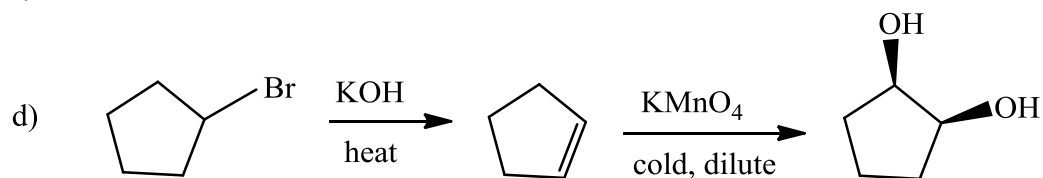


2. Propose a synthesis of each of these compounds, from the given starting material and any needed inorganic reagent and/or solvent.

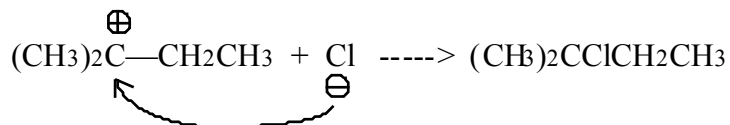
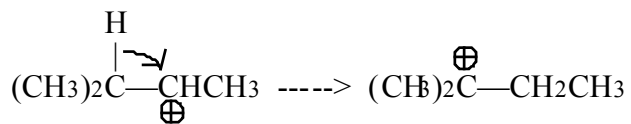
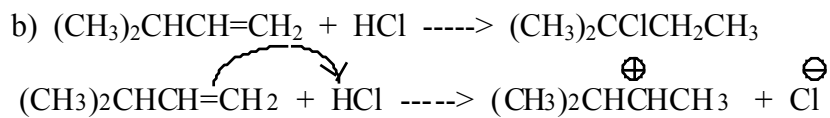
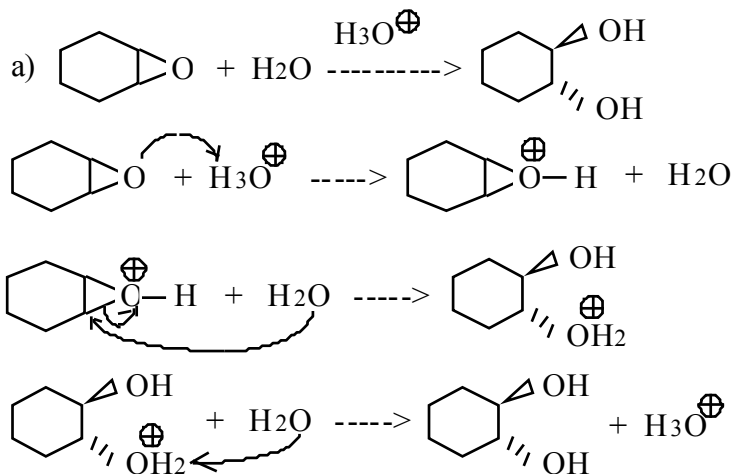


OR this could be accomplished using $\text{BH}_3\text{-THF}$, then H_2O_2 , OH^- , no RAR.

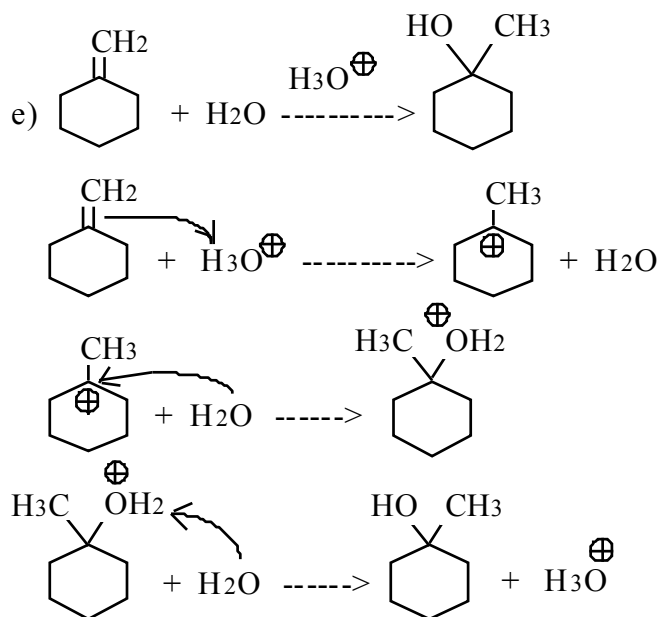
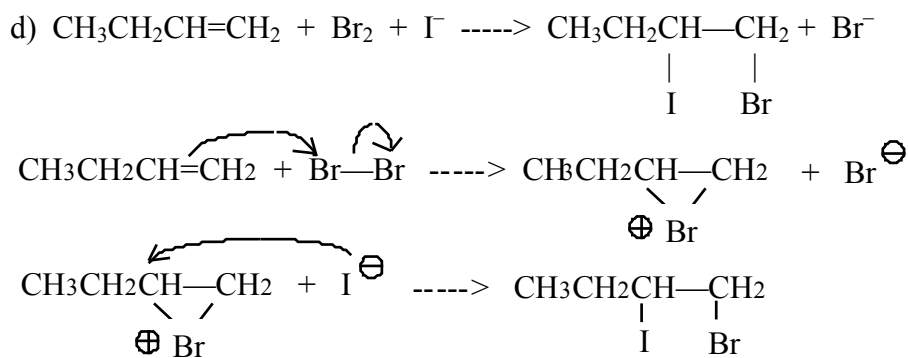
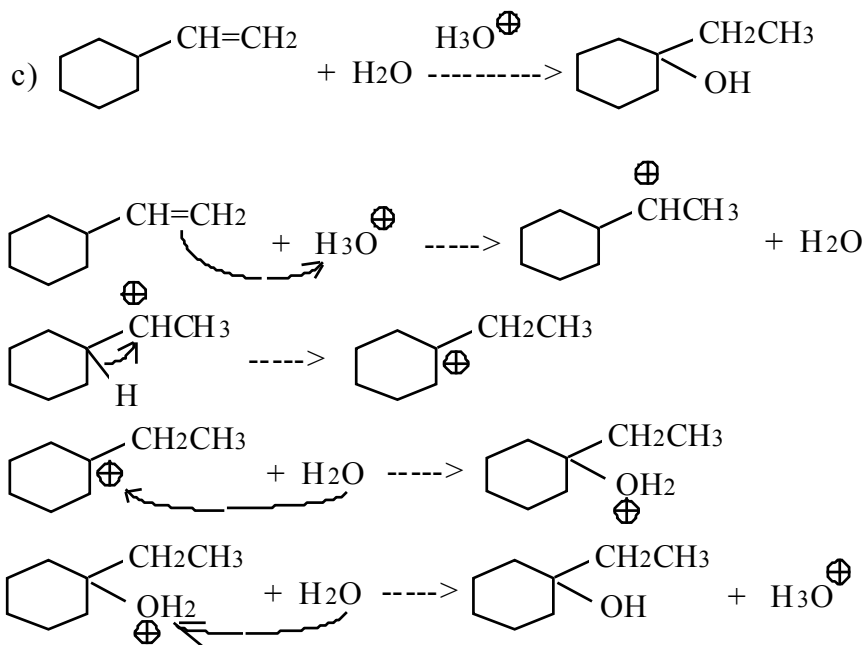
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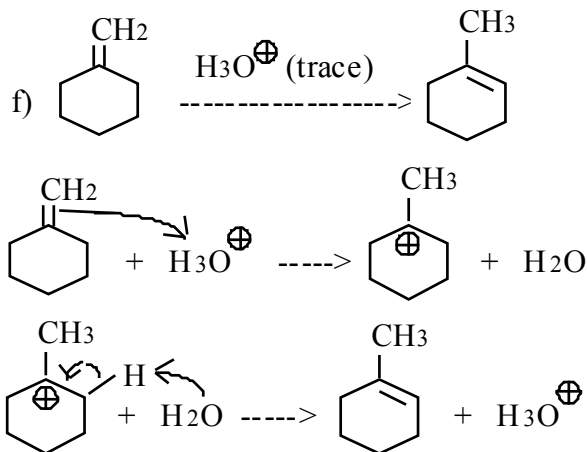
3. Mechanisms. Note that balanced equations are used throughout.



3.

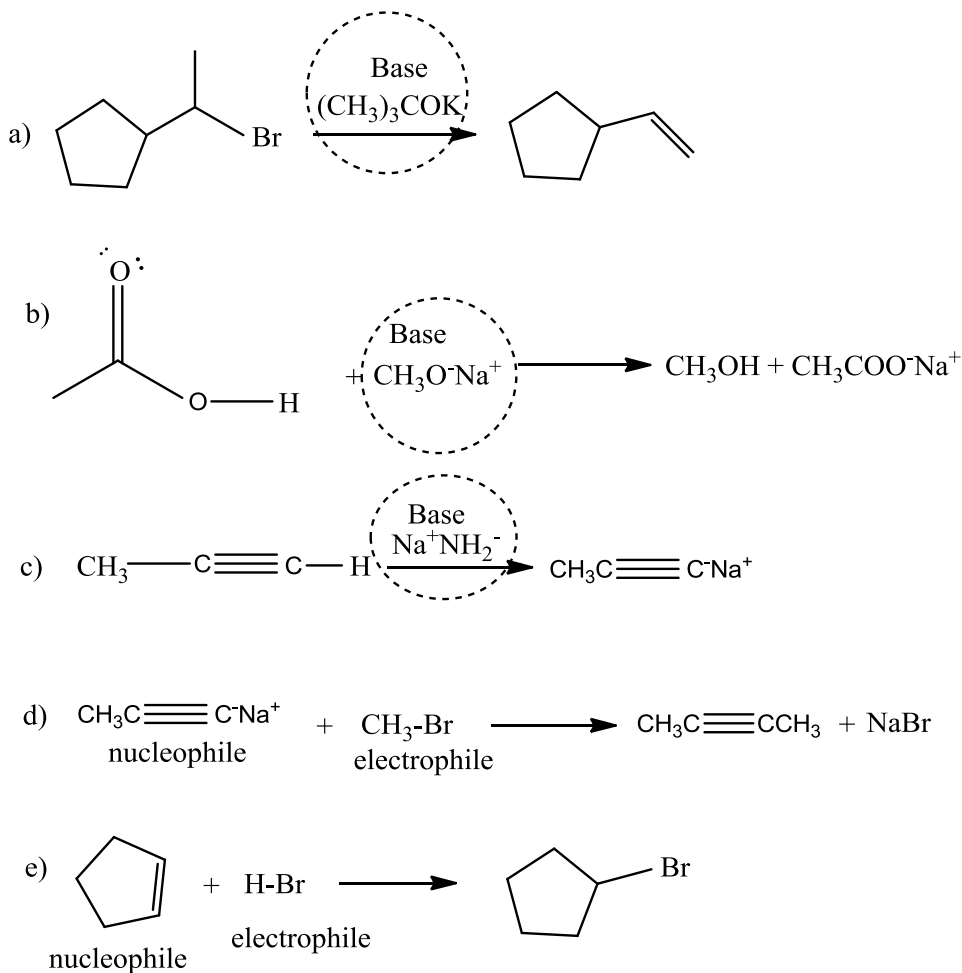


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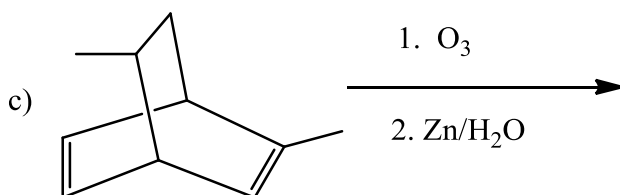
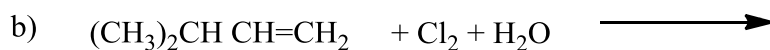
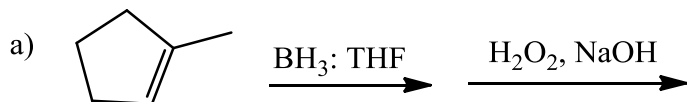


4.1. Reaction b) is stereospecific because the two hydrogens are added to the same face of the alkene in so called *syn* fashion. As a result, only the *cis* pair of enantiomers of the product forms. No diastereomeric *trans* enantiomers will be found in the product mixture. Reaction a) is not stereospecific because the carbocation that forms and then rearranges is trigonal planar (note sp^2 -hybridization of the carbon) and can be attacked from both sides. As a result, both possible enantiomers will form in approximately equal amounts, so the product will be racemic.

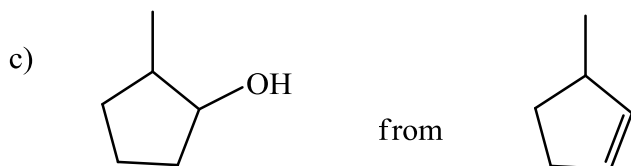
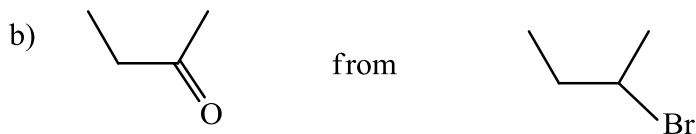
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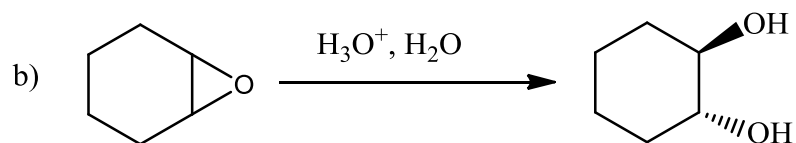
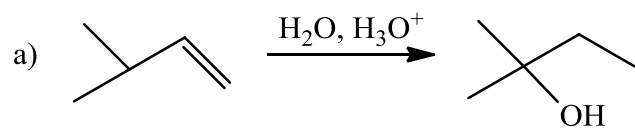
1. Predict the major organic product or products the following reactions. Show correct stereochemistry where appropriate. Also label regioselective and stereospecific reactions.



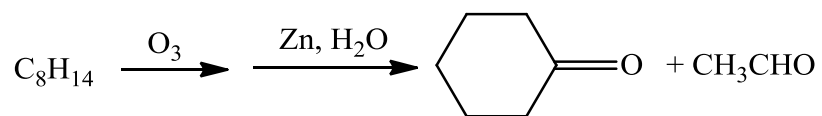
2. Propose a synthesis of each of the following compounds from the given starting material and any needed inorganic reagents or solvents.



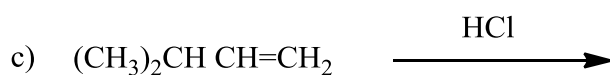
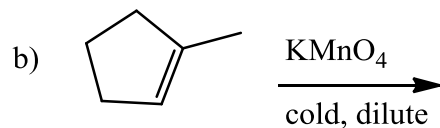
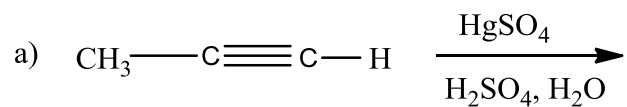
3. Propose a mechanism for each of the reactions shown.



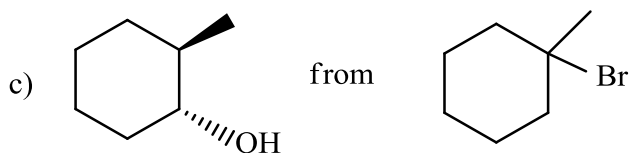
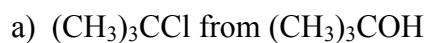
4. Give the structure of the unknown from the information given.



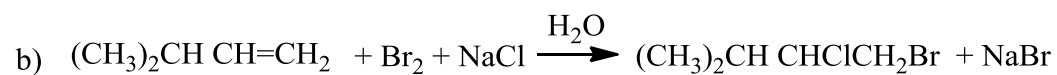
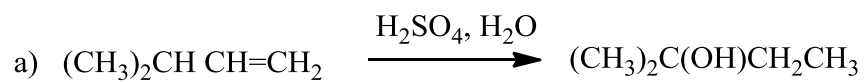
1. Predict the major organic product of each of the following reactions.



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



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



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

