

Chemistry 218, Problem Set 5

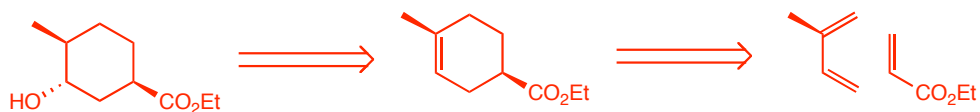
Recommended problems from the text: 16.15-16.17, 16.40-16.41, 16.43-16.45, 16.57

(Recommended problems from 1st ed.): 16.13-16.15, 16.38-16.39, 16.41-16.42, 16.55,

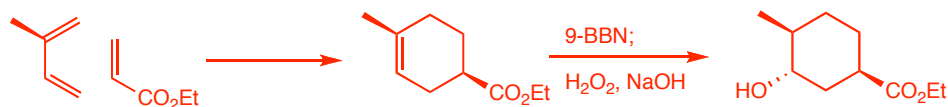
1. Starting with any diene and dienophile, propose a synthesis of the following molecules:

(a)

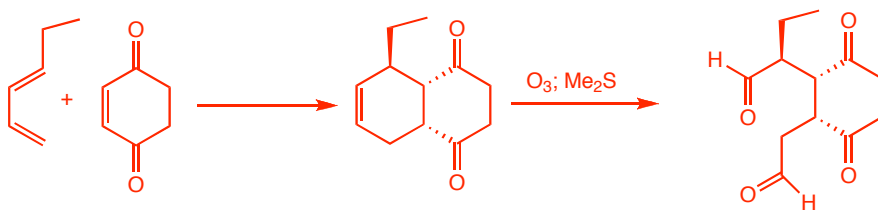
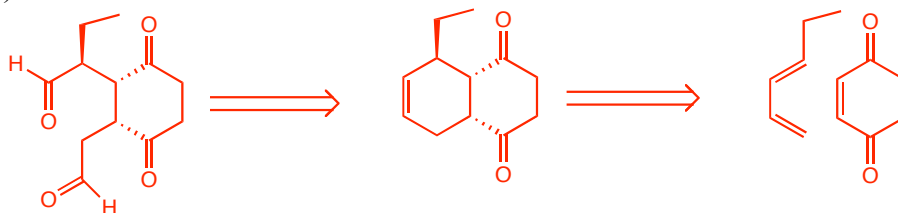
Retrosynthesis:



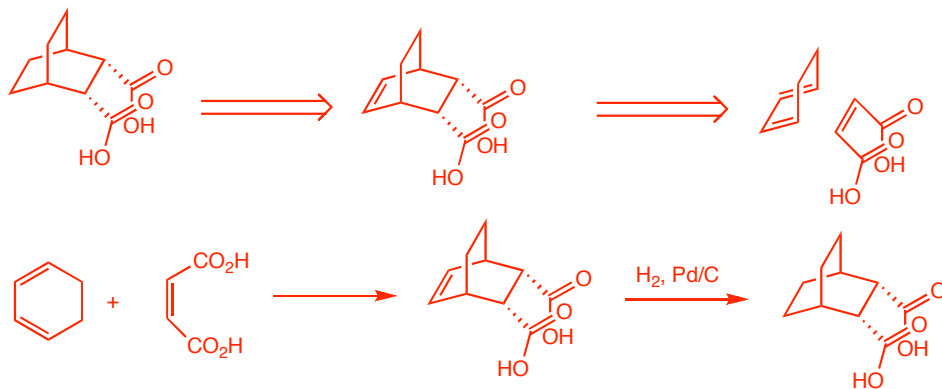
Forward Plan:



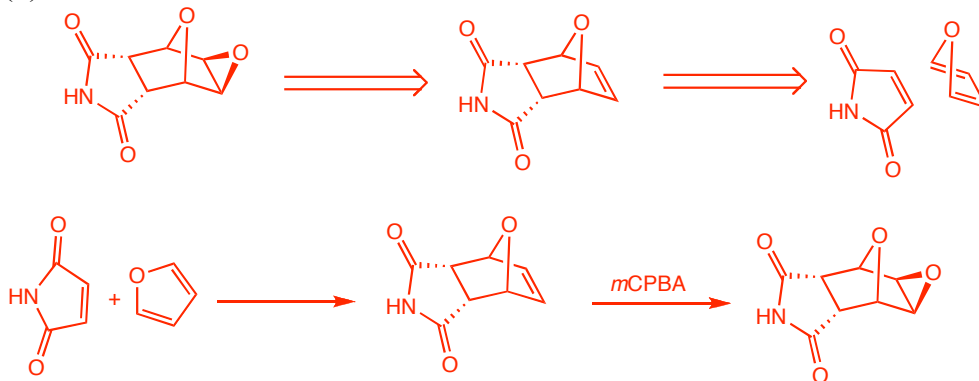
(b)



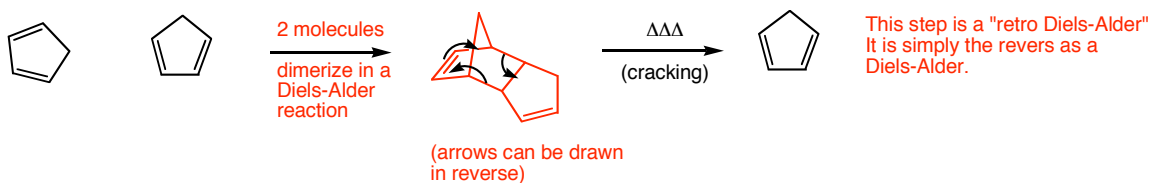
(c)



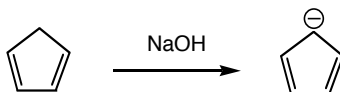
(d)



2. (a) When you buy cyclopentadiene, it actually exists as a dimer, which is the result of a Diels-Alder reaction between two molecules of cyclopentadiene. But, you can get the monomer back by heating (cracking) it. Draw the structure of the dimer and the mechanism for cracking.

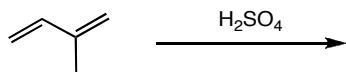


(b) One of the reasons that cyclopentadiene is used quite a bit in research is that it is much more acidic than would be expected. Explain why.

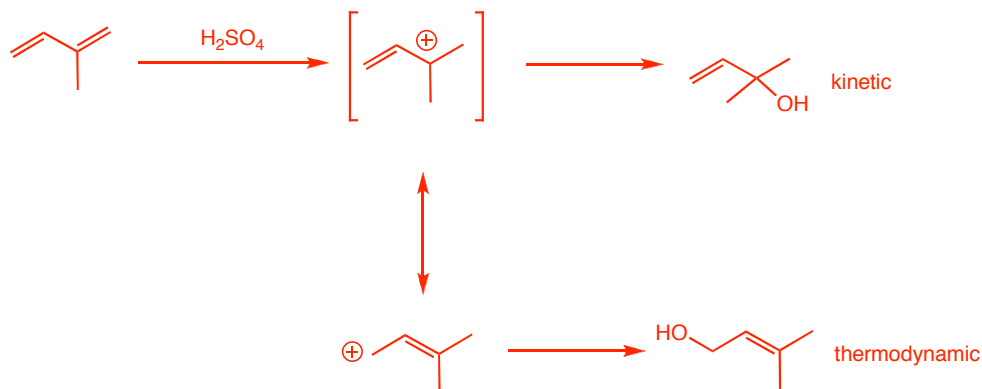


When it is in the protonated form (left side of the reaction), the system is not fully conjugated. In the deprotonated form, the entire ring is conjugated. Because the conjugate base is very stable, the acid is stronger than expected.

3. Other types of ionic reactions besides hydrohalogenations can also give 1,4 or 1,2 addition. Determine the kinetic and thermodynamic products of the following reaction:



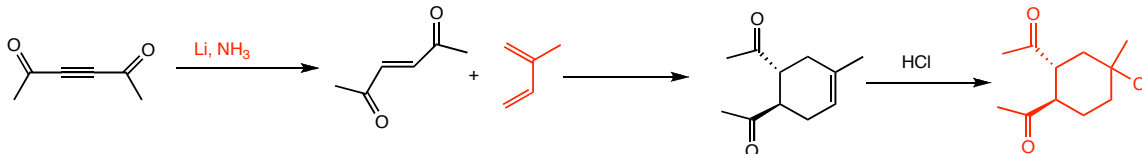
The initial carbocation is formed to give the most stable, conjugated cation:



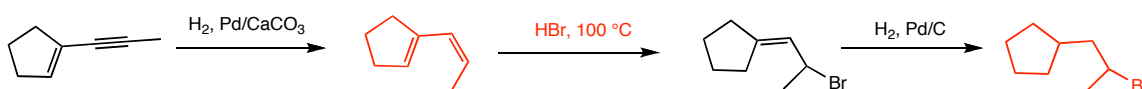
4. Provide

structures for the bolded letters:

(a)



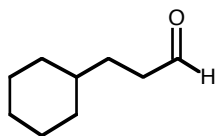
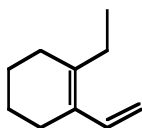
(b)



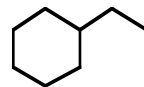
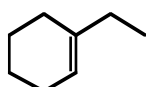
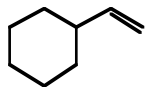
5. Propose a synthesis of the following molecules, with the stipulations given for each one.

(a) Both of the target compounds below, using only the starting materials given (you may use them more than once if you need to).

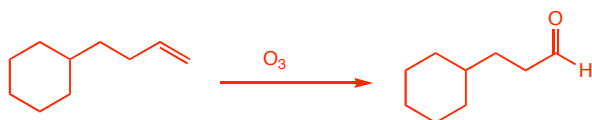
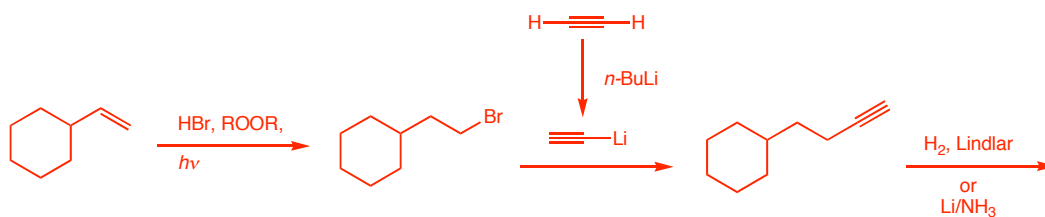
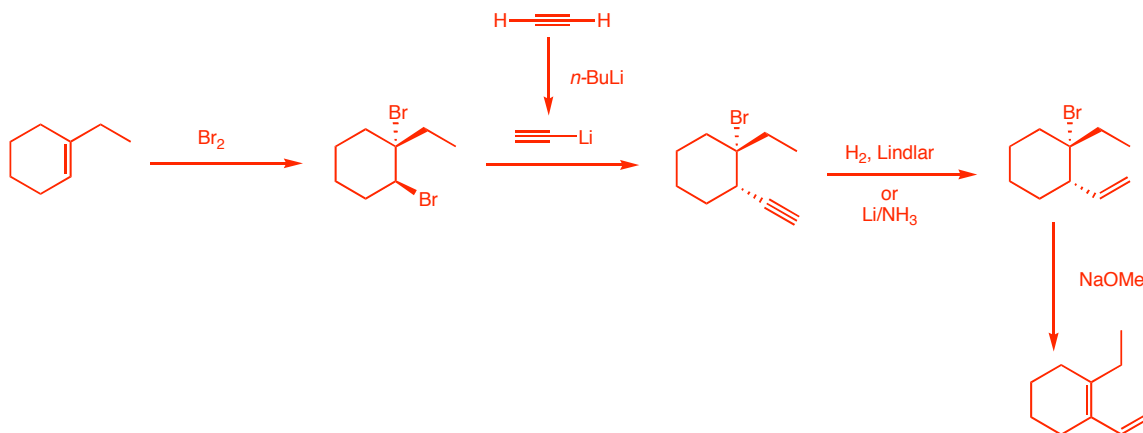
Target compounds:



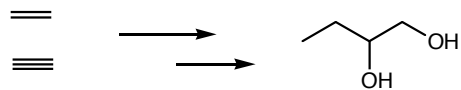
Starting materials:

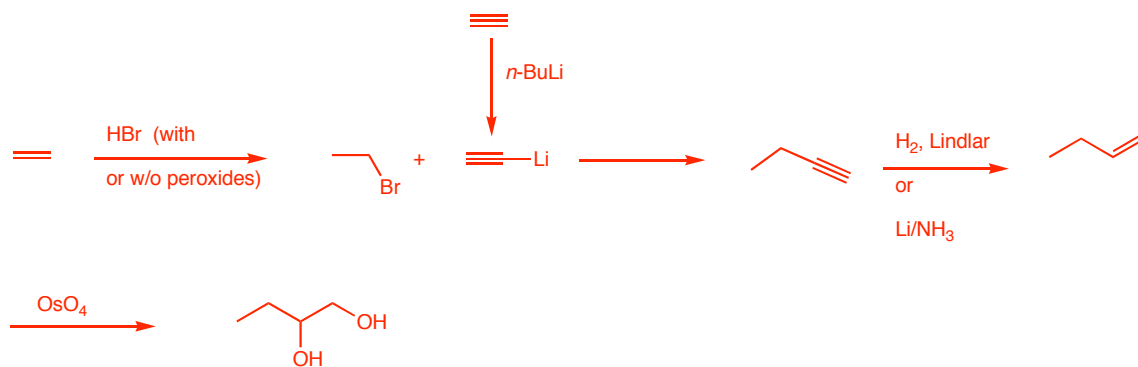


There are a couple of options: here is one for each:



(b) the following diol using only acetylene and ethylene as starting materials.





(c) the product shown from 2-methylbutadiene and no other organic compounds (inorganic reagents o.k.)

