Chemistry 217, Problem Set 10

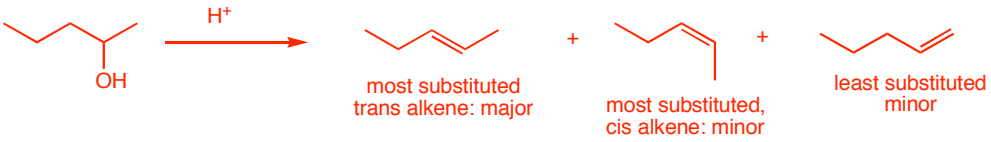
Recommended Problems from the Text: 9.2-9.4, 9.11-9.30, 9.31 (a-e), 9.32-9.37, 9.38, 9.39 (only ethers), 9.40 (a-f), 9.43, 9.44 (a-g), 9.45-9.54, 9.56-9.71, 9.73, 9.76, 15.1-15.2, 15.4-15.8, 15.11-15.14, 15.15 (a-c), 15.17-15.24, 15.38-15.47, 15.48 (a-d, i) 15.51-15.53, 15.55

(1st ed.: 9.2-9.4, 9.11-9.31, 9.32 (a-e), 9.33-9.37, 9.38, 9.39 (only ethers), 9.40 (a-f), 9.43, 9.44 (a-g), 9.45-9.53, 9.55-9.69, 13.1-13.2, 13.4-13.8, 13.11-13.14, 13.15 (a,b), 13.16-13.19, 13.21-13.22, 13.35-13.44, 13.45 (a-d,i), 13.47-13.49, 13.51)

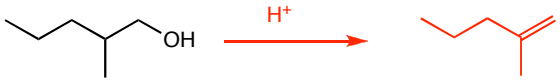
1. Give the dehydration product(s) for the following alcohols. For extra practice draw the mechanism for every reaction.

(a)

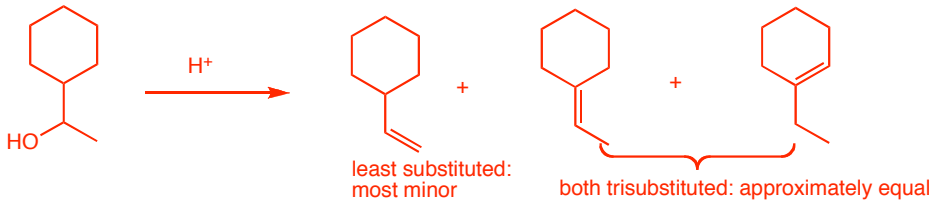
(b)



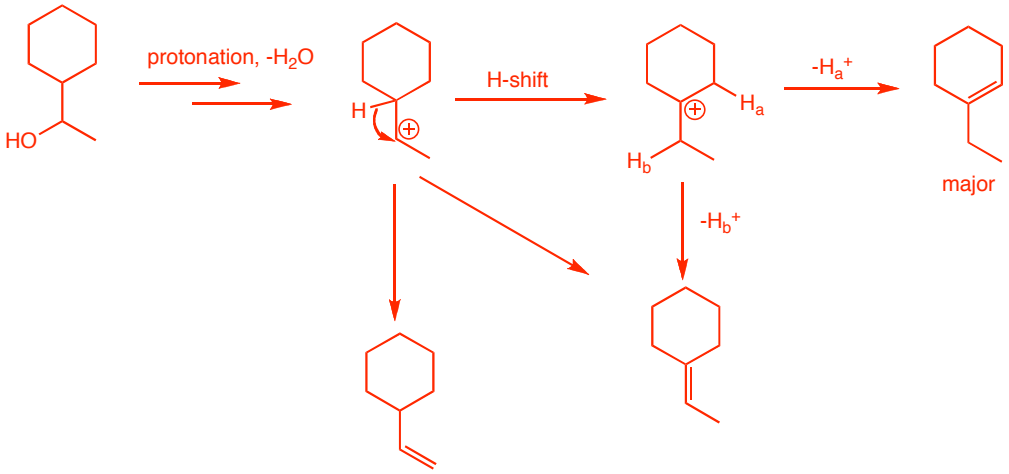
(c)



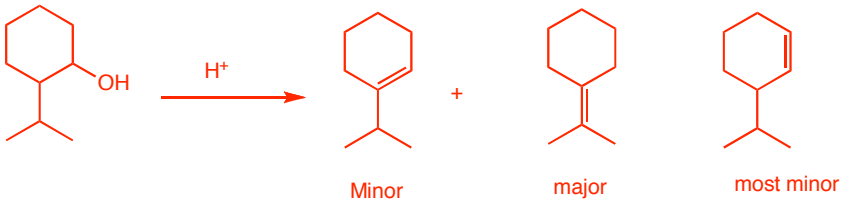
(d)



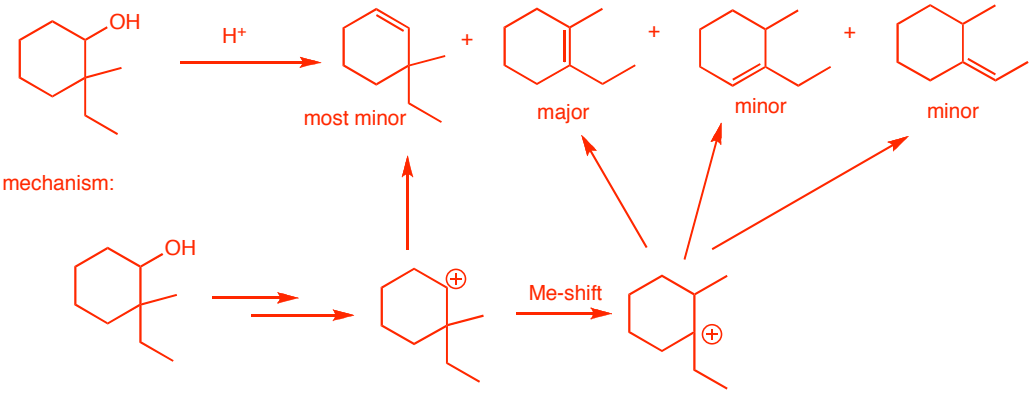
abbreviated mechanism:



(e)

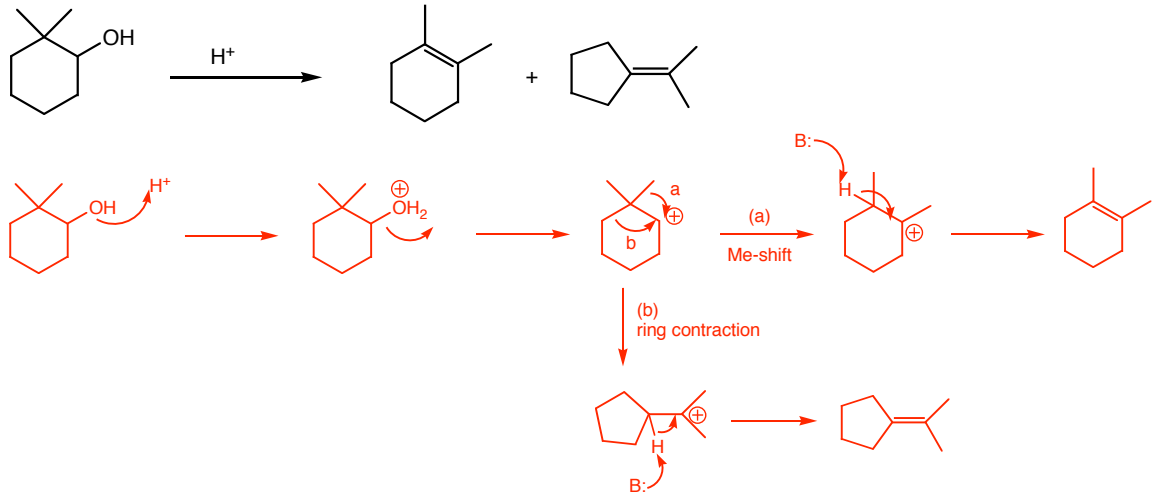


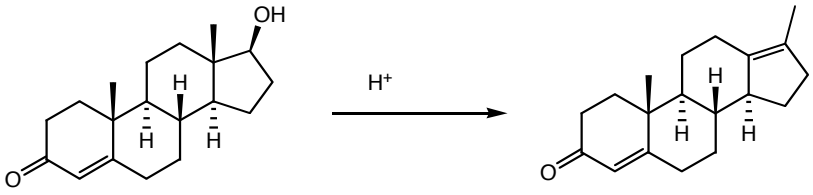
(f)



2. Draw mechanisms that account for the following observations:

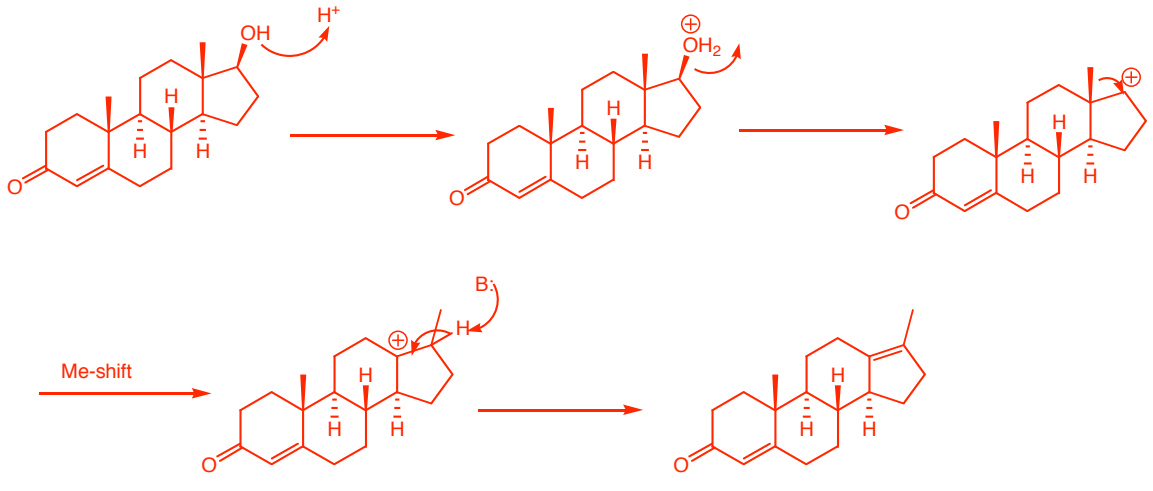
(a)



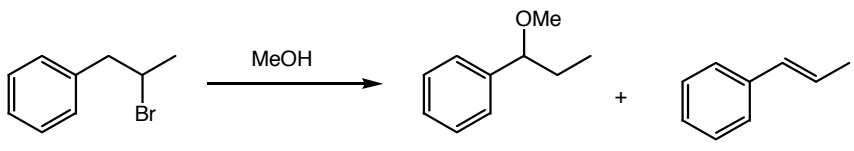


testosterone

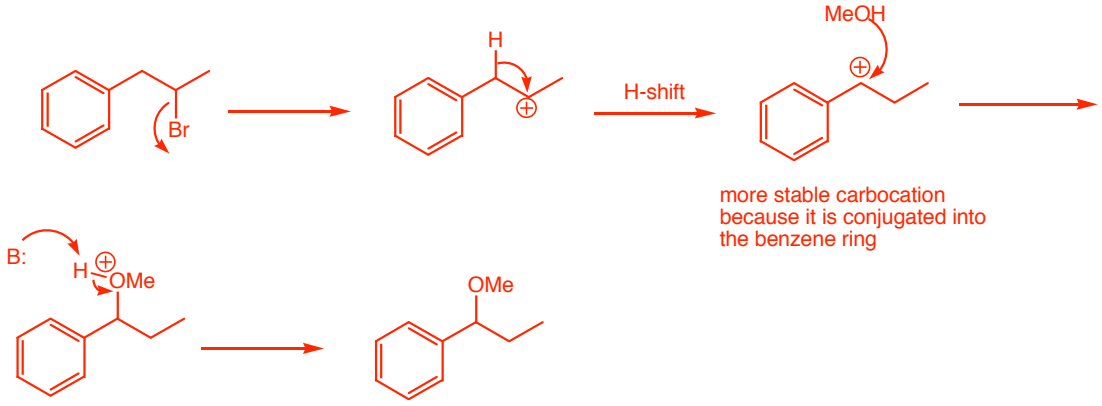
(b)



(c)

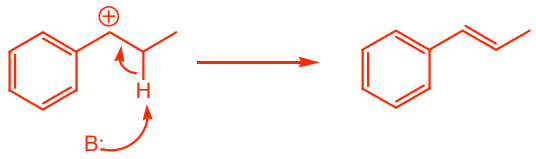


This is an $S_N1/E1$ reaction with a cation rearrangement

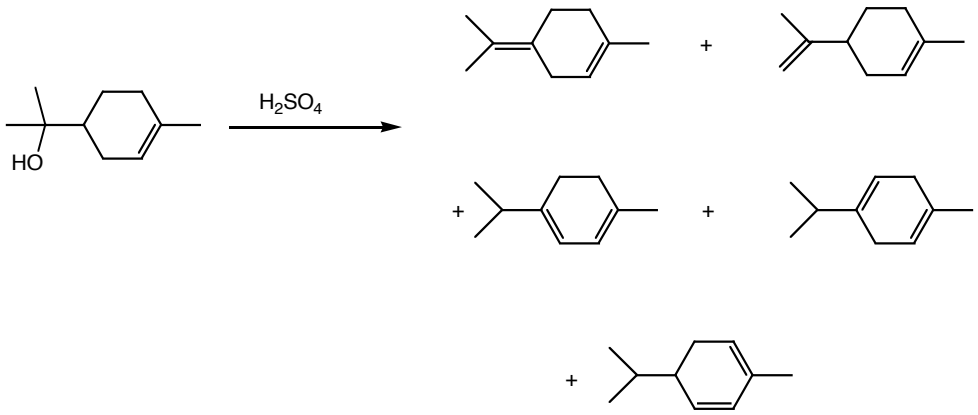


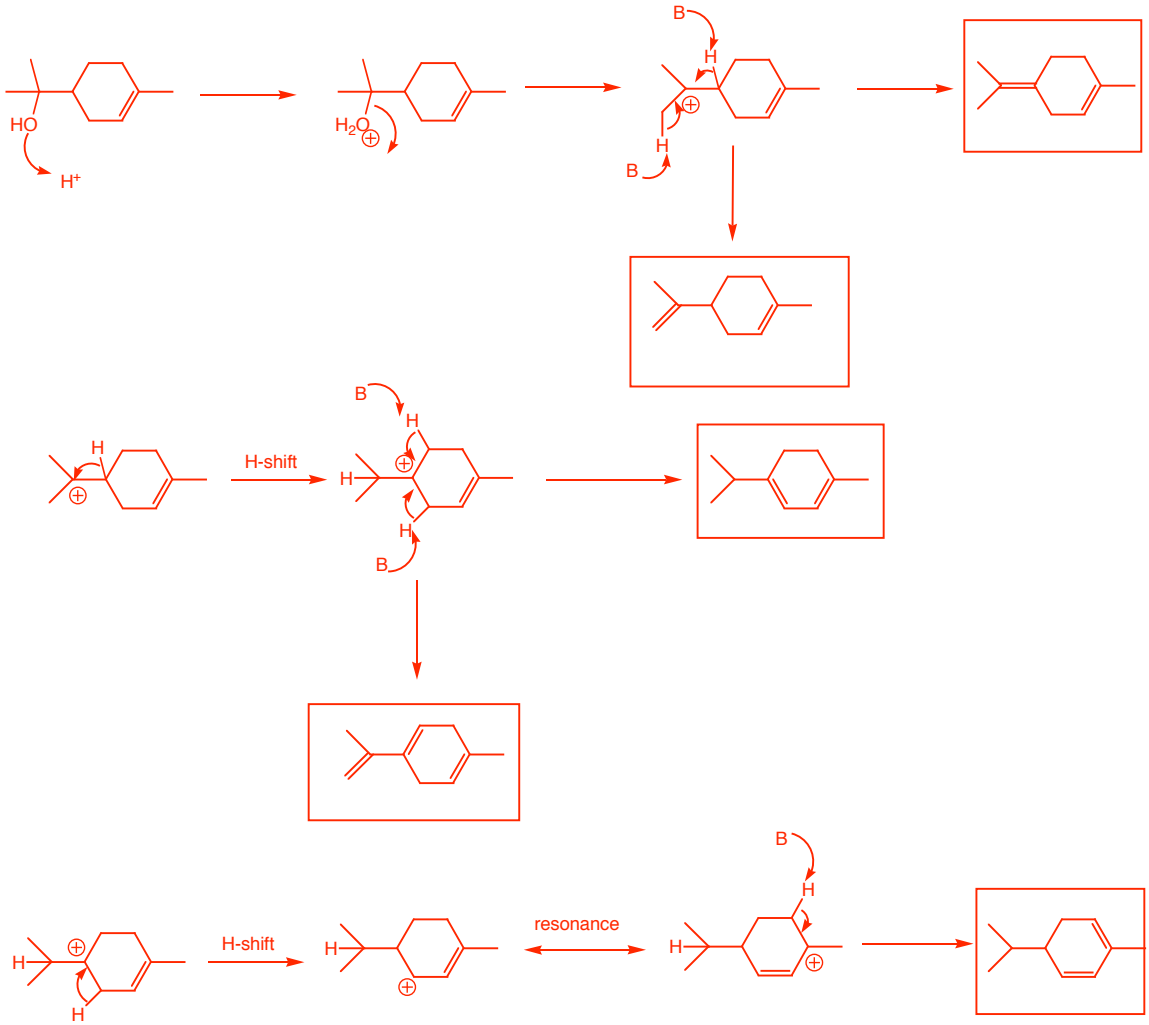
more stable carbocation
because it is conjugated into
the benzene ring

Formation of the alkene comes from the same carbocation as the S_N1 reaction:

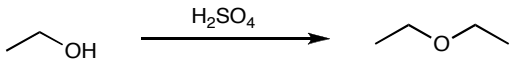


(d)

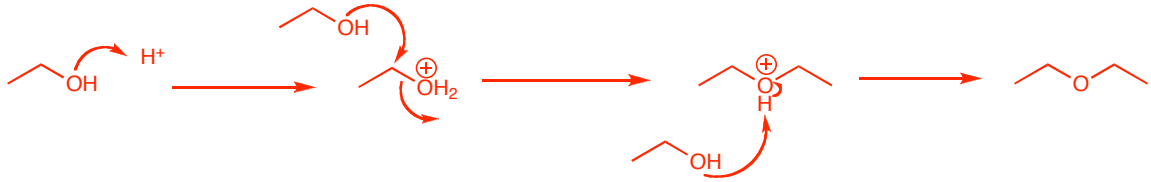




3. The industrial method for preparing diethyl ether is to treat ethanol with sulfuric acid:

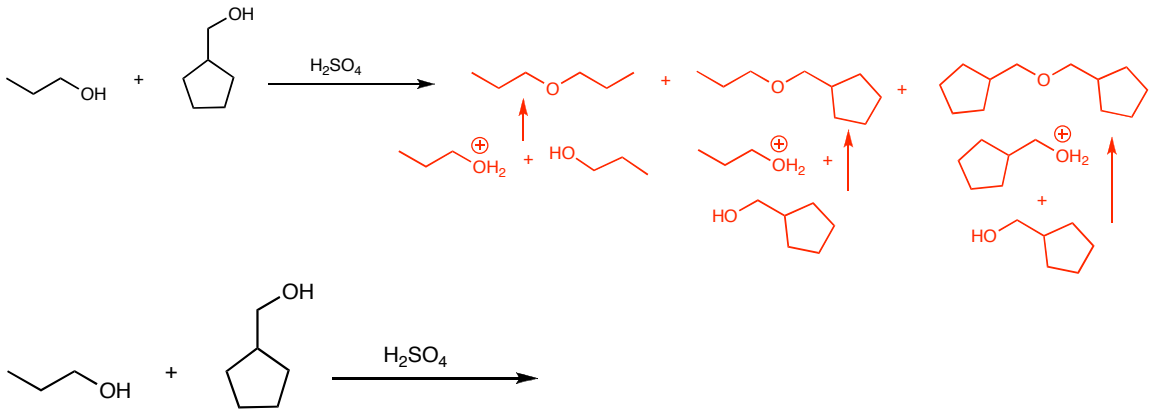


(a) Propose a mechanism for the formation of ether shown above.



(b) In general, 1° alcohols will form an ether in the presence of acid, but 2° and 3° form an alkene. Why? For 1° alcohols, S_N2 is fast, and E2 is slow, since there is no strong base in the reaction mixture to deprotonate. For 2° and 3° alchols though, the rate of S_N2 is slower than 1° due to sterics, so the E1 mechanism becomes the major pathway.

(c) What ether(s) would be formed in the following reaction?

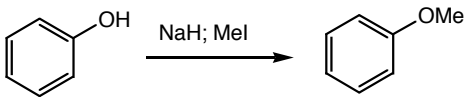


(d) Is this a suitable method for forming asymmetric ethers (ethers in which the R groups are different)? No, because as shown above, at least three products are formed when there are two different alcohols in the reaction.

4. Show how each of the following ethers can be prepared using the Williamson ether synthesis. If there are two possible methods, choose the one that is the best.

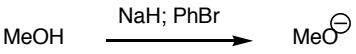
(a)

Works well:

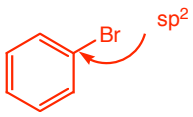


(note: for this particular alcohol, you can use a weaker base (such as K_2CO_3) for Williamson ether synthesis. (Why?)

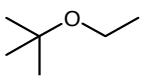
Does not work at all:



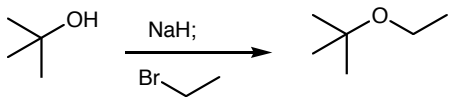
In this reaction, the only thing that would happen is that the methanol is deprotonated. The S_N2 part of the reaction cannot occur because the leaving group is on an sp^2 carbon. Only tetrahedral carbons can be electrophiles in an S_N2 reaction.



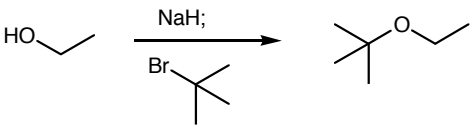
(b)



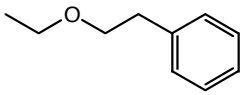
The two options are:



1° alkyl halide: better electrophile
This reaction would work better

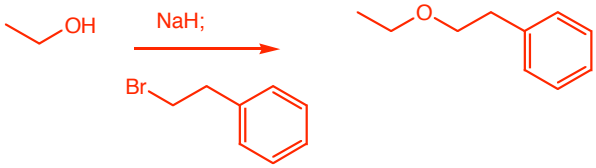


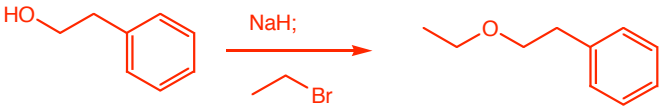
3° alkyl halide: very sterically hindered

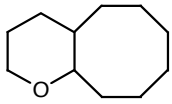


(c)

Both options would work equally well:

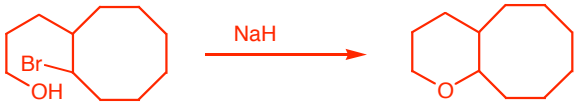




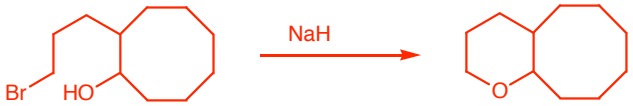


(d)

The two options are:



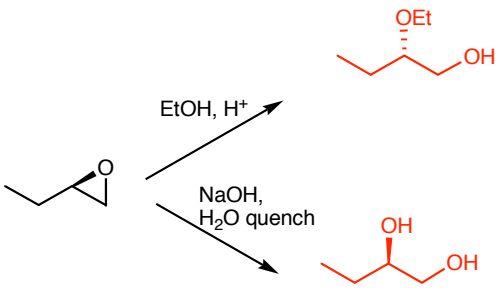
2° alkyl halide: less reactive



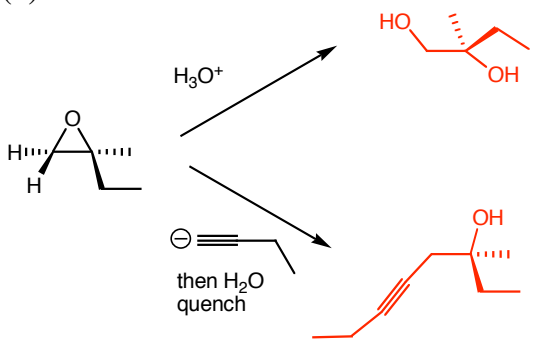
1° alkyl halide: more reactive

5. Give the products of the following reactions. Be sure to indicate the relevant stereochemistry of the product.

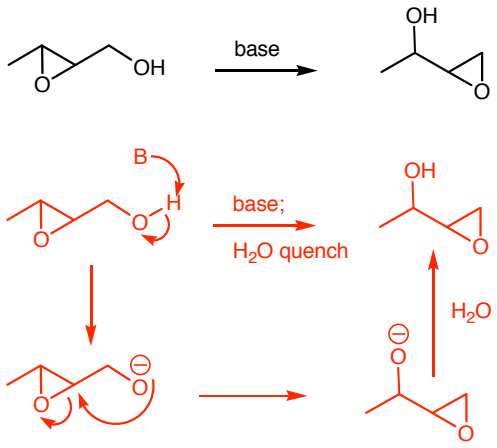
(a)



(b)

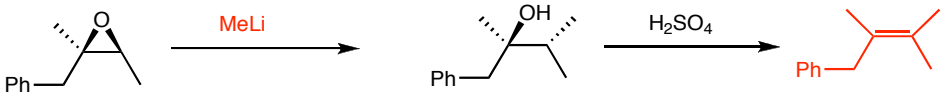


6. Propose a mechanism for the following rearrangement, called the Payne rearrangement:

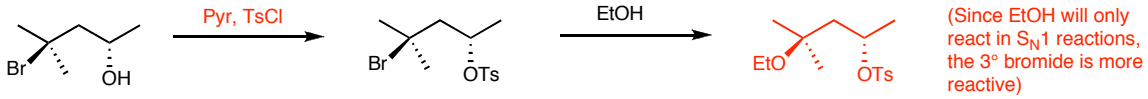


7. Fill in the blanks:

(a)

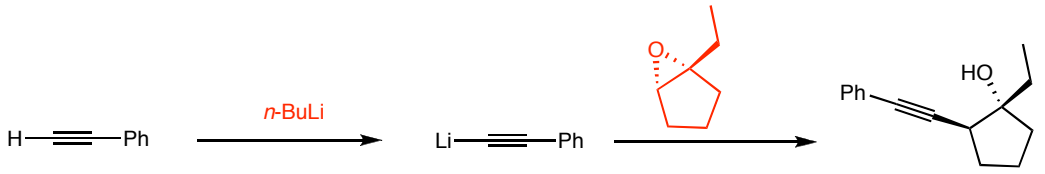


(b)



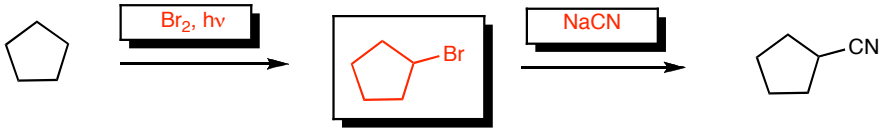
(Since EtOH will only react in S_N1 reactions, the 3° bromide is more reactive)

(c)

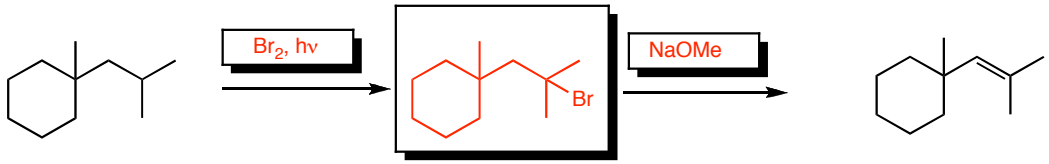


8. The first reaction of each of the following begins with a halogenation of some sort. Fill in all of the blanks.

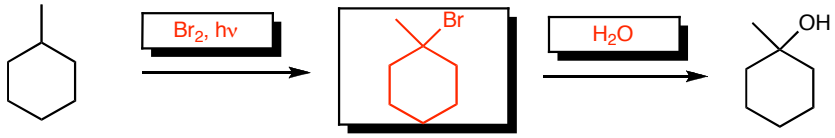
(a)



(b)



(c)



(d)