
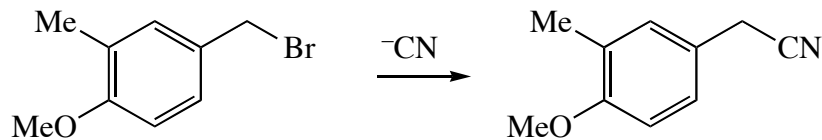
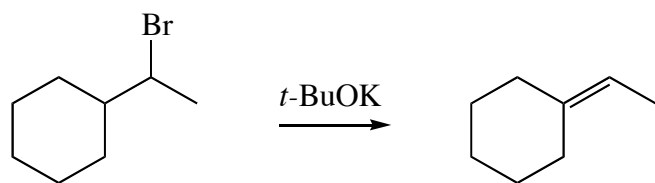


1. (4 pts. each, 24 pts. total) Draw the *major* product of each of the following reactions. If no reaction is expected to occur, write "No reaction." Be sure to indicate the stereochemistry of the product, if appropriate. (A mixture of configurations should be indicated with a squiggly bond  to one of the groups attached to the stereogenic C atom.)

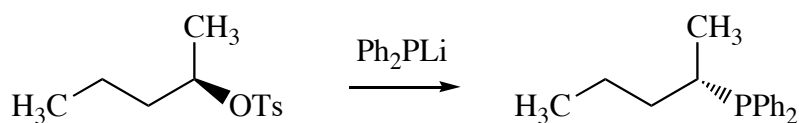
(a)



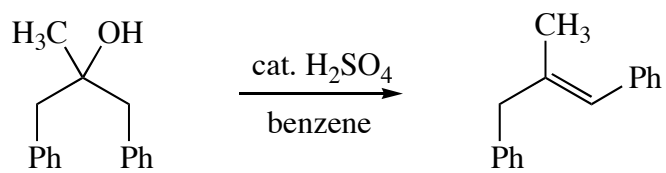
(b)



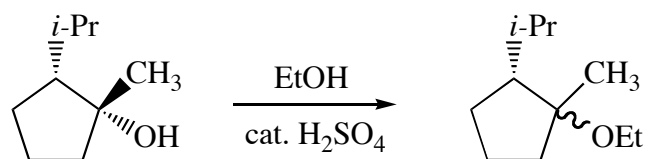
(c)



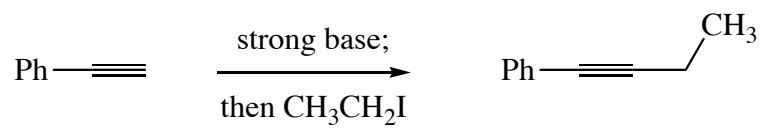
(d)



(e)

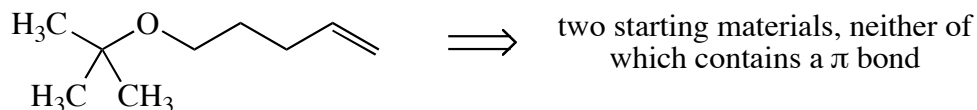


(f)

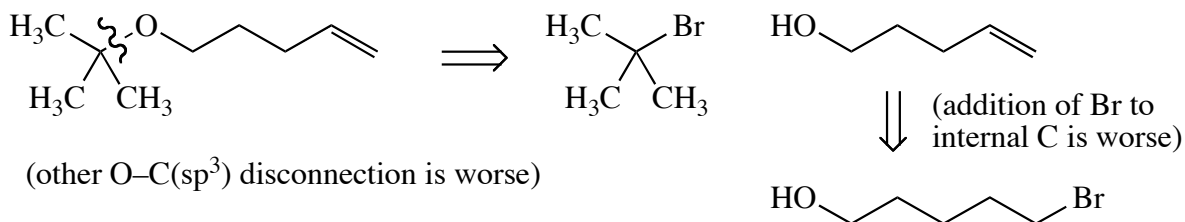


2. (16 pts. each, 32 pts. total) Design syntheses of each of the following compounds from the indicated starting materials. Show all reagents required for each transformation. You are advised to conduct a retrosynthetic analysis before working in the forward direction. *Either synthesis may require more than one step.*

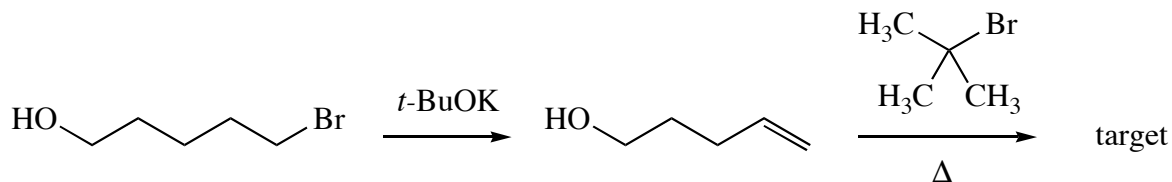
(a)



Retrosynthetic analysis:

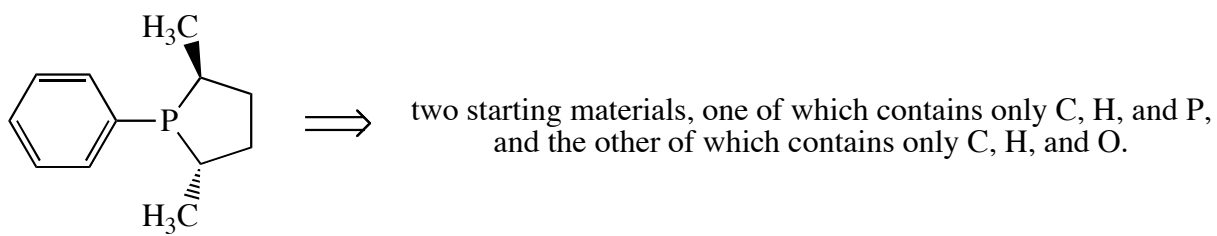


Forward synthesis:

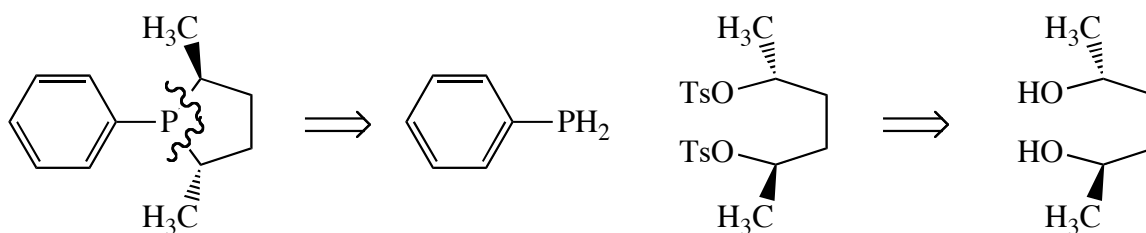


Actually, it's better to do these two steps in the reverse order, because treatment of the bromoalcohol with strong base is likely to induce cyclization to a cyclic ether instead of elimination. But you'll get full credit for doing it this way, anyway.

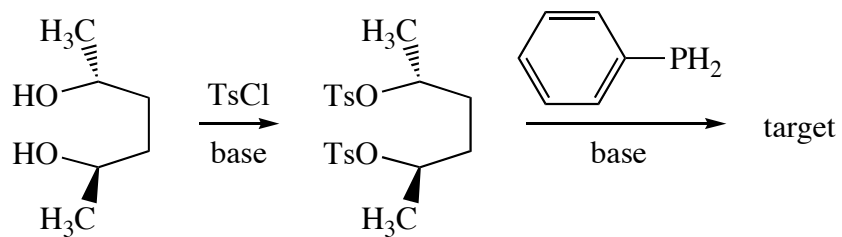
(b)



Retrosynthetic analysis:

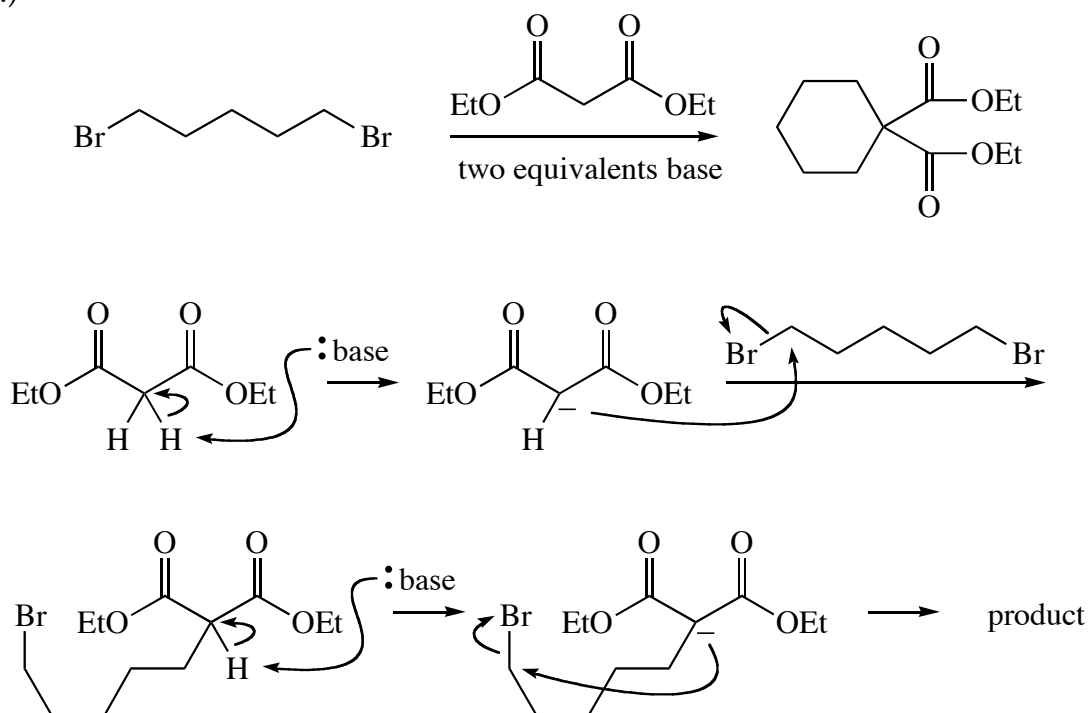


Forward synthesis:

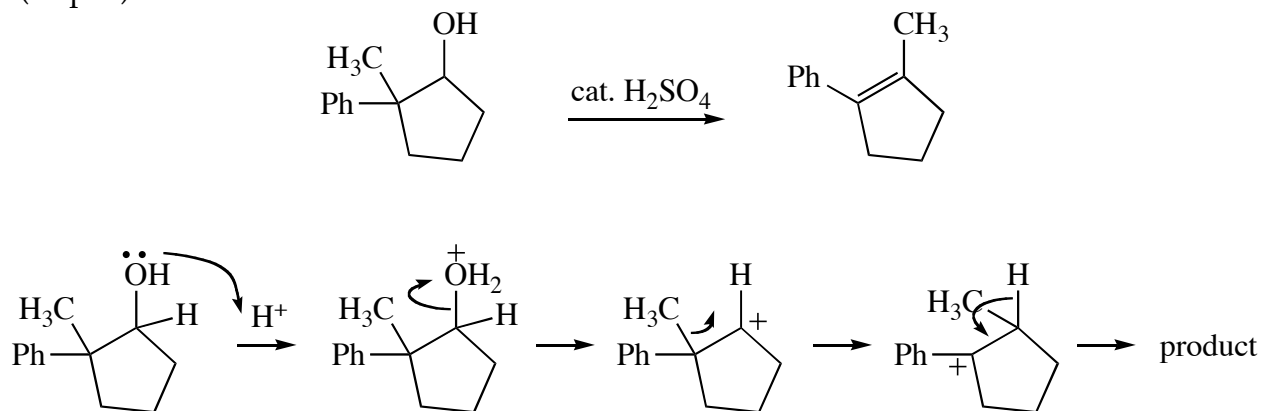


3. (22 pts. total) Draw reasonable mechanisms for each of the following reactions. Use the curved arrow convention to show the movement of electrons. Remember to obey Grossman's Rule!

(a) (8 pts.)

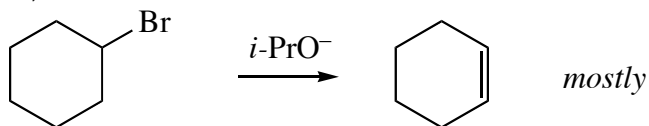


(b) (14 pts.)

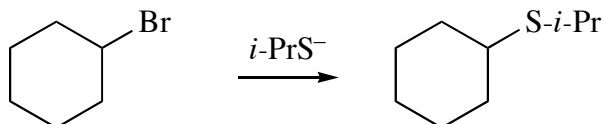


4. (22 pts. total) Explain each of the following observations in one or two brief, coherent, and grammatically correct sentences.

(a) (4 pts.)

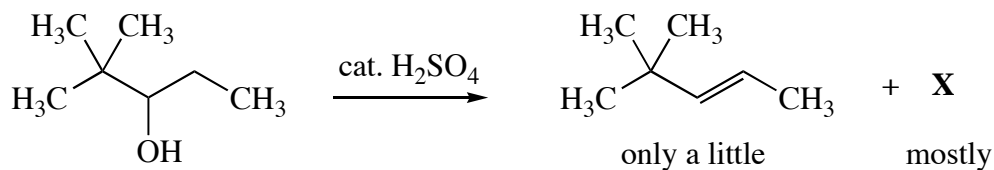


BUT



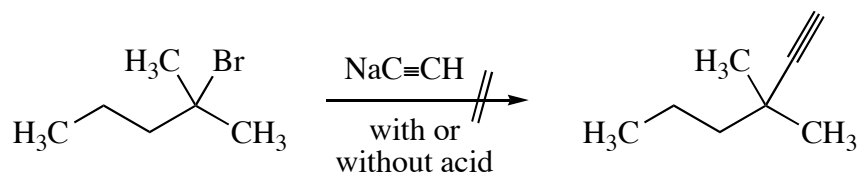
S is lower in the periodic table, so it's a better nucleophile and a worse base than O, so it favors a greater proportion of substitution.

(b) (4 pts.) Only a little of the product shown is obtained; the major product is entirely different.



In this reaction, a 2° carbocation is obtained. It undergoes a rearrangement to give a lower-energy 3° carbocation, and loss of H^+ then gives the observed product.

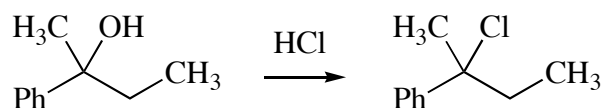
(c) (4 pts.) The reaction below fails regardless of whether or not acid is added. (Explain both cases.)



Under basic conditions, the 3° halide does not like to undergo substitution reactions; elimination will occur instead.

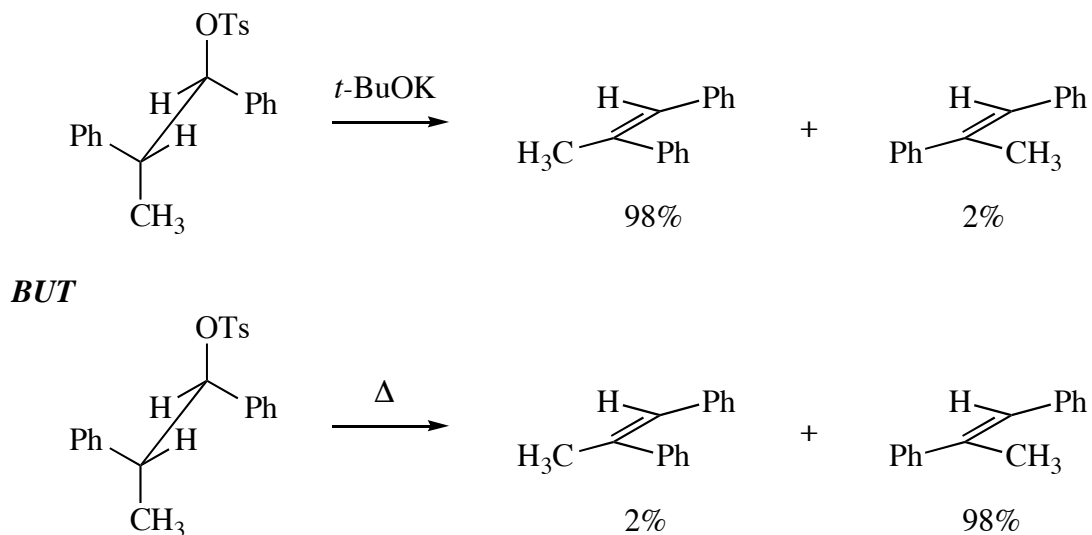
Under acidic conditions, the nucleophile will be protonated, so it will no longer be a nucleophile.

(d) (4 pts.) Undergraduate research assistant Sally Humdinger tries to double the rate of the reaction below by adding twice as much HCl, but it has no effect.



Under acidic conditions, the mechanism of substitution is $\text{S}_{\text{N}}1$, and the rate of the $\text{S}_{\text{N}}1$ reaction is not dependent on the concentration of the nucleophile.

(e) (6 pts.) The non-Zaitsev product is obtained predominantly under basic conditions, but the Zaitsev product is obtained predominantly when no base is included.



Under basic conditions, there is a requirement for antiperiplanar alignment of the breaking C–H and C–OTs bonds. In this conformation, the compound has the two Ph groups gauche, so they must be cis in the product.

Under acidic conditions, there is no requirement for antiperiplanar alignment of the breaking C–H and C–OTs bonds, so the lower-energy product, in which the Ph groups are trans, is mostly obtained.