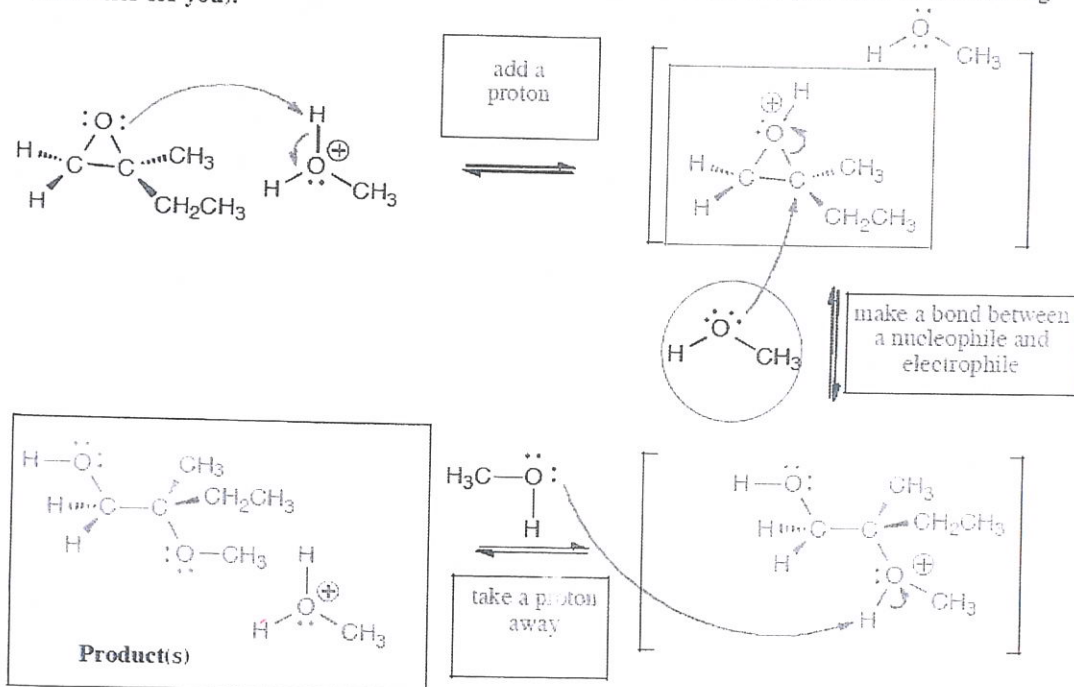
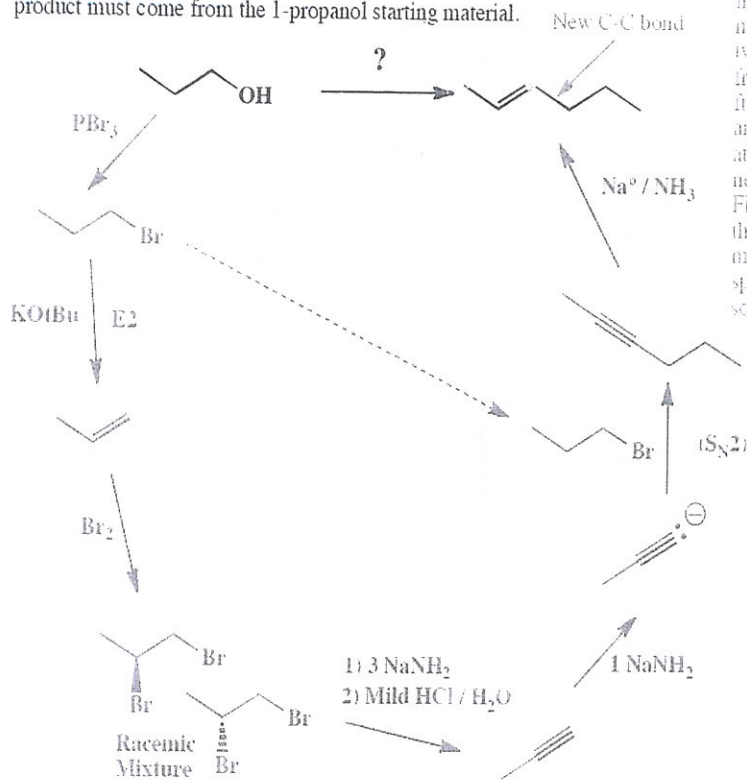


20. (25 pts.) For the reaction of this epoxide with methanol in acid, fill in the details of the mechanism. Draw the appropriate chemical structures and use arrows to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". MAKE SURE TO NOTICE THE QUESTIONS AT THE BOTTOM. Use wedges and dashes to indicate stereochemistry where appropriate. BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer for this problem (we are making this easier for you).



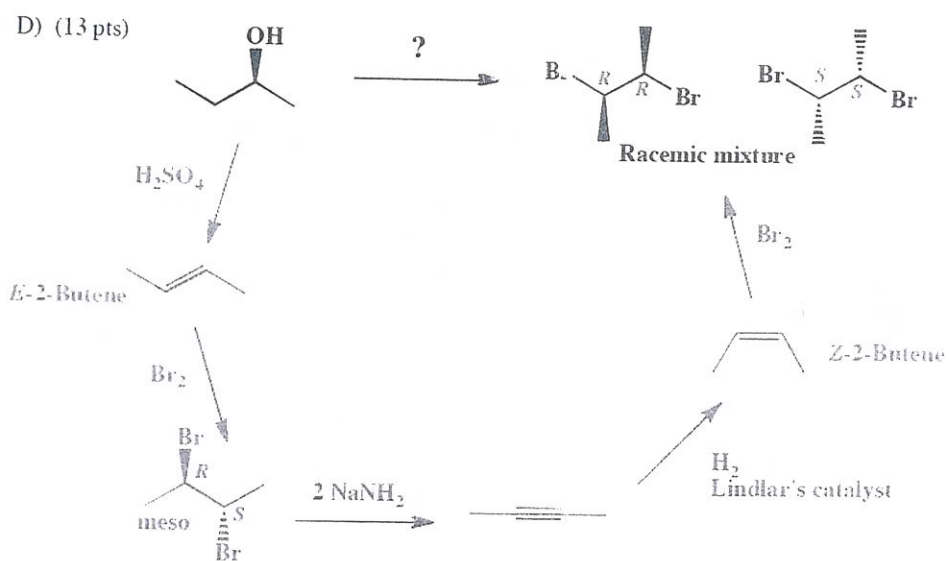
17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate.

C) (18 pts) For this one, all of the carbon atoms of the product must come from the 1-propanol starting material.



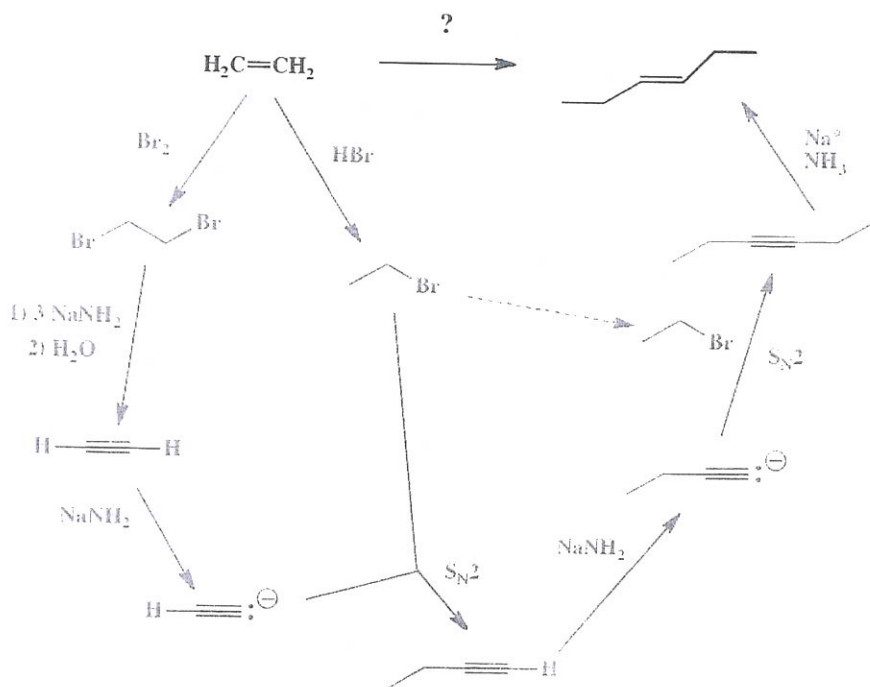
Recognize that the product has six carbons in a chain so you need to make a C-C bond from two three carbon fragments. Recognize further that an alkyne anion must be involved at precisely where the new C-C bond is formed. Finally, recognize also that the only way to make an *E* alkene at that spot from an alkyne uses sodium in ammonia.

Recognize that the required alkyne (DFW) can be made from the starting alcohol by conversion to the haloalkane followed by an  $E2$  to give the alkene (Austin) followed by reaction with  $N_3$  to give the vicinal dihaloalkane (Waco) then elimination using  $NaNH_2$  followed by a mild acid treatment. Recognize also that the 1-bromopropane needed for the key C-C bond forming step (as well as the first step overall) can be made from 1-propanol by reaction with  $PBr_3$ .



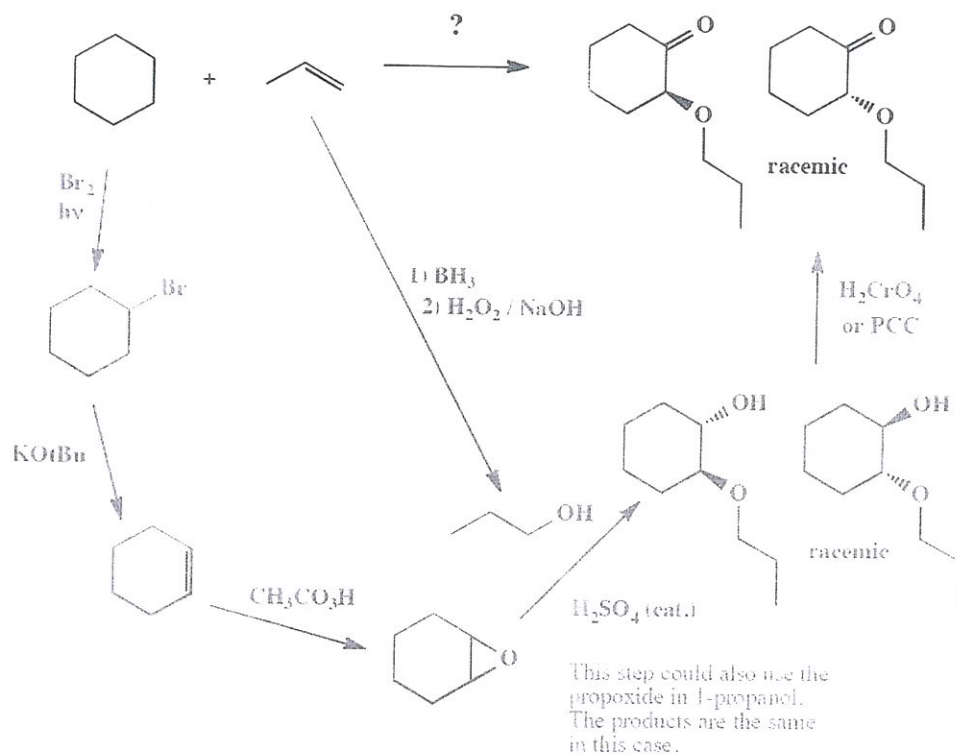
Recognize that the product vicinal dihaloalkane could only come from anti addition of  $Br_2$  to *Z*-2-butene. Recognize further that the only way you know to make a *Z* alkene is through the syn addition of  $H_2$  to an alkyne using  $H_2$  and Lindlar's catalyst. Recognize therefore that you must get to the alkene from the starting alcohol. The most efficient way to do this is to start by dehydrating the alcohol as in part A), then follow 1-35 to the meso vicinal dihaloalkane (Waco) followed by reaction with  $NaNH_2$  to give the alkyne (DFW).

C) (21 pts)



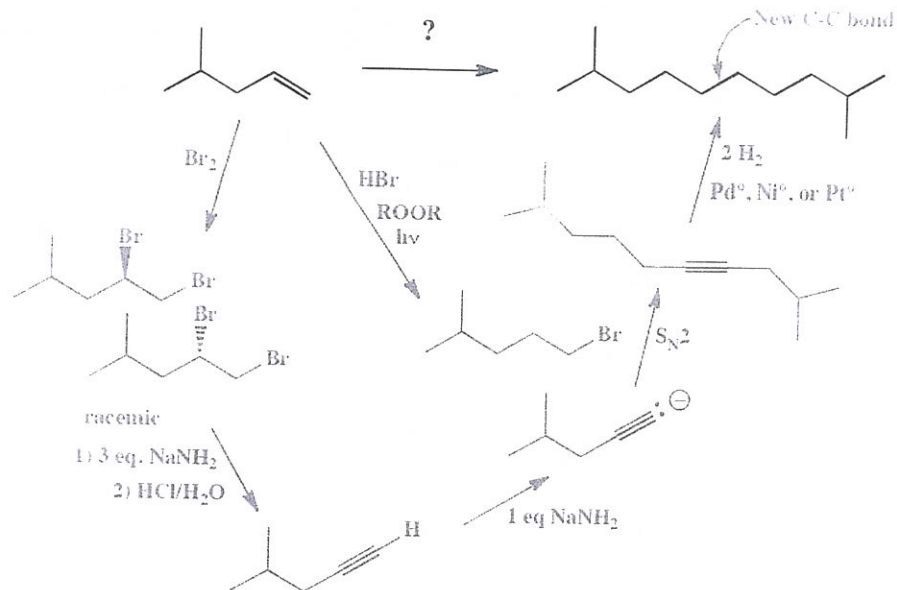
Recognize that this molecule can be assembled from three different 2-carbon pieces, using the alkyne alkylation strategy each time. Therefore, an alkyne is required, so recognize that the last step must be the reduction of the alkyne group using  $\text{Na}^+$  and  $\text{NH}_3$  to give the *E*-alkene product. The rest is standard chemistry at this point.

D) (16 pts)



Recognize the product as having a ketone, which in this class can only be made through ozonolysis of an alkene or oxidation of an alcohol. We can rule out ozonolysis because counting carbons makes it clear there are no C-C bonds broken, thus propose the last step as an oxidation of the alcohol. The hard part of this synthesis is to recognize that to make the vicinal ether-alcohol in high yield you must use 1-propanol to open an epoxide in either acid (shown) or basic conditions. Alkylating a vicinal diol would not work for this because the yield would be seriously compromised by creating a statistical mixture of products. The rest of the required chemistry is fairly straightforward.

C) (15 pts)



Recognize that there are 12 carbons in the product and even in the starting material. Assume you need to put two starting material molecules together at the central bond as shown. The only way this can be done using the reactions you know is to react the anion of a terminal alkyne with a primary haloalkane. Therefore, assume there was once an alkyne in the molecule so predict that the last step is the hydrogenation of the alkyne to give the alkane. Continuing to work backwards, the required 12 carbon alkyne can be derived from the reaction of the 6 carbon primary haloalkane shown and the corresponding 6 carbon terminal alkyne. The primary haloalkane can be made in a single step from the starting alkene by using HBr in the presence peroxide and light. The terminal alkyne can be made using the familiar "1-35" sequence of steps involving reaction with  $\text{Br}_2$  followed by reaction with the strong base  $\text{NaNH}_2$ .