NAME (Print): ______________________________

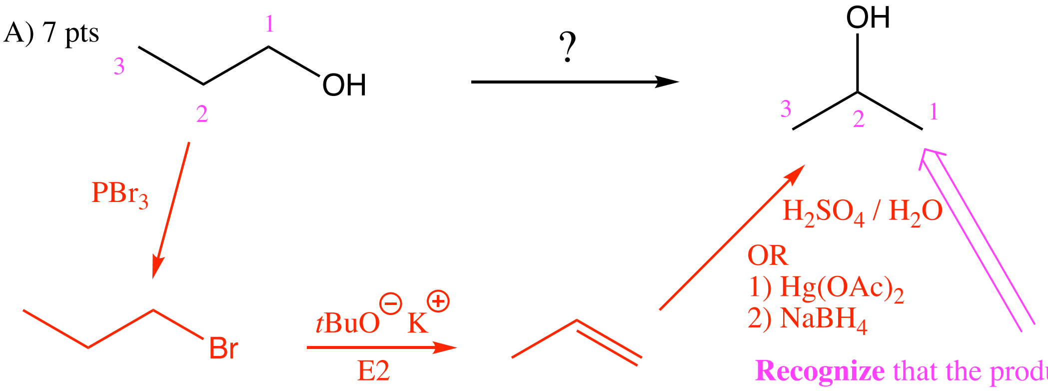
SIGNATURE: ______________________________

Chemistry 320M/328M
Dr. Brent Iverson
10th Homework
November 13, 2024

Please print the first three letters of your last name in the three boxes

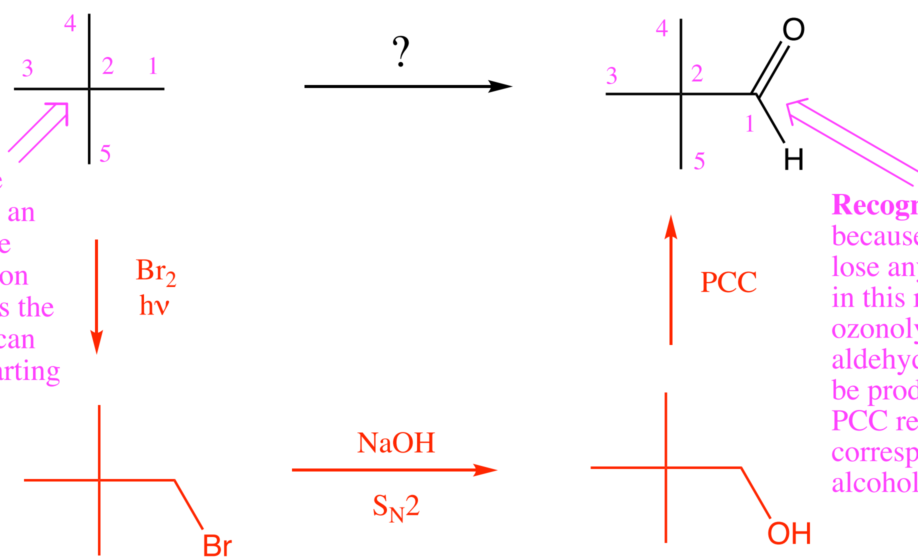
1. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction because only predominant products can be used. All the carbon atoms of the product(s) must come from the starting material(s) shown.

A) 7 pts



Recognize that the product is the result of Markovnikov addition of water to propene. Propene can easily be produced from the starting alcohol through an E2 reaction of bromopropane, which is produced using PBr_3 from the starting 1-propanol.

B) 7 pts



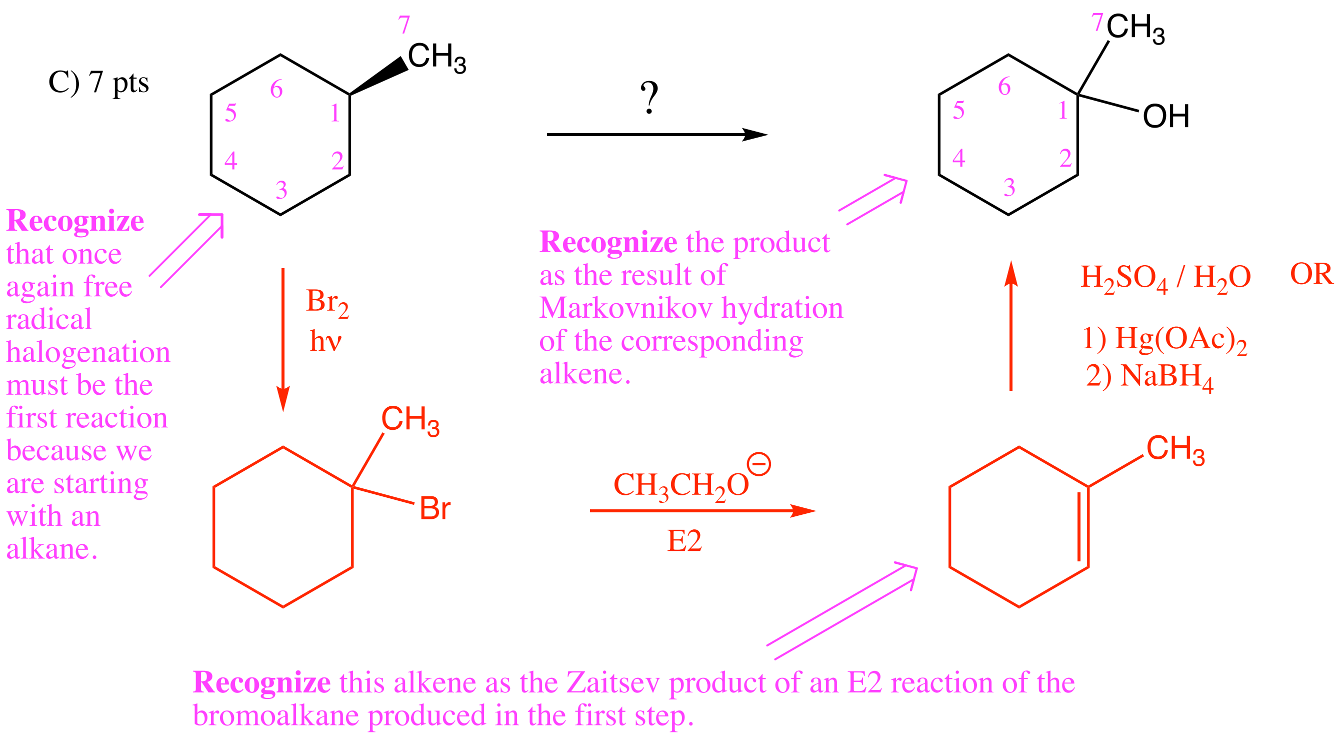
Recognize that the starting material is an alkane, and the free radical halogentation reaction with Br_2 is the only reaction you can use with alkane starting materials.

Recognize that because you do not lose any carbon atoms in this reaction (no ozonolysis) the aldehyde could only be produced through a PCC reaction of the correspongind primary alcohol

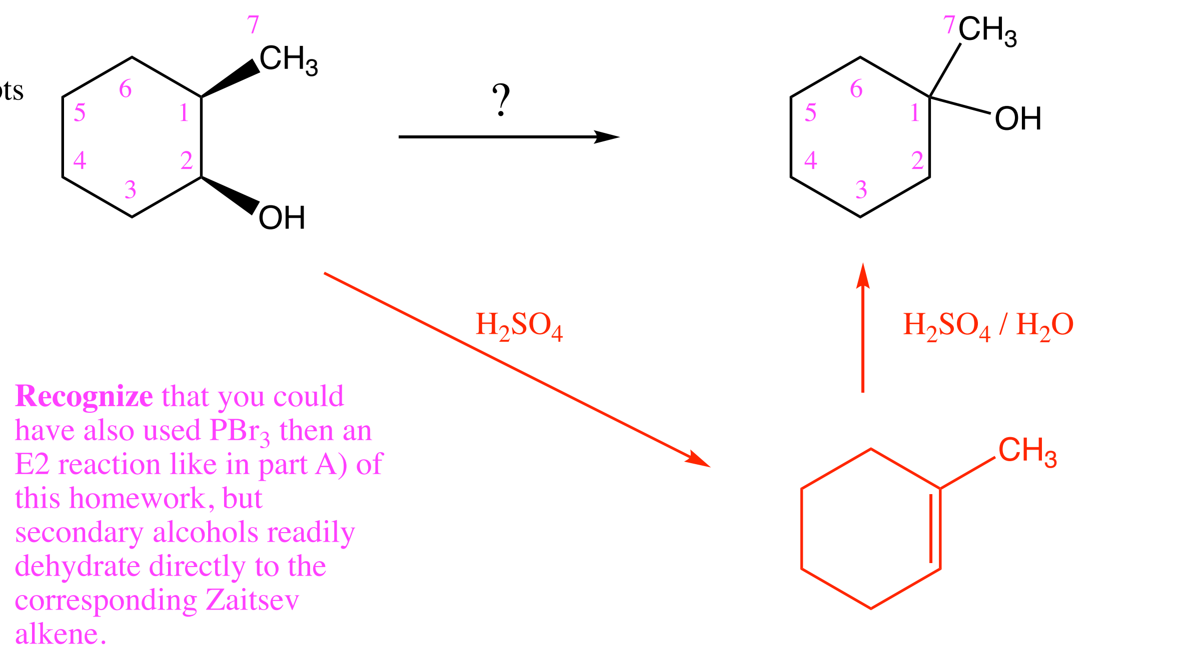
Recognize that this is a primary bromoalkane with no hydrogen atoms on the adjacent (central) carbon atom (i.e. no E2 possible here), so reaction with NaOH gives the desired S_N2 product

1. (cont.) All the carbon atoms of the product(s) must come from the starting material(s) shown.

C) 7 pts

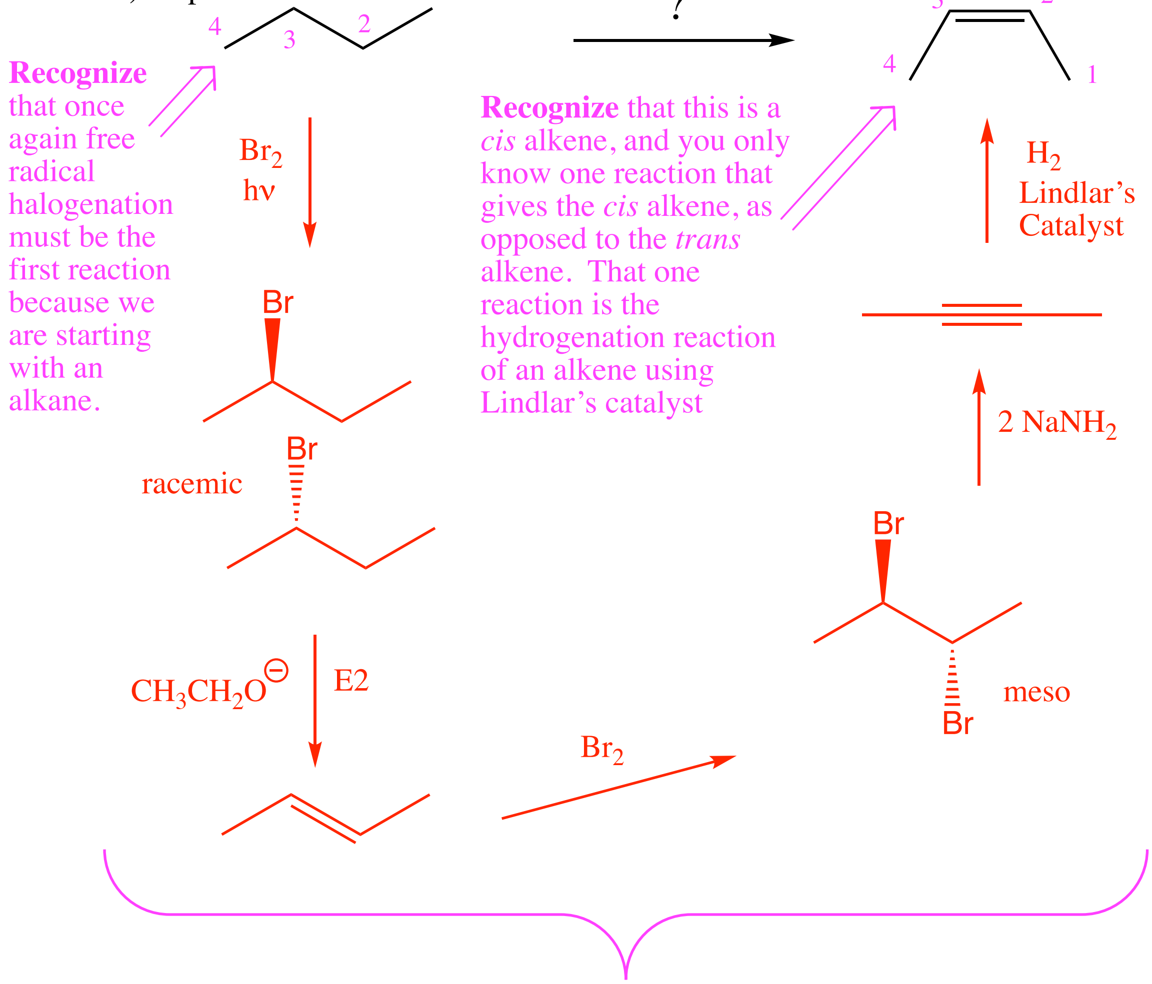


D) 4 pts



1. (cont.) All the carbon atoms of the product(s) must come from the starting material(s) shown.

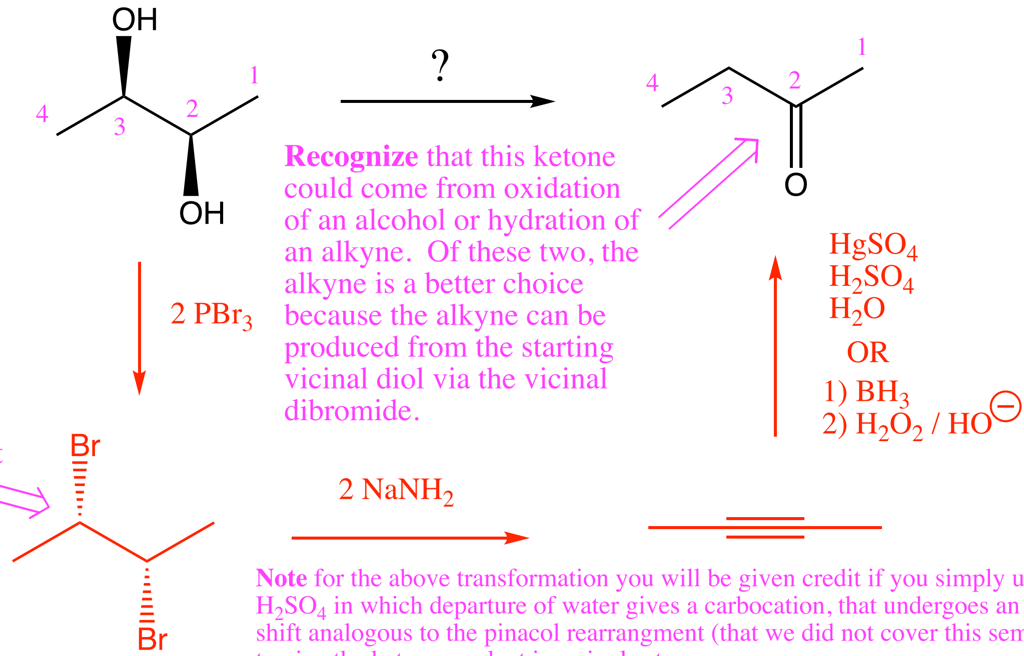
E) 13 pts



Recognize that the rest of the process is just taking the alkane to an alkyne, which is the set of reactions we refer to as "I-35" on your roadmap. You should be very familiar with all of these reactions, because they show up quite often in synthesis problems.

1. (cont.) All the carbon atoms of the product(s) must come from the starting material(s) shown.

F) 7 pts

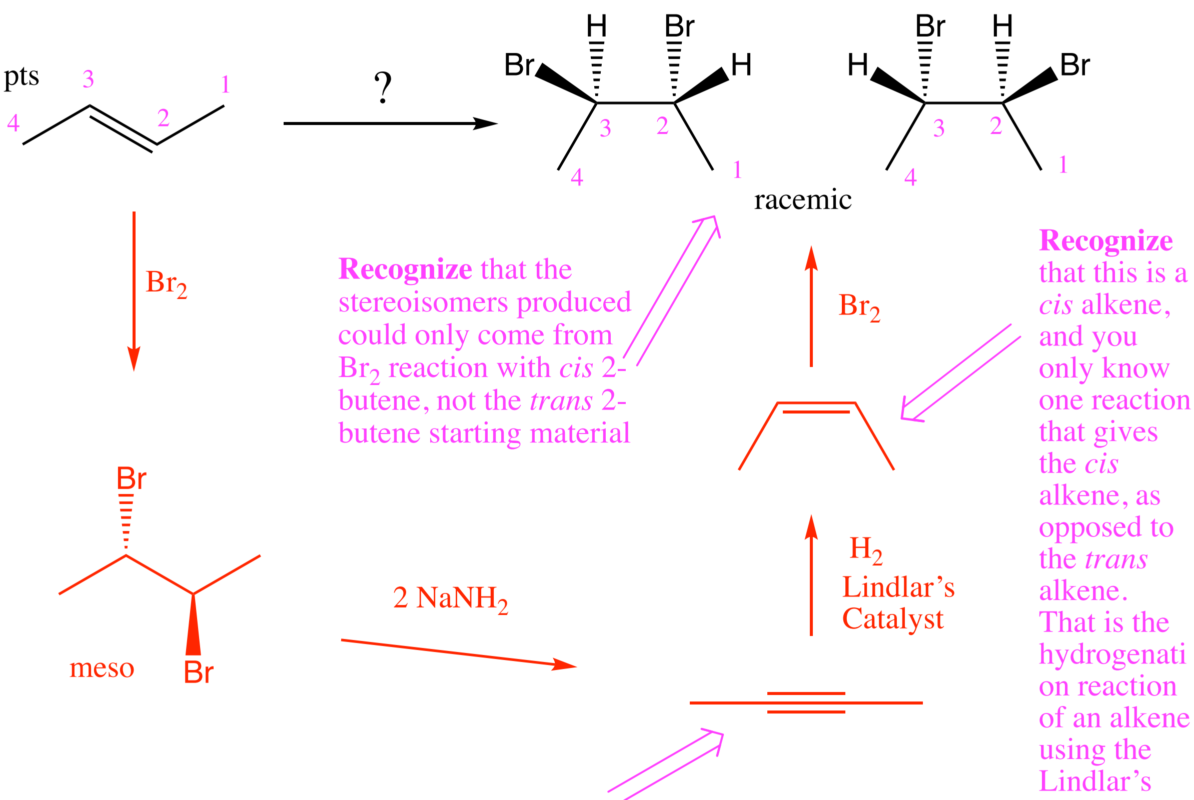


Recognize that you need two equivalents of PBr_3 to convert both OH groups to Br with inversion of configuration at the chiral ceners.

Recognize that this ketone could come from oxidation of an alcohol or hydration of an alkyne. Of these two, the alkyne is a better choice because the alkyne can be produced from the starting vicinal diol via the vicinal dibromide.

Note for the above transformation you will be given credit if you simply used H_2SO_4 in which departure of water gives a carbocation, that undergoes an H atom shift analogous to the pinacol rearrangement (that we did not cover this semester) to give the ketone product in a single step.

G) 10 pts



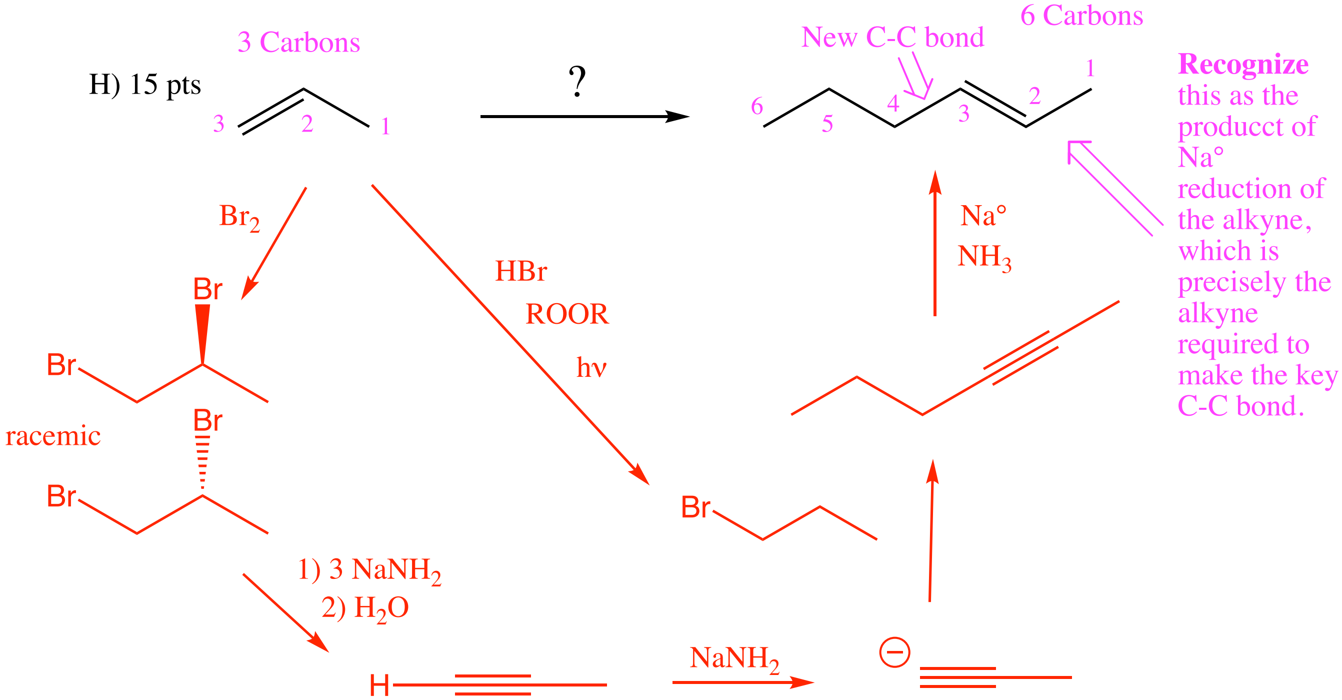
Recognize that the stereoisomers produced could only come from Br_2 reaction with *cis* 2-butene, not the *trans* 2-butene starting material

Recognize that this is a *cis* alkene, and you only know one reaction that gives the *cis* alkene, as opposed to the *trans* alkene. That is the hydrogenation reaction of an alkene using the Lindlar's catalyst

Recognize that the desired alkyne can come from the starting alkene via the often used reaction sequence of halogenation of the alkene, followed by double elimination of the vicinal dihalide.

1. (cont.) All the carbon atoms of the product(s) must come from the starting material(s) shown.

H) 15 pts



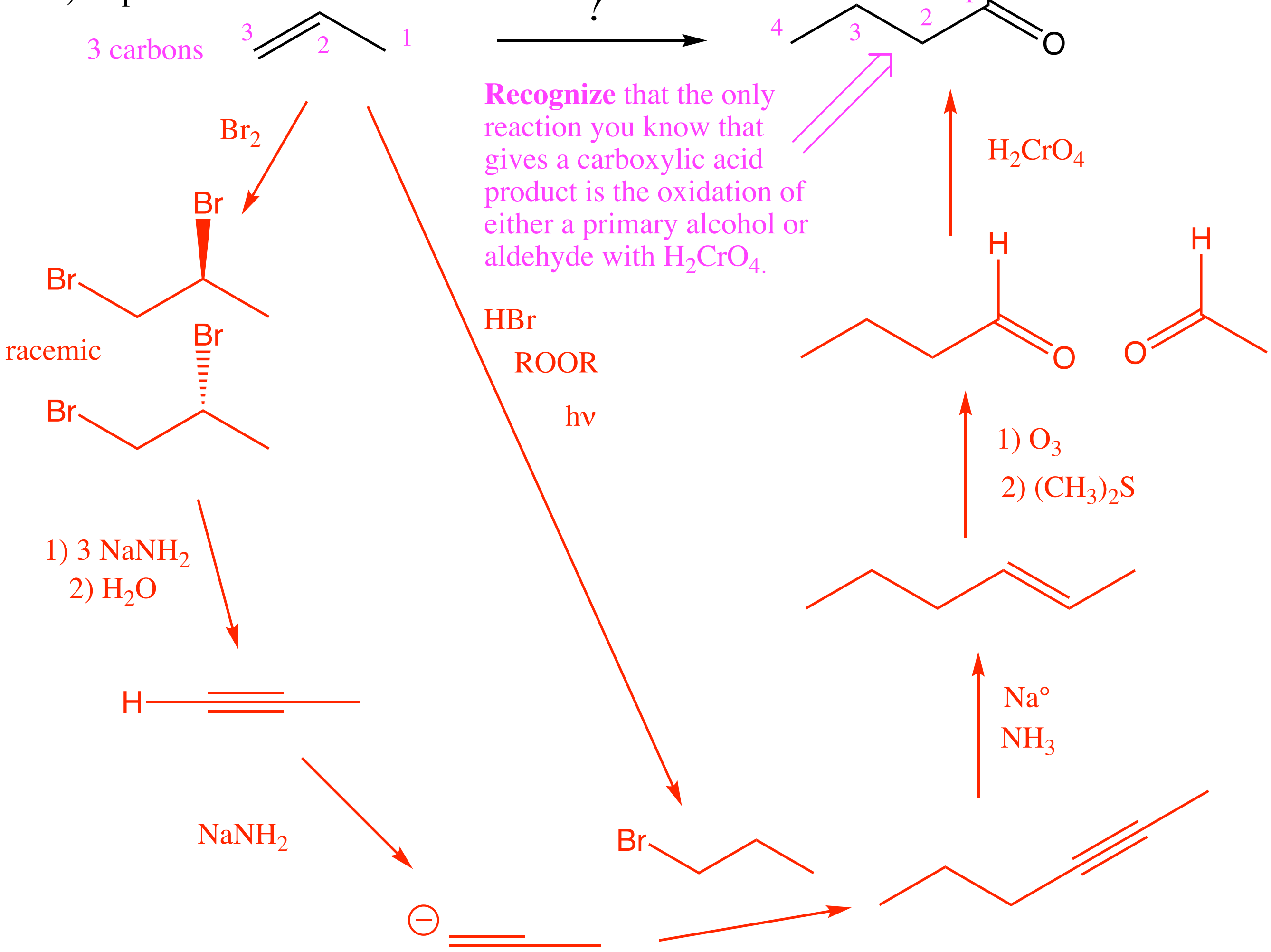
Recognize that the alkene product has 6 carbons, exactly twice the number of the starting material. That means two molecules derived from the starting material were reacted to make a new carbon-carbon bond. The only reaction you know that can generate a new carbon-carbon bond is the S_N2 reaction of a deprotonated terminal alkyne with a primary haloalkane. Thus, the problem comes down to conversion of the staring propene into an alkyne using halogenation and double elimination. Propene can be converted into 1-bromopropane in one step using the non-Markovnikov, free radical addition of H-Br in the presence peroxide (ROOR) and light.

Note Besides the reduction of an alkyne using Na°, the alkene product could have been the Zaitsev product derived from E2 elimination of an haloalkane or dehydration of an alcohol. We can rule out these latter two reactions in favor of the alkyne reduction reaction because we know that the alkyne must be involved since a C-C bond was made.

1. (cont.) All the carbon atoms of the product(s) must come from the starting material(s) shown.

(Hint: This one is very much related to the last problem)

I) 20 pts



Recognize that the key to this problem is counting carbons correctly. We have four carbons in the product, but only three in the starting material. From this you conclude that in this synthesis there must be a C-C bond forming reaction to give a molecule with 6 carbon atoms, followed by an ozonolysis to give a product with only 4 carbons. In addition, we gave the hint that the last problem's answer was related, so we hoped you would realize that an ozonolysis of the product from problem H) would give an aldehyde with the required 4 carbon atoms. Oxidation of the 4-carbon aldehyde product of ozonolysis gives the carboxylic acid product.