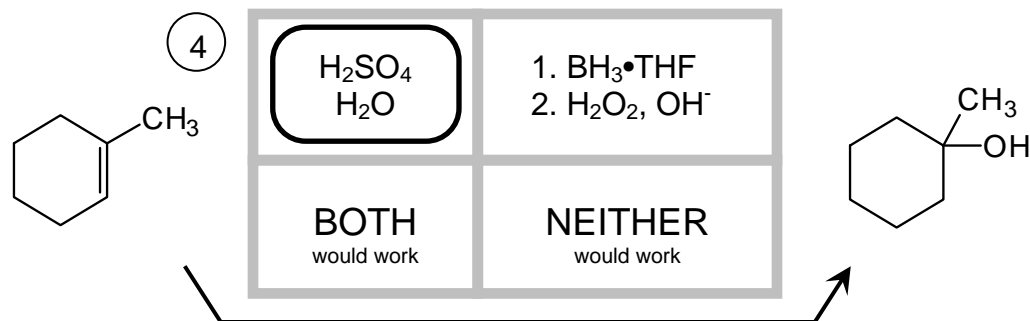
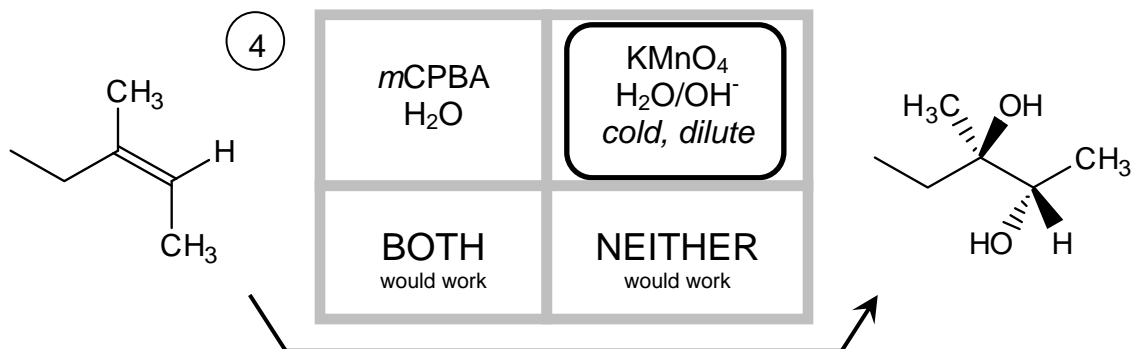


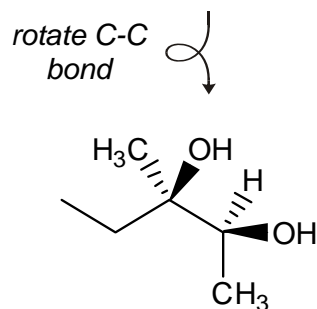
1. (16 pts) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**

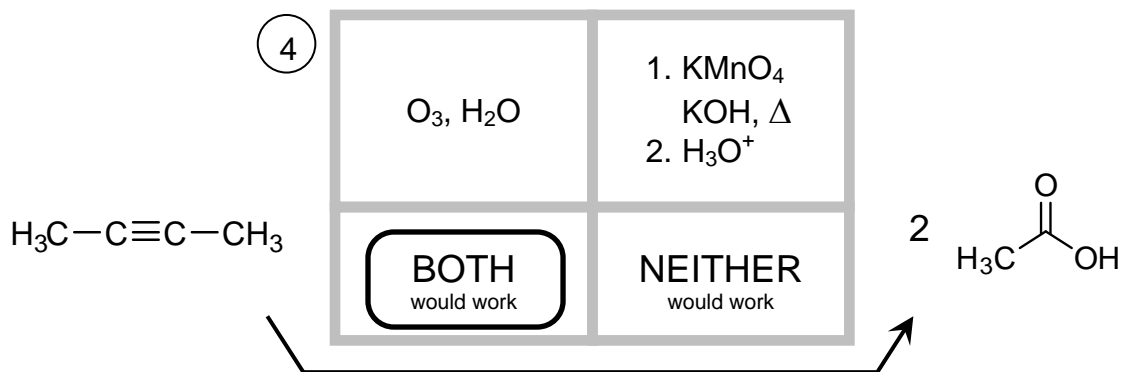


Both of these are methods for adding H-OH across a double bond. The first protocol adds Markovnikov (with -OH attached to the more substituted carbon), while the second adds anti-Markovnikov. The product here has -OH attached to the more substituted carbon of the starting alkene (Markovnikov).

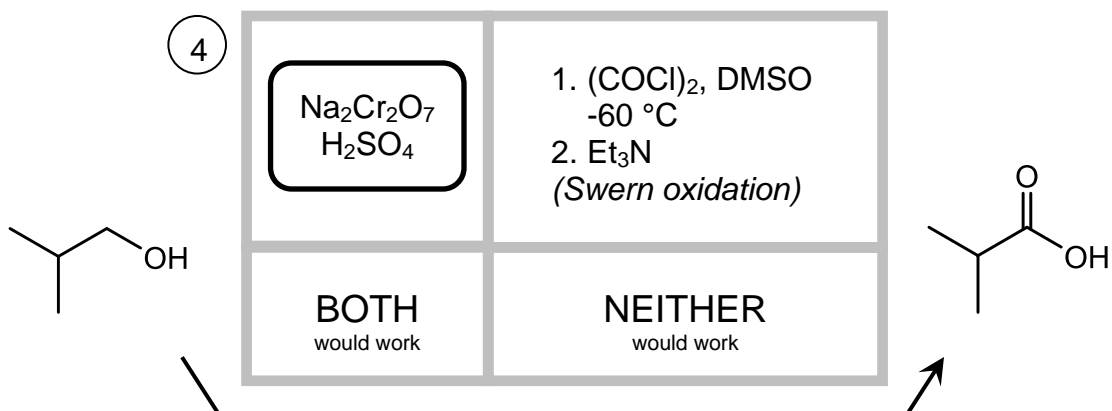


Both of these are methods for dihydroxylation of an alkene—the first accomplishes *anti*-dihydroxylation, and the second *syn*-dihydroxylation. If we redraw the product so that the groups are where they started, we can see that the -OH's were added to the same (*syn*) face.



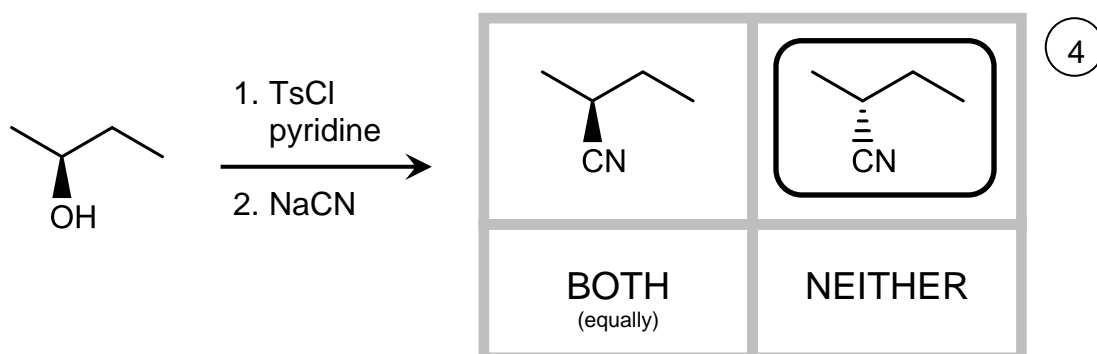


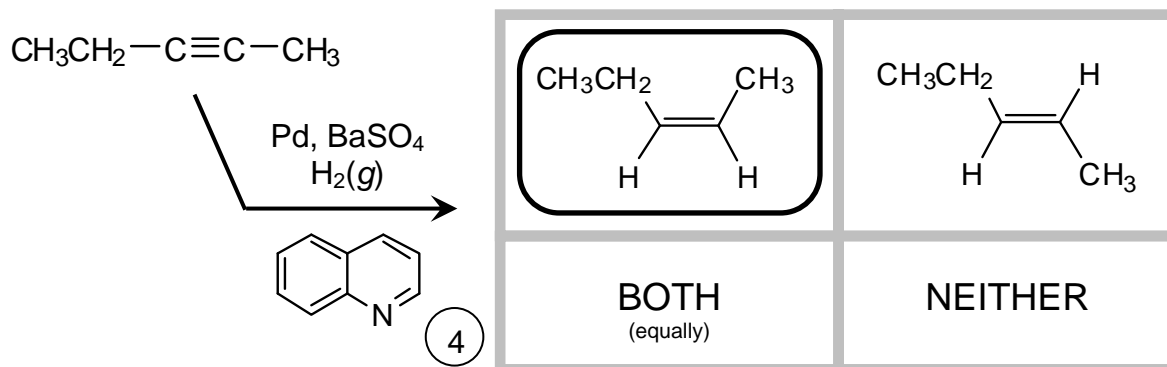
Both methods cleave triple bonds and convert each triple-bonded carbon atom to a carboxylic acid.



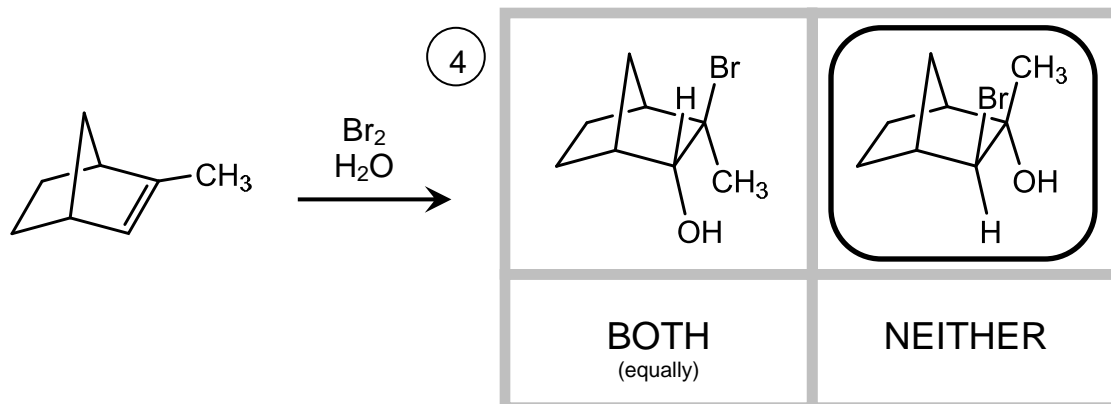
Here, the alcohol is oxidized all the way to a carboxylic acid. This requires a strong oxidizing agent, like $Na_2Cr_2O_7$, rather than a mild oxidizing method, like Swern oxidation.

2. (8 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**



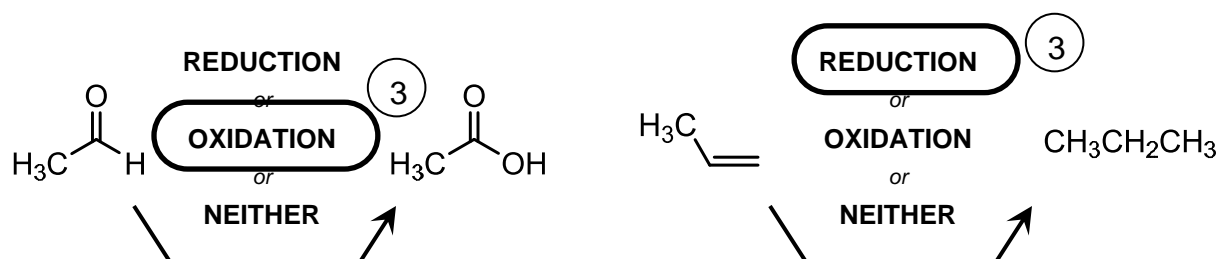


Hydrogenation with a “poisoned” Pd/BaSO₄ catalyst accomplishes *syn*-hydrogenation of an alkyne, just once, to give the *cis*-alkene.

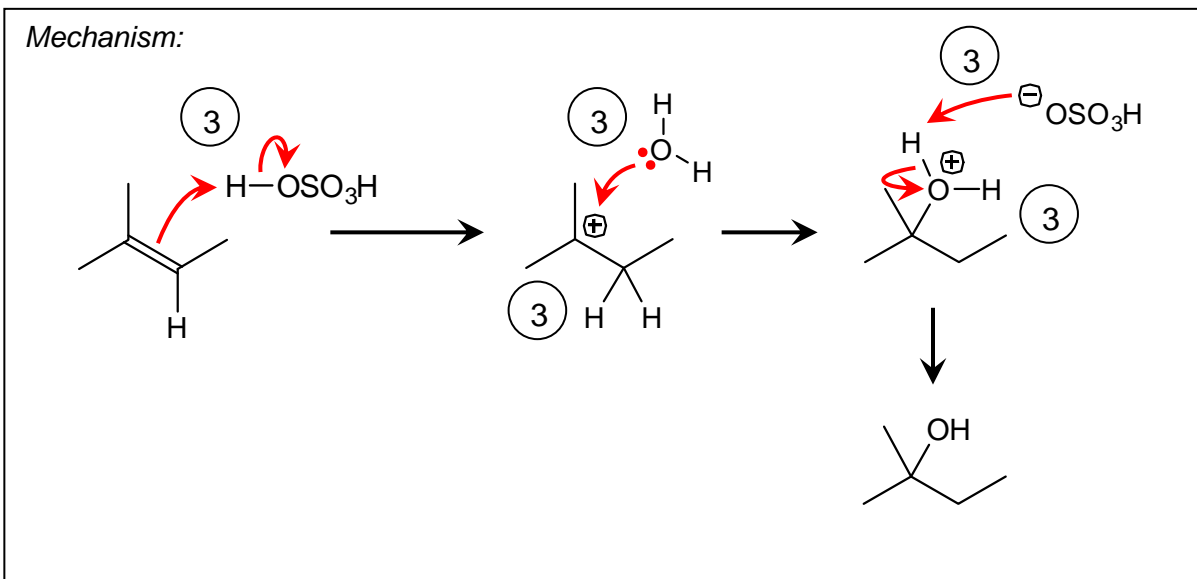
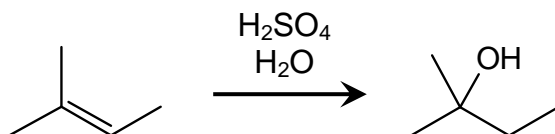


Rubric (Problems 1 & 2): 4 points each.

3. (6 pts) Is each of the model reactions below an oxidation, a reduction, or neither? **Circle one answer only for each reaction.**



4. (30 pts) **Draw a mechanism** (using “electron pushing”) for each of the reactions shown below. Draw each mechanistic step explicitly; don’t cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don’t invoke generic species. (E.g., don’t use “H-A” as a generic acid.)



Rubric for both parts: (15 points total each)

Overall notes:

Overall, the minimum score for each step is zero; errors in a step cannot earn you negative points that count against another, correct step.

Things that have left (e.g., HSO_3^- from H_2SO_4) and spectators may be omitted. Each proton transfer must be shown explicitly, with two arrows (one to proton, one from proton-acid bond).

-2 points, for each arrow in each step, for errors (including omission) in drawing one arrow in a multi-arrow step. Arrow must start at an electron pair (either a bond or a lone pair), and end at nucleus or bond where electrons will newly interact.

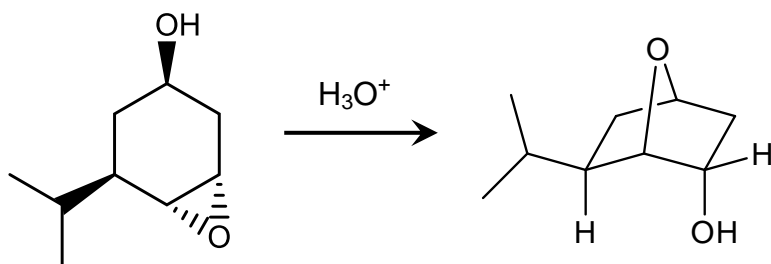
-2 points for each error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.

-2 points for each step combined with another, taken off each step. (So, you would get 6 points total for combining two 6-point steps.)

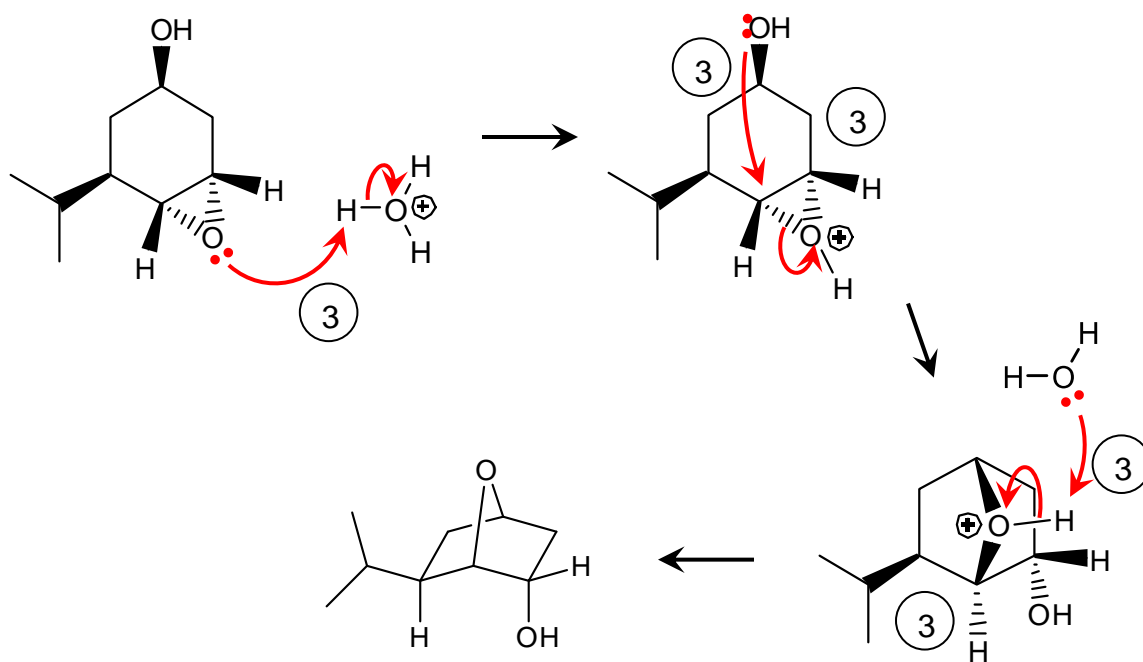
-2 points for each use of a generic or incorrect acid/base. Only H_3O^+ or H_2SO_4 can be used as the acid, and only H_2O or HSO_3^- can be used as the base—that’s it.

3 points for each arrow-pushing step.

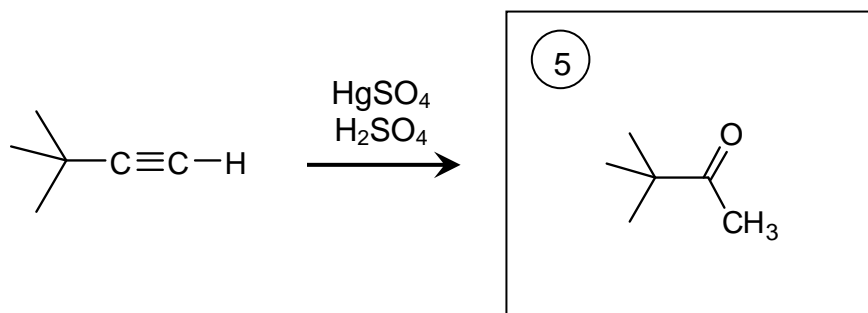
3 points for each intermediate.



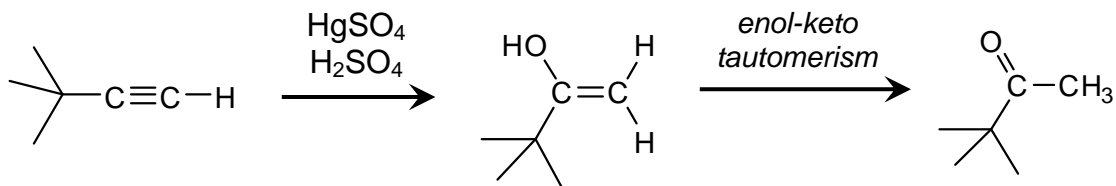
Mechanism:



5. (15 pts) For each of the reactions below, **fill in the empty box corresponding to products**. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".



This reagent set accomplishes Markovnikov addition of H-OH (with the -OH attached to the more substituted alkyne carbon); the resulting enol then isomerizes to form the ketone.

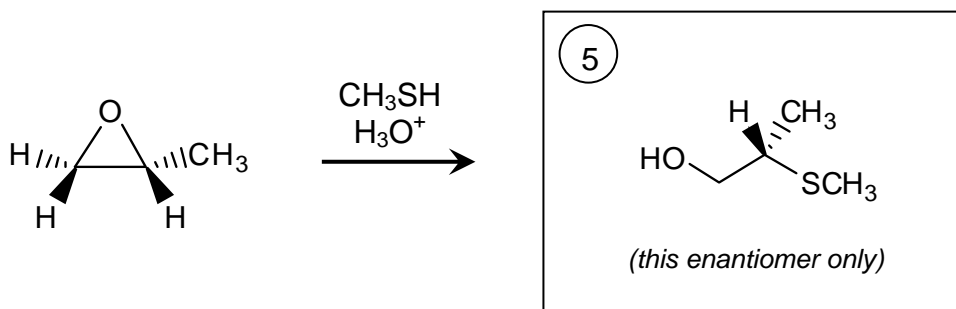


Rubric:

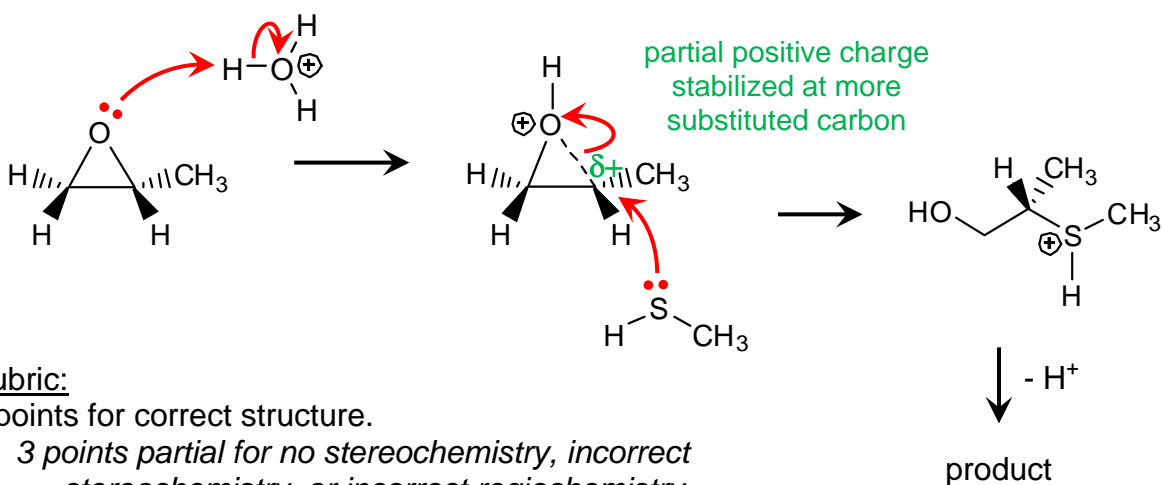
5 points for correct structure.

3 points partial for terminal aldehyde, or for enol intermediate.

-2 points for each clearly trivial structure mistake (especially too many or too few carbons).



In acid, epoxides are attacked by nucleophiles at the more substituted carbon:

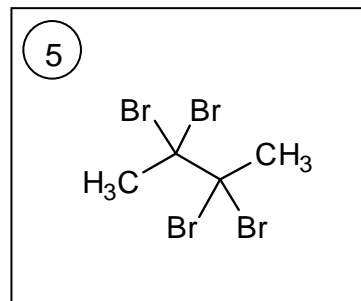
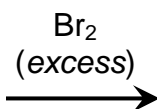
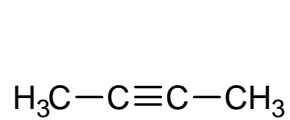


Rubric:

5 points for correct structure.

3 points partial for no stereochemistry, incorrect stereochemistry, or incorrect regiochemistry (nucleophile attacks other carbon)

-2 points for each clearly trivial structure mistake.



If there's at least two equivalents of Br_2 available, it adds twice.

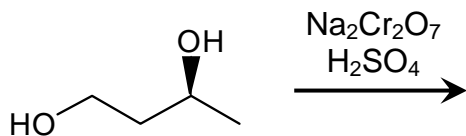
Rubric:

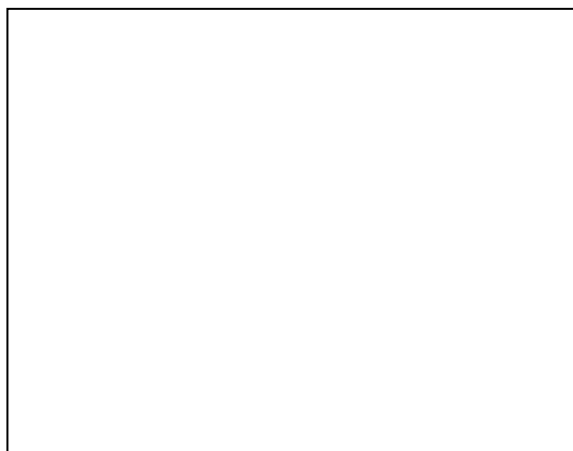
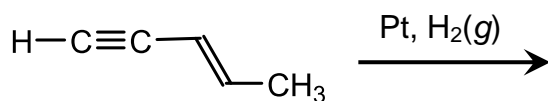
5 points for correct structure.

3 points partial for incomplete halogenation (fewer than four), or for HBr adduct.

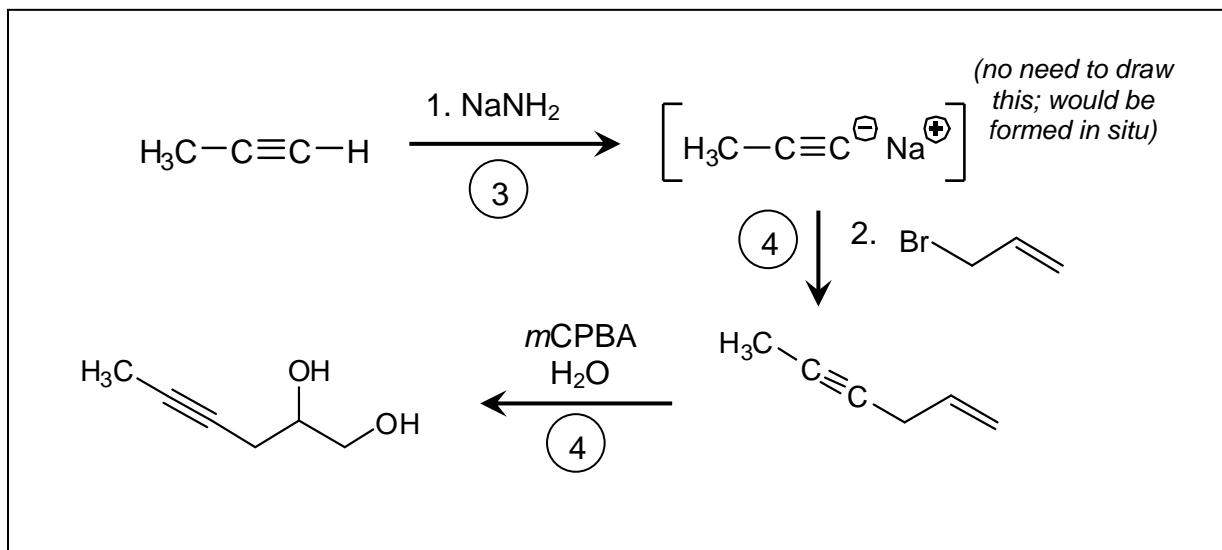
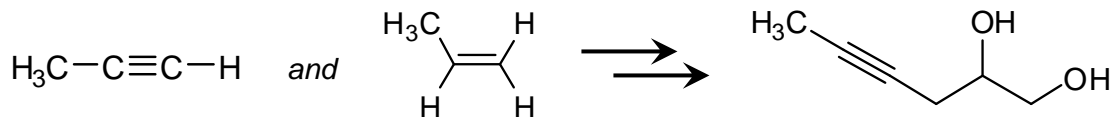
This includes brominated alkene products.

-2 points for each clearly trivial structure mistake.





6. (11 pts) For the starting materials and product shown below, **propose a multistep synthesis**. In addition to the molecules shown, you can use any reagents and reactions we've learned about in class. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.



The product of this synthesis has six carbons, and each of our starting materials has three. So if we can form a new C-C bond between the two starting pieces, that might lead us toward the product. Right now, you know of only one way to form a new C-C bond: by using an alkynyl anion to attack a carbon electrophile. You start with both of the pieces you need.

Once those pieces are connected, the last thing that needs to be done is to form a diol (a di-alcohol) from the alkene. But many methods that transform alkenes also transform alkynes, and so we need to choose a reaction that doesn't affect the alkyne. KMnO_4 is not a good choice, because it reacts with both; $m\text{CPBA}/\text{H}_2\text{O}$, on the other hand, selectively forms a diol at the alkene, because an intermediate epoxide can't be made at the triple bond. (The intermediate would be a three-membered ring with a double bond in it, and that's just too strained to exist.)

We required that your synthesis have three elements:

- (1) The alkyne needs to be deprotonated to make an alkynyl anion. The product needs a new C-C bond between the two starting materials, and this is the only way you've got so far in this class to make one. (There will be plenty more in the future.)
- (2) The two parts need to be combined in a way that they will react, and that gets us towards the product.
- (3) The alkene needs to be converted into a diol, without affecting the alkyne.

Rubric: *General notes:*

Each task is judged separately, and does not require that the synthesis makes sense, or that other tasks are correct.

-1 point for each clearly minor error in structures or reagents; if error propagates, points are taken off only for initial error.

-2 points if step reagents are incorrect, but reaction could otherwise be accomplished with correct reagents.

-2 points if reagents are correct/reasonable, but wrong step product, except for the last step (where the step product is obviously the final product).

We only gave points for correct reagents if they connected a starting material and a product in an understandable way. So, for example, just writing " NaNH_2 " in the box was not enough; it needed to connect an alkyne with something in a mechanistically meaningful way.

3 points for deprotonating alkyne with NaNH_2 .

Do not have to draw intermediate alkynylide, but if you don't, it needs to be clear from synthesis what you are doing with it next.

4 points for combining alkynyl anion with alkenyl halide.

4 points for converting alkene to diol with $m\text{CPBA}/\text{H}_2\text{O}$.

2 points partial credit for using KMnO_4 (cold, dilute), $\text{H}_2\text{O}/\text{OH}$.

2 points partial for using OsO₄.

2 points partial for converting alkene to diol (using any chemistry above) before connecting to alkyne.