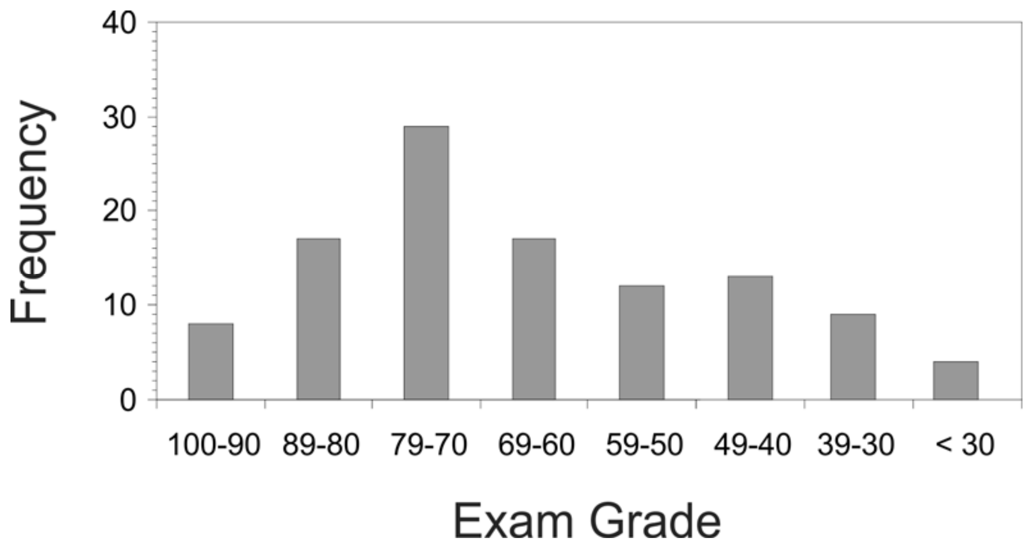
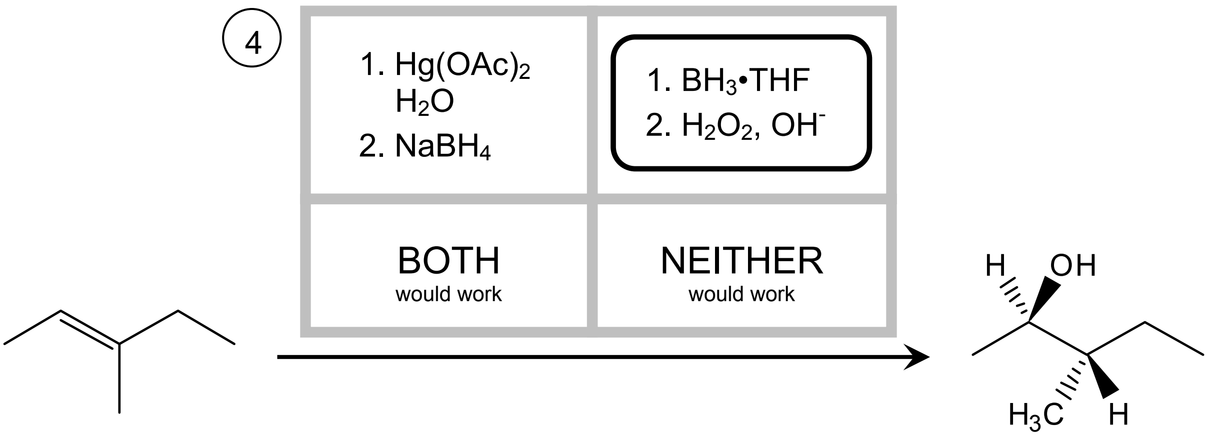
Exam 3
Answer Key

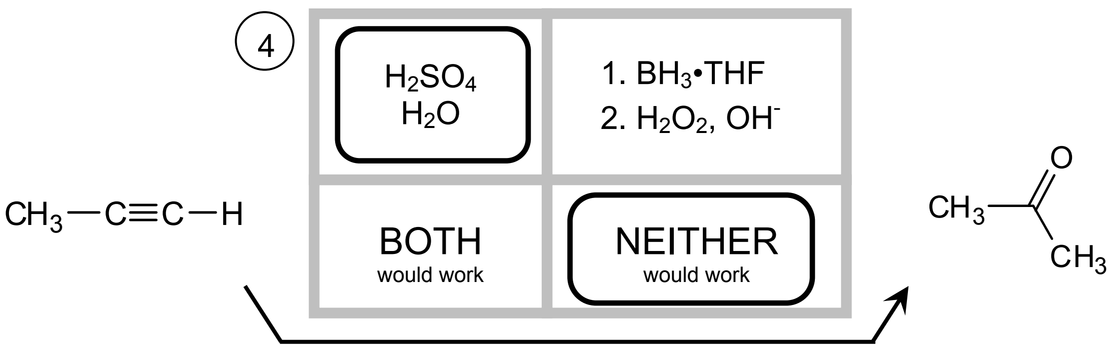
Exam 3 Mean:	65
Exam 3 Median:	69
Exam 3 St. Dev.:	19



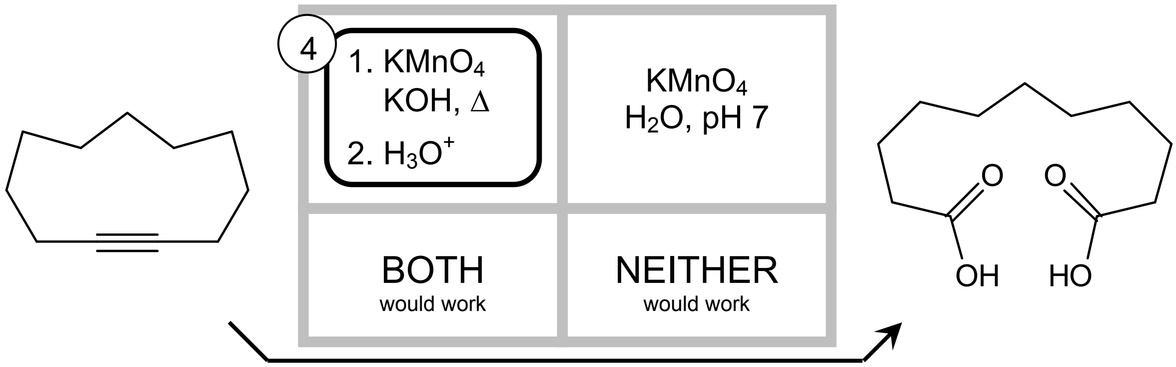
1. (12 pts) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of 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 less substituted carbon of the starting alkene (anti-Markovnikov).

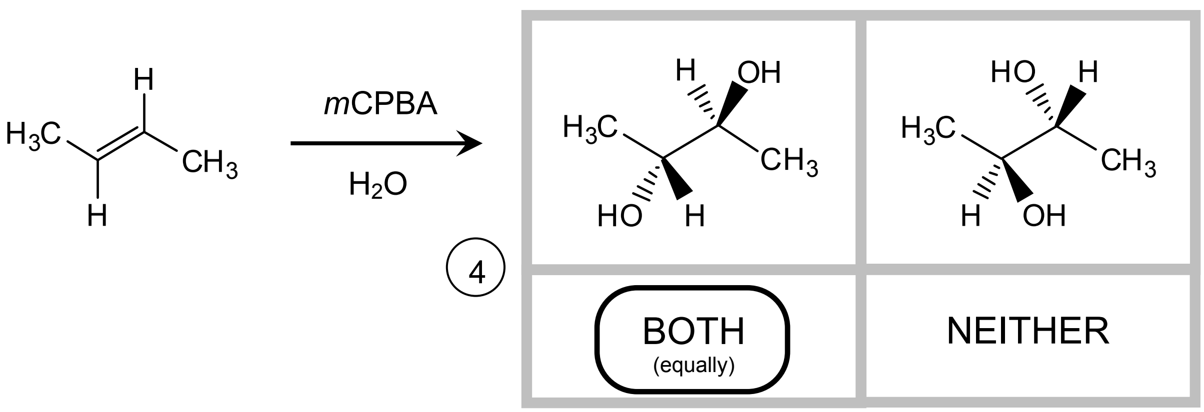


Both of these are methods, in principle, for converting an alkyne to a carbonyl (via addition of H-OH to the alkyne, followed by enol-keto tautomerism). The first would generate a ketone (via Markovnikov addition of H-OH), if I had included $HgSO_4$ in the list of ingredients (which I intended to do, but didn't). The second set of reagents generates an aldehyde (via anti-Markovnikov addition of H-OH). So the correct answer was "NEITHER", but I thought the first box was misleading, so we accepted it as well.

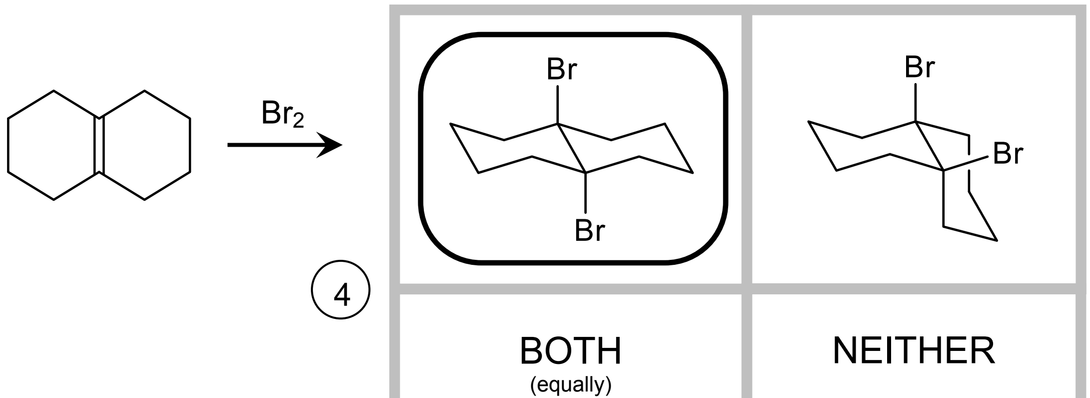


Only harsh, basic conditions will lead $KMnO_4$ to cleave the alkyne.

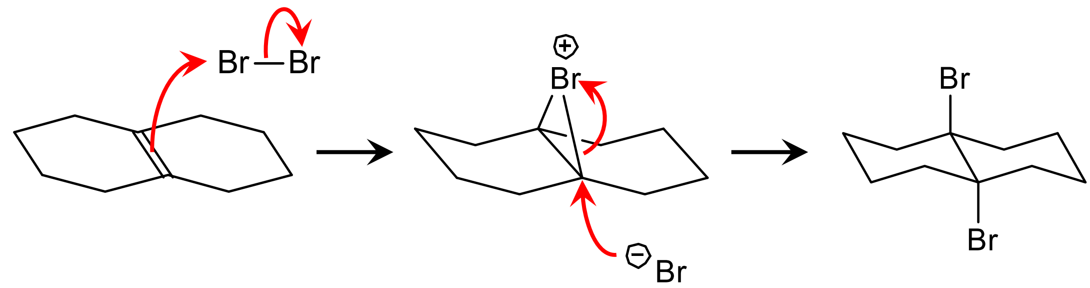
2. (16 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

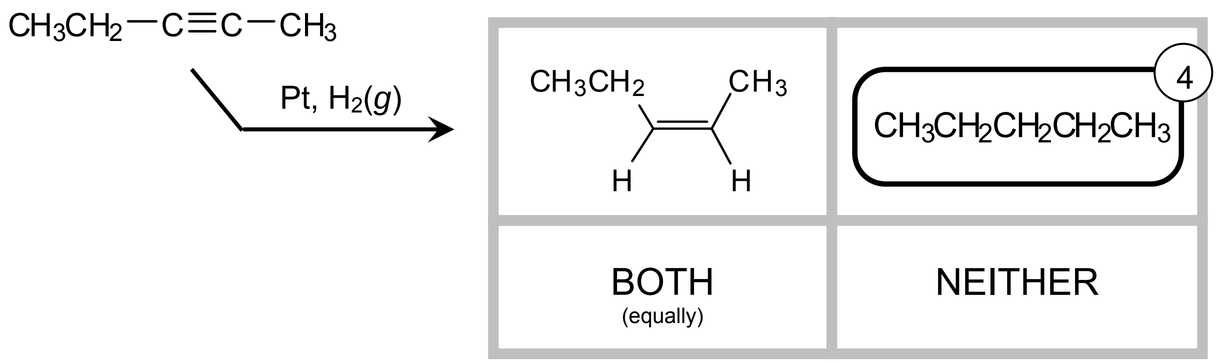


*m*CPBA/H_2O accomplishes *anti*-dihydroxylation of an alkene, such that one –OH adds to one face and the other –OH adds to the other face. That is true for both of the products shown on the right; these two molecules are actually the same molecule, and illustrate addition to either face of the alkene.

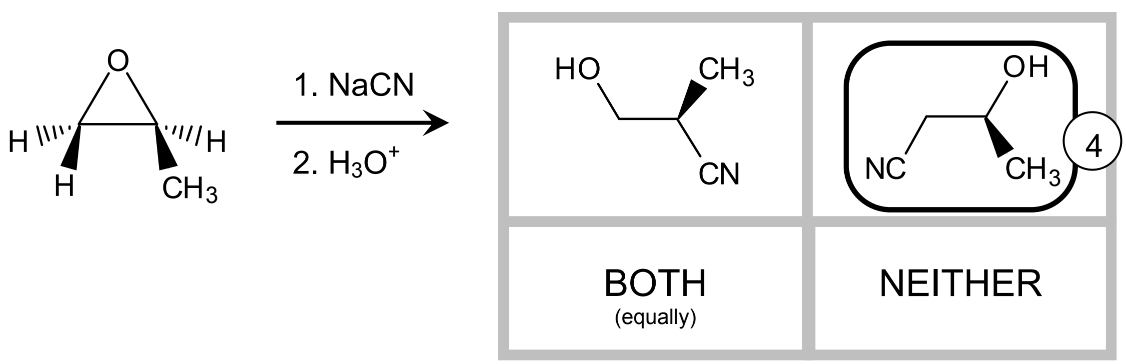


Br_2 adds *anti*- to a double bond, via backside attack of Br^- on a bromonium ion:

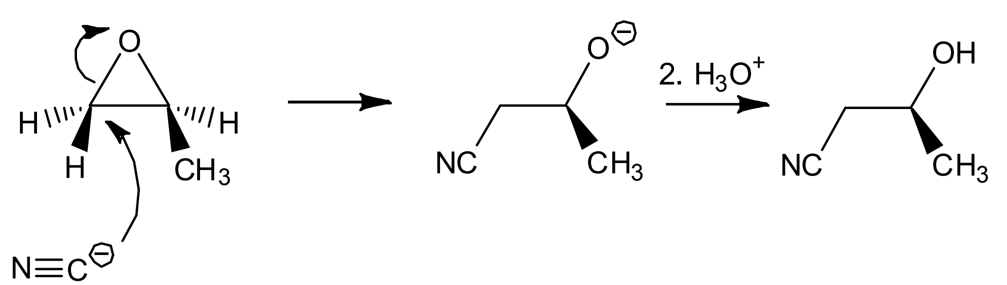




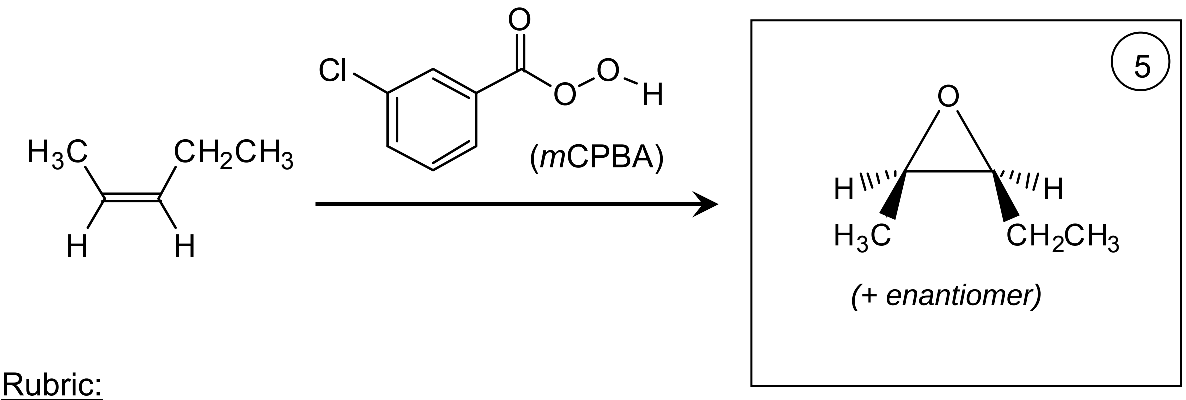
Pt/H_2 hydrogenates (adds H_2 to) both alkynes and alkenes. As a result, once this alkyne is hydrogenated to the alkene on the left, that alkene is immediately and unavoidably hydrogenated to the alkane on the right.



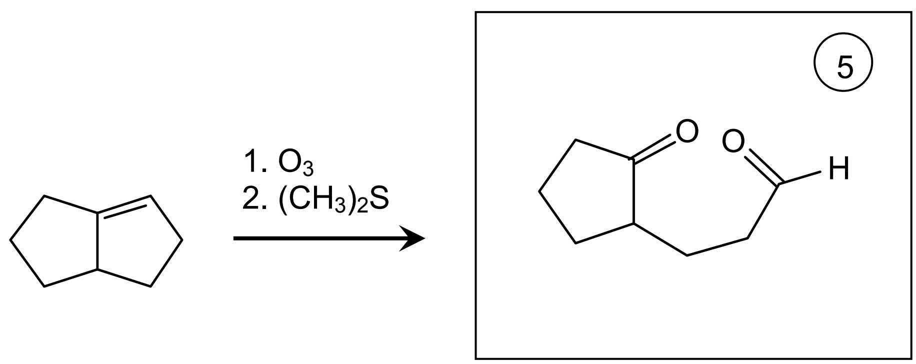
Under basic conditions (in other words, using ^-CN rather than HCN as the nucleophile), the nucleophile adds to the epoxide at the less sterically hindered position.



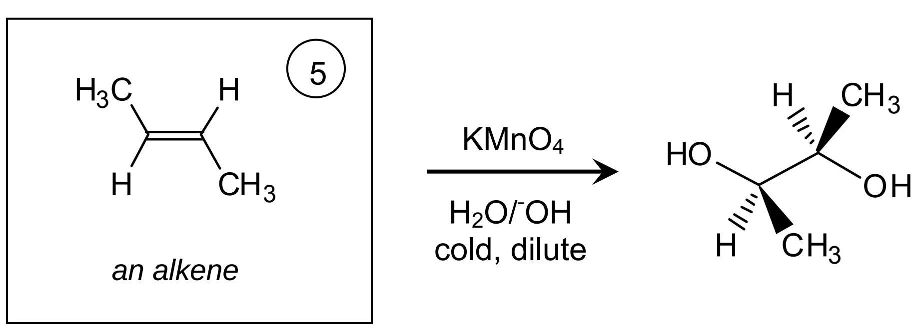
3. (20 pts) For each of the reactions below, **fill in the empty box corresponding to reactants or products**. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".



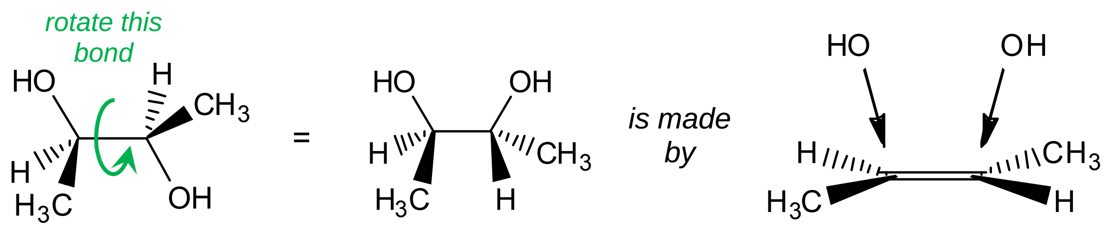
Rubric:
5 points for correct structure.
4 points partial for omitting "+ enantiomer".
3 points partial for incorrect stereochemistry, or for not indicating stereochemistry. (We won't also take a point for omitting "+ enantiomer" here.)
-2 points for each clearly trivial structure mistake.



Rubric:
5 points for correct structure.
No grading on stereochemistry for this problem.
-2 points for each clearly trivial structure mistake (including too many or too few carbons in the open chain).

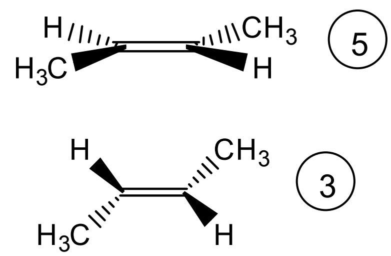


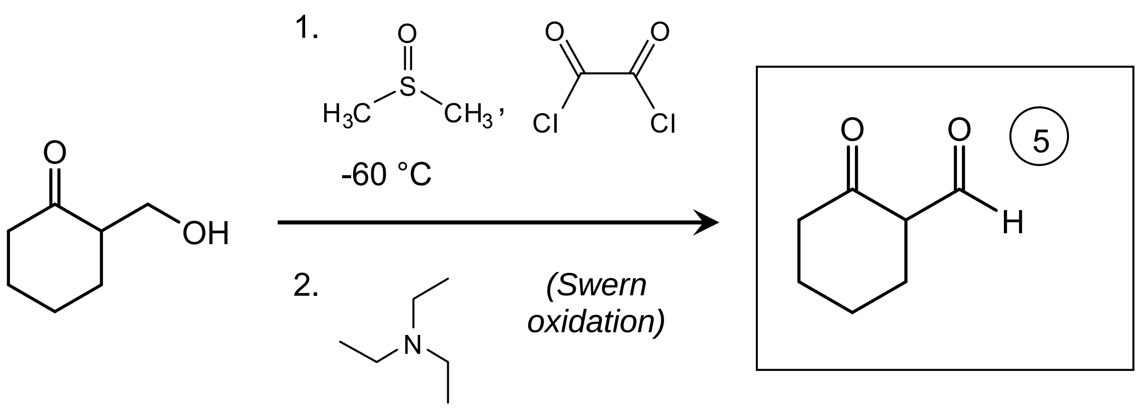
$KMnO_4$ performs *syn*-dihydroxylation on alkenes. The diol product of this reaction isn't drawn in a way that makes it clear how *syn*-dihydroxylation would happen; the two –OH groups are opposite each other in this drawing. But if we rotated the central C-C bond, it would be more obvious:



So this is your starting material.

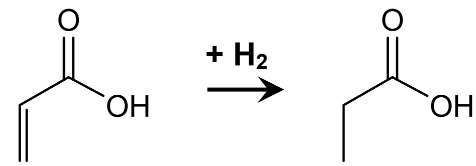
Rubric:
5 points for correct structure. You can draw your alkene in 3-D if you want, as long as it's flat.
3 points partial for cis-alkene, or for unclear stereochemistry. That includes drawing an alkene that isn't flat. Alkenes that look like this one on the right get three points.
-2 points for each clearly trivial structure mistake.





Rubric:
5 points for correct structure.
No grading on stereochemistry for this problem.
*2 points partial for aldehyde **and** changing ketone.*
2 points partial for oxidizing to carboxylic acid.
-2 points for each clearly trivial structure mistake (including too many or too few carbons in the open chain).

4. (9 pts) Identify each of the transformations shown as a reduction, an oxidation, or neither. **Circle only one answer for each transformation**.



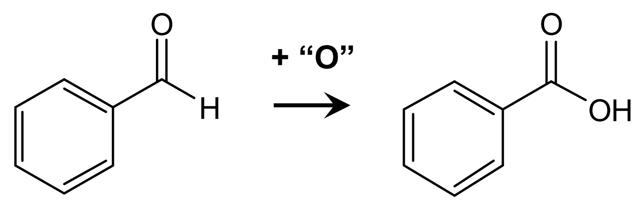
3 **REDUCTION**

or

OXIDATION

or

NEITHER



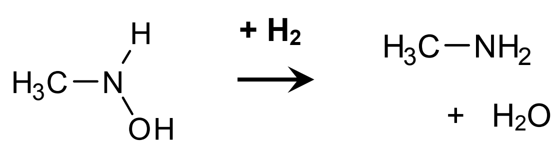
REDUCTION

or

3 **OXIDATION**

or

NEITHER



3 **REDUCTION**

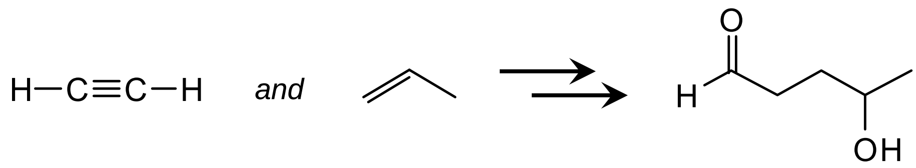
or

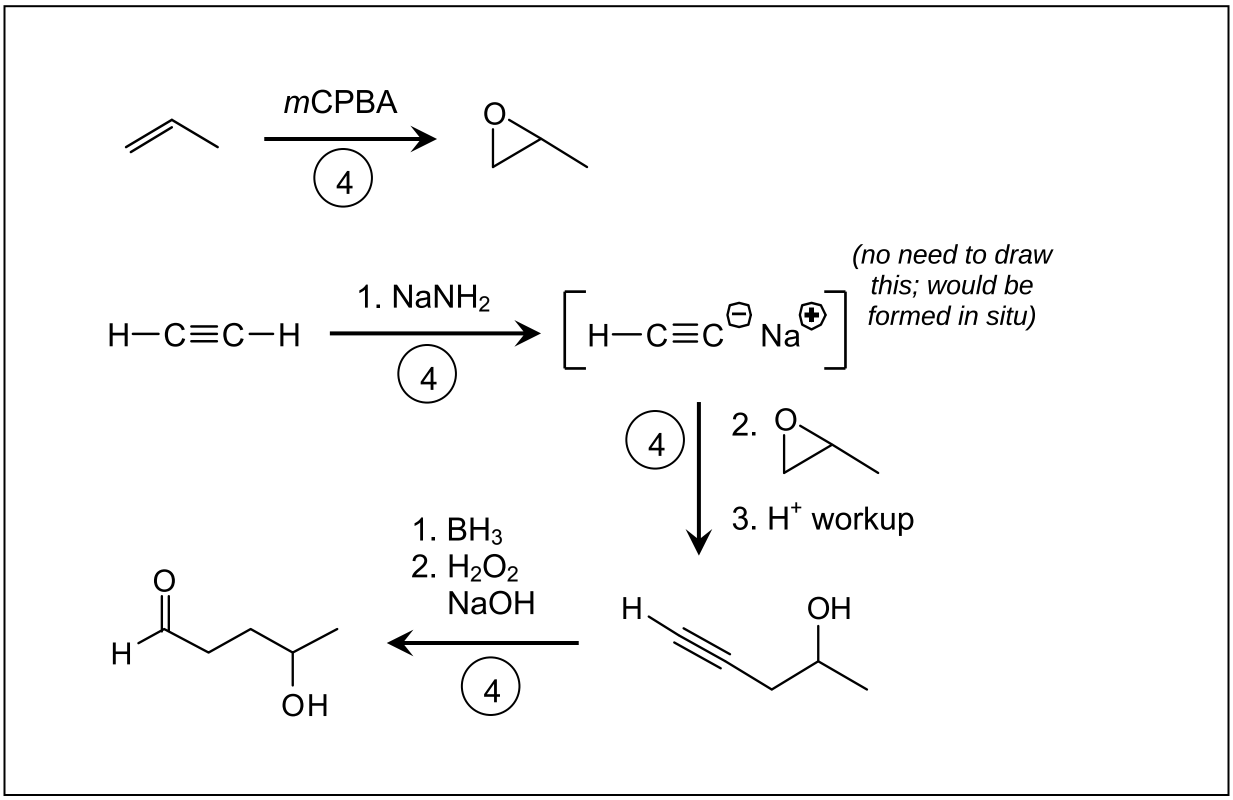
OXIDATION

or

NEITHER

5. (16 pts) For the starting materials and product shown on the next page, **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.

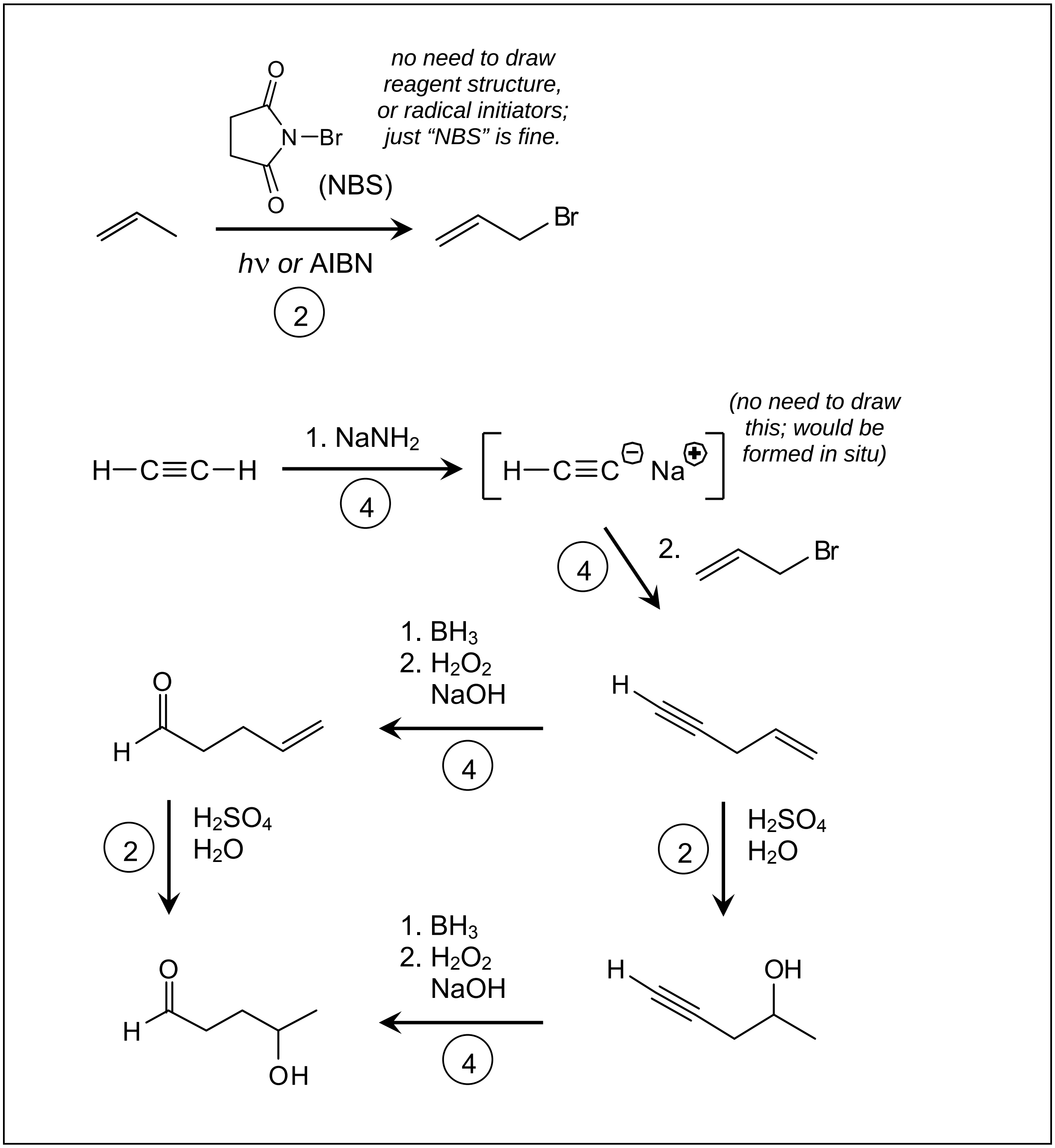




We required that your synthesis have four elements:

(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 alkene needs to be prepared to accept that alkynyl anion, preferably in a way that will lead directly to the product alcohol. There are a couple of ways to do this.
(3) The two parts need to be combined.
(4) The alkyne needs to be converted into an aldehyde.

So, alternately (next page),



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, as long as synthesis still works toward target presented in the problem.

-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.

4 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 preparing alkene to react with alkynylide and become an alcohol.

Can be via epoxide (4 points), or allylic halogenation (2 points) followed by Markovnikov addition of H-OH (2 points).

2 points partial for any other reaction that introduces a halogen. Any other method will either fail in alkynyl step (Br_2/H_2O), not be selective or capable in later chemistry (Br_2, HBr, HBr/peroxide), or have side reactions ($Br_2/h\nu$).

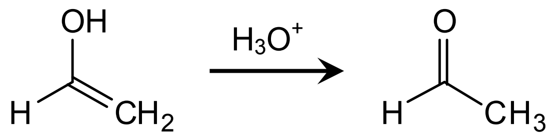
4 points for combining alkynyl anion with any alkyl halide or epoxide to create new C-C bond.

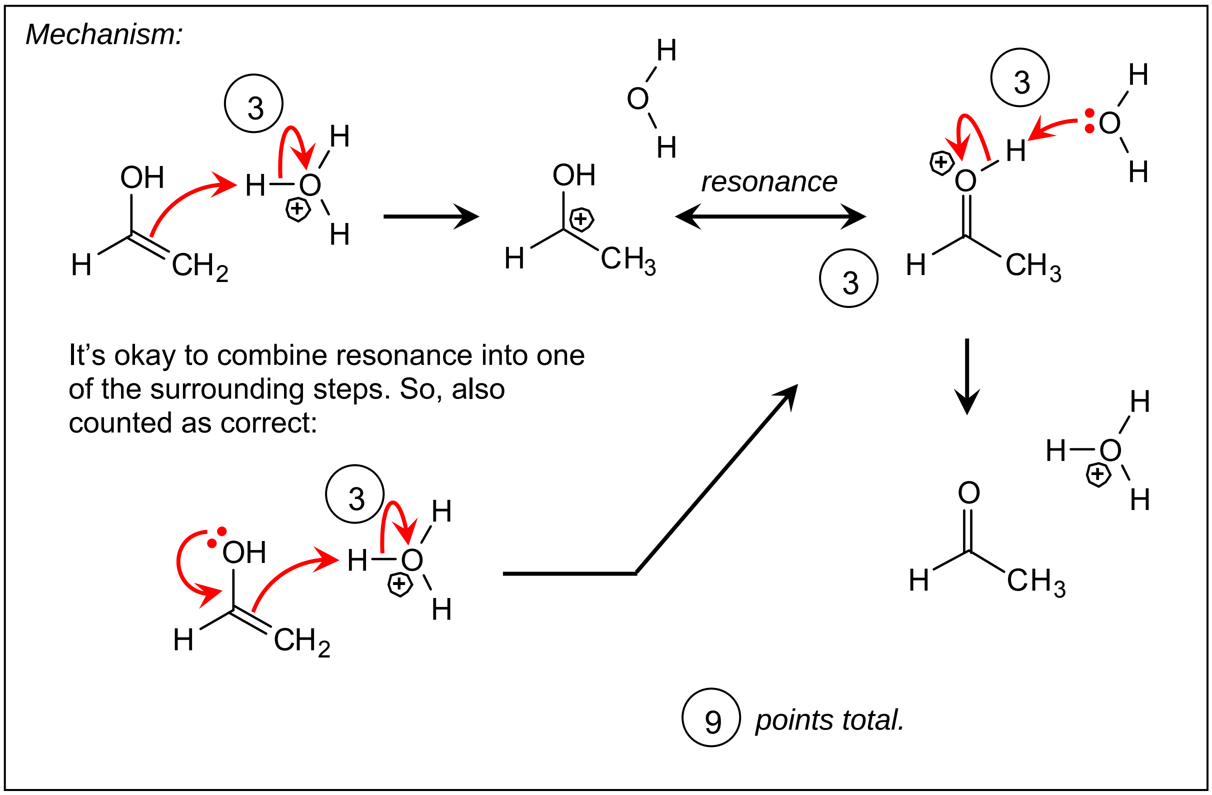
Reaction must work to receive these points. No points for combining alkynylide with any alcohol.

4 points for converting alkyne to aldehyde using BH_3.

2 points partial for using $HgSO_4$ (Markovnikov) instead.

6. (27 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: *(9 points total)*

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., H_2O from H_3O^+) and spectators may be omitted.

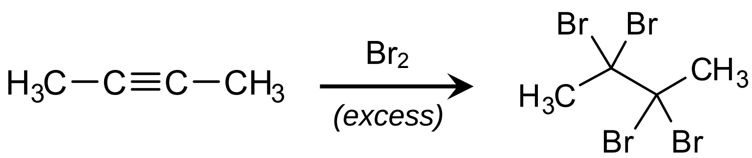
Each proton transfer must be shown explicitly, with two arrows (one to proton, one from proton-acid bond).

Resonance is not technically a mechanistic "step"; it is just two ways of illustrating the same structure. As a result, we did not judge arrow pushing on resonance. In addition, resonance could be integrated into either previous or subsequent mechanistic step by adding an arrow.

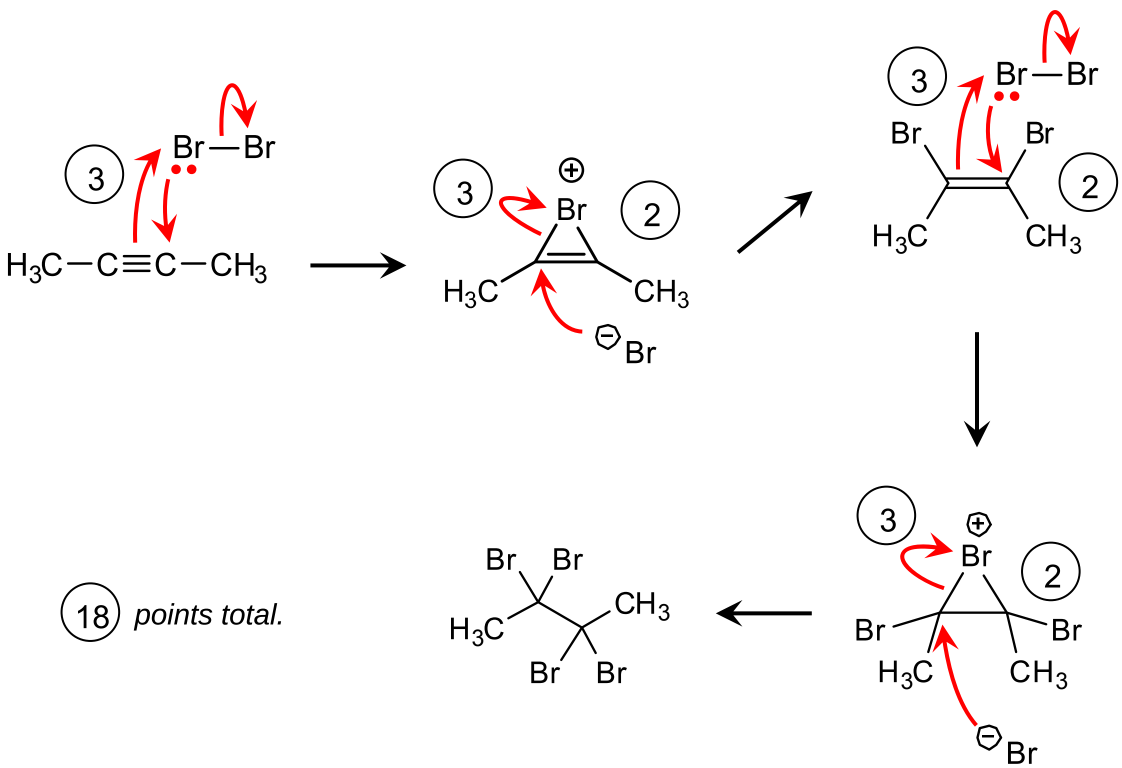
-2 points, for each arrow in each step, for errors (including omission) in drawing arrows. Arrow must start at an electron pair (either a bond or a lone pair), and end at nucleus or bond where electrons will newly interact.

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

3 points for each set of curved arrows.
3 points for cation intermediate (illustrated in either resonance form).



Mechanism:



Rubric: *(18 points total)*
Same as previous problem, except:
3 points for each set of curved arrows.
2 points for each intermediate.