

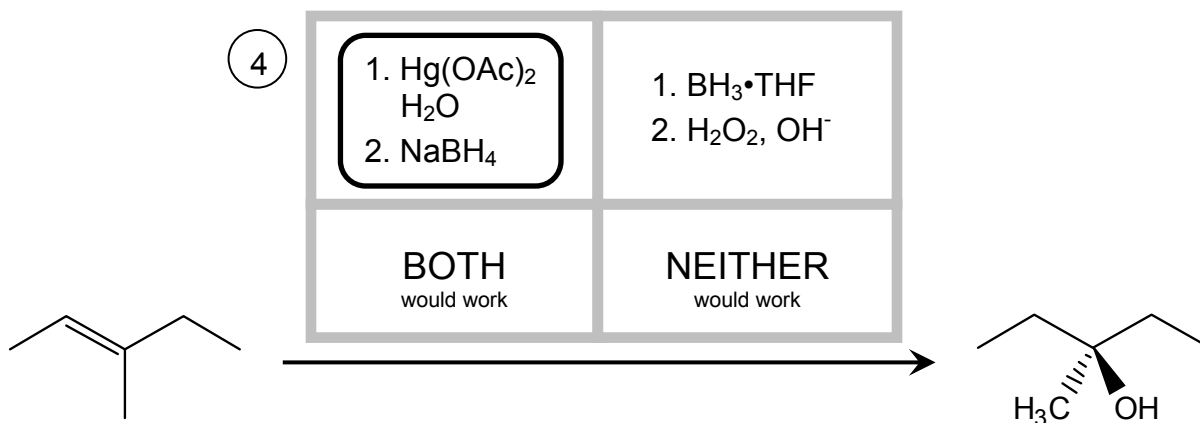
**Exam 3
Answer Key**

Exam 3 Mean: 67

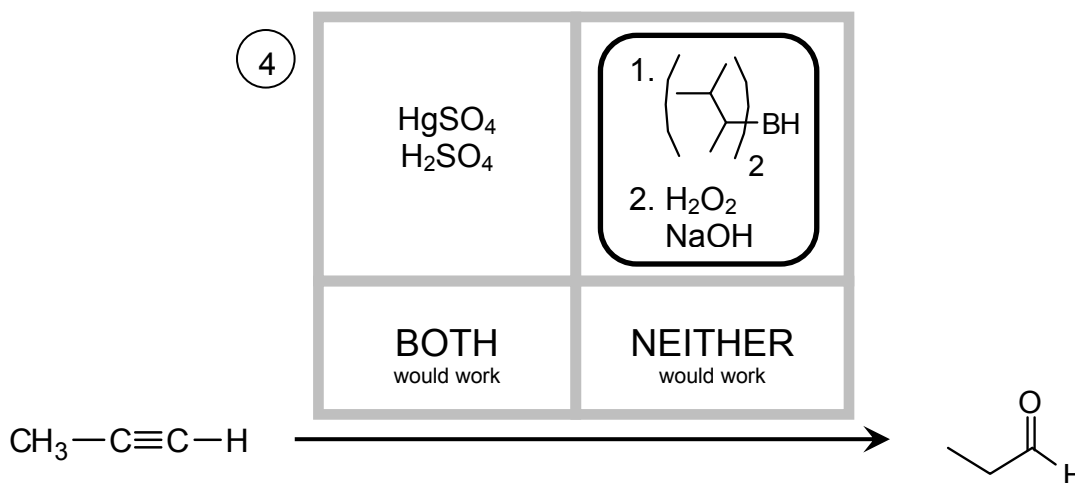
Exam 3 Median: 68

Exam 3 St. Dev.: 21

1. (8 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.**

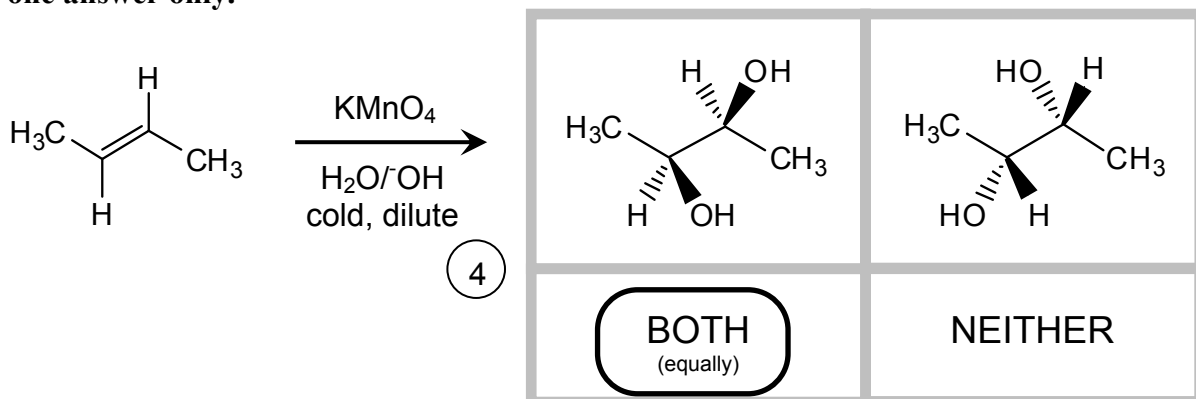


Both of these are methods for adding H-OH across a double bond. The first protocol adds Markovnikov (with -OH attached to the more substituted carbon), while the second adds anti-Markovnikov. The product here has -OH attached to the more substituted carbon of the starting alkene (Markovnikov).

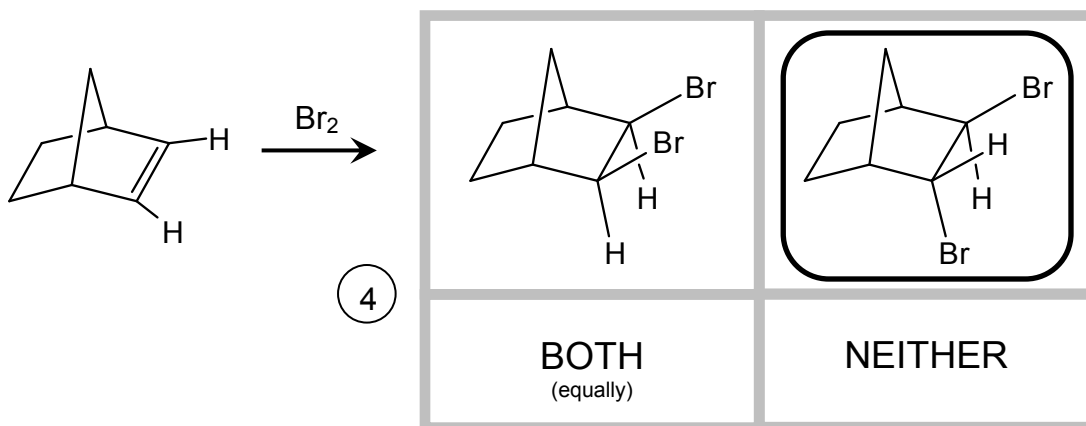


Both of these are methods for converting an alkyne to a carbonyl (via addition of H-OH to the alkyne, followed by enol-keto tautomerism). The first generates a ketone (via Markovnikov addition of H-OH), while the second generates an aldehyde (via anti-Markovnikov addition of H-OH).

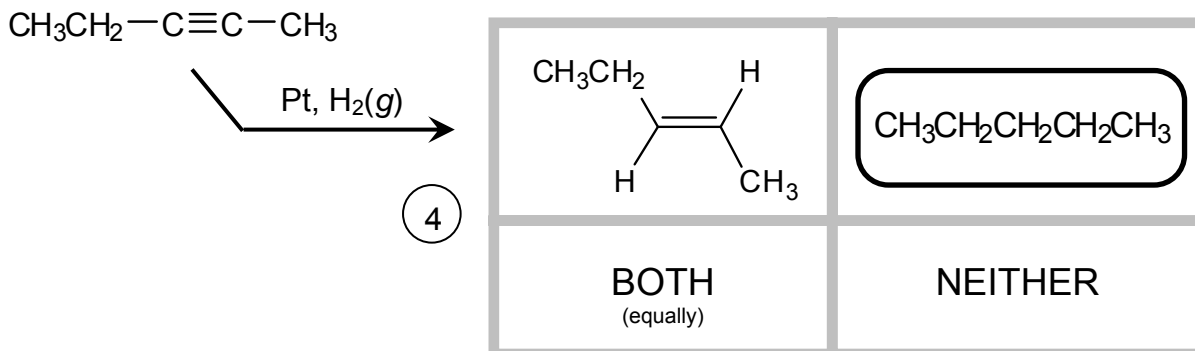
2. (16 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**



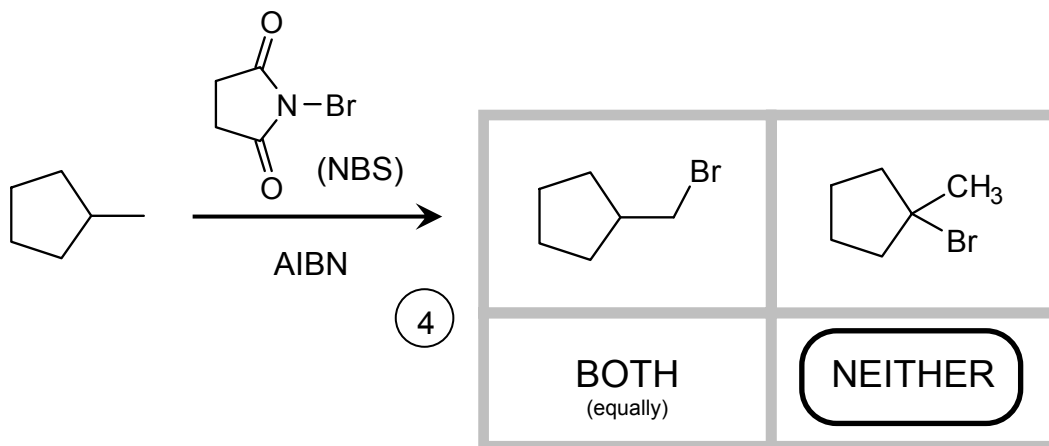
KMnO_4 accomplishes *syn*-dihydroxylation of an alkene, such that two $-\text{OH}$ groups add to the same face. That is true for both of the products shown on the right; the two are enantiomers of one another, and both enantiomers would be made here (via addition to the top and bottom faces, respectively).



Br_2 adds *anti*- to the double bond, to generate a *trans*-dibromo product.

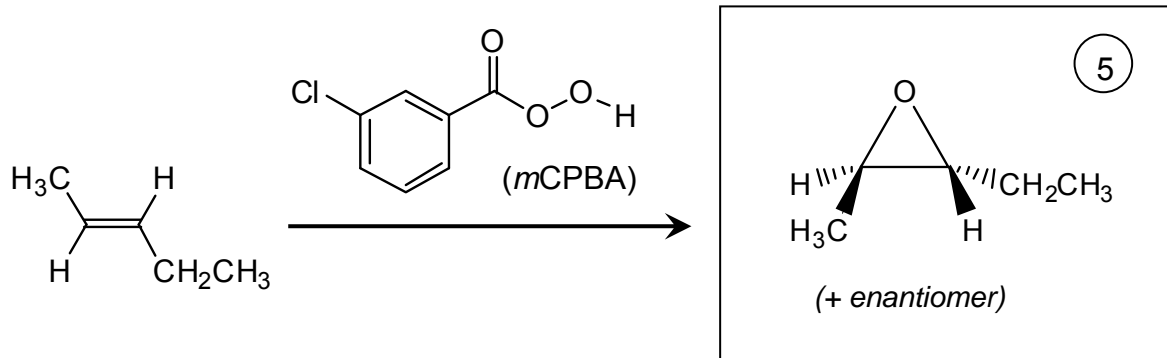


Pt/H₂ hydrogenates (adds H₂ to) both alkynes and alkenes. As a result, once this alkyne is hydrogenated to form the *cis*-alkene, that alkene is immediately and unavoidably hydrogenated to the alkane on the right. (The *trans*-alkene on the left is never made by this process, not even as an intermediate.)



NBS is a reagent for allylic and benzylic halogenation—it converts an H to a Br only when the H is next door to a double bond or benzene ring. None of the H's in this starting material is allylic or benzylic, so NBS will do nothing.

3. (15 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:

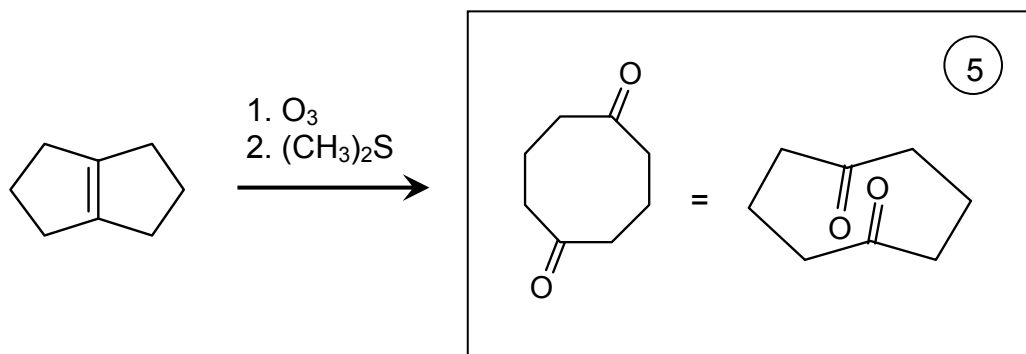
5 points for correct structure.

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.)

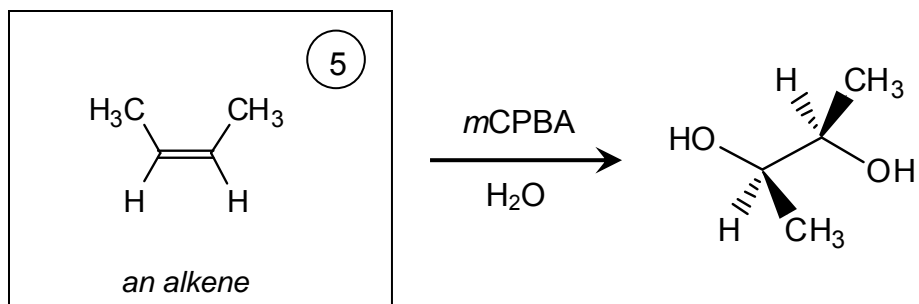
-2 points for each clearly trivial structure mistake.



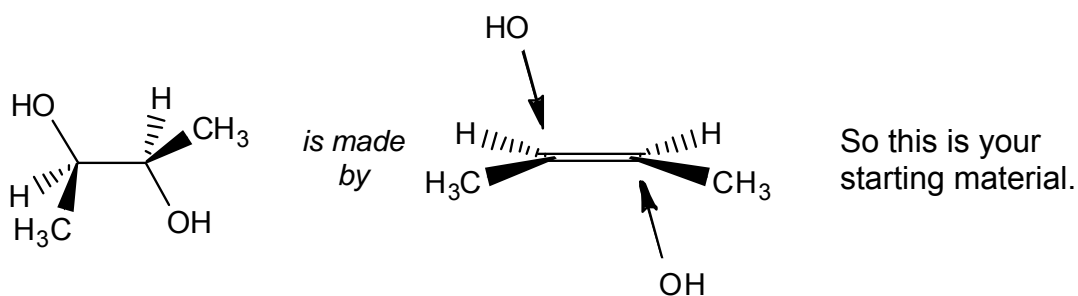
Rubric:

5 points for correct structure.

-2 points for each clearly trivial structure mistake (including too many or too few carbons in the cycle, or mispositioning of carbonyls).



mCPBA/H₂O performs *anti*-dihydroxylation on alkenes. The diol product of this reaction is drawn pretty well, that makes it clear how *anti*-dihydroxylation would happen:

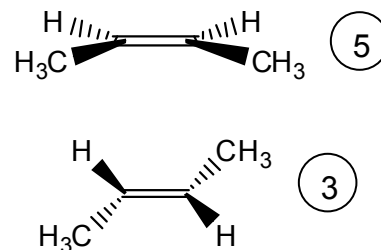


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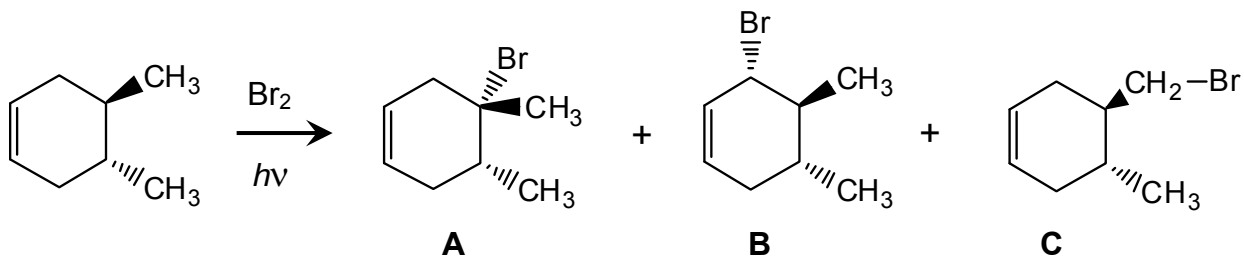
5 points for correct structure. You can draw your alkene in 3-D if you want, as long as it's flat.

3 points partial for *trans*-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.

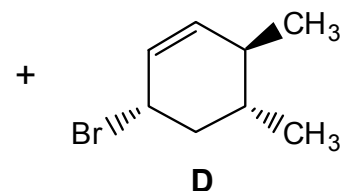
-2 points for each clearly trivial structure mistake.



4. (19 pts) When the starting material below is exposed to the conditions of free-radical bromination, four monobrominated products (A-D) are isolated.



- a) How would these four molecules relate in terms of product ratio? Which product would be most prevalent, and which would be least prevalent? In the boxes below, rank the four molecules (by letter) from highest to lowest product ratio. If any two molecules would be observed at equal ratios, circle the “≈” sign between those two boxes.



Rubric:

2 points for each box.

No partial credit. Each box is graded individually.

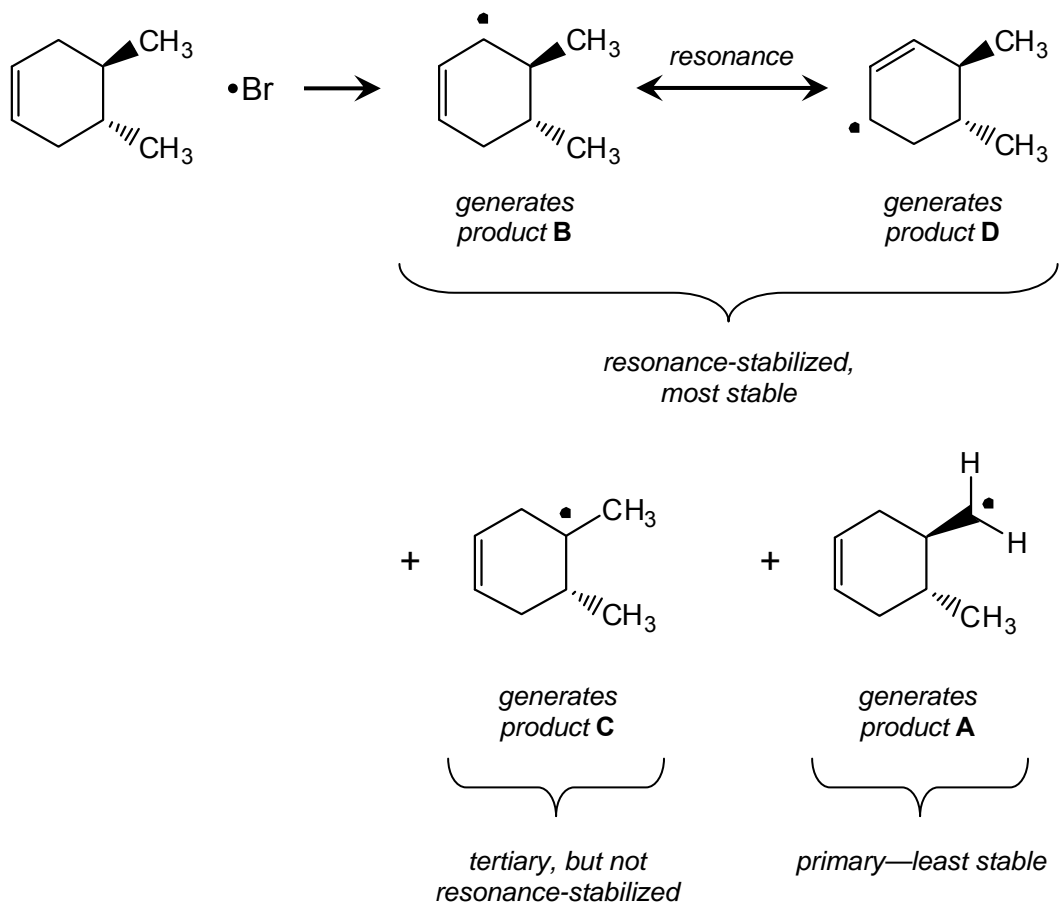
First two boxes can be either B or D (order doesn't matter).

2 points for saying B and D are equal.

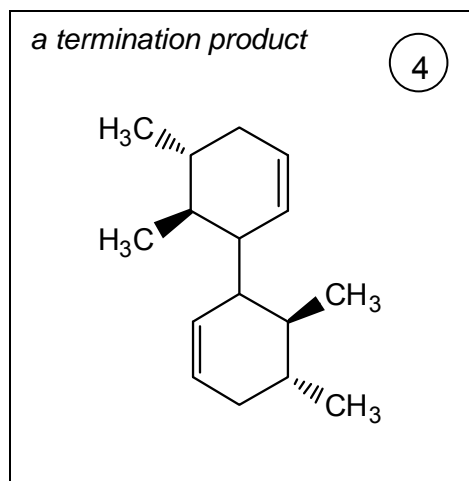
You get these points regardless of where B and D are in sequence. For example, C > A > D ≈ B gets these 2 points.

2 points for not having any other equal signs circled.

The selectivity of this radical halogenation will be determined by the stability of the intermediate radical produced. An allylic radical is the most stable radical that can be made here, followed by a tertiary radical, and then a primary radical. This is backed up by the bond dissociation energy (BDE) table, which shows an allylic C-H bond is weakest, followed by a tertiary C-H bond and then a primary C-H bond.



- b) The free-radical chain reaction that generates products **A-D** is slowed by termination reactions that remove radicals from the reaction cycle. In the box on the right, draw one termination product that would be observed for the reaction above, *other than* Br_2 and *products A-D*. (So, do not draw Br_2 or any of the products **A-D** above as an answer to this part.)

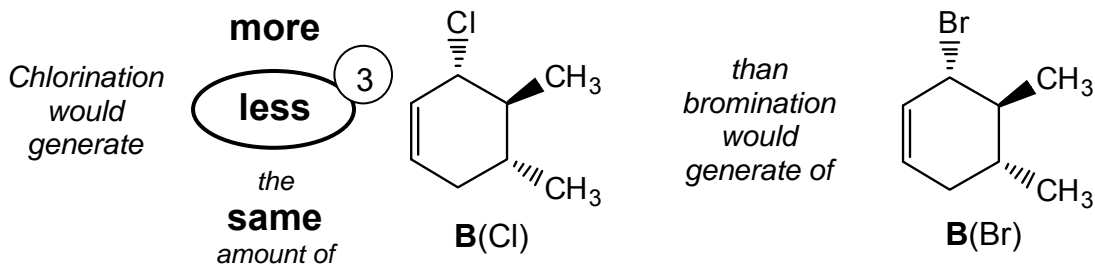


Termination is the process by which two radicals in the free-radical chain reaction combine to form a stable product. (We described it as step “4” in lecture.) That can involve combination of any two of the radicals above.

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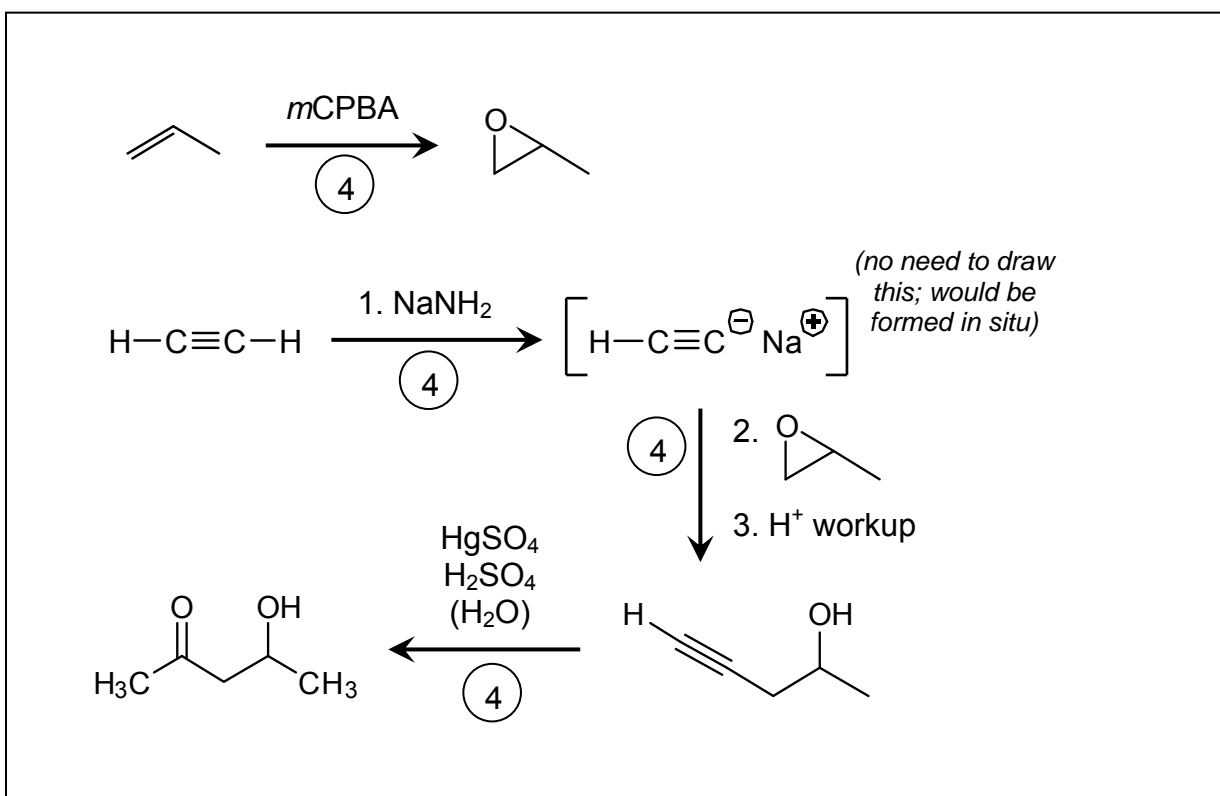
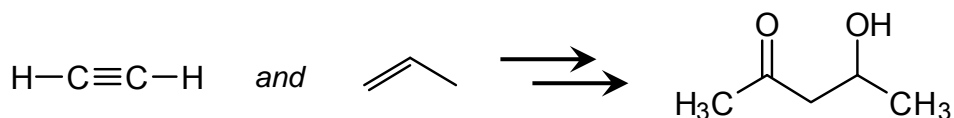
4 points for any combination of any of the radicals above (homo- or hetero-dimer).
 -2 points for each clearly trivial structure mistake.

- c) If the reaction on the previous page were a chlorination instead of a bromination—using Cl_2 instead of Br_2 —would the amount (ratio) of product **B(Cl)** be more, less, or the same as the amount (ratio) of product **B(Br)** made in the bromination? (Circle one answer.)



Chlorination is less selective than bromination is, so it would generate less of the favored product than bromination.

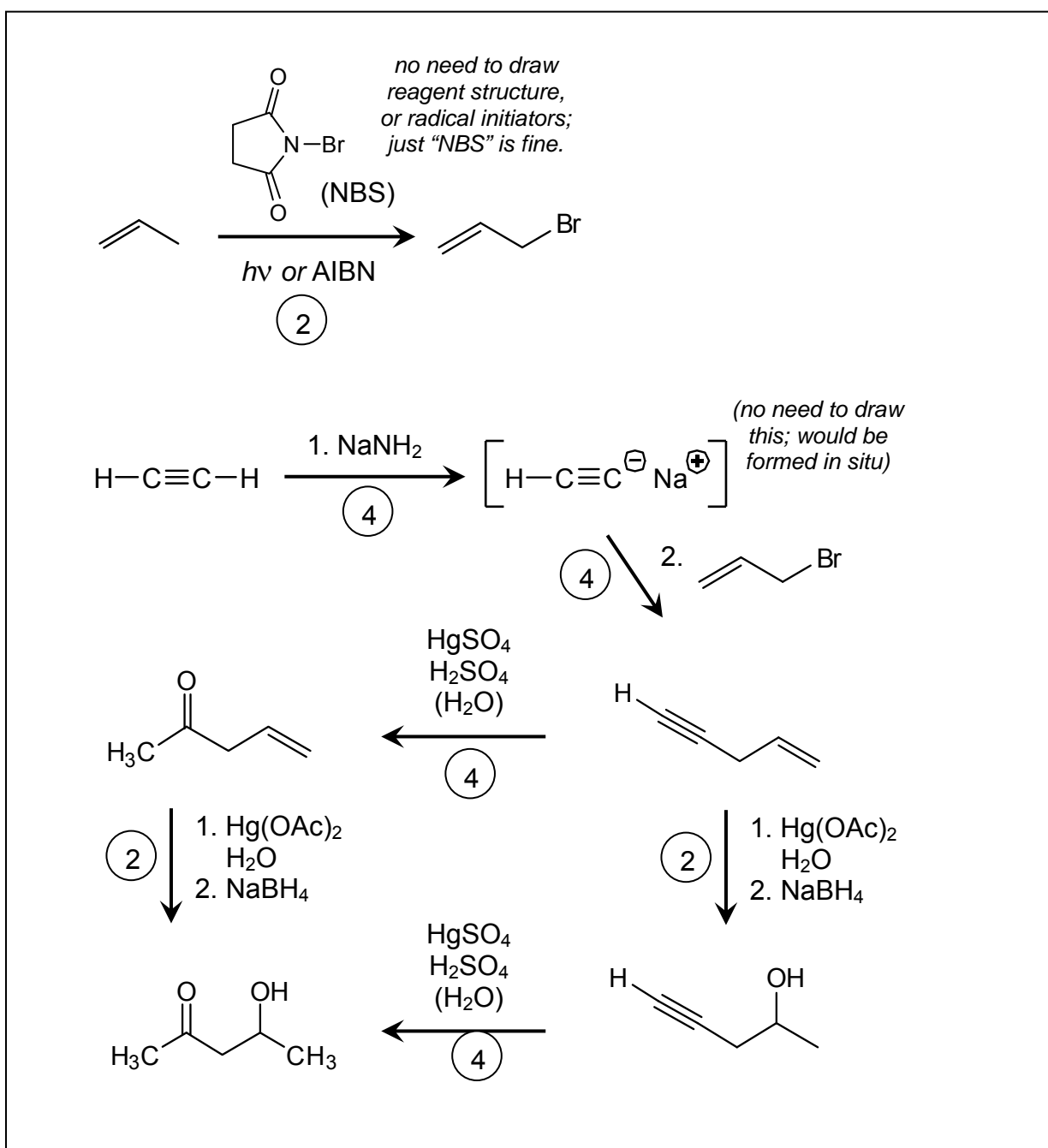
5. (16 pts) For the starting materials and product shown below, **propose a multistep synthesis**. In addition to the molecules shown, you can use any reagents and reactions we've learned about in class. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.



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 a ketone.

So, alternately,



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 "NaNH₂" 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 NaNH₂.

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 (Br₂/H₂O), not be selective or capable in later chemistry (Br₂, HBr, HBr/peroxide), or have side reactions (Br₂/hν).

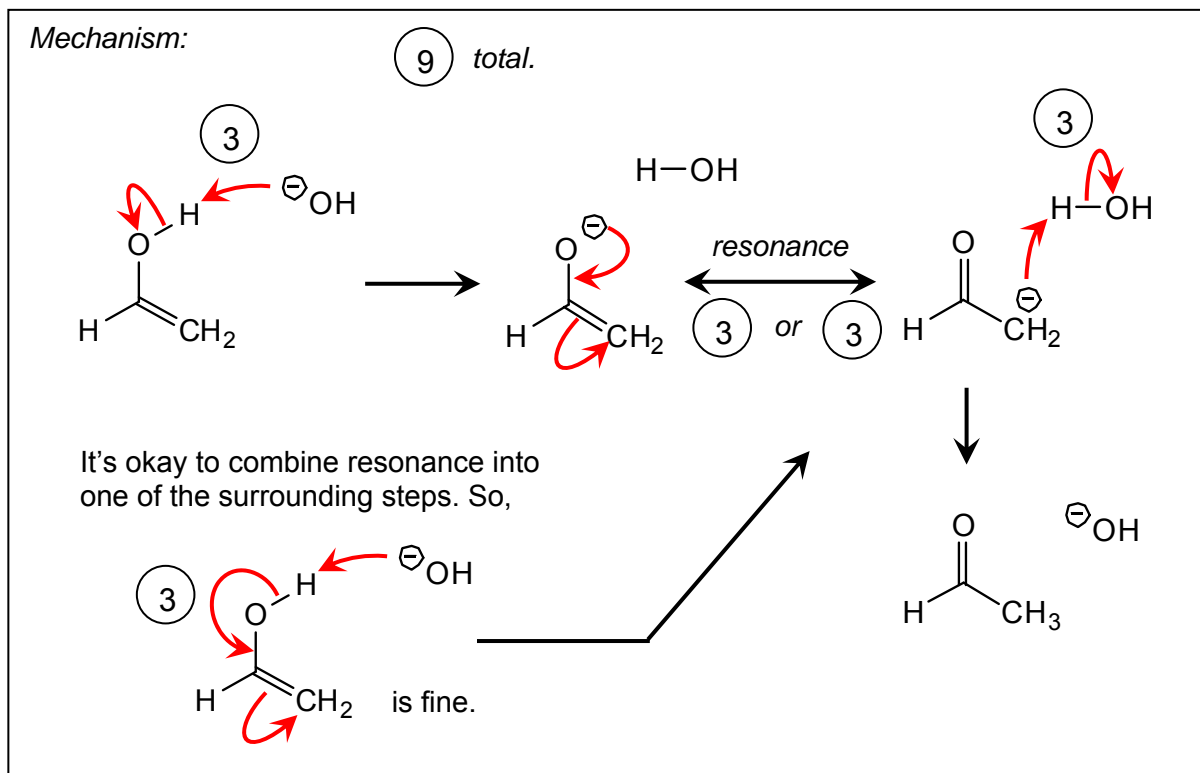
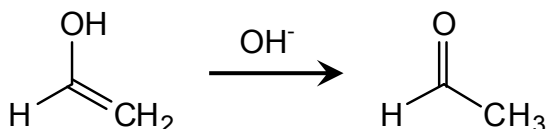
4 points for combining alkynyl anion with any alkyl halide or epoxide to create new C-C bond.

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

4 points for converting alkyne to ketone using HgSO₄.

2 points partial for using (Sia)₂BH (anti-Markovnikov) instead.

6. (26 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 OH^-) 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 step. In addition, resonance could be integrated into either previous or subsequent mechanistic step by adding an arrow.

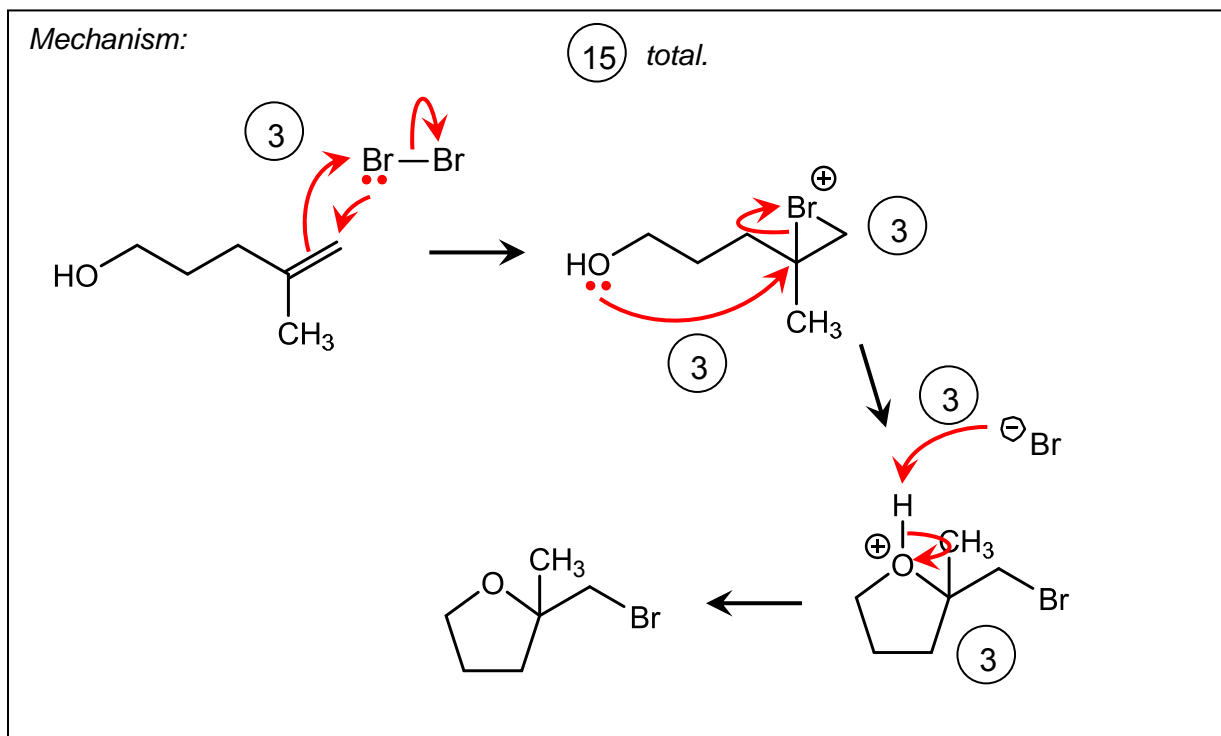
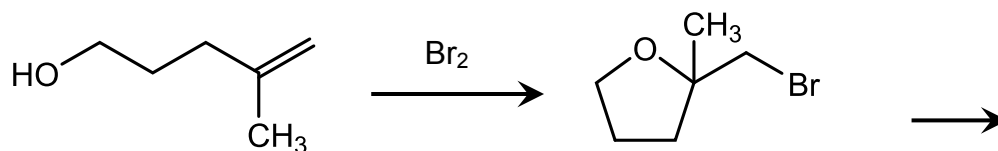
-2 points, for each arrow in each step, for errors (including omission) in drawing arrows. Arrow must start at an electron pair (either a bond or a lone pair), and end at nucleus or bond where electrons will newly interact.

- 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 OH⁻ can be used as the base, and only H₂O can be used as the acid—that's it.

3 points for each step of arrow pushing. There are two steps, so 6 points for arrow pushing.

3 points for each intermediate. There is only one intermediate—the enolate—so just 3 points for that. The enolate can be illustrated as either resonance structure.

+2 POINTS AUTOMATIC FOR PROBLEM 6.



Rubric: (15 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.

-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.

3 points for each step of arrow pushing. There are three steps, so 9 points total for arrow pushing.

3 points for each intermediate. There are 2 intermediates, so 6 points for intermediates.