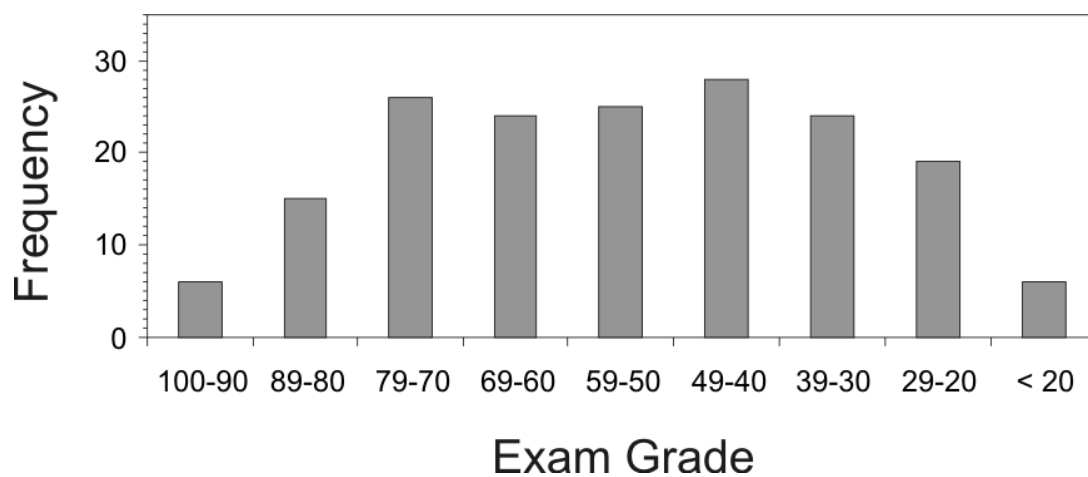


**Exam 3
Answer Key**

Exam 3 Mean: 55
Exam 3 Median: 55
Exam 3 St. Dev.: 21

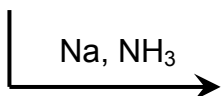
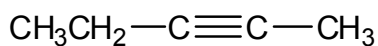


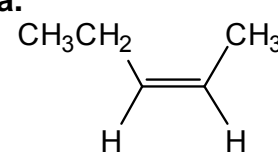
Multiple-Choice Problems

Please answer these problems on the bubble sheet.

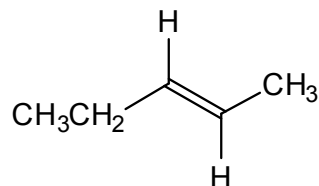
(4 pts each) Each of the reactions below is drawn with two possible products, marked (a) and (b). If one of the two products predominates, answer with the letter corresponding to the correct product. If the two products are produced equally, answer (c) BOTH. If neither product would result from the reaction, answer (d) NEITHER.

1.

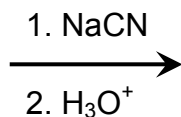
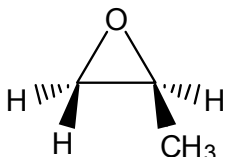


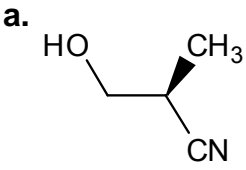
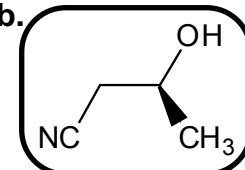
<p>a.</p> 	<p>b.</p> $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
<p>c.</p> <p>BOTH (equally)</p>	<p>d.</p> <p>NEITHER</p>

This protocol adds two H's to form a *trans*-alkene. Neither of the products shown is a *trans*-alkene. The correct product would be:

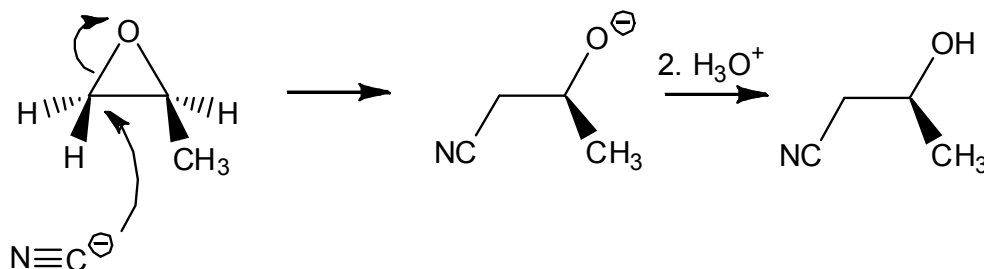


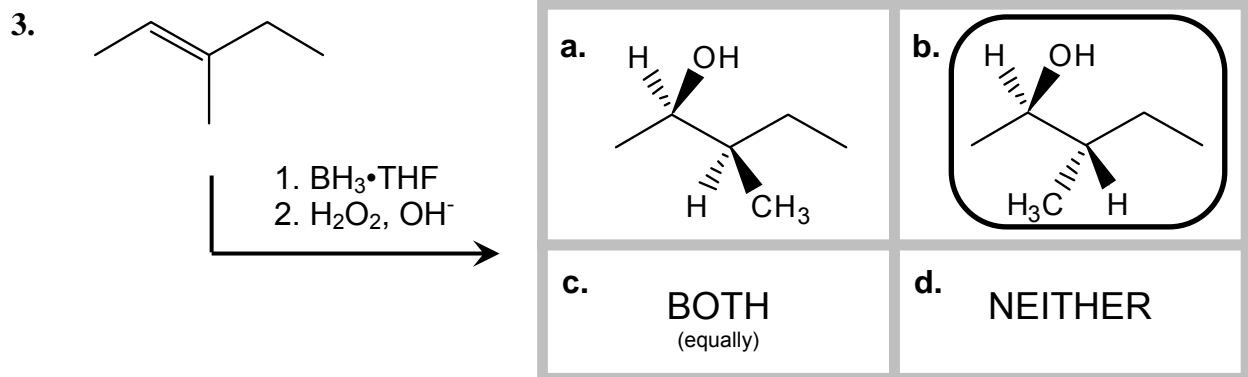
2.



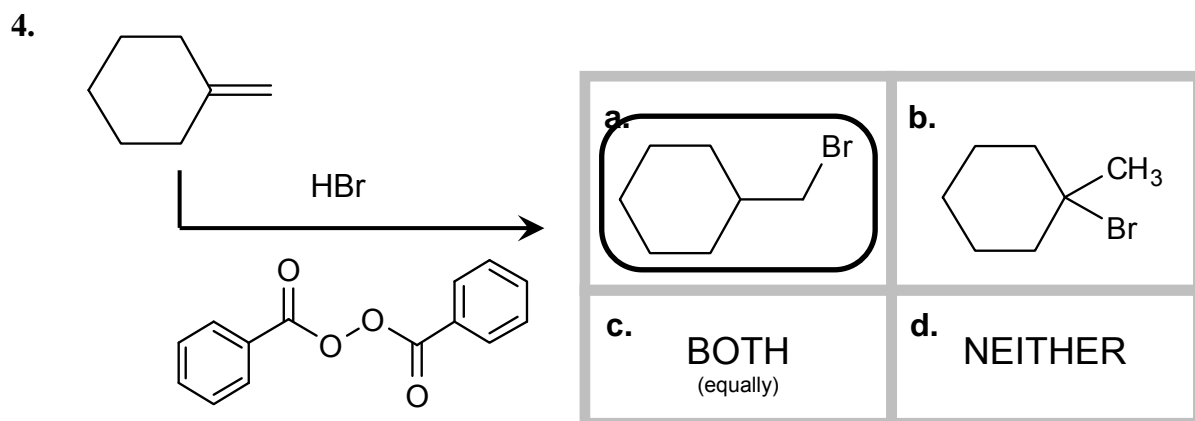
<p>a.</p> 	<p>b.</p> 
<p>c.</p> <p>BOTH (equally)</p>	<p>d.</p> <p>NEITHER</p>

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.

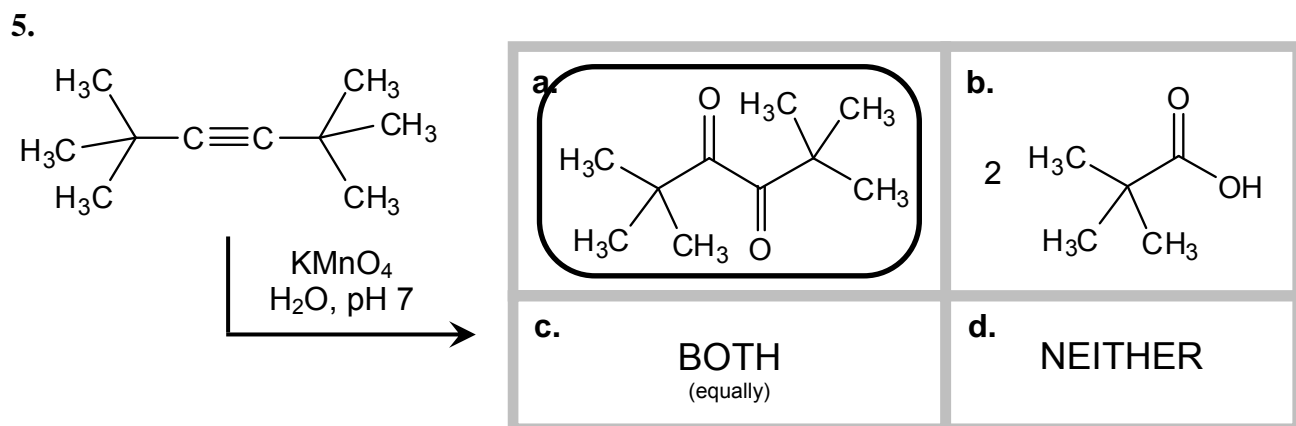




Hydroboration adds H-OH to the same side of an alkene, anti-Markovnikov. Both structures have the -OH added to the less substituted carbon, but only in the structure on the right have the H and OH been added to the same (top) face of the alkene. (They are pointed above the plane of the page.)

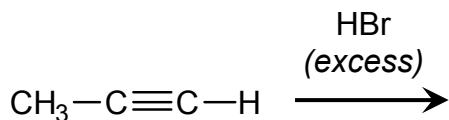


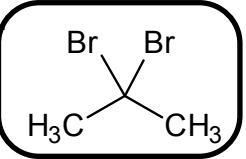
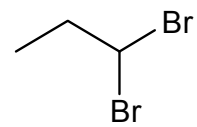
In the presence of peroxides (like the benzoyl peroxide above), H-Br adds anti-Markovnikov to the double bond; in other words, it adds such that the Br ends up at the less substituted carbon.



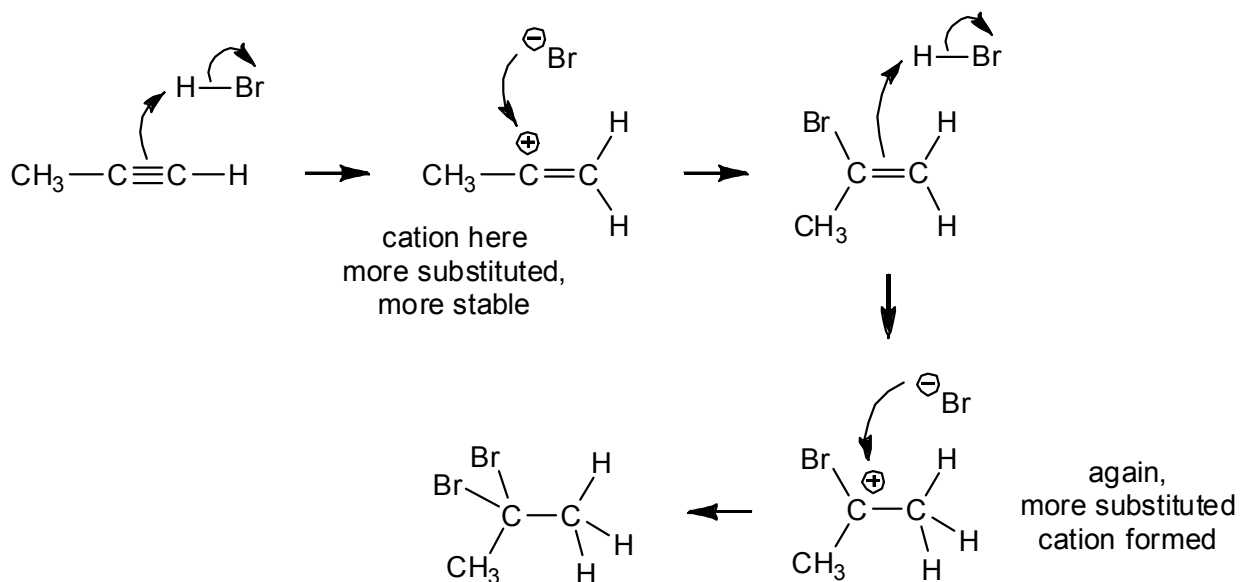
As long as the KMnO_4 isn't warm or basic, it won't cleave the $\text{C}\equiv\text{C}$ bond—it converts it into a diketone instead.

6.

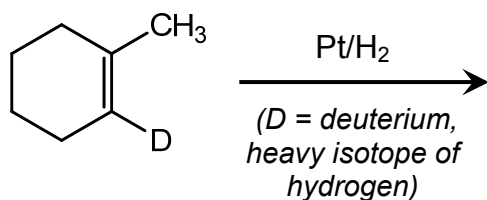


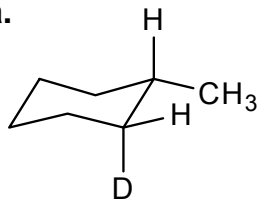
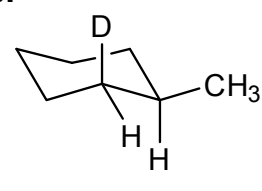
a. 	b. 
c. BOTH (equally)	d. NEITHER

H-Br will add Markovnikov to the alkyne, twice, to form the secondary dibromide preferentially.

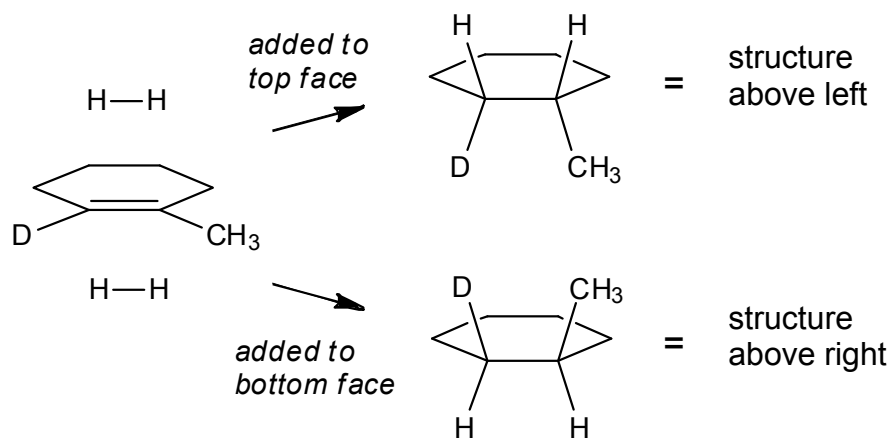


7.

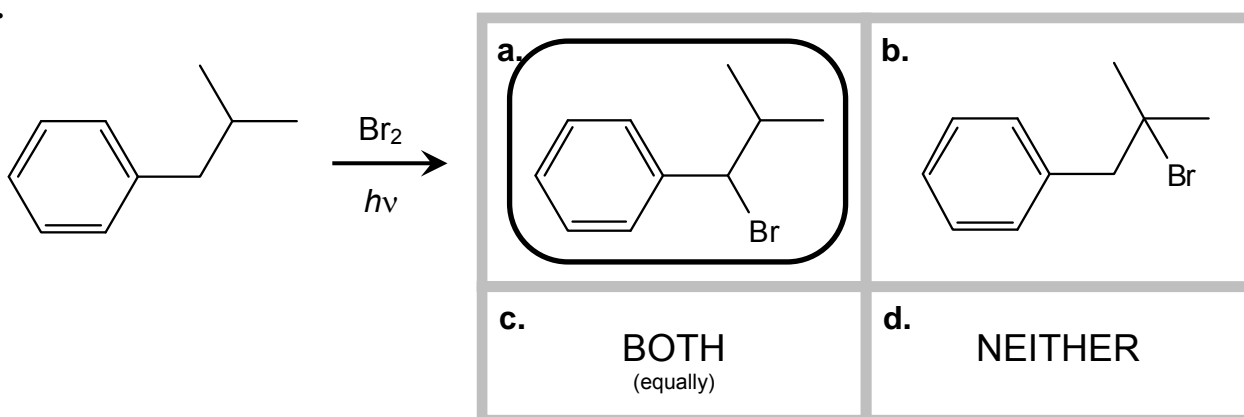


a. 	b. 
c. BOTH (equally)	d. NEITHER

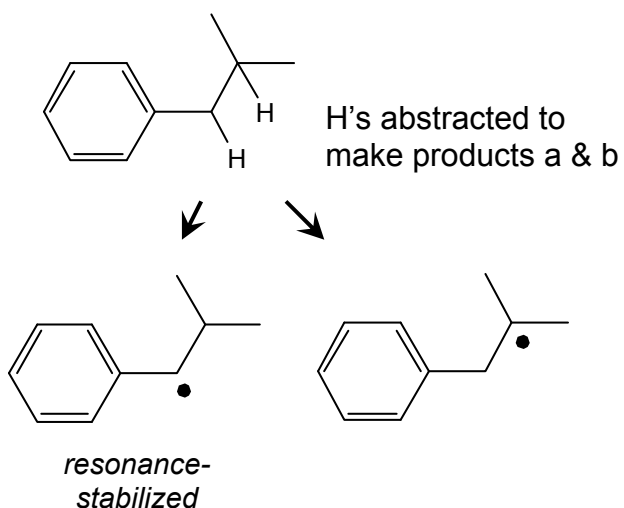
Catalytic hydrogenation adds two hydrogen atoms to the same side of an alkene. The two H's can be added either to the top or bottom faces of the alkene:



8.

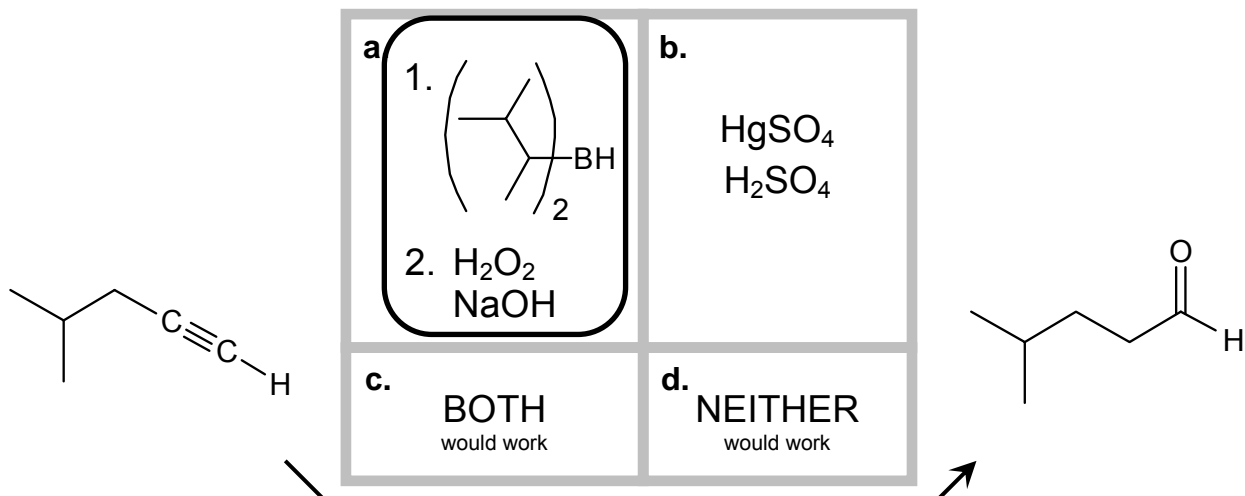


Radical halogenation goes through the most stable radical intermediate. Radicals are stabilized by two things—substitution and resonance, with resonance being the more powerful effect. As a result, even though the secondary radical associated with the product on the left is less substituted, it is benzylic and resonance-stabilized, and the product on the left is favored.



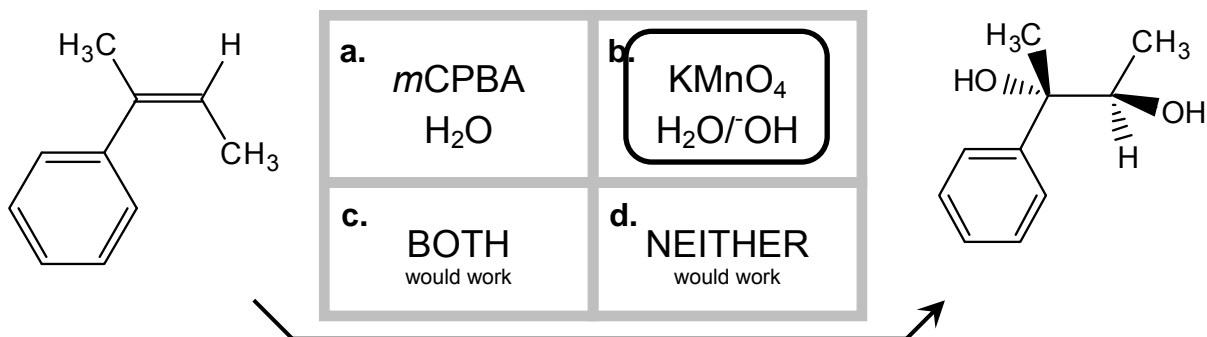
(4 pts each) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, answer with the corresponding letter. If both sets of conditions would accomplish the reaction, answer (c) "BOTH". If neither set of reaction conditions would succeed, answer (d) "NEITHER".

9.

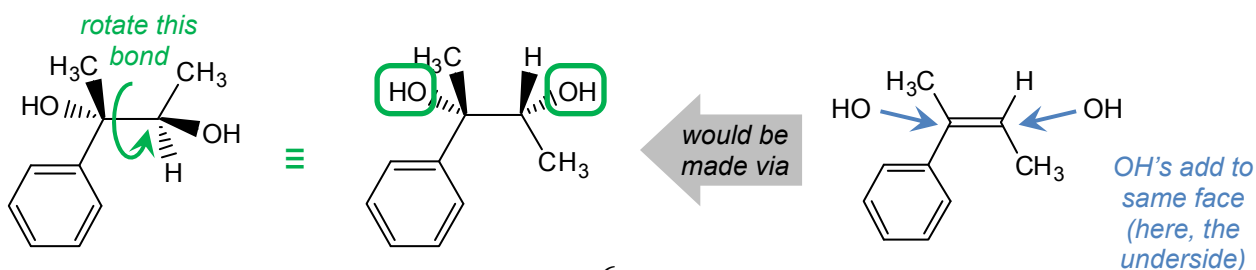


Both of these reagent sets add H-OH to the alkyne group to yield an enol intermediate, which tautomerizes to form a carbonyl (C=O). $\text{HgSO}_4/\text{H}_2\text{SO}_4$ adds the -OH to the more substituted, internal position of a terminal alkyne to eventually yield a methyl ketone. Disiamylborane, on the other hand, adds the -OH to the less substituted terminal carbon (anti-Markovnikov), and the resulting enol tautomerizes to an aldehyde.

10.

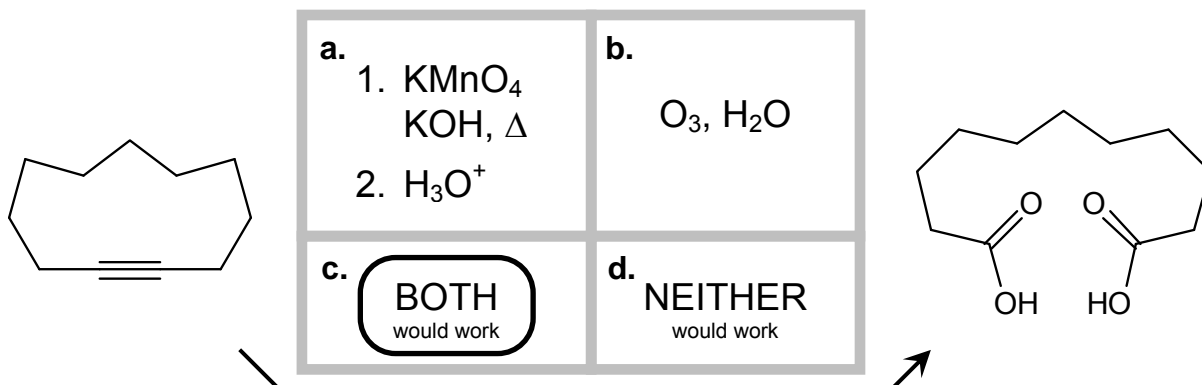


This reaction is a dihydroxylation, adding one -OH to each of the alkene carbons. But we don't know whether it's a *syn*- or an *anti*-dihydroxylation. Unfortunately, the product isn't drawn in a way that allows us to compare it to the starting material; we can see things better if we rotate the central bond in the product:



Because the addition needs to be *syn* (with both OH groups added to the same face of the starting alkene), KMnO_4 is the appropriate reagent here; *m*CPBA/ H_2O yields the anti-addition product.

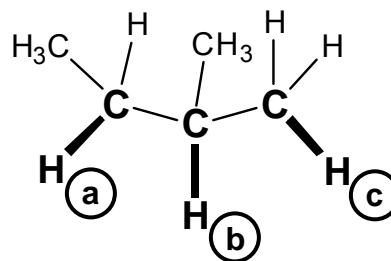
11.



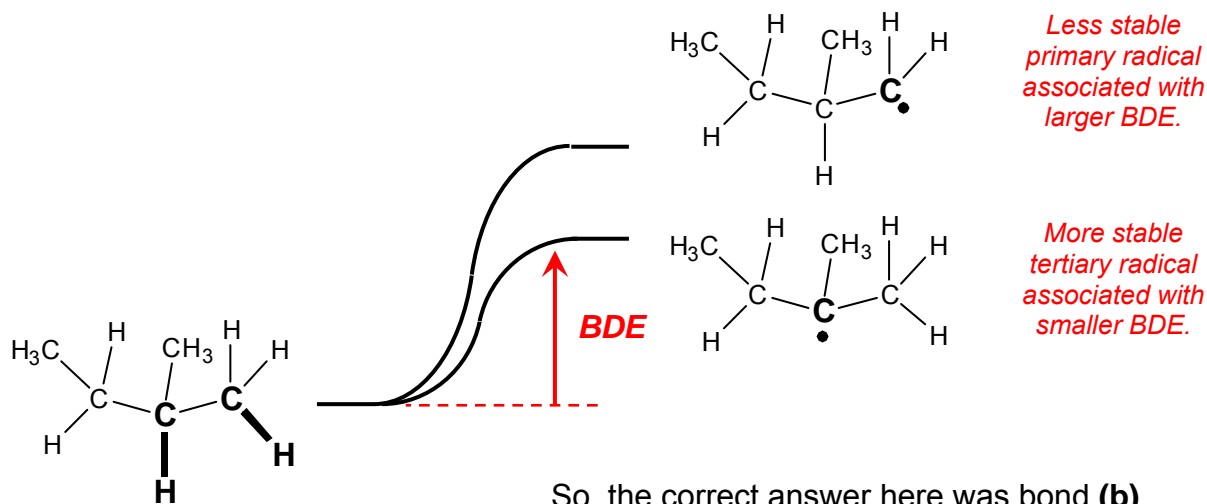
Both of these reaction conditions cleave the alkyne to yield carboxylic acids.

(3 pts each) The chemical structure of isopentane shown on the right has three C-H bonds labeled.

12. Which of the three bonds has the smallest bond dissociation energy (BDE)?



Bond dissociation energy (BDE) is the energy required to break a bond and form two product radicals. This process is always endothermic, but the more stable the resulting radical, the less endothermic it is.

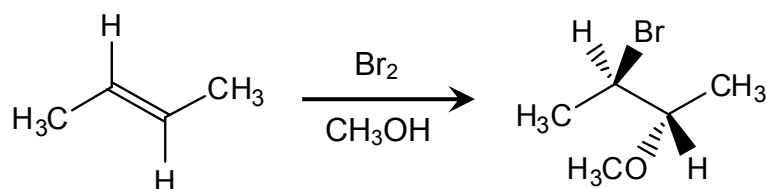


13. Which C-H would be most likely replaced by a C-Cl in a radical chlorination with Cl₂ and UV light?

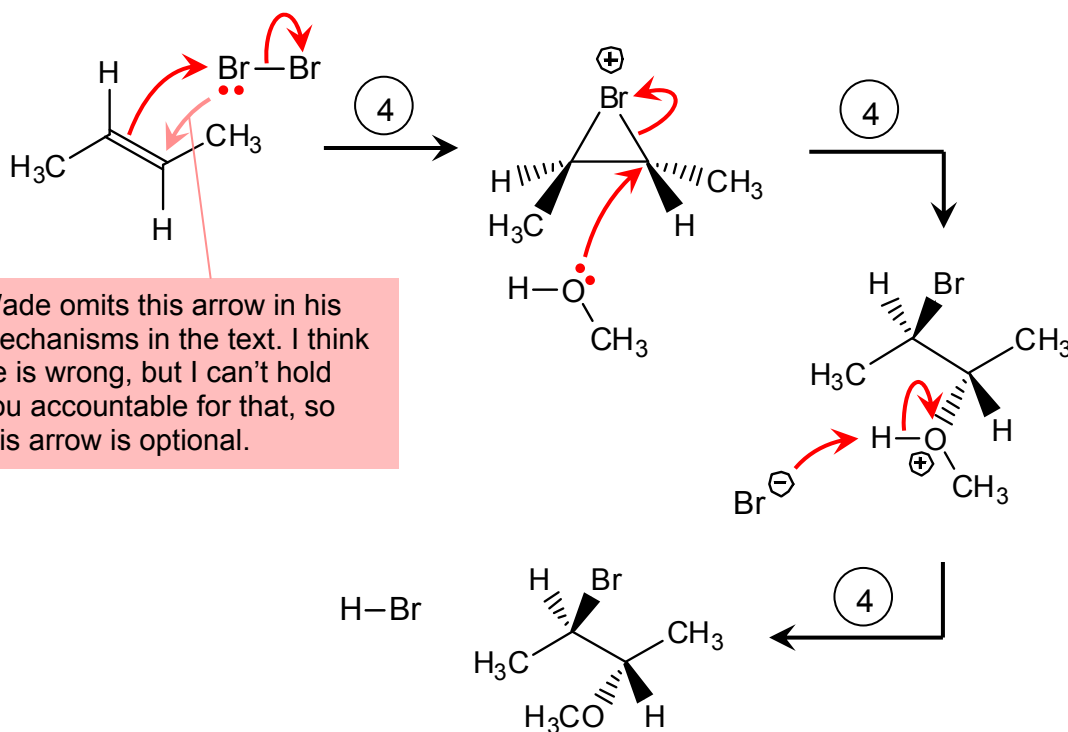
The reaction that goes through the most stable radical intermediate is favored here. So, the bond most likely to be replaced is bond **(b)**.

14. (20 pts) For each of the reactions shown below, draw a mechanism that explains how the product is generated from the starting material. In your answer, make sure that you:

- Draw each step of the mechanism separately;
- Use “electron pushing” to show where the electrons in each step go;
- Use only the molecules that you are given; do not invoke reactants or solvents that aren't in the problem.

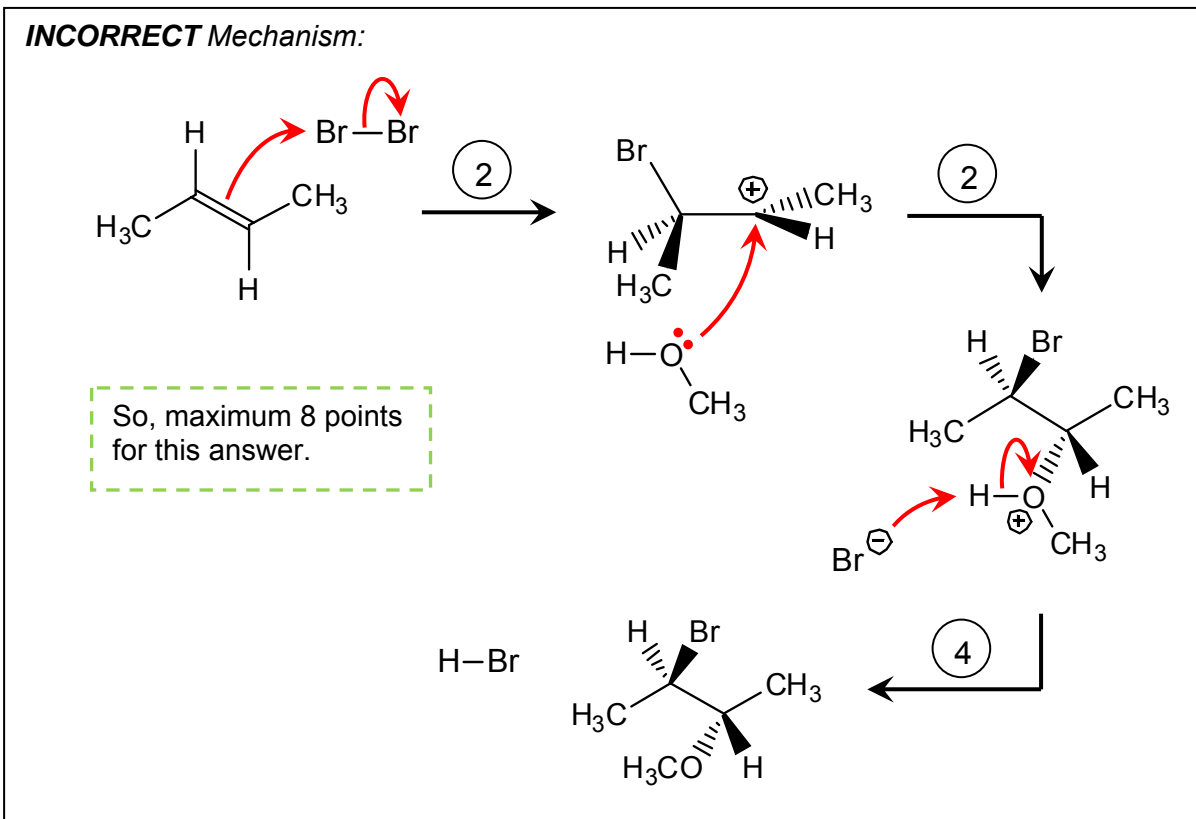


Mechanism:



Wade omits this arrow in his mechanisms in the text. I think he is wrong, but I can't hold you accountable for that, so this arrow is optional.

The mechanism of electrophilic bromination passes through a three-membered-ring bromonium ion; the structure of this ion dictates the stereochemistry in the final product. Some of you drew the mechanism passing through a carbocation instead; if you did this, we gave you only 2 points for each step going to and from the cation. So, that **incorrect** mechanism would look like:



Rubric for this part: (12 points total; 8 points if mechanism goes through carbocation rather than bromonium ion)

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., HBr from last step) and spectators (e.g., Br⁻ that sits around and waits until the end) may be omitted.

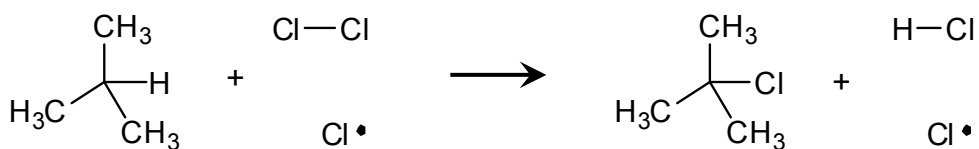
Proton transfer must be shown explicitly, with two arrows (one from base to proton, one from proton-acid bond to conjugate base).

-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.

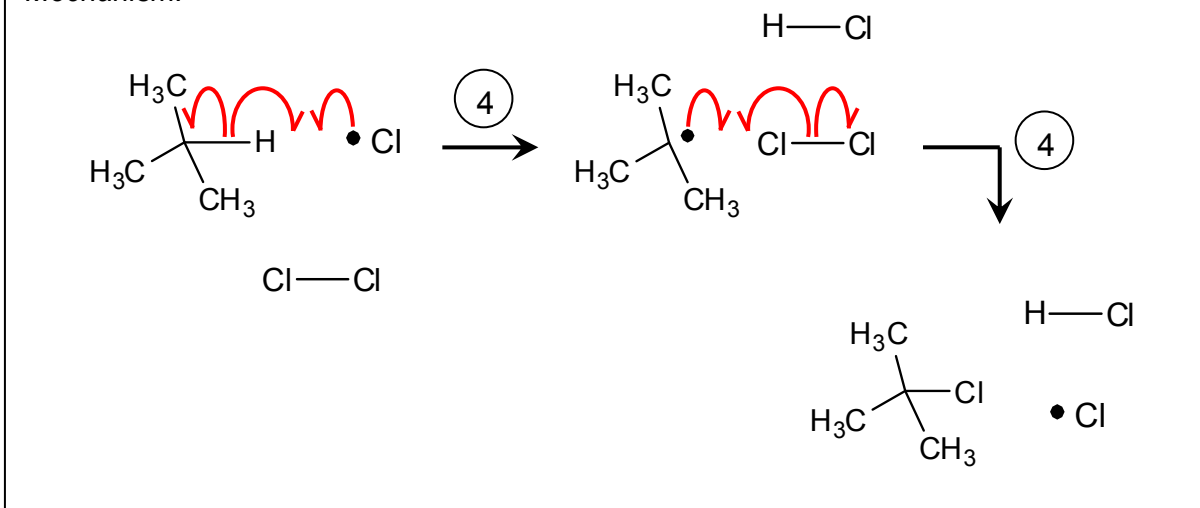
-2 points for each error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.

-2 points for each step combined with another, taken off each step.

-2 points for each use of a generic or incorrect acid/base. Here, either Br⁻ or CH₃OH could be used as the base in the final step.



Mechanism:



Rubric for this part: (8 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.

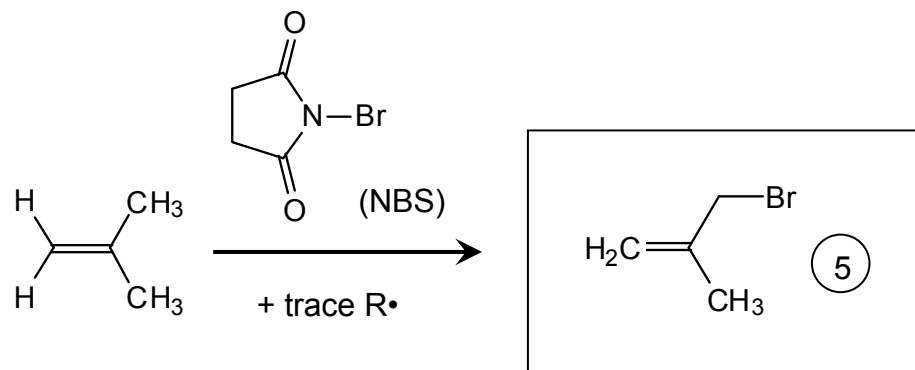
Things that have left (e.g., HCl produced in first step) and spectators (e.g., Cl₂ in first step) may be omitted. Only organic things that change need to be drawn.

-2 points, for each arrow in each step, for errors (including omission) in drawing arrows. Each arrow in this problem must be *single-barbed*. Double-barbed arrows earn no partial credit. Arrow must start at an unpaired electron or an electron pair, and end at a nucleus or newly formed bond.

-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. Don't know how you'll do this here, but there you go.

15. (15 pts) Draw the missing reactant or product in the empty boxes. For products, give the predominant, most favored product. Illustrate stereochemistry in your answer where appropriate. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note “+ enantiomer”.



NBS does allylic bromination—it replaces an H with a Br one carbon away from a double bond. The reaction can be run under conditions where mainly the monobrominated product is formed, but multiple brominations can also occur, so we also gave full credit for multi-allylic-bromination products.

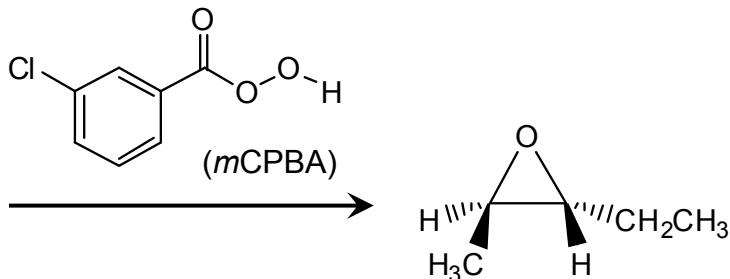
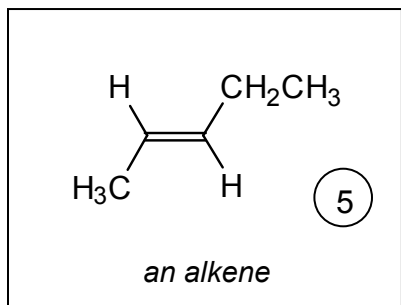
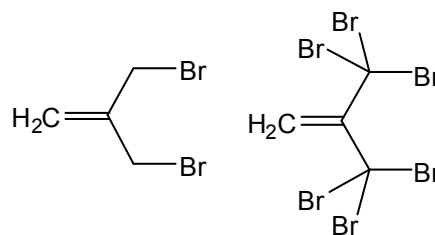
Rubric:

4 points for correct structure.

Full credit for any number of allylic additions of Br.

-2 points for each clearly trivial structure mistake. (I.e., where it is clear that correct answer was intended, but simple omission or error made the answer incorrect. Intent must be clear.)

Full credit for (for example):



Rubric:

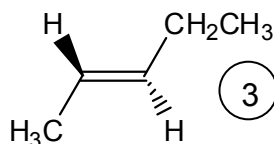
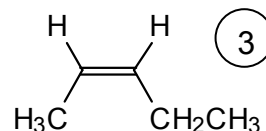
5 points for correct structure.

3 points partial for *cis*-alkene.

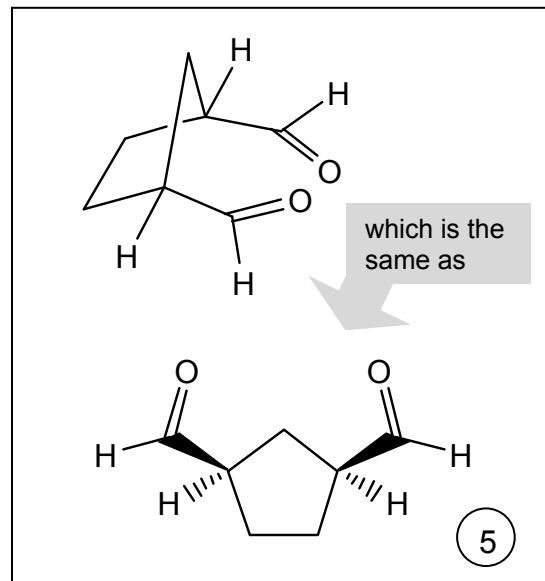
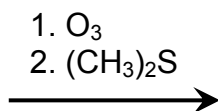
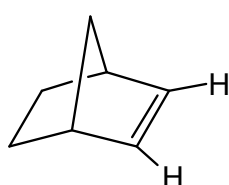
-2 points for each clearly trivial structure mistake.

This includes drawing an alkene that's not flat.

Alkenes are flat.



this makes no sense—it's not flat.



Ozonolysis breaks double bonds, and adds a double-bonded oxygen to each of the carbons that used to be in the double bond. The result here is two aldehyde groups on the same side of the remaining cyclopentane.

Rubric:

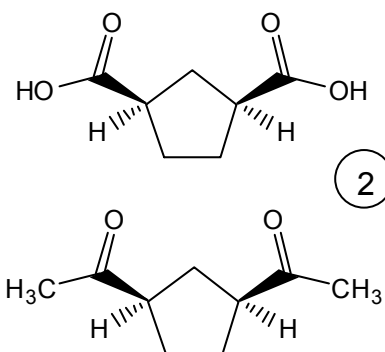
5 points for correct structure.

Can also draw structure without changing perspective, as shown on top, with or without bridgehead hydrogens.

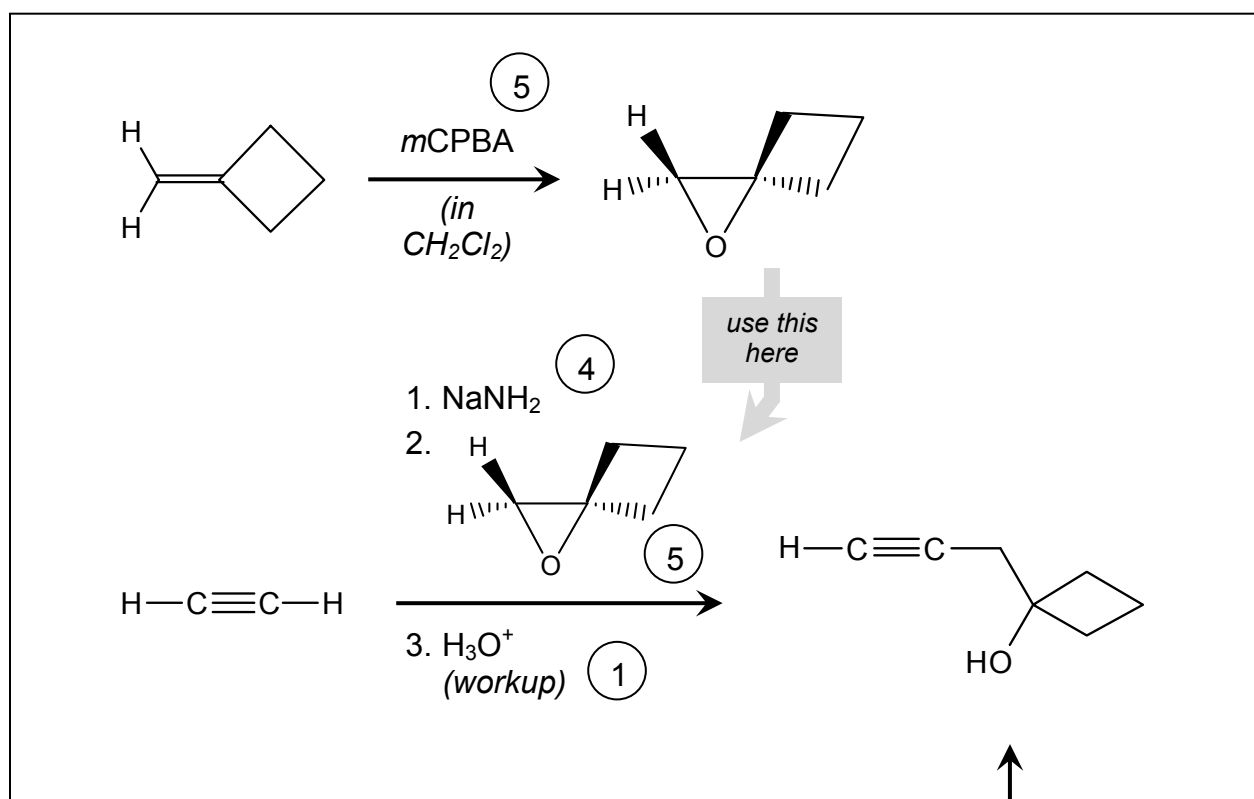
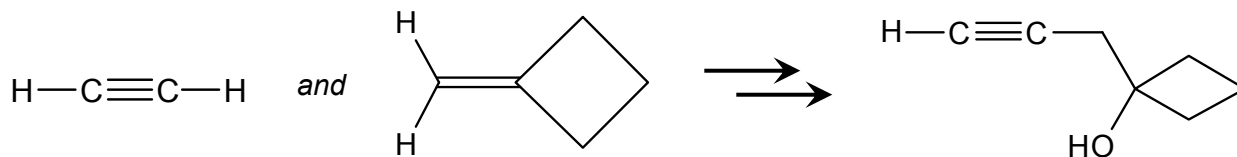
2 points partial for di(carboxylic acid), di(methylketone), or any other cleaved dicarbonyl product instead of dialdehyde.

-2 points for incorrectly or not illustrating cis-stereochemistry at cyclopentane carbons. (I am arguing that the drawing on top accomplishes this.)

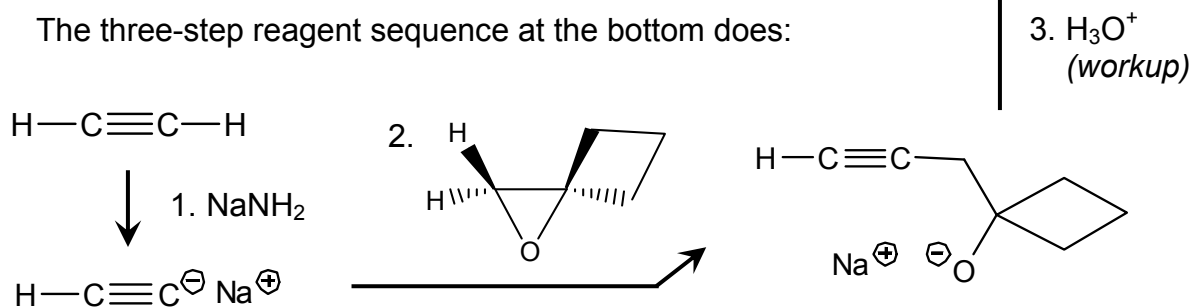
-2 points for each clearly trivial structure mistake.



16. (15 pts) For each set of starting materials and products 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 three-step reagent sequence at the bottom does:



Neither of the two starting materials has enough carbon atoms in it alone to make the product, so the two need to be combined. In order to do this, your answer would have required 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 alkene needs to be prepared to accept that alkynyl anion. There are a couple of ways to do this.
- (3) The two parts need to be combined in a way that they will react, and that gets us towards the product.

Rubric: 15 points total for the three elements described above.

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

I've drawn deprotonation of acetylene, attack on epoxide, and protonation of the resulting alkoxide on one arrow, because a chemist would carry out the reaction in one pot. However, if you wrote out each of these as an individual step, that's just fine--full credit, as long as what you've drawn makes sense.

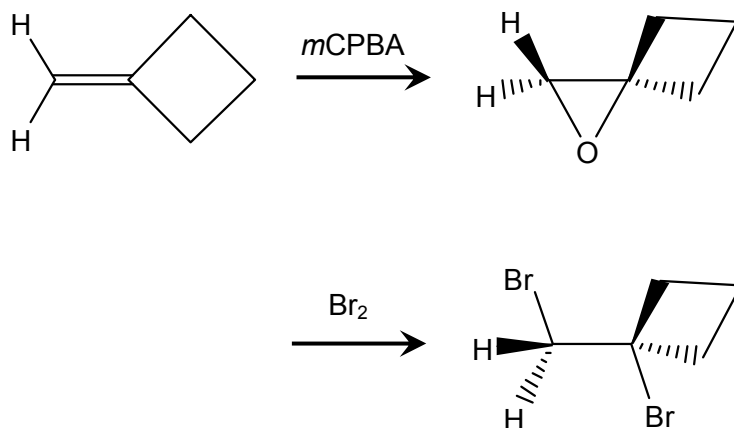
-1 point for each clearly minor error in structures or reagents; if error propagates, points are taken off only for initial error.

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

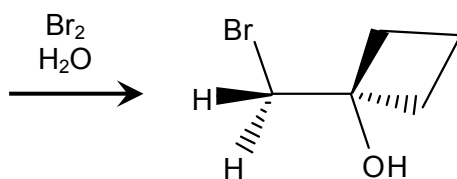
We only gave points for correct reagents if they connected a starting material and a product in an understandable way. So, for example, just writing "NaNH₂" in the box was not enough; it needed to connect acetylene with something in a mechanistically meaningful way.

5 points for generating an alkynyl-reactive electrophile from alkene.

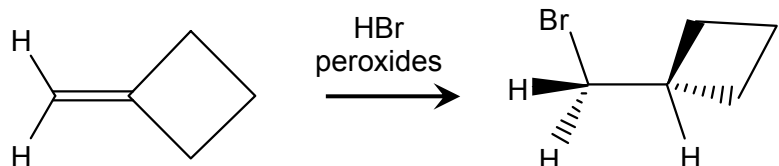
Examples of reactions that could react with an alkynyl anion, and so receive full credit:



(continued on next page)



This will fail at a later step, but it receives full credit here.



This fails to put alcohol in, but receives full credit for this step.

2 points partial for any reaction that generates an -OH group at the more substituted carbon, but doesn't allow for subsequent addition of alkynyl anion.

4 points for generating alkynyl anion using NaNH_2 .

6 points for combining alkynyl anion with electrophile to generate alcohol.

Routes that receive full credit:

- *Alkynyl + epoxide. 5 points for combining, 1 point for acid workup at the end.*
- *Alkynyl + dibromide, followed by $\text{S}_{\text{N}}1$ (H_3O^+) to generate alcohol.*
3 points partial if only alkynyl + dibromide is done successfully.
- *Alkynyl + deprotonated halohydrin. It's not clear whether deprotonating alcohol would then cause intermolecular decomposition of halohydrin, but we'll give the benefit of the doubt.*
3 points partial for alkynyl + halohydrin without prior deprotonation of alcohol.
Alkynyl anion would deprotonate alcohol before attacking bromide.

2 points partial for any other combination that successfully makes C-C bond, but does not generate -OH.