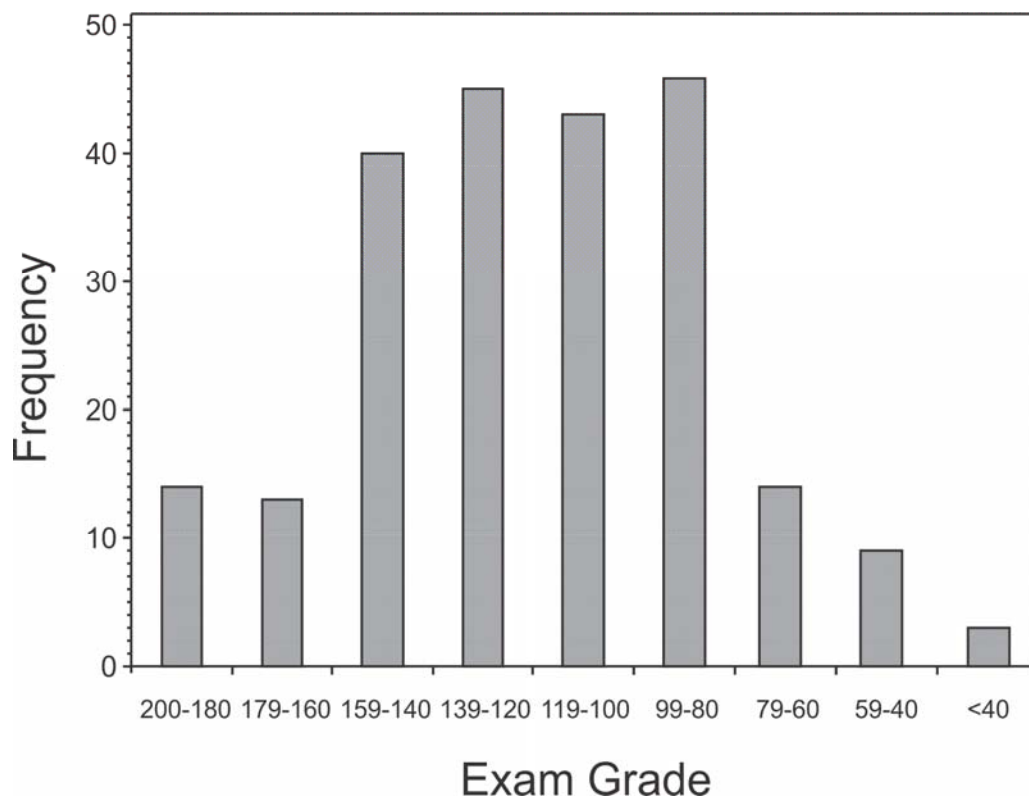
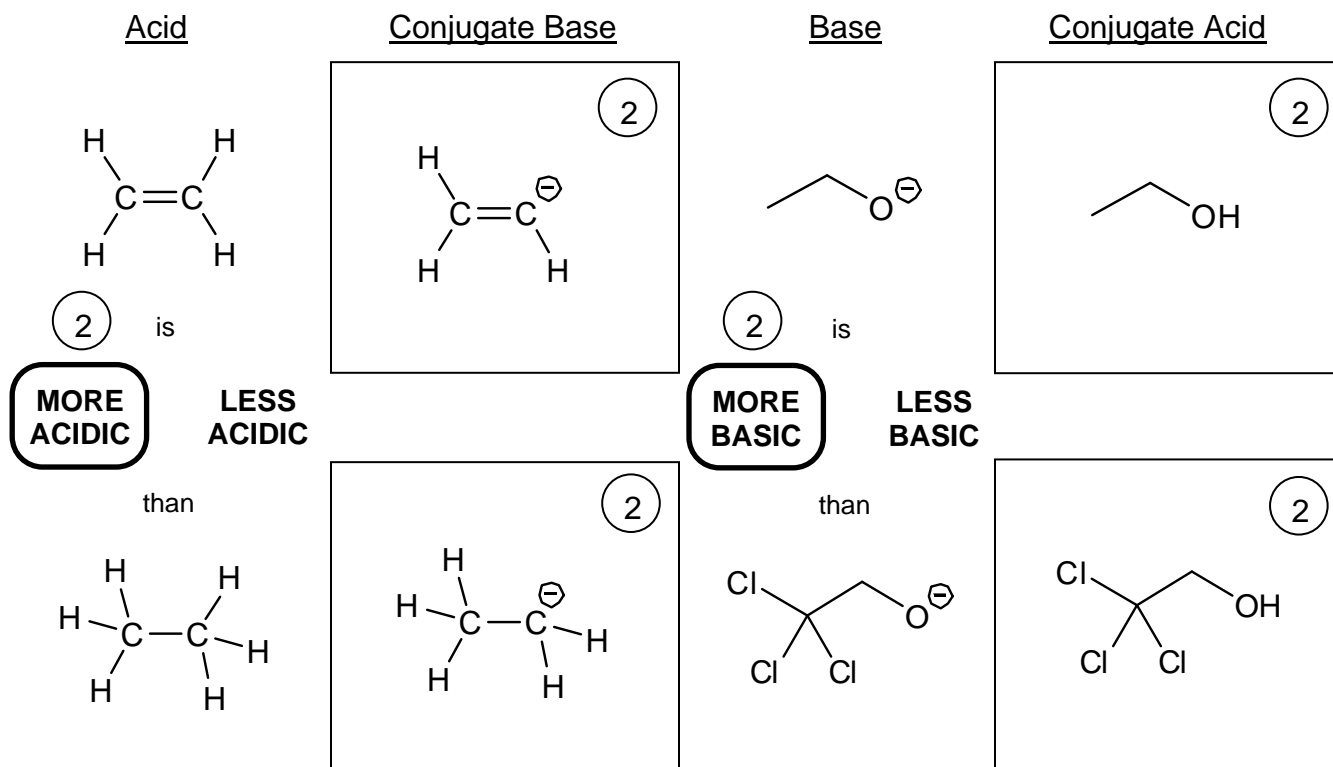


**Final Exam
Answer Key**

Final Exam Mean: 120
Final Exam Median: 120
Final Exam St. Dev.: 35



1. (12 pts) For each of the pairs of acids (or bases) below,
- Draw the conjugate base (or acid).
 - Circle whether you think the first acid (or base) is more or less acidic (or basic) than the second.



The extra lone pair of electrons is in an sp^2 hybrid orbital in the upper carbanion, and in an sp^3 hybrid orbital in the lower carbanion. The sp^2 orbital has more s character; as a result its electrons are held closer to the carbon nucleus, and are better compensated by the nuclear (positive) charge. The upper anion is more stable, and so the upper acid is more acidic.

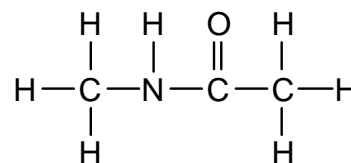
The lower oxyanion is stabilized by inductive effects (from the electronegative chlorine atoms) that are not present in the upper anion. So the upper alkoxide is less stable, and more basic.

Rubric:

2 points per conjugate acid/base structure. *No partial credit.*

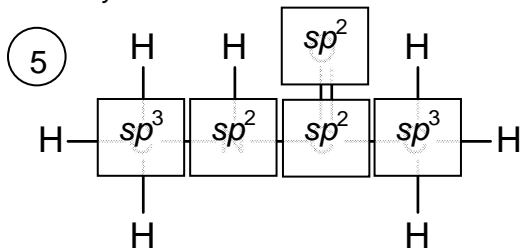
2 points per circled more/less acidic/basic.

2. (17 pts) For methyl acetamide (drawn at right), in the boxes provided:



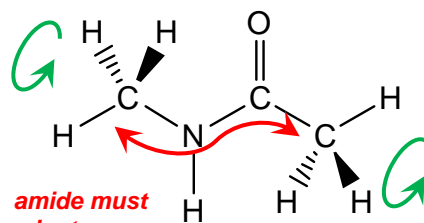
- Draw all significant resonance structures. In each structure, draw all atoms, bonds, lone pairs of electrons, and formal charges. Then, circle which resonance structure you think is the most significant, and which is the least. **Circle only one MOST and one LEAST.**
- Draw a Lewis wedge/dashed-bond structure that illustrates the most stable three-dimensional conformation of the molecule. Draw all atoms, bonds, and charges, but omit lone pairs.
- In the boxes provided, write the hybridization state on any atom heavier than hydrogen.

atom hybridizations:



(2) **MOST** or **LEAST** significant?

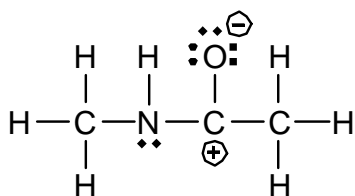
3-dimensional representation



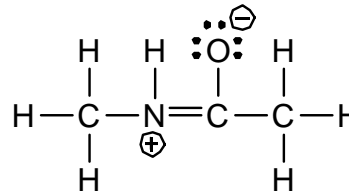
amide must be trans

methyl groups can be in any rotation (as long as they are tetrahedral)

resonance structure



resonance structure



MOST or **LEAST** significant?

MOST or **LEAST** significant?

(2)

Rubric:

-1 point for each trivial mistake in structure (left out an H, extra C, etc.)

Hybridizations: 1 point each. (5 points this part.)

3-D drawing: 4 points total.

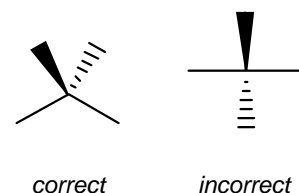
1 point for flat amide.

1 point for *trans* amide, i.e., flat, *anti* (180°) C-N-C-C.

The *trans* conformation puts the two largest groups—the two methyl groups—farthest away from each other.

2 points for illustrating tetrahedral carbons correctly.

Tetrahedral centers are illustrated as having two bonds in the plane of the page on one side of the center, and two bonds out of the plane (one forward, one back) on the other side.



Resonance structures: 2 points each.

1 point for formal charges (both charges must be correct).

1 point for lone pairs and bonds (all must be correct).

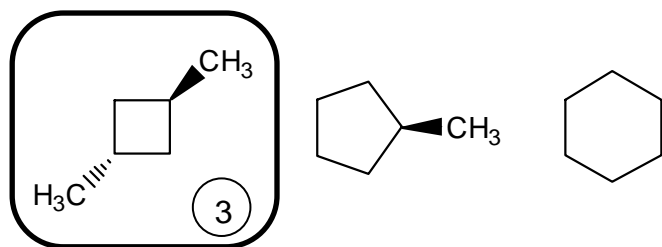
Resonance structures need not be in 3-D, or have correct bond angles.

Contributions (MOST/LEAST): 2 points each.

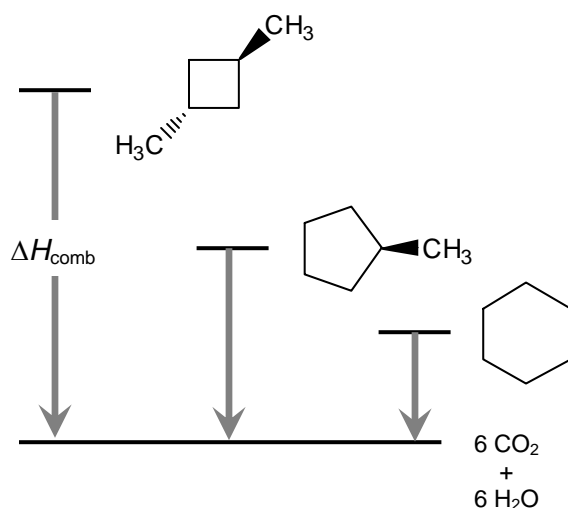
If you circle more than one of either, 0 points (out of 2) for that one.

You can only get these points if your resonance structure is a correct one.

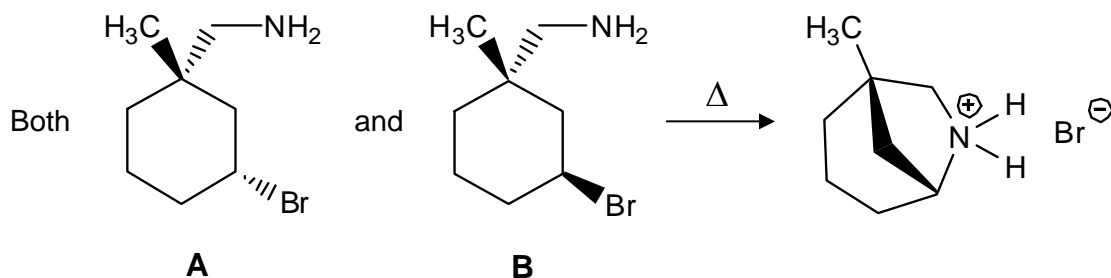
3. (3 pts) Each of the C_6H_{12} cycloalkanes on the right combusts in O_2 exothermically (with $\Delta H_{\text{comb}} \ll 0$) to CO_2 and H_2O . **Which one combusts the most exothermically?** (Circle one molecule.)



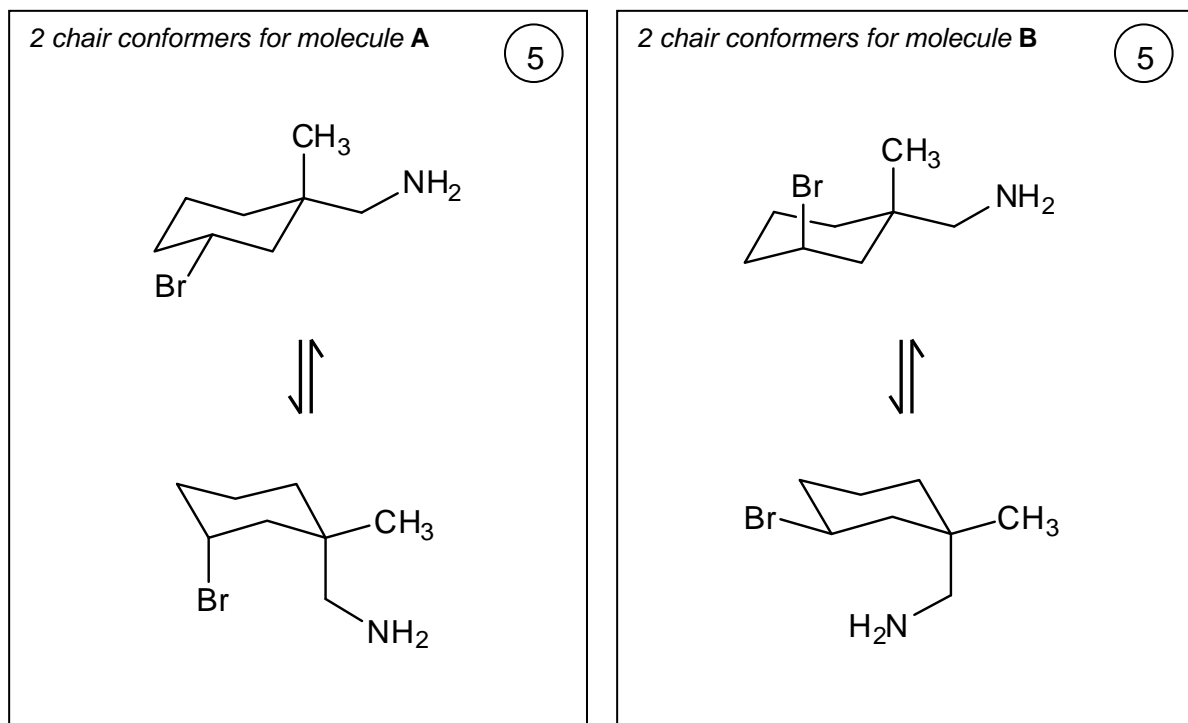
These molecules all have the same molecular formula— C_6H_{12} —and they all combust to form the same number of molecules of CO_2 and H_2O . But they have different heats of combustion because of differences in ring strain between the three molecules. The cyclobutane is the most strained, the highest in energy, and so it combusts to give off the most energy.



4. (34 pts) Each of the starting materials below, when heated, is transformed into the same product. However, the two starting materials react via different mechanisms. In this problem, you will explain why.



- (a) Each of the starting cyclohexanes (which I've labeled **A** and **B**) has two equilibrating chair conformers. In the boxes below, draw the two chair conformers for each starting material. Feel free to omit the ring hydrogens, but draw all non-hydrogen substituents.



Rubric for part (a): 5 points per box. (10 points total for this part.)

1 point, in each box, for drawing two chairs. (*Not including substituents, just the chairs*).

2 points for all substituent positions correct on each chair. (4 points total per box.)

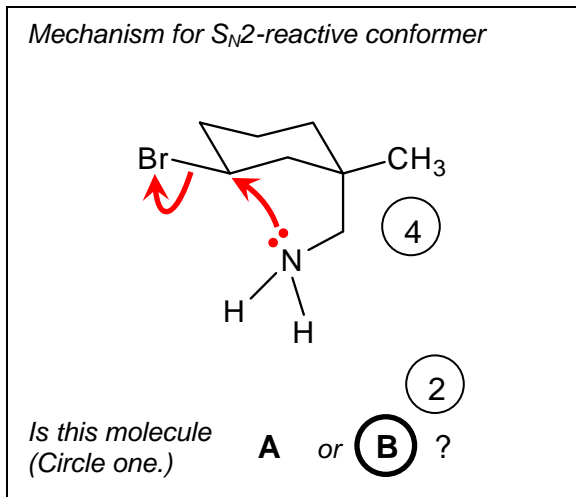
To receive these points, it must be clear which substituents are axial and which are equatorial. Equatorial substituents must be co-linear with a ring bond.

If substituents are correct in the first chair, and then not flipped in the second chair, credit for first set of substituents only.

1 point partial, per chair, for drawing two out of three substituents correctly.

- (b) Of the four conformers you drew on the previous page, only one will react to make product via S_N2 . In the box on the right, re-draw that conformer. Then, “push electrons” (using curved arrows) to show how the product would be generated from this conformer. (You don’t need to re-draw the product, just push electrons.)

Only in the conformation shown can the amine nitrogen reach across, and be anti-co-linear with the bromine leaving group, the geometry required by the S_N2 mechanism.



Rubric for part (b): 5 points for this part.

2 points for identifying correct conformer (and **B** as S_N2 -active molecule).

2 points for each arrow.

Arrow must start at an electron pair, and end at nucleus where electrons will newly interact.

You do not need to have drawn the correct conformer to get these 4 points.

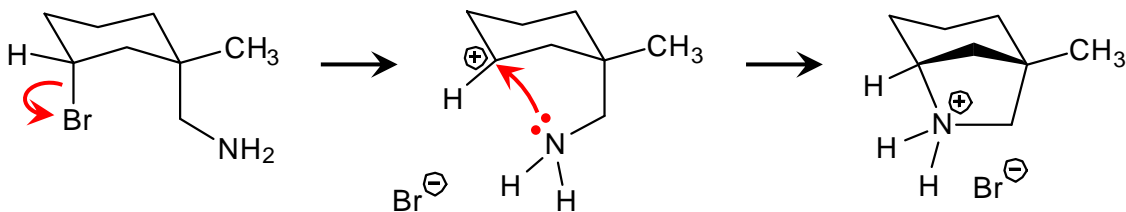
Grading is on arrow pushing only.

- (c) Your answer to part (b) explains how one of the starting materials is converted to product. How is product generated from the other starting material? Please be brief; you can probably answer this question in less than 5 words. You do not need to draw a mechanism to answer this question.

Explain how: S_N1 .

3

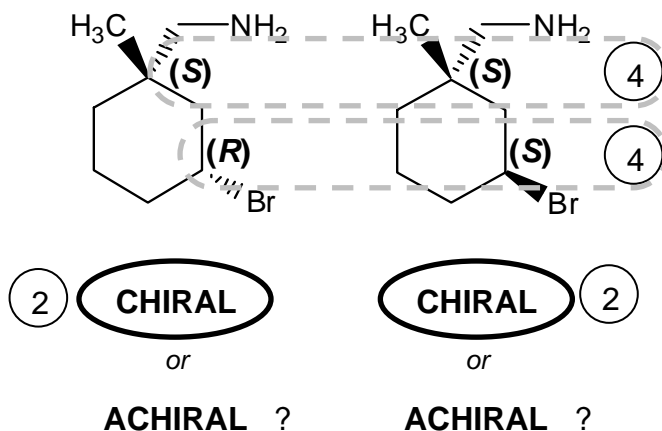
When the nitrogen nucleophile and the bromine leaving group can't be opposite each other, the reaction can still take place via an S_N1 mechanism:



Rubric for part (c):

3 points for "S_N1" in your answer.

- (d) Are the two starting materials chiral? For each starting material, **circle** whether you think the molecule is chiral or achiral. Then, **label each chiral center** with its appropriate Cahn-Ingold-Prelog designation [(*R*) or (*S*)]. Make it clear which atom in the drawing you are labeling.



- (e) What is the stereochemical relationship between the two starting materials? (Circle one answer.) Are they

ENANTIOMERS or **DIASTEREOMERS** or NEITHER ?

Rubric for parts (d) and (e):

4 points for each pair of Cahn-Ingold-Prelog designations. (8 points total.)

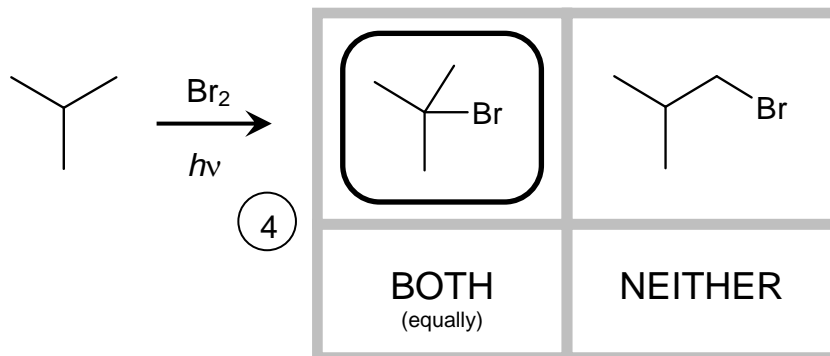
We graded these in pairs because of the obvious (same or opposite) relationship each has with another. If you got both assignments correct you get the points, but if you miss one, say by hedging your bets, you got no points.

-2 points for each achiral center labeled as chiral.

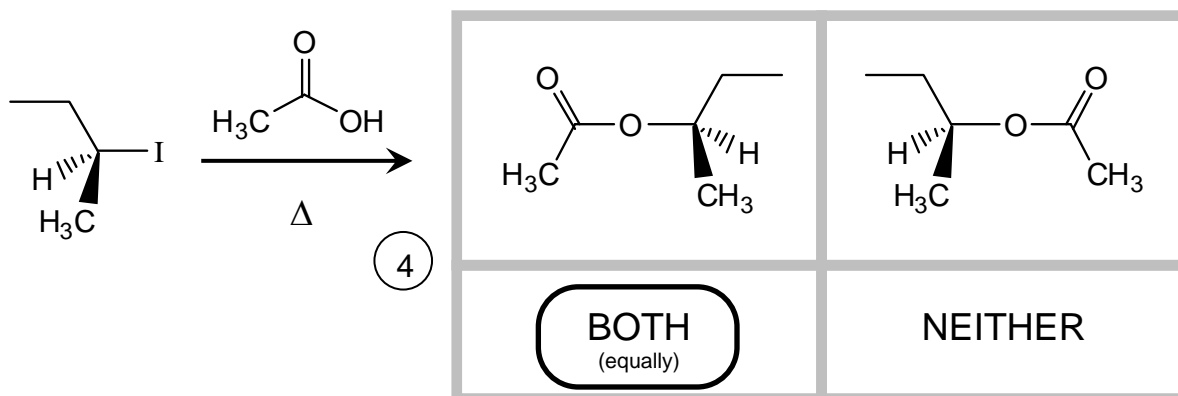
2 points for each circled chiral/achiral assignment.

3 points for diastereomer assignment.

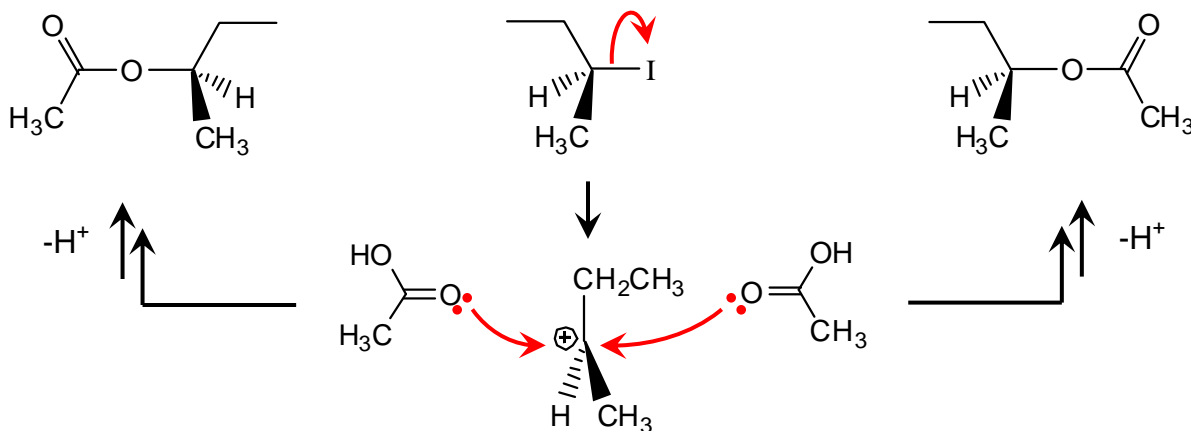
5. (12 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

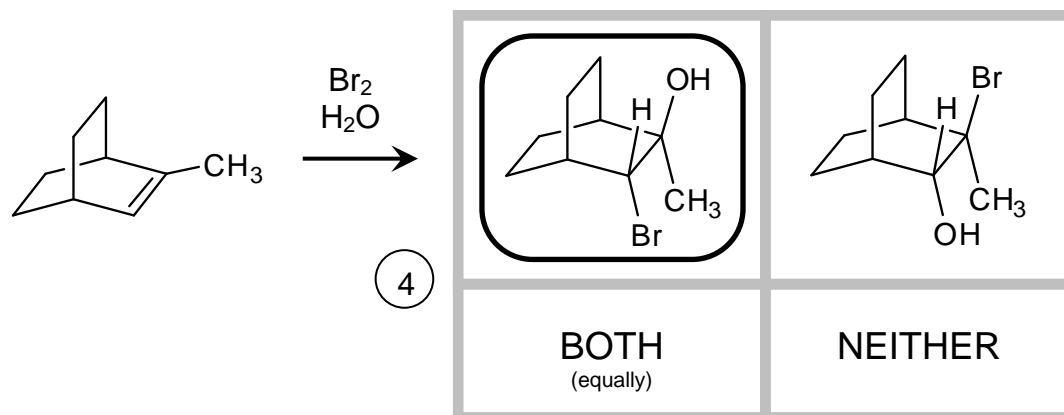


Radical bromination prefers the most substituted carbon, because reaction at that carbon goes through the most substituted radical.

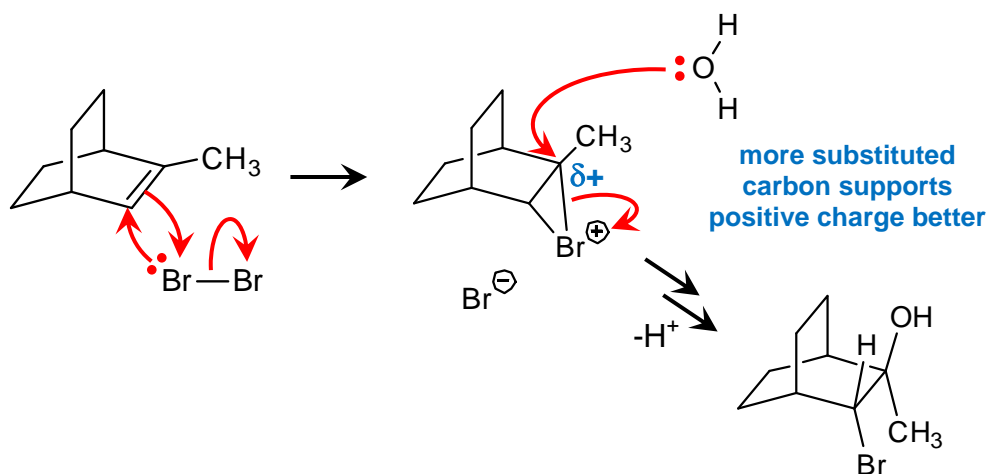


This reaction goes via S_N1 , because acetic acid is a poor nucleophile, but an even poorer base. The reaction goes through a planar carbocation intermediate, which can react on either face to give the two enantiomers shown.

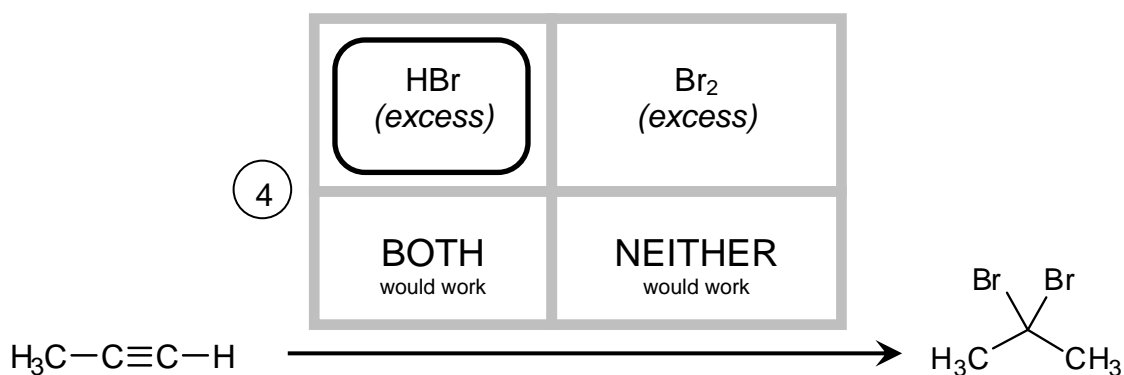




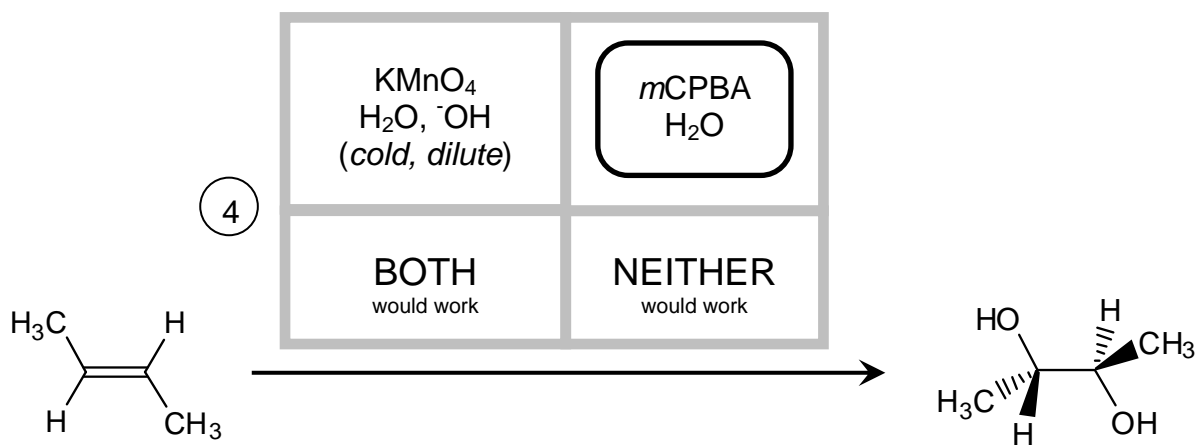
Formation of a halohydrin via $\text{Br}_2/\text{H}_2\text{O}$ places the $-\text{OH}$ group at the more substituted carbon. This is because the intermediate bromonium ion accommodates a partial positive charge better, and is thus more electrophilic, at the more substituted carbon:



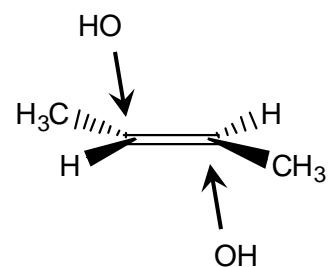
6. (16 pts) Each of the reactions *on the next page* is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle “BOTH”. If neither set of reaction conditions would succeed, circle “NEITHER”. **Circle one answer only.**

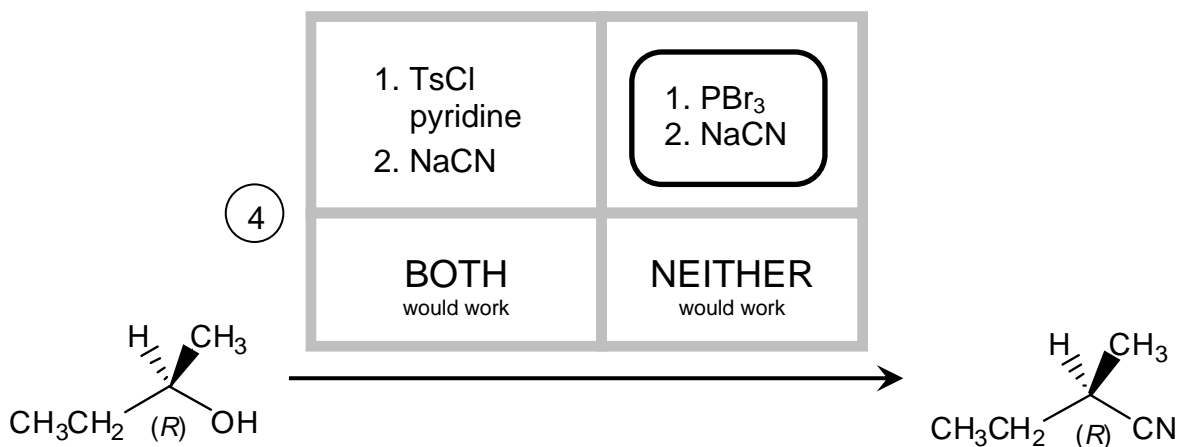


Both of these reagent systems will add H-Br to alkynes: the system on the left will add Markovnikov, with the Br attached to the more substituted carbon; and the system on the right will add anti-Markovnikov, with the Br attached to the less substituted carbon. (And the “excess” means that each will add twice rather than once.) The product is Markovnikov.

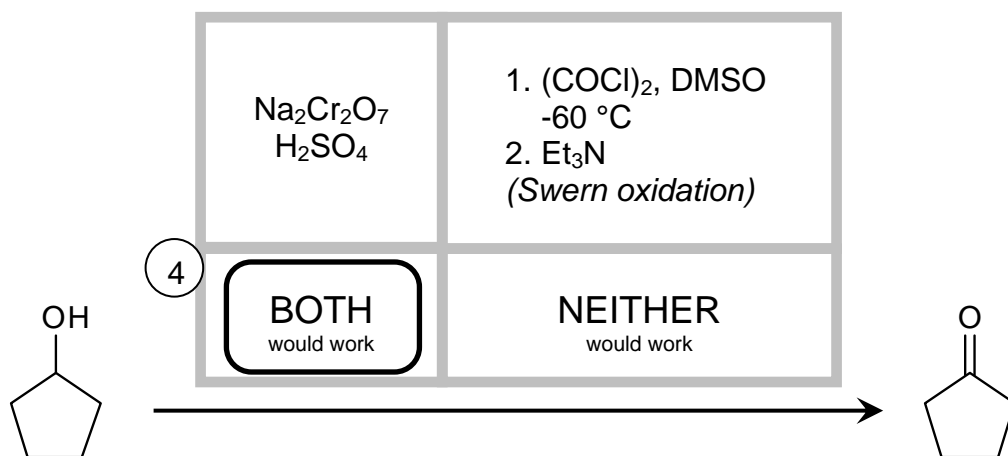
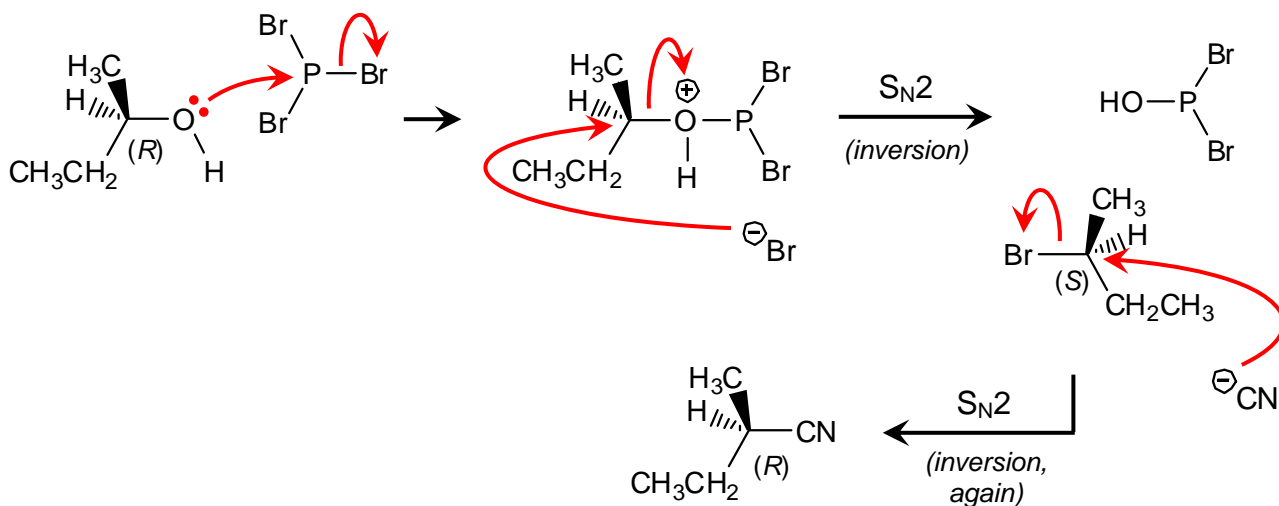


Both of these reagent systems will perform dihydroxylation on alkenes; the first adds two -OH groups *syn* (on the same face of the alkene), and the second adds them *anti* (on opposite faces of the alkene). Here, the addition is *anti*.

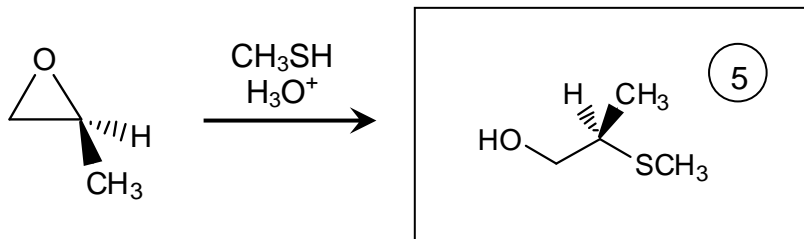




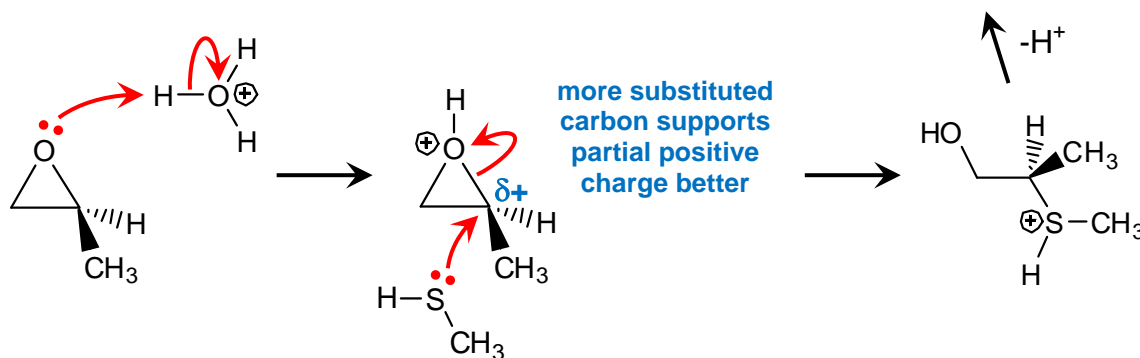
Both of these sets of reaction conditions would replace the -OH with a -CN . The first set would invert stereochemistry at the reacting carbon; tosylation retains stereochemistry, but the subsequent $\text{S}_{\text{N}}2$ reaction with CN^- would invert the (R) center to an (S) product. The second set would invert stereochemistry twice, giving net retention:



7. (15 pts) For each of the reactions on the following pages, fill in the empty box corresponding to the major product. Wherever appropriate, illustrate stereochemistry in your drawings (using wedge and dashed bonds). If multiple enantiomers or diastereomers are produced, indicate this in the answer box (e.g., by writing "+ enantiomer", etc.)



In acid, the epoxide is attacked at the more substituted carbon.



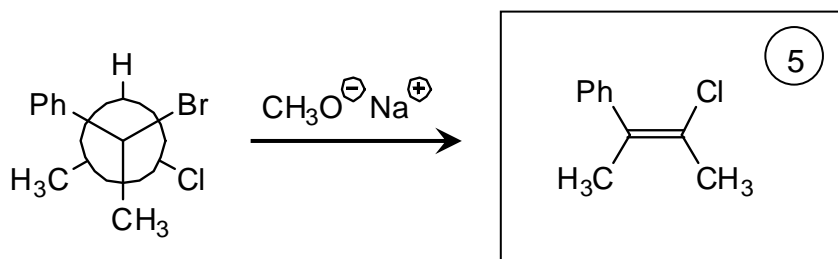
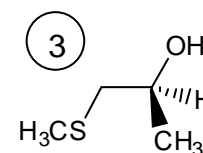
Rubric:

5 points for correct structure.

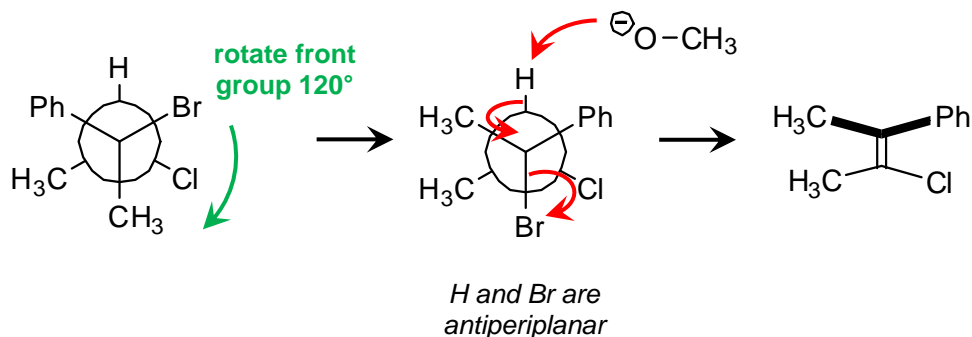
-2 points for incorrect or unclear stereochemistry.

-2 points for incorrect regiochemistry (attack at less hindered carbon).

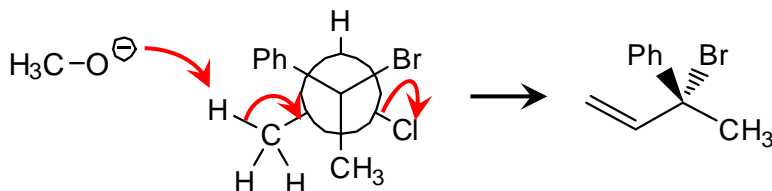
-2 points for each clearly trivial structure mistake. (This includes leaving out or adding a carbon.)



CH_3O^- is a strong base, a better base than it is a nucleophile, and will react primarily via E2. The molecule drawn in the problem, however, isn't in the geometry it needs to be to react by E2, so we have to rotate the central bond:



There was actually another elimination reaction that could happen—elimination of HCl instead of HBr—but because Cl is a worse leaving group, and because the alkene product would be less substituted (and thus less stable), it would be a minor product here.



Rubric:

5 points for correct structure.

3 points partial for (E)-alkene.

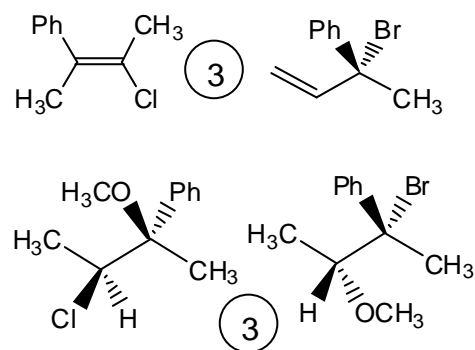
3 points partial for eliminating HCl instead of HBr.

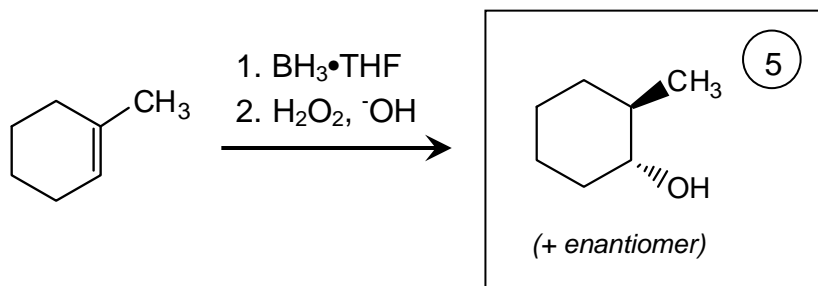
3 points partial for substitution product at either Br or Cl, as long as stereochemistry is correct.

1 point partial for any substitution product with incorrect or unclear stereochemistry.

-2 points for each clearly trivial structure mistake.

(This includes leaving out or adding a carbon.)





Hydroboration adds H-OH to alkenes in anti-Markovnikov fashion, such that the -OH ends up attached to the less substituted carbon. It is also a stereoselective reaction, which adds the -H and -OH *syn* (to the same face of the alkene). In the box above, I've drawn the -H and -OH having added to the underside of the alkene, but they could also both add to the top, which would give the enantiomer.

Rubric:

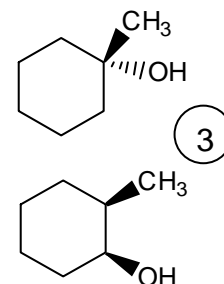
5 points for correct structure.

4 points partial for omitting "+ enantiomer".

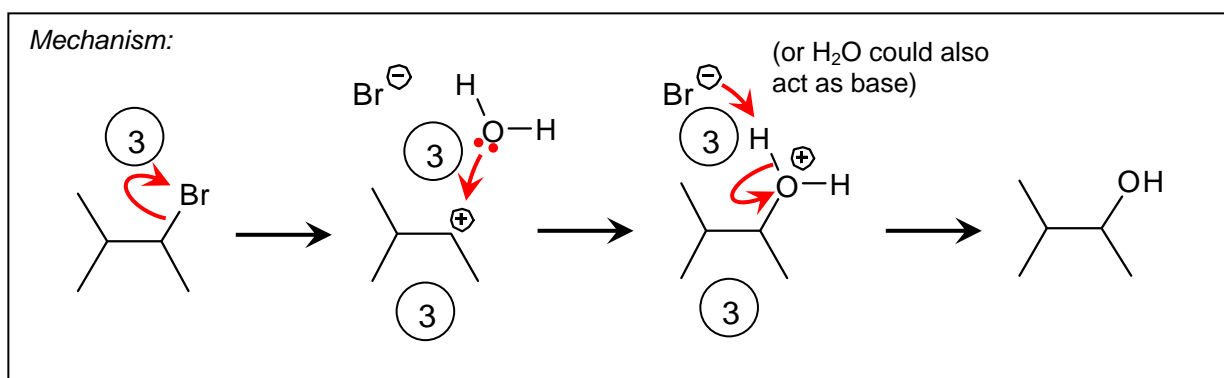
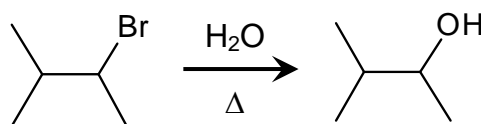
3 points partial for incorrect stereochemistry (including anti-addition of H-OH), or for not indicating stereochemistry.

(You won't lose a point for also omitting "+ enantiomer" here—still 3 points.)

3 points partial for Markovnikov addition of H-OH.



8. (34 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: (15 points total this part)

Overall notes:

Must be these steps, in this order.

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) and spectators may be omitted.

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

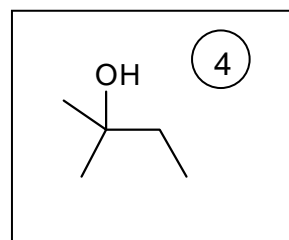
-2 points for each error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.

-6 points (out of 12) for combining two steps into one.

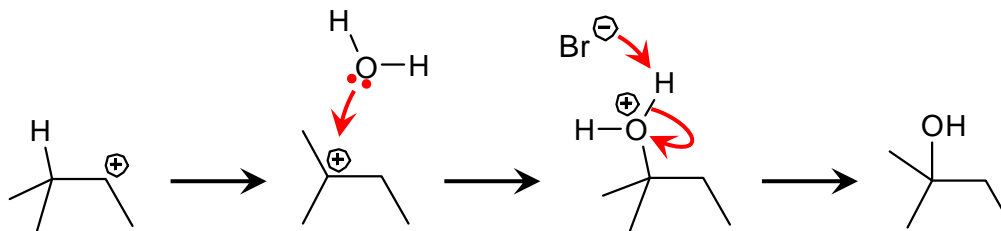
3 points per electron-pushing step.

3 points per intermediate.

One of the intermediates you drew in this mechanism could be stabilized by a 1,2-hydride shift. What alcohol product would be generated if this shift occurred?

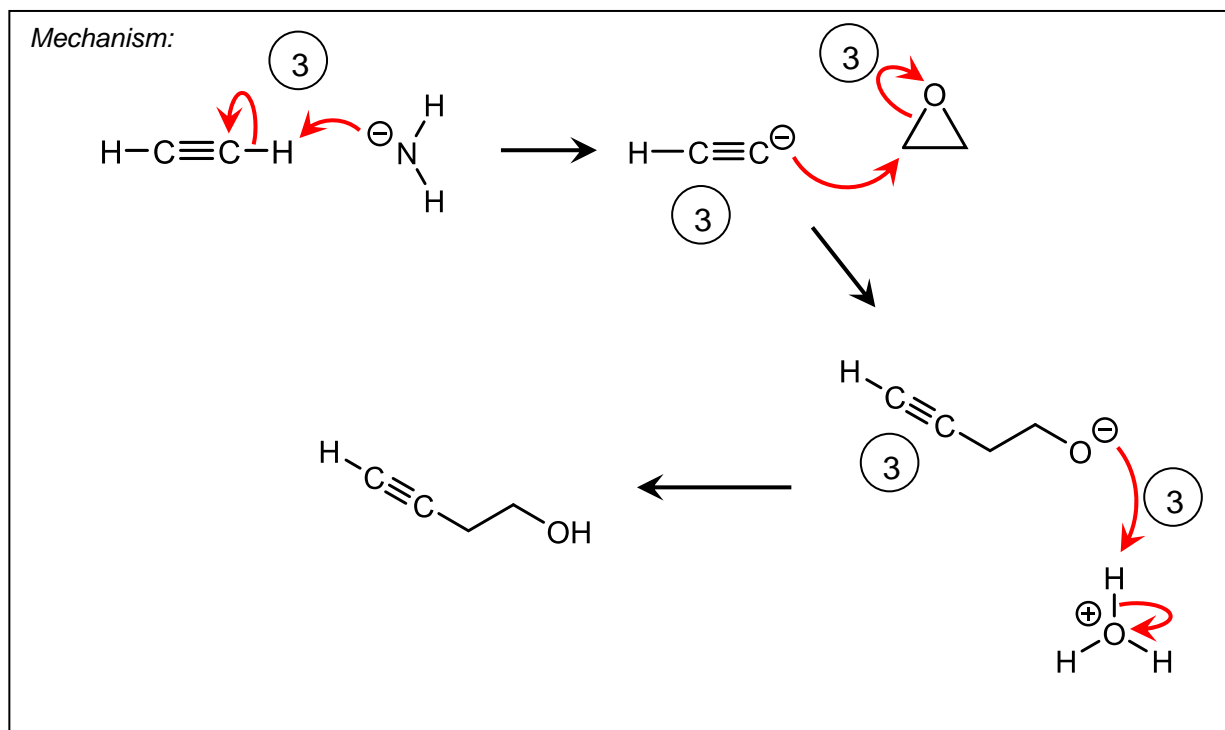
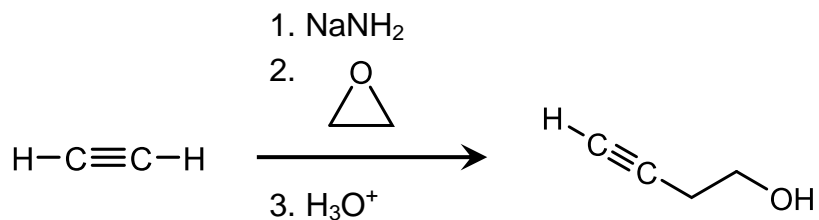


The carbocation intermediate in the mechanism above is a secondary carbocation—stable, but not as stable as it could be. A 1,2-hydride shift can convert this secondary cation to a tertiary one:



Rubric:

4 points for correct answer. *No partial credit.*



Rubric: (15 points total this part)

Overall notes:

3 points per arrow-pushing step.

3 points per intermediate.

Must be these steps, in this order.

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

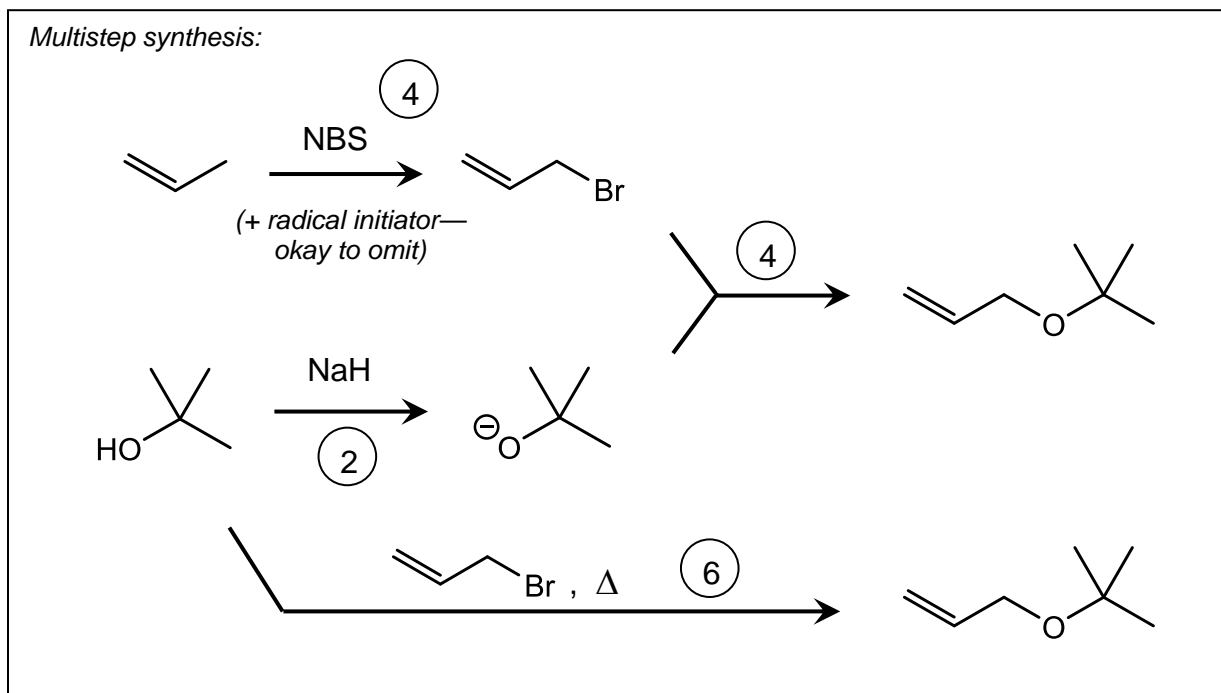
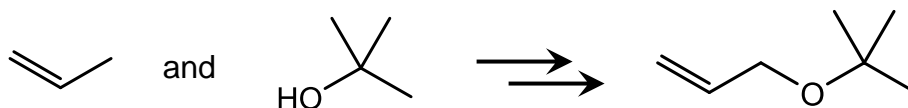
Things that have left (e.g., NH₃) and spectators may be omitted.

-2 points, for each arrow in each step, for errors in drawing arrows. Arrow must start at an electron 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.

-6 points (out of 12) for combining two steps into one.

9. (18 pts) For each set of starting materials and products 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.



Rubric: (10 points total this part)

General notes:

- 1 point for each 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, but product is wrong. If this happened, and you were led down an incorrect synthetic path by your mistake, you can also lose later points.

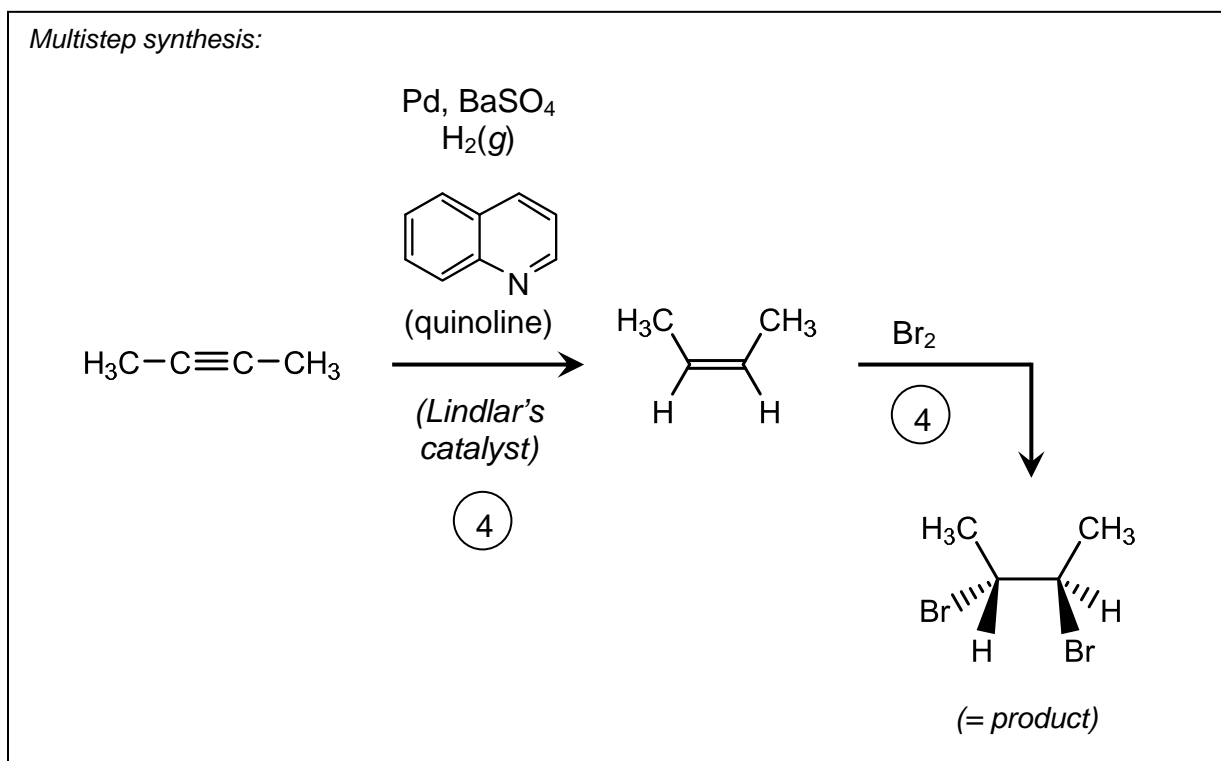
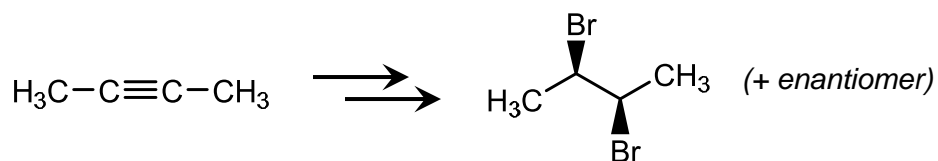
4 points for initial halogenation w/ NBS.

Though this reaction requires a radical initiator ($h\nu$ or AIBN) we didn't grade that here; just writing "NBS" was enough.

3 points partial for using $\text{Br}_2/h\nu$.

6 points for combining alcohol and alkyl halide in a way that makes them react.

This could be $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}1$; I think both would work in this case, because there is no competing elimination pathway.



Rubric: (8 points total this part)

General notes:

- 1 point for each 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. (So, if anti-hydrogenation is used for first step.)
- 2 points if reagents are correct, but product is wrong..

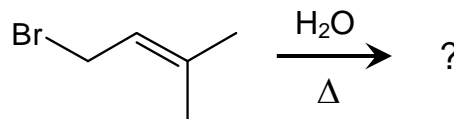
4 points for syn-hydrogenation.

2 points partial for using Na/NH₃, regardless of intermediate drawn.

4 points for bromination of alkene.

Altogether, 4 points partial for exposing alkyne to HBr. This would create the desired product, but also lots of other regio- and stereo-chemical products.

10. (38 pts) The bromoalkene starting material on the right reacts with water and heat to give a number of S_N1 substitution and $E1$ elimination products. One product was isolated and characterized by NMR and IR spectroscopy and mass spectrometry; the spectra of this product are shown on the following pages. High-resolution mass spectrometry determined an exact mass of 86.0732 amu for the highest-mass (parent, M^+) peak in the MS spectrum, which corresponds to a molecular formula of $C_5H_{10}O$.



(a) Four of the peaks in the IR spectrum below are labeled with their x -axis (wavenumber) value. What type of bond in the product does each peak correspond to? Match each peak to its bond vibration by writing its wavenumber value in the appropriate box. *There are seven boxes, so please leave three of them empty.*

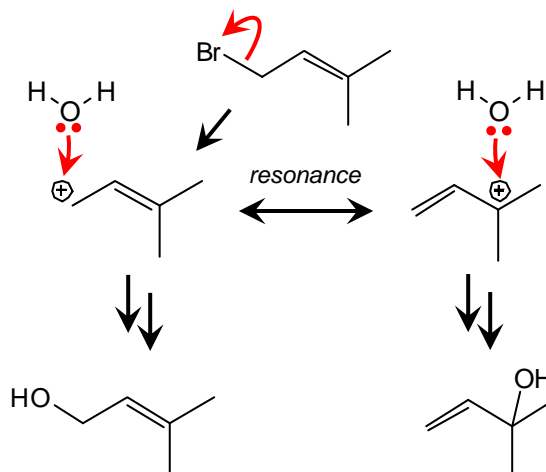
$\equiv C-H$ (sp)	$=C-H$ (sp^2)	$-C-H$ (sp^3)	$-O-H$
<input type="text"/>	<input type="text" value="3090 cm<sup>-1</sup>"/> 3	<input type="text" value="2979 cm<sup>-1</sup>"/> 3	<input type="text" value="3385 cm<sup>-1</sup>"/> 3
$-C\equiv C-$	$C=C$	$C=O$	
<input type="text"/>	<input type="text" value="1656 cm<sup>-1"/> "/> 3	<input type="text"/>	

Rubric for part (a):

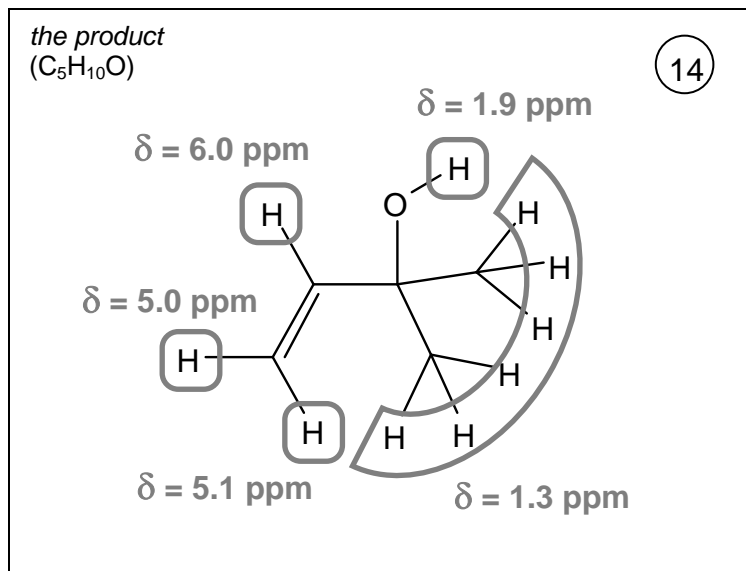
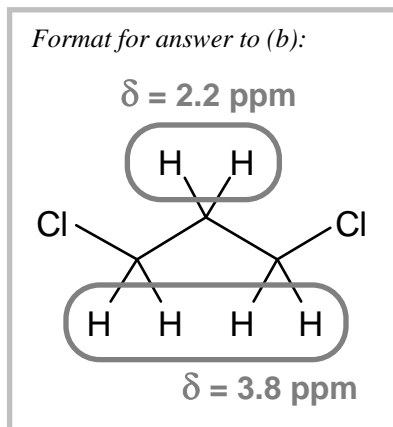
3 points for each correct box.

If any one value is written multiple times—say, in the correct box, but also in an incorrect box—no points.

At this point, we now know our product has an alcohol group in it. That means we must be dealing with a substitution (S_N1) product; an elimination ($E1$) product would contain a new double bond (in addition to the one that's already there), but no other functional groups. There are only two possible S_N1 products here:



(b) **What is the structure of the product?** In the box at right, draw the molecule's structure, including all hydrogens. Then, considering the ^1H NMR spectrum below, circle each set of equivalent $\text{H}'\text{s}$, and label each circle with its unique ^1H NMR chemical shift to within 0.1 ppm. (You do not need to label coupling constants J .)



Rubric for part (b):

Structure need not be correct to receive points in this problem.

4 points for the correct molecule.

2 points for assigning each δ value. (10 points total.) To get 2 points, circle must include all equivalent protons for your structure, match the integration intensity of the peak, and match the type of proton that would appear at that frequency.

6.0, 5.1, 5.0 ppm: Must be alkene protons. Full credit for the substitution pattern shown: 6.0 for lone H, 5.1 ppm, for H *trans* to the lone one, and 5.0 ppm for H *cis* to the lone one.

1 point partial for single circled alkene proton with mixed up δ assignment. This includes situations where alkene is not trisubstituted. (Splitting pattern would be inconsistent with other substitution patterns, but we gave partial credit anyway.)

2.9 ppm: Any alcohol proton (even nominally coupled ones).

1 point partial for ether protons. (Intensity wouldn't match.)

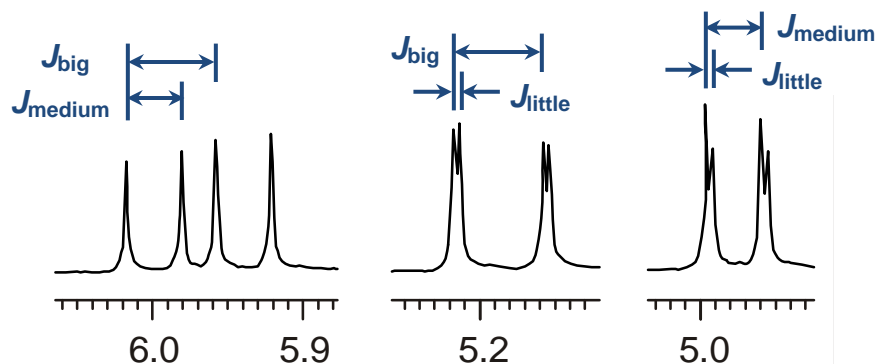
1.3 ppm: Two equivalent methyl groups.

1 point partial if two methyls are inequivalent, or if only one methyl group is circled. This is inconsistent with data, but we gave credit anyway.

The assignments for the alcohol proton and the methyl groups, in my opinion, are pretty clear. We know that the molecule has an alcohol group in it from the IR data, and there's only one resonance with intensity 1 in the NMR spectrum that's in the right region for it. Singlets with intensity 3, or multiples of 3, are often isolated methyl groups, so the singlet with intensity 6 at 1.3 ppm is probably two

equivalent methyl groups with no neighbors. The other three resonances in the $\delta = 5\text{-}6$ ppm region must be due to three inequivalent H's attached to a double bond. Of the two possible products listed on the previous page, the only one that makes sense in terms of these assignments is the one shown.

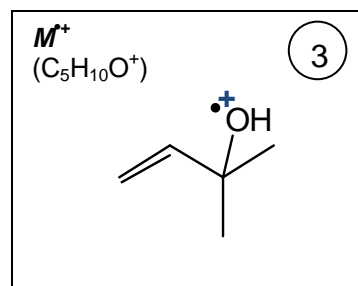
So then how do we assign the three alkene H's? Each multiplet of these three is a complex "doublet of doublets". I didn't list coupling constants J on the multiplets, but I think we can still imagine what they might be; on the diagram below, I've shown them as " J_{big} ", " J_{medium} ", and " J_{little} ".



Your coupling constant table says that, among the J coupling values felt by alkene H's for each other, J_{big} is J_{trans} (~15 Hz), J_{medium} is J_{cis} (10 Hz), and J_{little} is J_{geminal} (2 Hz). So the only H that should have a J_{big} and a J_{medium} —the one represented by the multiplet at 6.0 ppm—is the internal one. The other two can be assigned similarly.

- (c) By what mechanism was this product generated, 2 **S_N1** or **E1** ? (Circle one.)

- (d) In the electron-ionization (EI) mass spectrum, the parent mass peak at $m/z = 86$ corresponds to a radical cation (\mathbf{M}^+) that is generated by removing one electron from the original, neutral molecule \mathbf{M} . In the box on the right, draw \mathbf{M}^+ ; re-draw the structure you drew in part (b), but specifically indicate which electron is removed by drawing the molecule with one less electron.

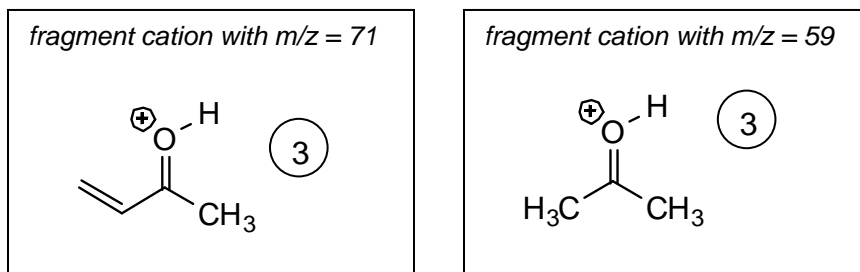


Rubric for part (d):

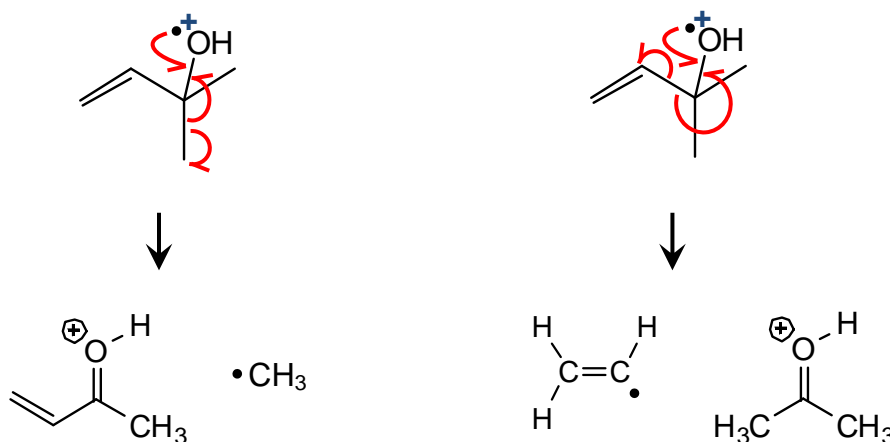
Structure need not be correct to receive points in this problem.

3 points for any molecule that (i) has formula $\text{C}_5\text{H}_{10}\text{O}$ and (ii) has a lone-pair electron on oxygen removed (leaving a radical cation).

- (e) What are the structures of the two predominant daughter (fragment) cations in the mass spectrum that have $m/z = 71$ and 59 ? *You do not need to do electron pushing to answer this question—just draw the cations.*



These fragments come from the radical cation parent:



Out of each pair of fragments, only the cations are visible in the mass spectrum.

Rubric for part (e):

Structures need not be correct to receive points in this problem.

Structures can be drawn as any resonance structure form and receive full credit.

3 points for correct answer.

-or-

3 points for any fragments that are substructures of answer to (b), that have the right mass, and that are drawn as cations.

-2 points for omitting positive charge.