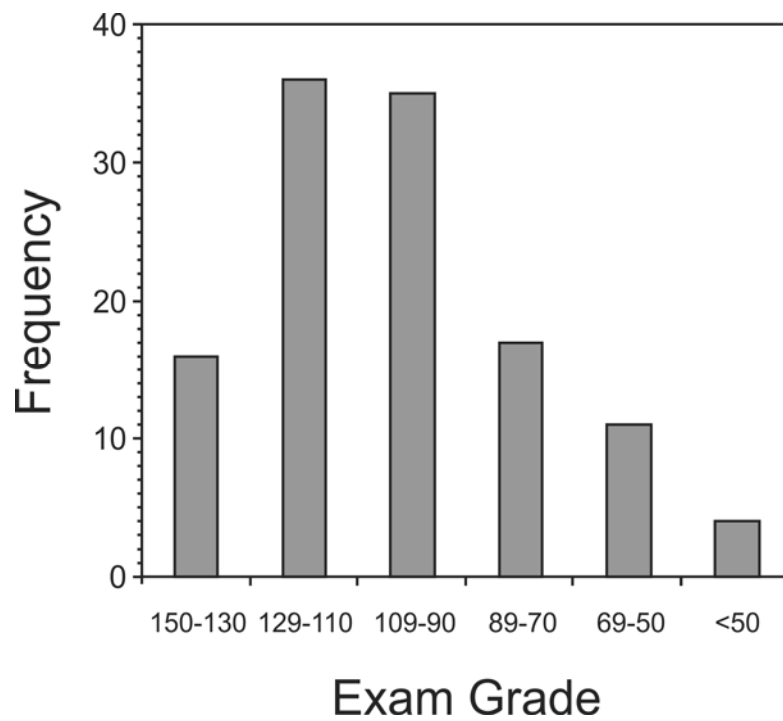


**Final Exam
Answer Key**

Final Exam Mean: 101
Final Exam Median: 105
Final Exam St. Dev.: 25



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.

<u>Acid</u>	<u>Conjugate Base</u>	<u>Base</u>	<u>Conjugate Acid</u>
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	<div style="border: 1px solid black; padding: 10px; width: fit-content; margin: 0 auto;"> $\text{H}-\text{C}\equiv\text{C}^{\ominus}$ </div>	$\text{F}_3\text{C}-\text{C}(=\text{O})\text{O}^{\ominus}$	<div style="border: 1px solid black; padding: 10px; width: fit-content; margin: 0 auto;"> $\text{F}_3\text{C}-\text{C}(=\text{O})\text{OH}$ </div>
(2) is <div style="border: 1px solid black; border-radius: 15px; padding: 5px; display: inline-block;"> MORE ACIDIC </div> LESS ACIDIC		is <div style="border: 1px solid black; border-radius: 15px; padding: 5px; display: inline-block;"> LESS BASIC </div> MORE BASIC	
than $\text{H}-\text{N}-\text{H}$	<div style="border: 1px solid black; padding: 10px; width: fit-content; margin: 0 auto;"> $\text{H}-\text{N}^{\ominus}-\text{H}$ </div>	than $\text{CH}_3\text{C}(=\text{O})\text{O}^{\ominus}$	<div style="border: 1px solid black; padding: 10px; width: fit-content; margin: 0 auto;"> $\text{CH}_3\text{C}(=\text{O})\text{OH}$ </div>

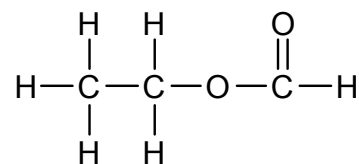
This is actually one you would just know. NaNH_2 is used to deprotonate alkynes, and it works because the $\text{p}K_a$ of ammonia (35) is higher than the $\text{p}K_a$ of an alkyne (25). So an alkyne like acetylene is more acidic.

The upper oxyanion is stabilized by both resonance and induction. So the upper alkoxide is more stable, and less basic.

Rubric:

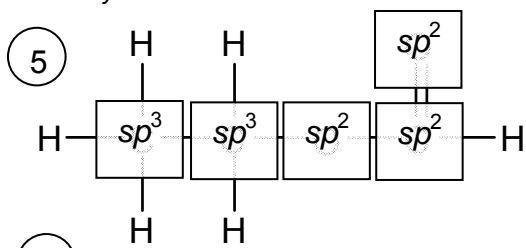
2 points per conjugate acid/base structure. *No partial credit.*
 2 points per circled more/less acidic/basic.

2. (18 pts) For ethyl formate (drawn at right), in the boxes provided:



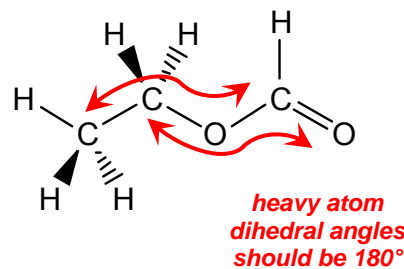
- Draw all significant resonance structures. In each structure, draw all atoms, bonds, lone pairs of electrons, and formal charges. Then, circle which resonance structure you think is the most significant, and which is the least. **Circle only one MOST and one LEAST.**
- Draw a Lewis wedge/dashed-bond 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:

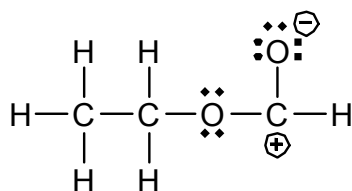


1 **MOST** or **LEAST** significant?

3-dimensional representation



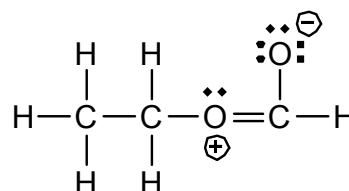
resonance structure



MOST or **LEAST** significant?

1

resonance structure



MOST or **LEAST** significant?

1

for **not** circling anything here.

Rubric:

- 1 point for each trivial mistake in structure (left out an H, extra C, etc.)
- Hybridizations: 1 point each (5 points this part.)
- (continued on next page)

3-D drawing: 3 points total.

2 points for *anti* (180°) dihedral angles; 1 point for C-C-O-C, 1 point for C-O-C-O.

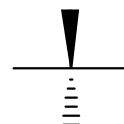
Anti conformation puts the largest groups farthest away from each other.

1 point 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.



correct



incorrect

Resonance structures: 3 points each.

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

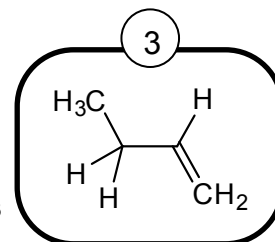
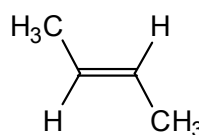
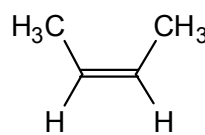
1 point for lone pairs (all must be correct).

1 point for bonds (all must be correct).

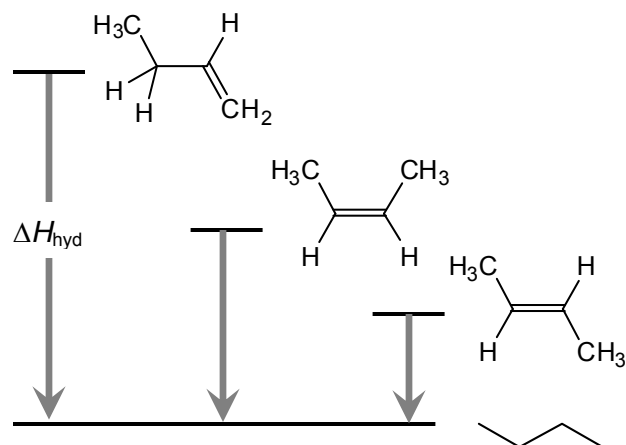
Resonance structures need not be in 3-D, or have correct bond angles.

Contributions (MOST/LEAST): 1 points each.

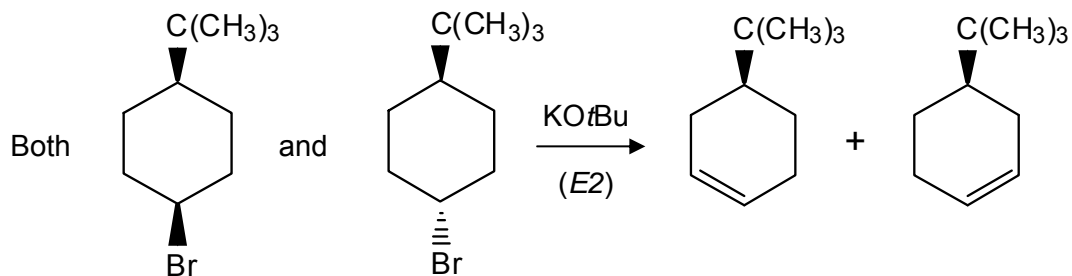
3. (4 pts) Each of the alkenes on the right hydrogenates—adds H_2 —exothermically (with $\Delta H_{\text{hyd}} < 0$) to form butane. **Which one hydrogenates the most exothermically?** (Circle one molecule.)



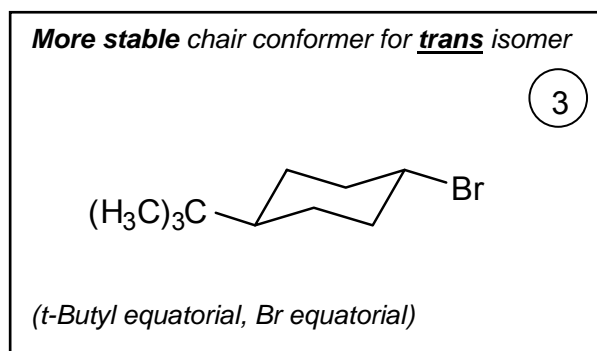
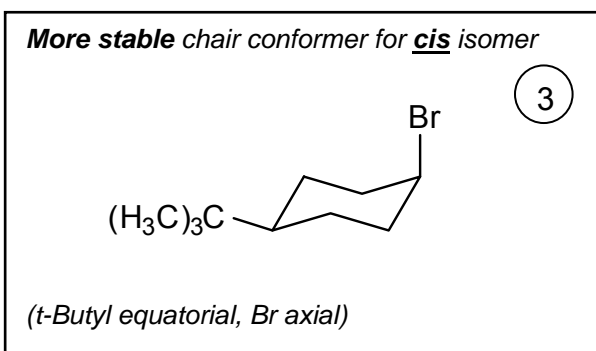
These molecules are all alkenes, and they all hydrogenate to form the same alkane, *n*-butane. But they have different heats of hydrogenation because of the different degrees of substitution between the three molecules. The monosubstituted alkene is the least stable, the highest in energy, and so it hydrogenates to give off the most energy.



4. (22 pts) In the presence of a strong base, each of the bromo-*tert*-butylcyclohexanes below undergoes E2 elimination to produce an alkene. However, one of the two reacts much faster than the other. In this problem, you will explain why.



- (a) Each of the starting cyclohexanes has two equilibrating chair conformers; in each case, one chair is much more stable than the other. In the boxes below, draw the two chair conformers for each starting material. Draw the more stable chair on top, and the less stable one below. Feel free to omit the ring hydrogens, but draw all non-hydrogen substituents.



The *tert*-butyl group is far more sterically demanding (bigger) than the bromine, so the chair conformer that puts the *tert*-butyl group equatorial will always be the most stable.

Rubric for part (a): 3 points per box. (6 points total for this part.)

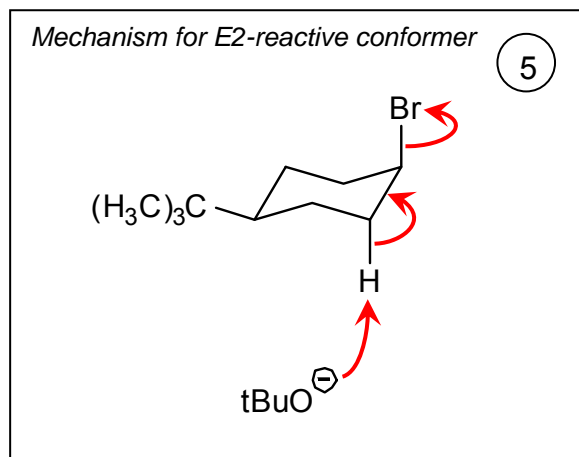
1 point per box for drawing any chair. (*Not including substituents, just the chair.*)

So if all you draw is 2 chairs, you get 2 points.

2 points per box for substituents correct.

If chair pairs are switched (trans on the left, cis on the right), you do not get these points.

- (b) Of the more stable conformers you drew on the previous page—the two on top—only one will react with $\text{KO}t\text{Bu}$ via E2. In the box on the right, re-draw the one stable conformer that will undergo E2. Then, “push electrons” (using curved arrows) to show how one of the two products would be generated from starting material and the $t\text{BuO}^-$ base. (You don’t need to draw the product, just push electrons.)

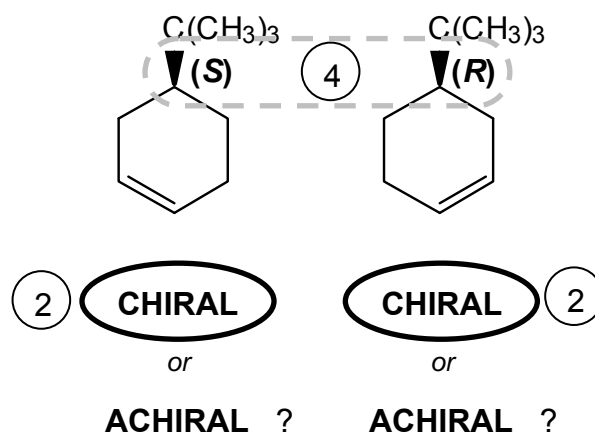


For E2 to work, the proton and leaving group must be anti-coplanar.

Rubric for part (b):

- 2 points for drawing the correct conformer in the box. *No partial credit.*
- 3 points for drawing arrows correctly.
- 2 points for each incorrect arrow. 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.

- (c) Are the two products chiral? For each structure, **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.



- (d) What is the stereochemical relationship between the two products? (Circle one answer.) Are they



Rubric for parts (d) and (e):

4 points for pair of Cahn-Ingold-Prelog designations.

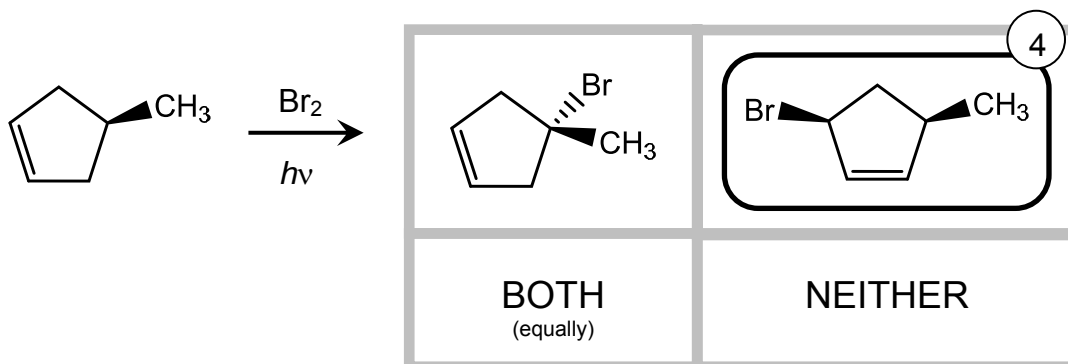
We graded these as a pair because of the obvious (same or opposite) relationship one center has with the other. If you got both assignments correct you get the points, but if you miss one, say by hedging your bets, you got no points.

-2 points for each achiral center labeled as chiral.

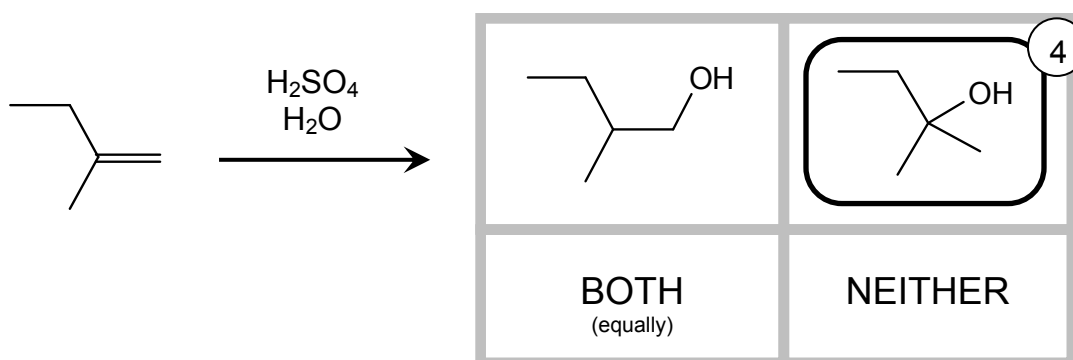
2 points for each circled chiral/achiral assignment.

3 points for enantiomer assignment.

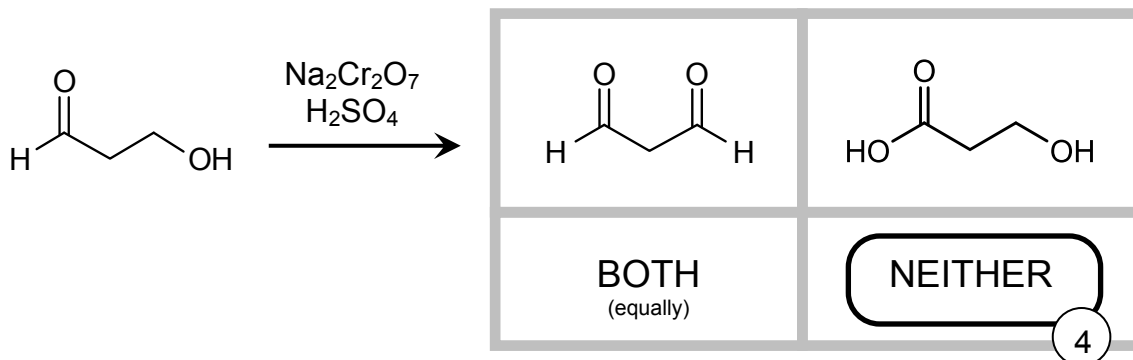
5. (12 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**



The reagents here perform radical halogenation on the substrate. The selectivity of radical halogenations is dictated by the stability of the intermediate radical; the allylic site will create a resonance-stabilized radical, which will be much more stable than the tertiary radical produced at the other site. So bromination at that allylic site is preferred.

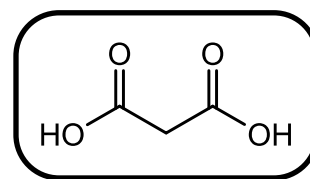


Hydration in strong acid performs Markovnikov addition of H-OH to alkenes; in other words, the -OH ends up bound to the more substituted position of the double bond. The product on the left is the anti-Markovnikov product.

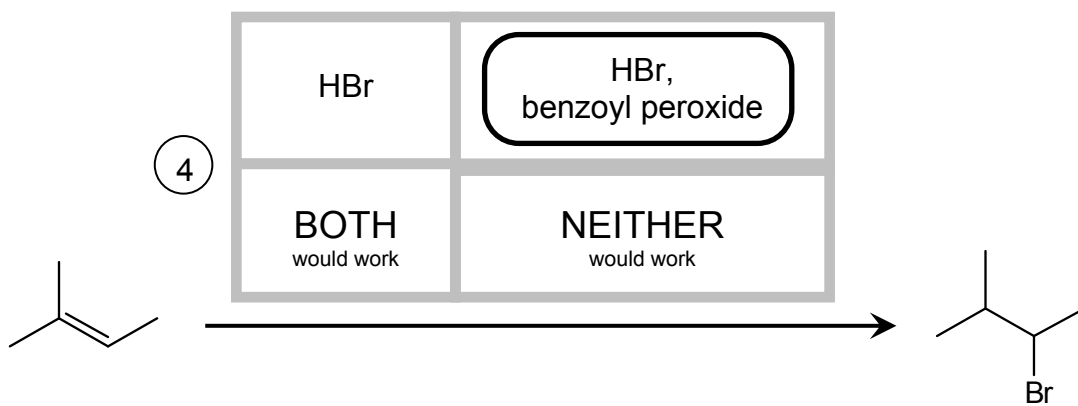


4

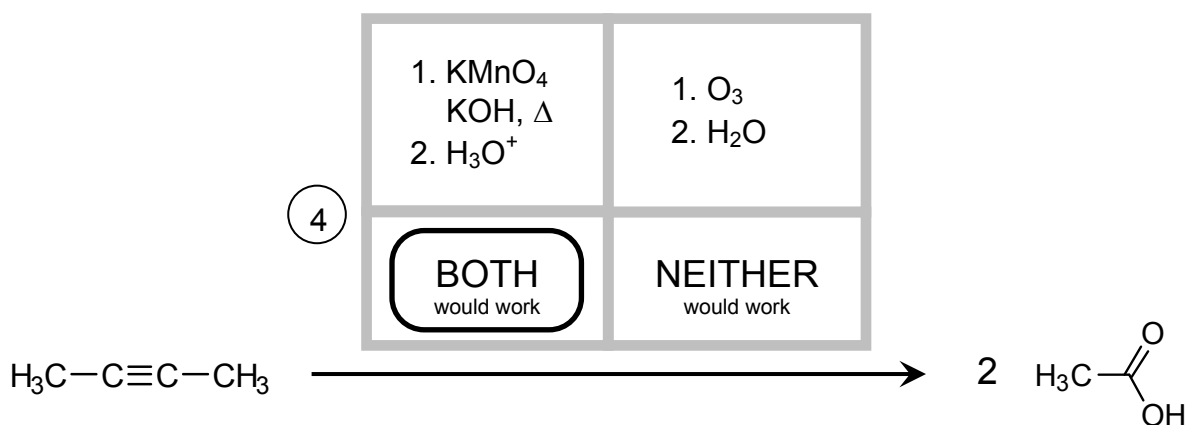
Chromate oxidizes all oxygen-containing functional groups as far as they can be oxidized. Here, both primary carbons would be oxidized to carboxylic acids, to:



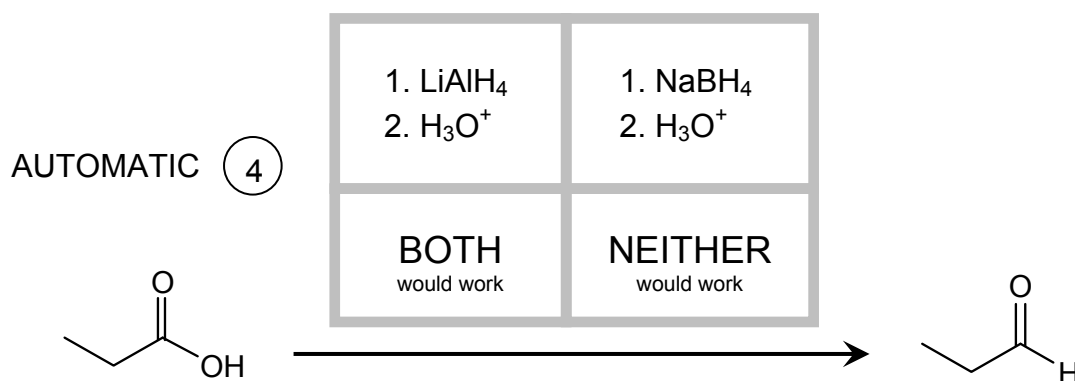
6. (16 pts) Each of the reactions *on the next page* is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If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



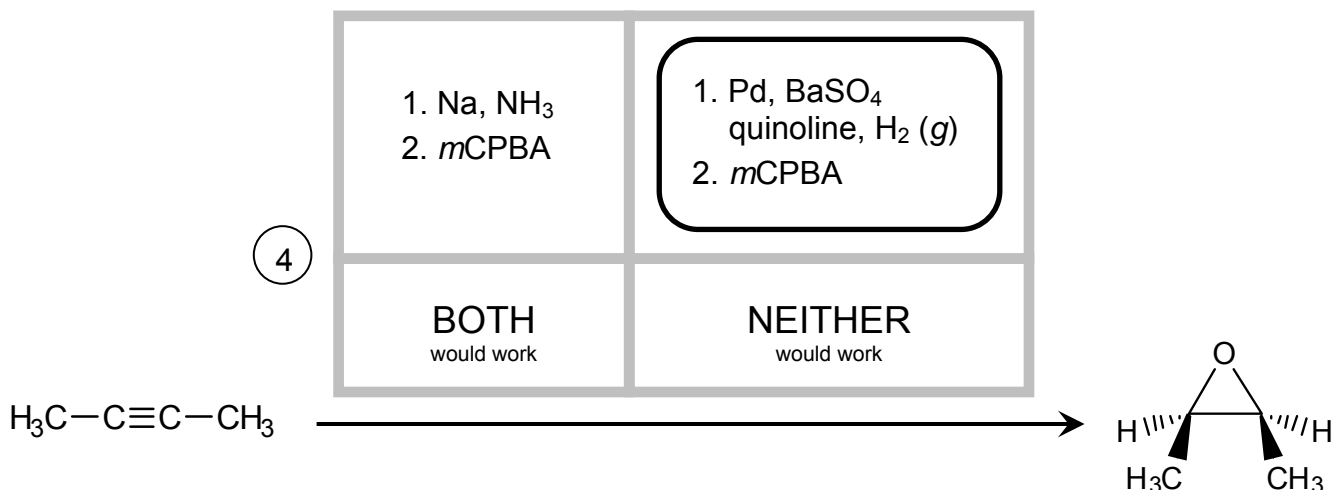
Both of these reaction conditions add H-Br to a double bond. The first adds Markovnikov (such that the Br is bound to the more substituted of the two alkene carbons), and the second adds anti-Markovnikov (such that the Br is bound to the less substituted carbon). The product is the anti-Markovnikov adduct.



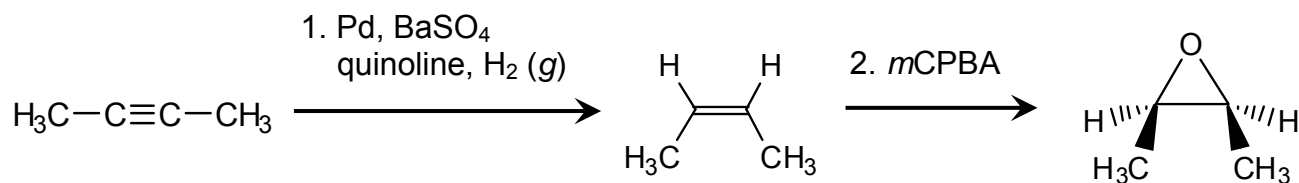
Both of these methods split an alkyne into two carboxylic acids.



I copied this problem from a CHEM 2302 exam, with the plan to use the boxes and one of the molecules to make a new problem for this test, but I must have forgotten to save the changes I made. You shouldn't have known the answer to this.

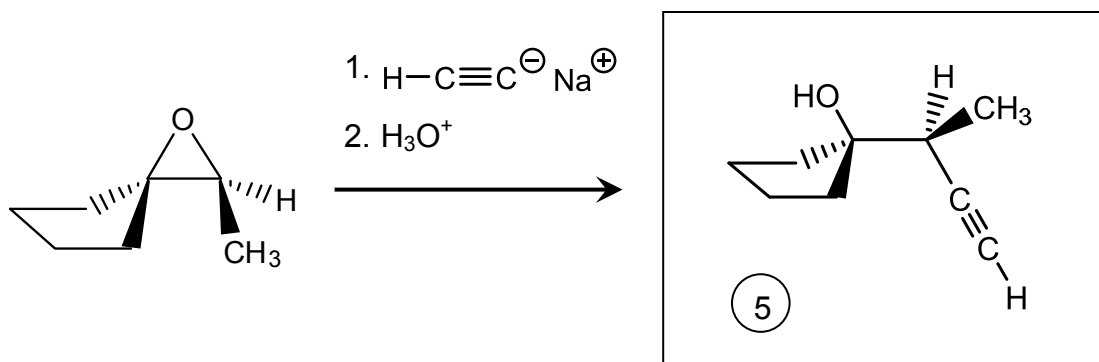


This problem involves a sequence of two transformations. In both boxes, the first step converts the alkyne to an alkene, and the second converts the alkene to an epoxide. To make the *cis*-dimethylepoide shown, we need a *cis*-alkene, and only Lindlar's catalyst (the second box) makes a *cis*-alkene from an alkyne:

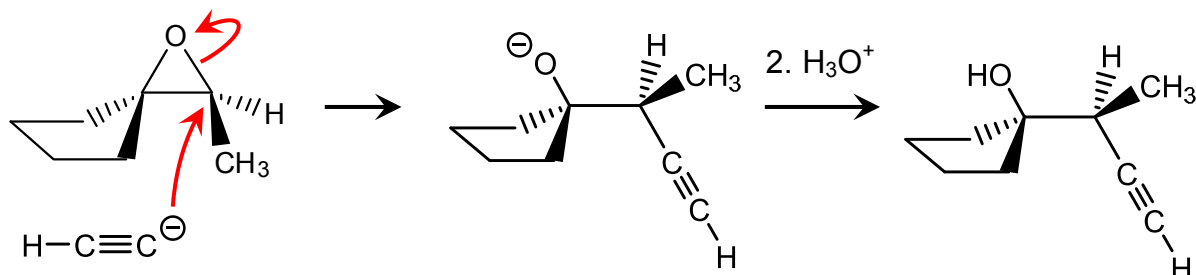


The other sequence would generate the *trans*-alkene, and then the *trans*-disubstituted epoxide.

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.)



The alkylmetal opens the epoxide at the less substituted, less sterically hindered carbon. (The epoxide's reactivity pattern here is under basic conditions, because alkylmetals are strong bases.) The stereochemistry on the right side is inverted by the S_N2 reaction.

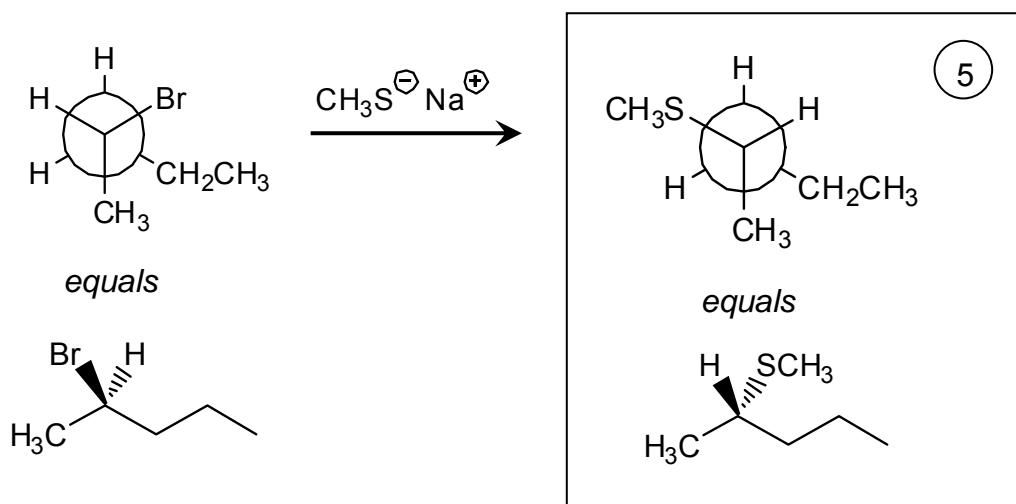


Rubric:

5 points for correct structure.

-2 points for incorrect or unclear stereochemistry.

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



Thiolates (like CH_3S^-) are much better nucleophiles than they are bases, so this will be an S_N2 reaction.

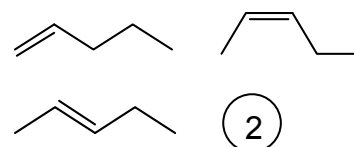
Rubric:

5 points for correct structure.

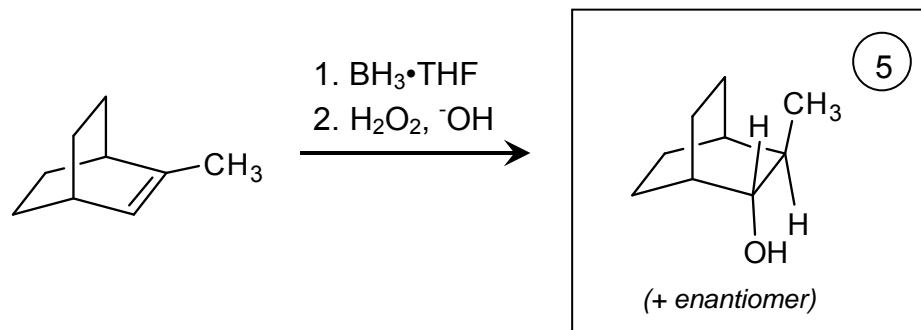
You did not have to draw your answer as a Newman projection; any correct drawing received full credit.

3 points partial for incorrect or unclear stereochemistry.

2 points partial for any elimination product.



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



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:

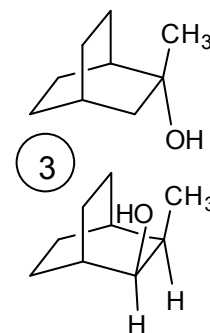
5 points for correct structure.

4 points partial for omitting "+ enantiomer".

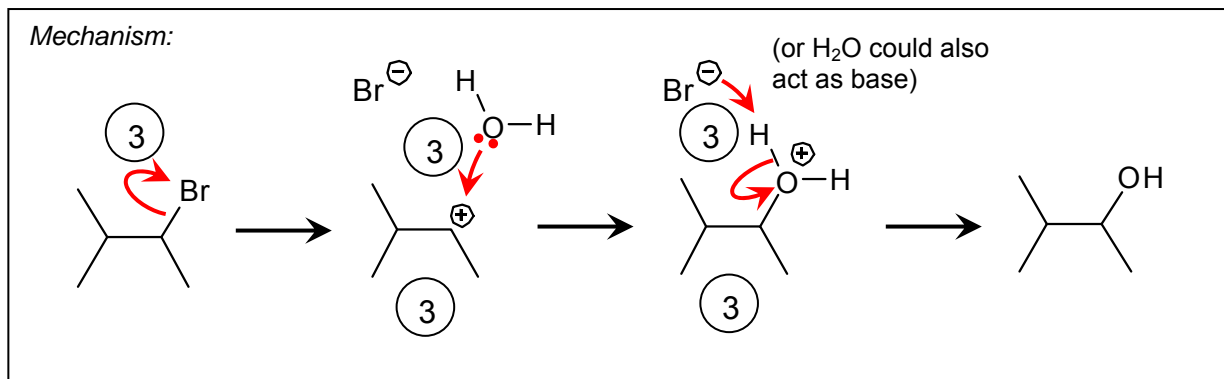
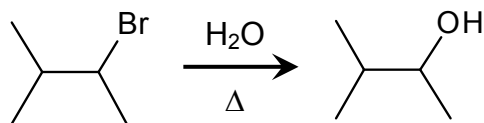
3 points partial for incorrect stereochemistry (including anti-addition of H-OH), or for not indicating stereochemistry.

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

3 points partial for Markovnikov addition of H-OH.



8. (19 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.

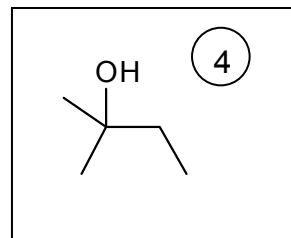
-2 points for each error in charge, valency, structure, base, etc.; if error propagates, points are taken off only for initial error.

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

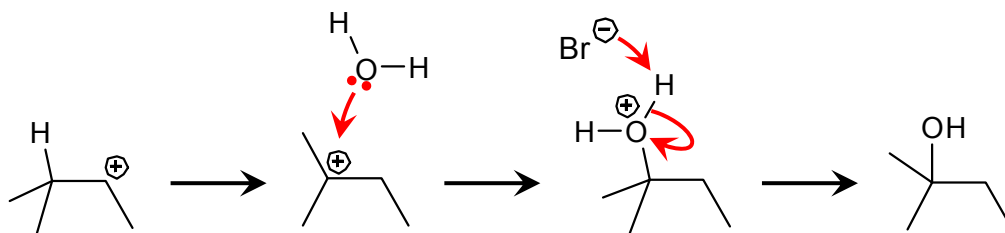
3 points per electron-pushing step.

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?



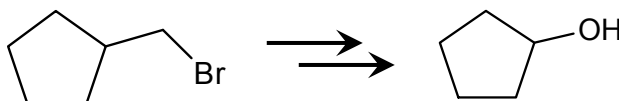
The carbocation intermediate in the mechanism above is a secondary carbocation—stable, but not as stable as it could be. A 1,2-hydride shift can convert this secondary cation to a tertiary one:



Rubric:

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

9. (12 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.



AUTOMATIC 12.

10. (22 pts)
- a. The ^1H NMR spectrum of the product is shown above. Given this spectrum, **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 H'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 .)

the product
($\text{C}_8\text{H}_{12}\text{O}$)

(10) total this box.

$\delta = 2.5$ ppm

$\delta = 5.8$ ppm

$\delta = 6.6$ ppm

$\delta = 1.9$ ppm

$\delta = 1.2$ ppm

Rubric for part (a):

Structure need not be correct to receive points in this problem. We did not evaluate your structure for correctness, but incorrect structures

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.

6.6, 5.8 ppm: Must be alkene protons with an adjacent H. Either value can be assigned to either proton.

1 point partial for assigning each ppm value to any alkene proton, regardless of neighbors.

2.5, 1.9 ppm: Must be alkyl protons with two adjacent H's. Once again, either value can be assigned to either proton.

1 point partial for assigning these to any C_{sp^3} -H.

1.2 ppm: Must be two equivalent $-CH_3$ groups with no neighbors.

1 point partial if methyl group has neighboring H's, or for assigning to inequivalent H's.

- b. How many peaks would you expect to observe in the 1H -decoupled ^{13}C NMR spectrum of the product?

7

3

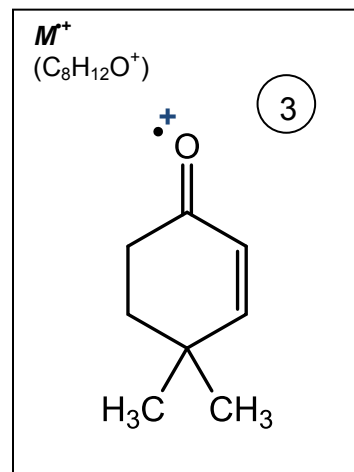
In our product, all of the 8 carbons are inequivalent except for the two methyl groups. That leads to 7 signals. We accepted any answer that was consistent with your answer to part (a).

Rubric for part (b):

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

3 points for any answer that has the correct number of carbons for your answer to (a).

- c. In the electron-ionization (EI) mass spectrum shown at the bottom of this page, the parent mass peak at $m/z = 124$ corresponds to a radical cation ($M^{+\bullet}$) that is generated by removing one electron from the original, neutral molecule **M**. In the box on the right, draw $M^{+\bullet}$; re-draw the structure you drew in part (a), but specifically indicate which electron is removed by drawing the molecule with one less electron.

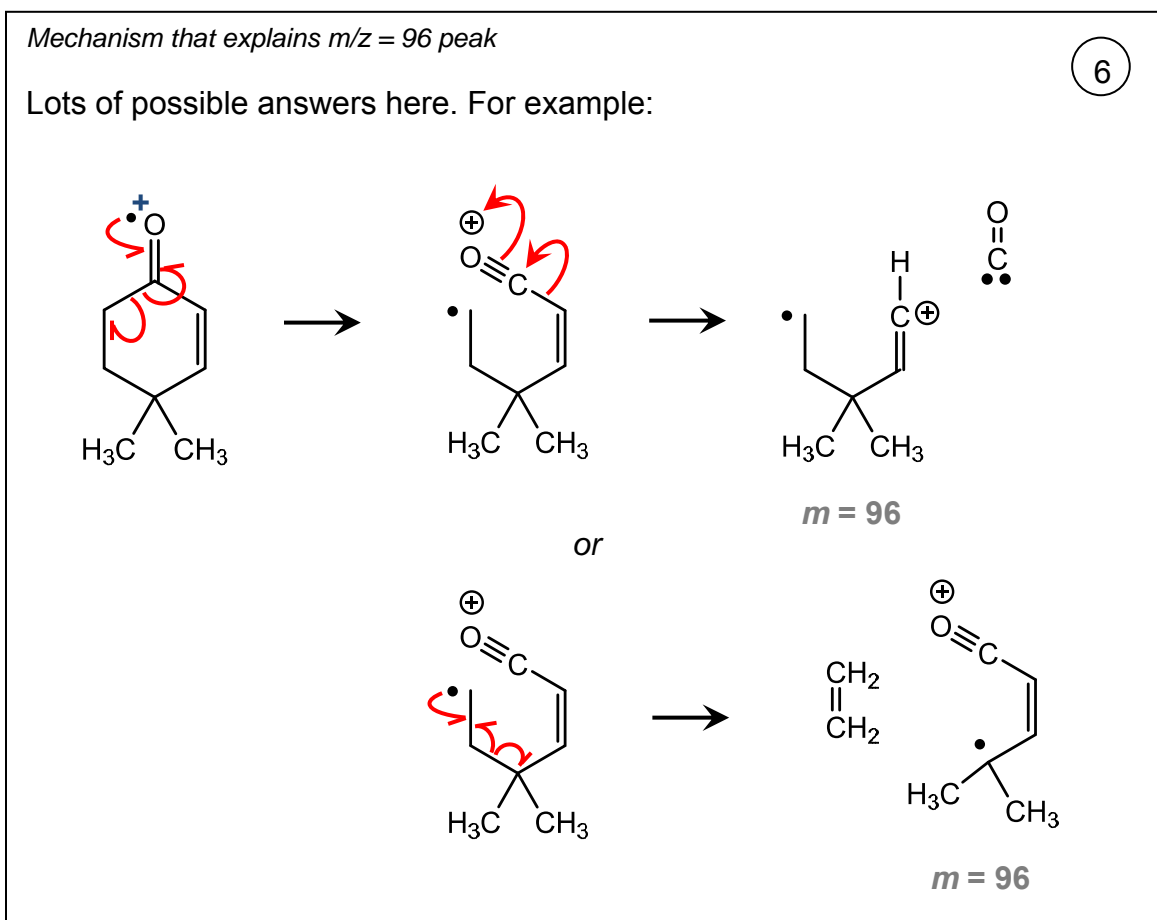


Rubric for part (c):

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

3 points for ionizing a lone pair in (a).

- d. The spectrum also shows a fragment peak at $m/z = 96$. In the box below, draw a mechanism (using “arrow pushing”) that shows how this fragment is generated from the parent ion you drew above.



Rubric for part (d):

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

3 points for a fragment related to the answer in (c) by loss of $m = 28$.

That includes losing carbon monoxide (CO) or ethylene (C₂H₄). These are both neutral, paired-electron molecules, so your fragment product needed to be a radical cation. In addition, I think you needed to start with an α -cleavage.

3 points for electron pushing to get to that product.