NAME ________________________

ID # ________________________

ORGANIC CHEMISTRY I (2301)

9:30 – 10:45 am, August 7, 2014

Final Exam

You will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Monday, August 12th at 1 PM. Exams that are not picked up within two weeks will be disposed of.

A periodic table and tables of typical NMR chemical shifts and coupling constants are attached to the back of this exam as aids. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

Right now, write your name and student ID number at the top of this page. When the exam begins, please write your name at the top of the next page.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

NAME _________________________

Scoring:	1. _________ / 12	6. _________ / 16
	2. _________ / 17	7. _________ / 15
	3. _________ / 3	8. _________ / 19
	4. _________ / 22	9. _________ / 12
	5. _________ / 12	10. ________ / 22

Total Score: _________ / 150

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.

Acid

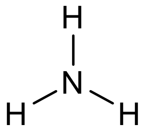
Conjugate Base

$H-C\equiv C-H$

is

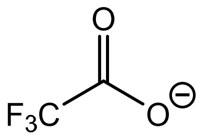
MORE ACIDIC **LESS ACIDIC**

than



Base

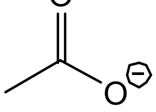
Conjugate Acid



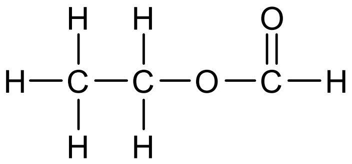
is

MORE BASIC **LESS BASIC**

than

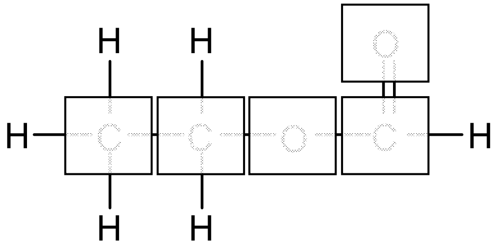


2. (17 pts) For ethyl formate (drawn at right), in the boxes provided:



- 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:



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

↕

3-dimensional representation

resonance structure

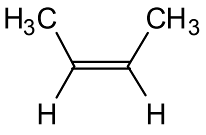
↔

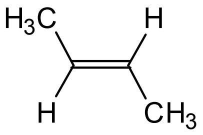
resonance structure

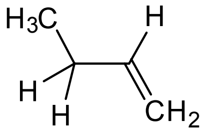
MOST *or* **LEAST** *significant?*

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

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







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.

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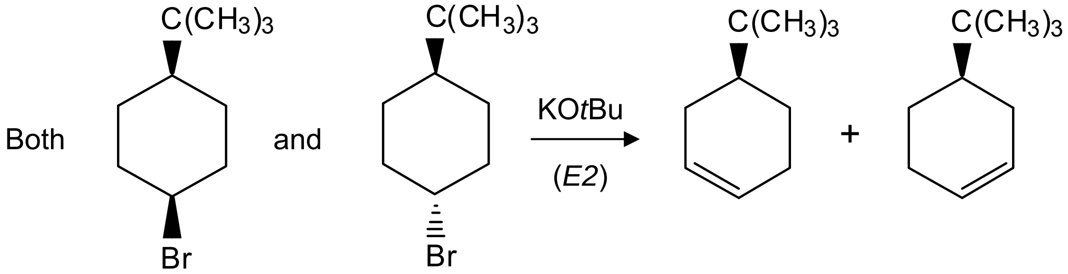


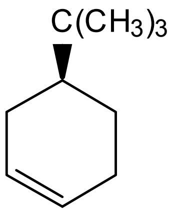
(a) Each of the starting cyclohexanes has two equilibrating chair conformers; for each starting material, one chair is much more stable than the other. In the boxes below, draw the more stable conformers for each starting material. Feel free to omit the ring hydrogens, but draw all non-hydrogen substituents.

More stable *chair conformer for* ***cis*** *isomer*	***More stable*** *chair conformer for* ***trans*** *isomer*

(b) Of the conformers you drew above, only one will react with KO*t*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*BuO^{-} base. (You don't need to draw the product, just push electrons.)

Mechanism for E2-reactive conformer

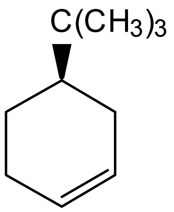
(c) Are the two products chiral? For each structure, **circle** whether you think the molecule is chiral or achiral. Then, **label each chiral center** with its appropriate Cahn-Ingold-Prelog designation [(*R*) or (*S*)]. Make it clear which atom in the drawing you are labeling.



CHIRAL

or

ACHIRAL ?



CHIRAL

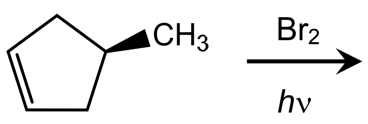
or

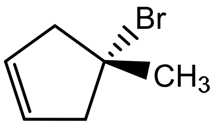
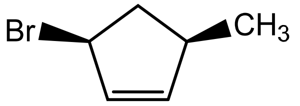
ACHIRAL ?

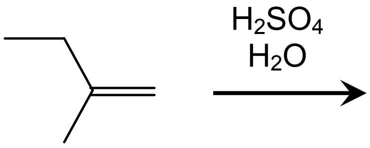
(d) What is the stereochemical relationship between the two products? (Circle one answer.) Are they

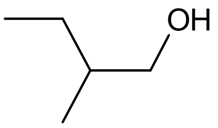
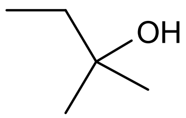
ENANTIOMERS *or* **DIASTEREOMERS** *or* **NEITHER** ?

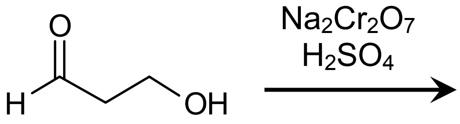
5. (12 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

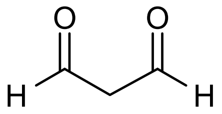
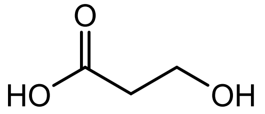


	
BOTH (equally)	NEITHER

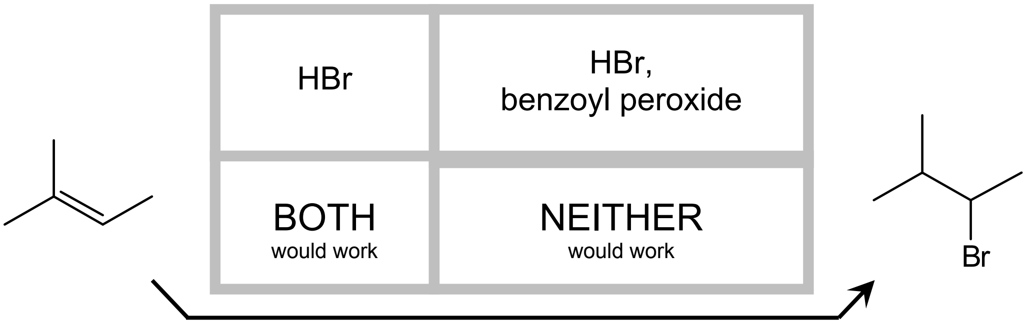


	
BOTH (equally)	NEITHER

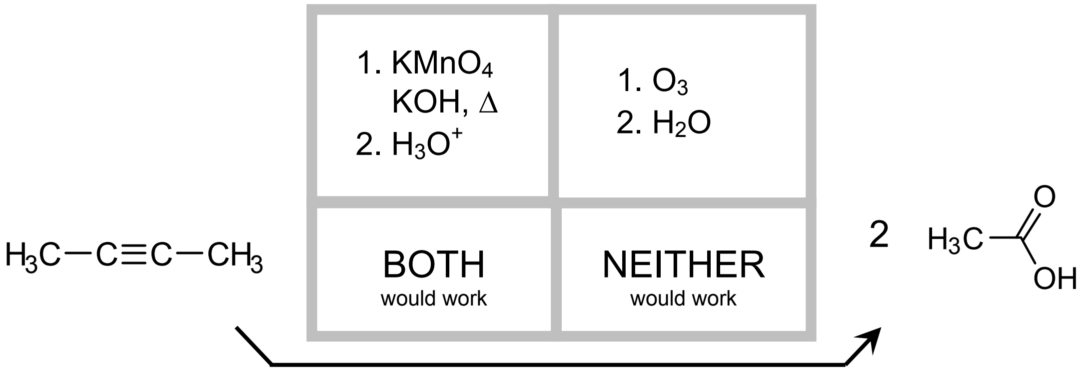


	
BOTH (equally)	NEITHER

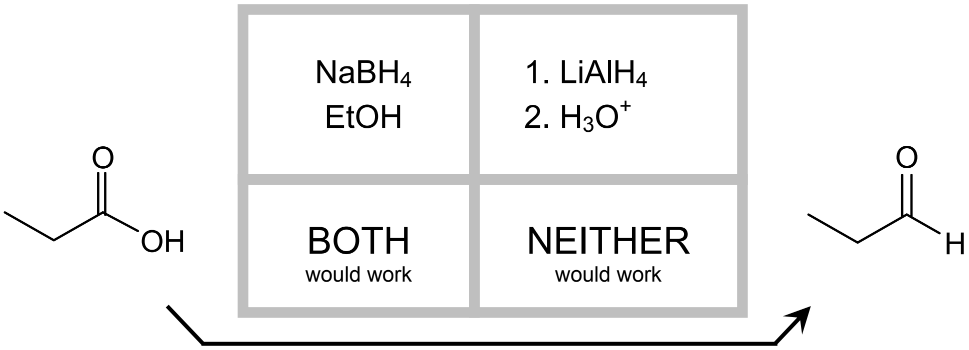
6. (16 pts) Each of the reactions below is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of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



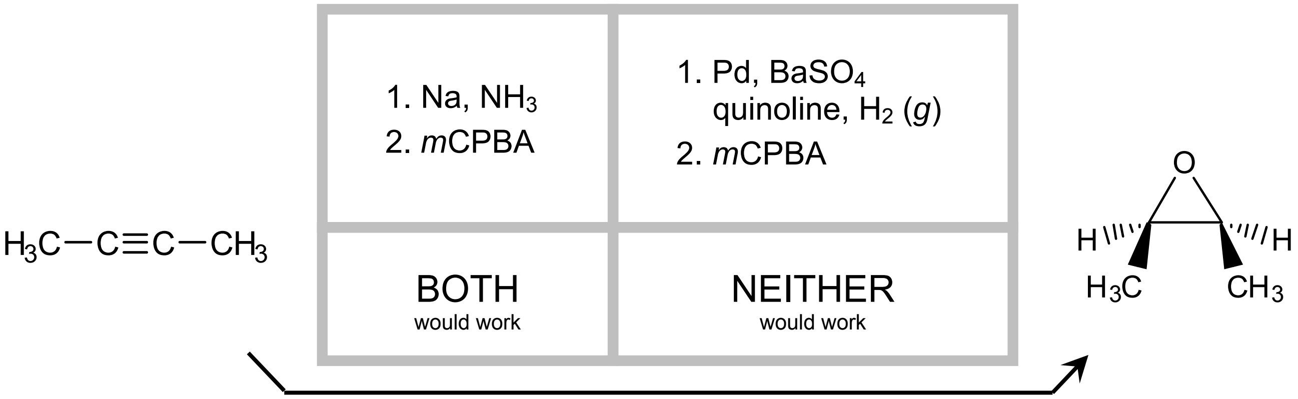
HBr	HBr, benzoyl peroxide
BOTH would work	NEITHER would work



1. $KMnO_4$ KOH, Δ 2. H_3O^+	1. O_3 2. H_2O
BOTH would work	NEITHER would work

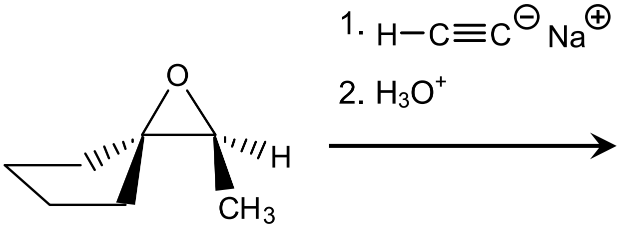


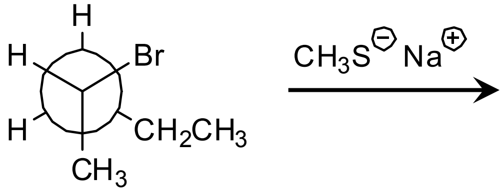
$NaBH_4$ EtOH	1. $LiAlH_4$ 2. H_3O^+
BOTH would work	NEITHER would work

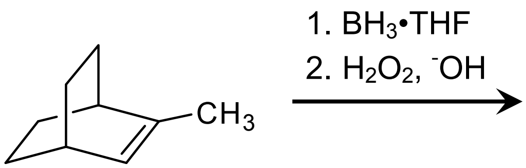


1. Na, NH_3 2. *m*CPBA	1. Pd, $BaSO_4$ quinoline, H_2 (*g*) 2. *m*CPBA
BOTH would work	NEITHER would work

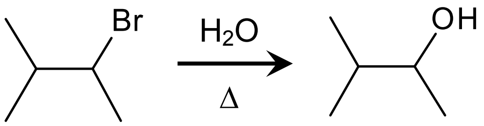
7. (15 pts) For each of the reactions on the following pages, fill in the empty box corresponding to the major product. Wherever appropriate, illustrate stereochemistry in your drawings (using wedge and dashed bonds). If multiple enantiomers or diastereomers are produced, indicate this in the answer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







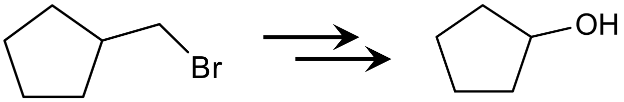
8. (19 pts) Draw a mechanism (using "electron pushing") for each of the reactions shown below. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don't invoke generic species. (E.g., don't use "H-A" as a generic acid.)



Mechanism:

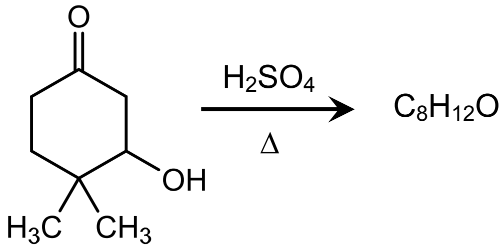
One of the intermediates you drew in this mechanism could be stabilized by a 1,2-hydride shift. What alcohol product would be generated if this shift occurred?

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.

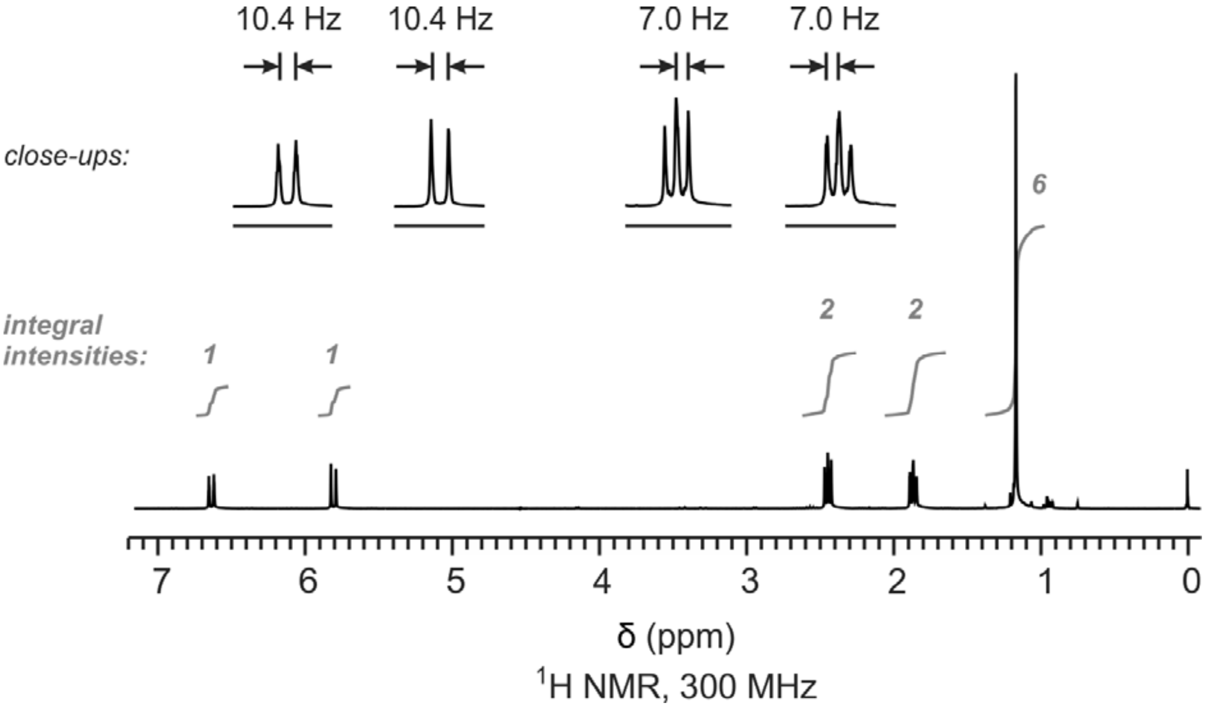


Multistep synthesis:

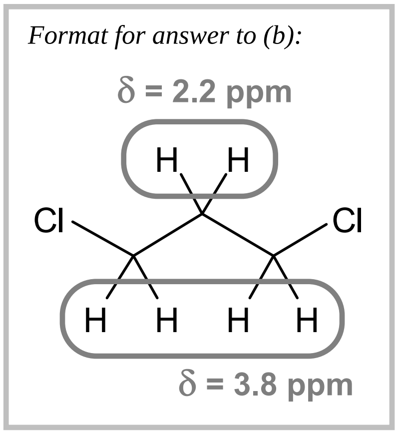
10. (22 pts) When exposed to H_2SO_4 and heat, the cyclohexenol starting material shown at right reacts to form primarily one product, which was characterized by ^{1}H NMR and mass spectrometry. The spectra of this product are shown on the following pages. High-resolution mass spectrometry determined an exact mass of 124.0888 amu for the highest-mass (parent, $\mathbf{M^+}$) peak in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_8H_{12}O}$.



^{1}H NMR:



a. The ^{1}H 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 ^{1}H NMR spectrum below, circle each set of equivalent H's, and label each circle with its unique ^{1}H NMR chemical shift to within 0.1 ppm. (You do not need to label coupling constants *J*.)


Format for answer to (b):

the product
($C_8H_{12}O$)

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

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 ($\mathbf{M}^{\bullet+}$) that is generated by removing one electron from the original, neutral molecule **M**. In the box on the right, draw $\mathbf{M}^{\bullet+}$; re-draw the structure you drew in part (a), but specifically indicate which electron is removed by drawing the molecule with one less electron.

$M^{\bullet+}$
($C_8H_{12}O^+$)

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.

Mechanism that explains m/z = 96 peak

Mass Spectrum: