

**FINAL EXAMINATION**  
CHEMISTRY 220a  
Thursday, December 16, 1999  
9:00 A.M.

NAME (print): \_\_\_\_\_

TA: \_\_\_\_\_ Section Day: \_\_\_\_\_ Section Time: \_\_\_\_\_

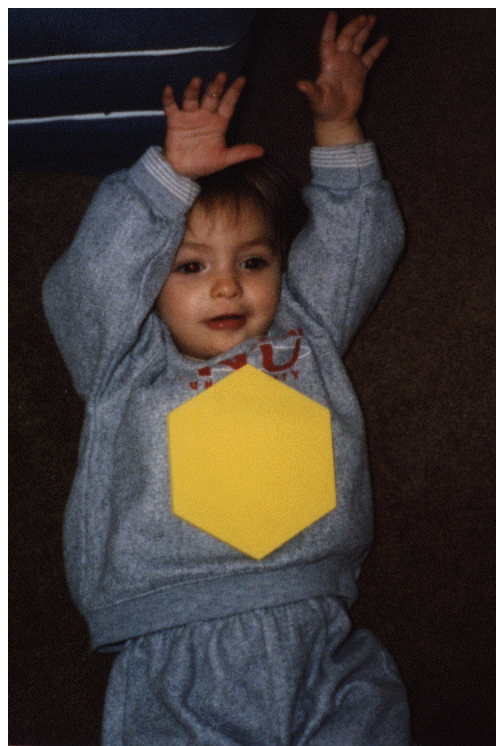
Take a few moments to look over the exam. Do problems first with which you are most comfortable. Important points and unknowns are in **bold** type. Do all **preliminary** work on the worksheets. The worksheets will **not** be graded. There is a Periodic Table on page 16 of the exam. The exam is 2 to 2-1/2 hours with 1/2 hour for review. **STOP** writing when you are asked to do so. Put your name on the cover sheet and subsequent pages where indicated.

Bonus: What is the name of the compound whose structure is on the front of your textbook?

**You are to do either 1a or 1b, not both of them.**

**REMEMBER:** Neatness is to your advantage. **Have a GREAT winter break! Best of Luck in Chem. 221b!**

1. (35 pts) Mechanism \_\_\_\_\_
2. (25 pts ) Reactions I \_\_\_\_\_
3. (25 pts) Reactions II \_\_\_\_\_
4. (32 pts) Potpourri \_\_\_\_\_
5. (30 pts) Radicals \_\_\_\_\_
6. (30 pts) NMR \_\_\_\_\_
7. (30 pts) Structure Proof \_\_\_\_\_
8. (43 pts) Synthesis/NMR \_\_\_\_\_
9. (5 pts) Bonus \_\_\_\_\_



Let's hear it for cyclohexane!!!

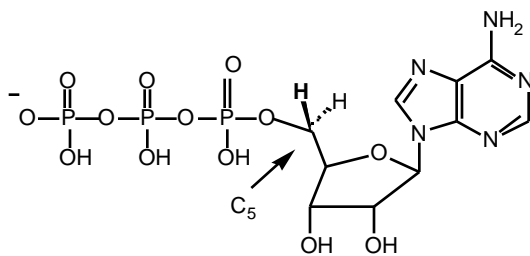
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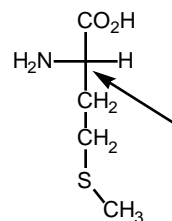
- 1a) Mechanism (35 pts.): **You are to do either 1a or 1b, not both. Mark the box in the left margin for 1a to be graded.**



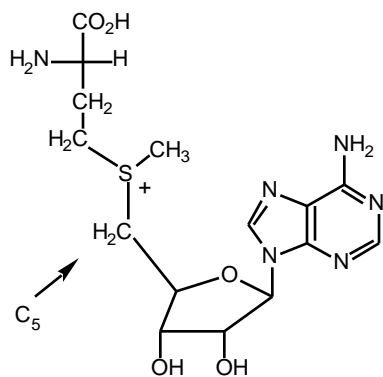
Nature employs the  $S_N2$  reaction **twice** in the formation of  $-OCH_3$  and  $-NCH_3$  groups where oxygen and nitrogen, respectively, are nucleophiles. Adenosine triphosphate (ATP) **1** reacts with the amino acid methionine **2** to form S-adenosyl methionine (SAM) **3**, Nature's methylating agent. For instance, SAM serves as a methylating agent to convert dihydroxy aldehyde **4**, acting as a nucleophile, into vanillin **5**.



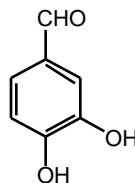
**1** (Adenosine Triphosphate - ATP)



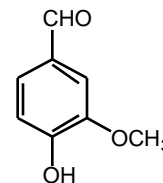
**2** (Methionine)



**3** (S-Adenosyl Methionine)



**4**



**5** (Vanillin)

- a) (5 pts.) *Why is the triphosphate group (or a phosphate group for that matter) in **1** a good leaving group?*
- b) (5 pts.) *What is the configuration (R,S) at the carbon designated by the arrow in methionine **2** (Fischer projection)?* \_\_\_\_\_

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Name: \_\_\_\_\_

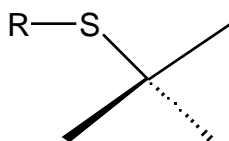
The mechanism of this reaction sequence has been unraveled using isotopic labeling. Assume that the **bold hydrogen** at C<sub>5</sub> in ATP **1** is a deuterium atom instead of hydrogen. Answer the following questions.

c) (5 pts.) What is the configuration (R,S) at C<sub>5</sub> in deuterium labeled ATP **1**? \_\_\_\_\_

d) (5 pts.) What is the configuration (R,S) at C<sub>5</sub> in deuterium labeled SAM **3**? \_\_\_\_\_

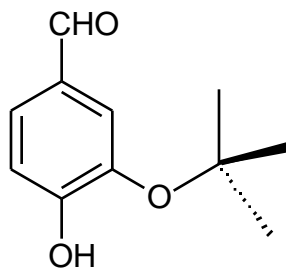
Assume that labeled methionine **2** is prepared such that the -SCH<sub>3</sub> group is now a chiral methyl group -SC(HDT) of the R-configuration containing hydrogen, deuterium and tritium.

e) (5 pts.) Draw this configuration using the template below.



f) (5 pts.) What is this configuration in the labeled methyl group in SAM **3**? \_\_\_\_\_

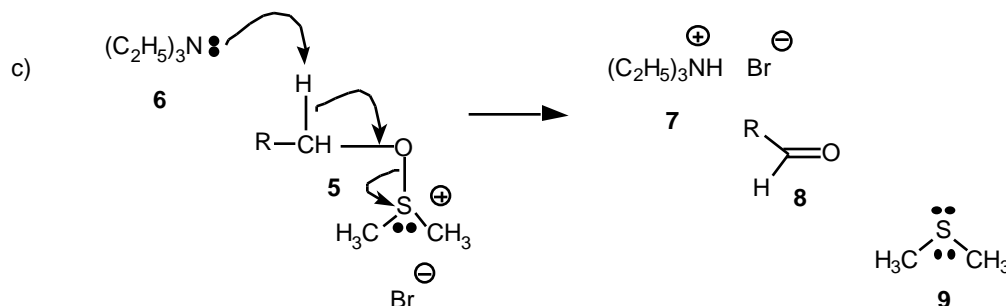
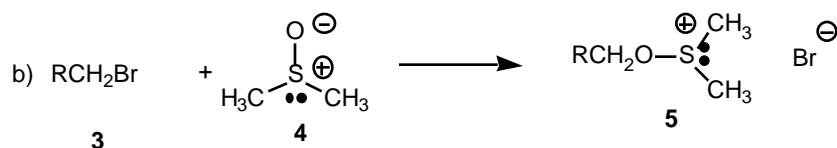
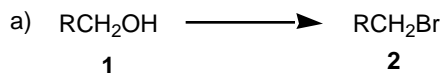
g) (5 pts.) Draw the configuration of the labeled methyl group in vanillin **5** using the template shown below. What is its configuration? \_\_\_\_\_



1b) Mechanism (35 pts): **You are to do either 1a or 1b, not both. Mark the box in the left margin for 1b to be graded.**



During the term we studied the oxidation of alcohols with Cr(VI) reagents. In particular, the use of PCC to oxidize primary alcohols to aldehydes was addressed. The sequence of reactions in equations a - c is a variation of the so-called Swern oxidation, which accomplishes the same goal. Your counterparts at "that other institution" were asked questions about this series of reactions during the past term. The questions in italics were asked of them.



a) (5 pts.) Provide an alternative to HBr for the conversion of alcohol **1** to bromide **2** in equation (a). [We have discussed two alternative methods]

b) (5 pts.) *Suggest a mechanism for the reaction of dimethyl sulfoxide **4** to form sulfoxonium salt **5** in equation (b). Use the curved arrow formalism. [The polarized S-O bond in **4** is the same as S=O.]*

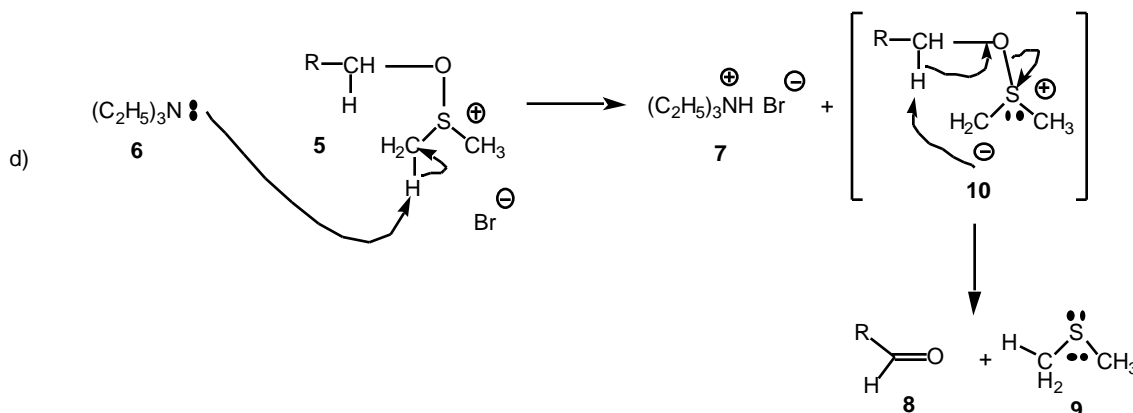
c) (5 pts.) *Classify the reaction in equation (b): (S<sub>N</sub>1, S<sub>N</sub>2, E2, E1, addition, etc.)*

(continued on the next page)

Name: \_\_\_\_\_

d) (5 pts.) What is the oxidizing agent? What is the reduction product?

They were asked to provide a mechanism for the decomposition of the sulfoxonium salt **5** formed in equation (b). They were given as the correct answer (after the exam) the E2 mechanism shown in equation (c). However, the mechanism shown below (equation d) is equally plausible. In this mechanism, intermediate **10** is formed. The same reactants **5** and **6** give the same products **7**, **8**, and **9** in both mechanisms! To decide between equation (c) or equation (d) as the correct mechanism, dimethyl sulfoxide **4** [(CD<sub>3</sub>)<sub>2</sub>S=O] having deuterium (six of them) in place of hydrogen was used.



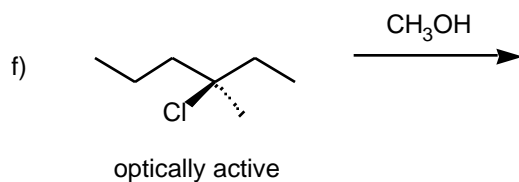
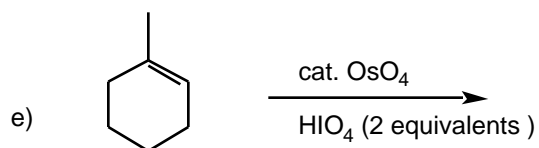
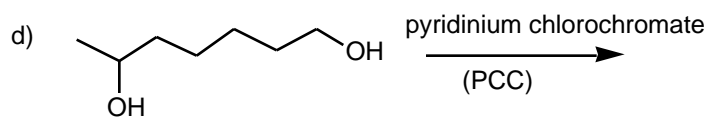
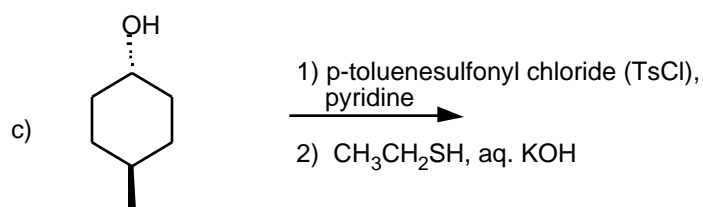
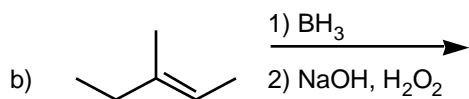
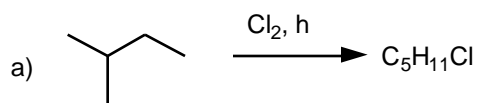
- **Here are the facts!**

When totally deuterated dimethyl sulfoxide **4** [(CD<sub>3</sub>)<sub>2</sub>S=O] is used to form sulfoxonium salt **5**, its reaction (i.e., **5**) with triethylamine **6** gives ammonium salt **7** [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>ND<sup>+</sup> Br<sup>-</sup>] containing **one** deuterium atom and dimethyl sulfide **9** [CD<sub>2</sub>HSCD<sub>3</sub>] containing only **five** of the original **six** deuterium atoms that were present in the (CD<sub>3</sub>)<sub>2</sub>S=O.

e) (15 pts.) Which of the two mechanisms does the data support? [Hint: Compare the location of the deuterium atoms in equation (c) and (d).] Illustrate and explain.

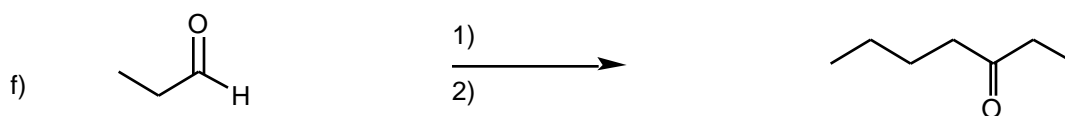
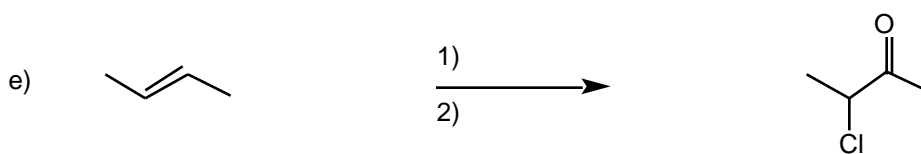
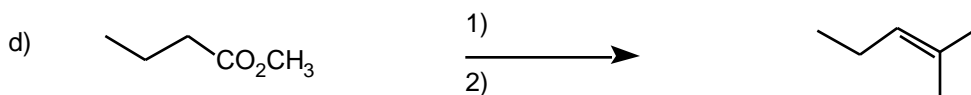
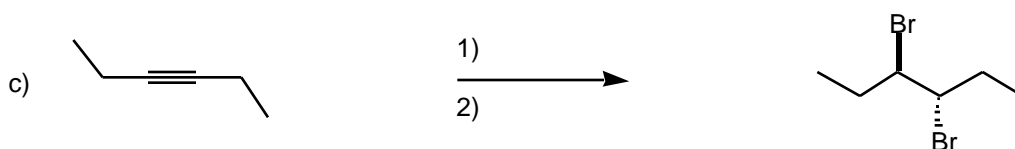
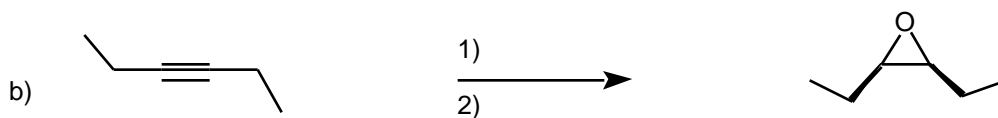
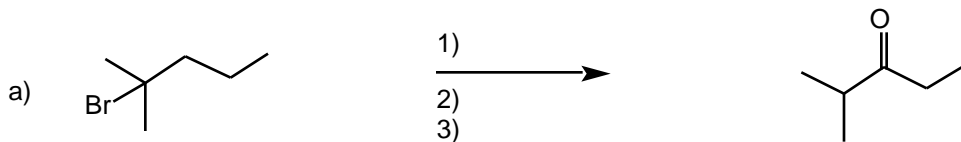
Name: \_\_\_\_\_

- 2) Reactions I (25 pts.) Provide the expected major product in **five** of the following six reactions. **Do only five**. If you did six, put a big "X" through the one you want excluded. **Pay attention to stereochemistry**.



Name: \_\_\_\_\_

- 3) Reactions II (25 pts.): Provide the reagents in **five** of the following six reactions. **Do only five**. If you did six, put a big "X" through the one you want excluded. **Pay attention to stereochemistry**. Each reaction requires the number of steps shown. (There may be alternatives.) Place the reagents by the arrows.



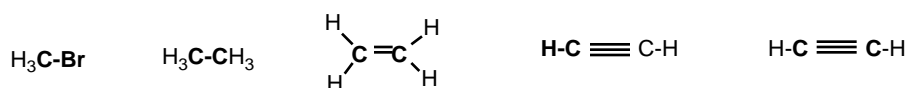
Name: \_\_\_\_\_

4) Potpourri (32 pts.): **Circle** the correct answer in each of the following:

a) The compound whose conjugate base will deprotonate only **two** of the other compounds. [Hydrogens are in **bold** type.]



b) The compound with the **shortest** bond (**bold**):



c) The best estimate of the rotational barrier (kcal/mol) about the C-C bond in ethane.

0.9                      3.0                      3.3                      3.9                      5.0

d) The hybridization of the central carbon of allene ( $\text{CH}_2=\text{C}=\text{CH}_2$ ).

s                                      sp                                      sp<sup>2</sup>                                      sp<sup>3</sup>                                      p

e) The heat of formation of n-butane is -30 kcal/mol. The heat of hydrogenation (2 moles) of 1-butyne is -70 kcal/mol. The **best estimate** for the heat of formation (kcal/mol) of 1-butyne is:

-100                      70                      -45                      -40                      +39                      +30

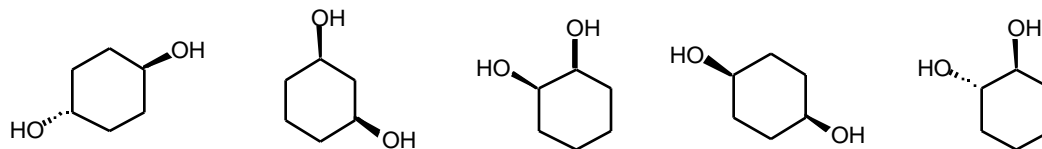
f) A one hydrogen triplet appears in a <sup>1</sup>H NMR spectrum with J = 6.0 Hz. The three peaks appear at 0.9, 1.0, and 1.1. What is the frequency (MHz) of the spectrometer?

indeterminate                      500                      100                      600                      60

g) The value of  $G^0$  (kcal/mol) for the equilibrium between the two chair conformations of trans-1,4-dimethylcyclohexane (gauche butane interaction: 0.9 kcal/mol).

0                      0.9                      1.8                      3.6                      5.0                      none of these

h) The compound with the **greatest** number of singlets in its broad band proton decoupled <sup>13</sup>C NMR spectrum.





Name: \_\_\_\_\_

5) Radicals (30 pts.): The free radical chain chlorination of cyclohexane affords chlorocyclohexane. Answer the following questions.

a) (10 pts) Write the propagation steps?

propagation step 1 --->

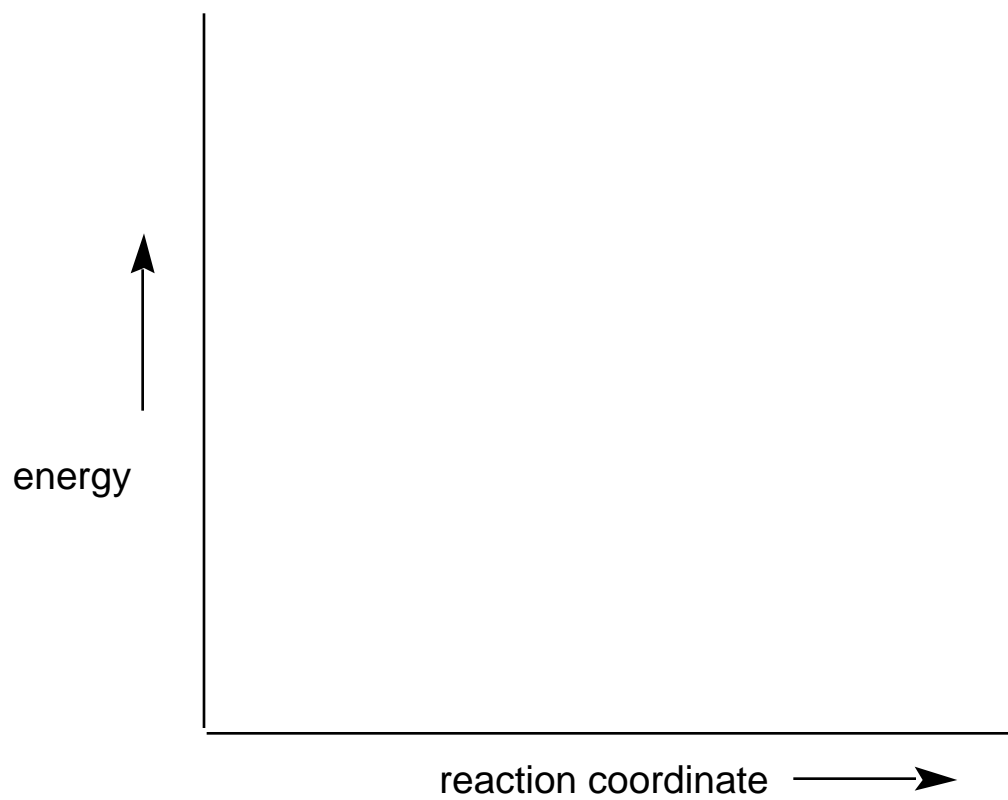
propagation step 2 --->

b) (10 pts) Determine the CH bond dissociation energy (BDE) for cyclohexane, the BDE for the CCl bond in chlorocyclohexane, and the  $H^\circ$  for propagation step 2. Show work. [  $H^\circ$  (overall rxn.) = -30 kcal/mol;  $H^\circ$  (propagation step 1) = -8 kcal/mol; BDE HCl = 103 kcal/mol; BDE Cl<sub>2</sub> = 58 kcal/mol]

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Name: \_\_\_\_\_

- d) (10 pts) Provide an energy diagram for this reaction. Include the three values of  $H^\circ$  and obey the Hammond postulate.

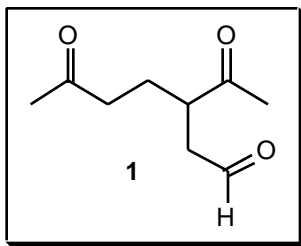


Name: \_\_\_\_\_

- 6) NMR (30 pts.): An unknown compound **A** ( $C_8H_{16}$ ) reacts with  $O_3$  followed by zinc reduction to give two compounds, **B** and **C**. Compound **B** has a singlet ( $\delta$  2.07) in its  $^1H$  NMR spectrum and two singlets (one singlet is weak;  $\delta$  20.4) in its broad band proton decoupled  $^{13}C$  NMR spectrum. The  $^1H$  NMR spectrum of **C** displays the following data ( $\delta$  values are estimated): 2.5 (quartet) and 1.2 (triplet). The integration of the two signals in the spectrum of **C** is in a **ratio** of 2:3 (quartet:triplet). What are the structures of **A**, **B**, and **C**? Explain.

Name: \_\_\_\_\_

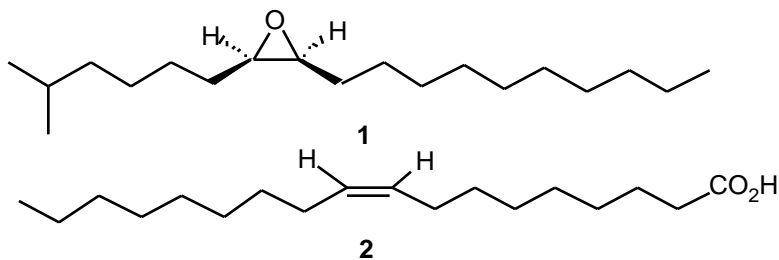
- 7) Structure Proof (30 pts.): (S)-(+)-Limonene, (C<sub>10</sub>H<sub>16</sub>, [α]<sub>D</sub> +124°) is a terpene found in the rind of lemons and oranges. Ozonolysis of (S)-(+)-limonene followed by treatment with dimethyl sulfide results in the isolation of **1**. Hydrogenation of limonene gives cis- and trans-1-isopropyl-4-methylcyclohexane.



- a) (5pts.) How many degrees of unsaturation are present in limonene?
- b) (5pts.) What important information is gained from the hydrogenation experiment?
- c) (5 pts.) What is the other product of ozonolysis?
- c) (5 pts.) Draw (S)-(+)-limonene.
- d) (10 pts.) (S)-(+)-Limonene reacts with 2 equivalents of HBr in Markovnikov fashion to give **two optically inactive** compounds C<sub>10</sub>H<sub>18</sub>Br<sub>2</sub>. **Draw** their structures and **explain briefly**. {Hint: Think about the hydrogenation experiment.]

Name: \_\_\_\_\_

- 8) Synthesis (43 pts): Gainfully employed in a laboratory during the summer, a graduate of Chem 220a is given the challenge of synthesizing disparlure (**1**), the optically-active sex attractant of the female gypsy moth. She uses 5-methyl-1-hexanol (**3**), part of oleic acid **2** for the n-alkane chain, and compounds with two or fewer carbon atoms as her sources of carbon. All other reagents are available to her.



- a) (25 pts) Show her synthetic plan.

(continued on the next page)

Name: \_\_\_\_\_

b) (10 pts.) She understands why her starting alcohol **3** ( $C_7H_{16}O$ ) contains only six singlets in its broad band proton decoupled  $^{13}C$  NMR spectrum, and she fully expects to see all nineteen carbons as unique singlets in the  $^{13}C$  spectrum of her synthetic disparlure **1**. [Note: There is no fortuitous overlap of singlets]. Explain her reasoning.

c) (9 pts.) The  $^1H$  and  $^{13}C$  NMR spectra of her synthetic material were identical to the corresponding spectra of the pheromone isolated from the female gypsy moth. What measurement that she took showed a difference between the synthetic and natural material? Why?

Name: \_\_\_\_\_

- 9) Bonus (5 pts) What is the name of the compound whose structure is on the front of your textbook?

Name: \_\_\_\_\_  
**Periodic Table**



Name: \_\_\_\_\_  
**Work Sheets** ---- They will not be graded.

Name: \_\_\_\_\_  
**Work Sheets** ---- They will not be graded.

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