FINAL EXAM
Organic Chemistry
Chemistry 220a
2 P.M., Friday, December 15, 2000

NAME (print): ____

TA:____________________ Section Day:____________ Section Time:____________

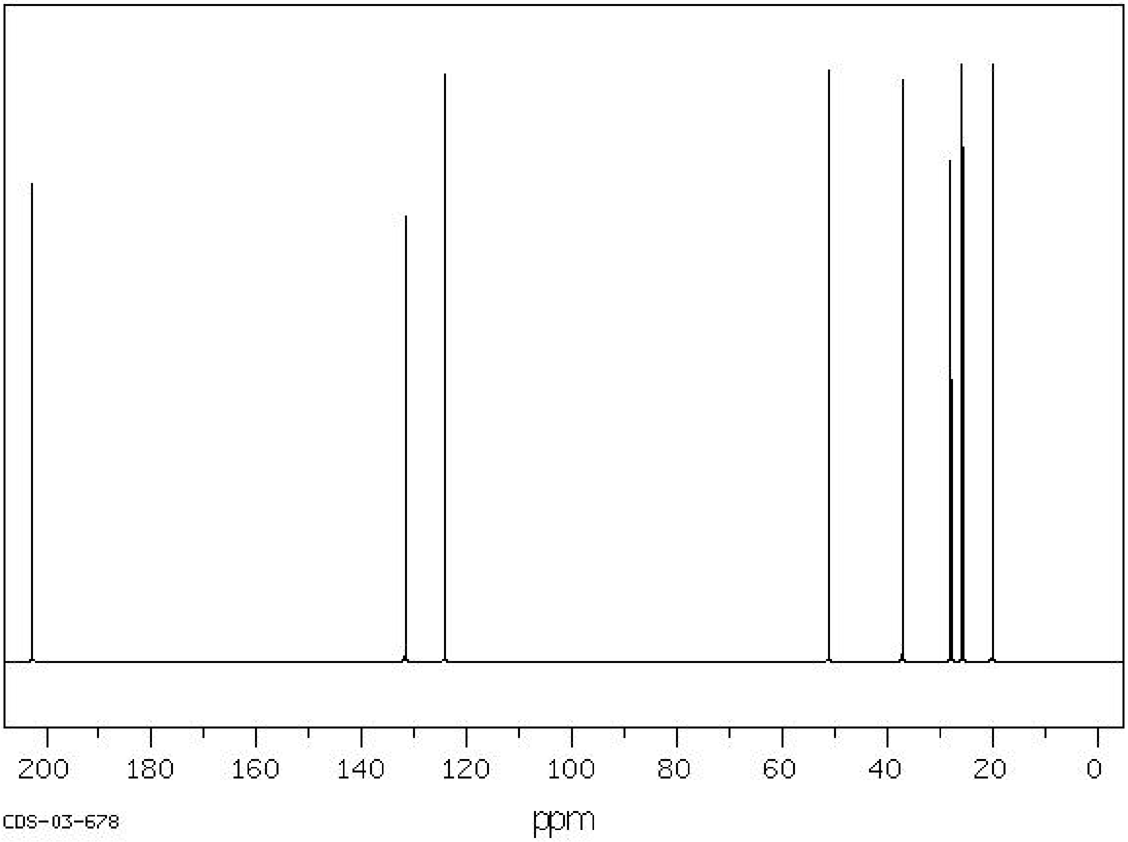
Take a few moments to look over the exam. Do problems first with which you are most comfortable. Important points and unknowns are in **bold** type. Do all **preliminary** work on the worksheets. The worksheets will **not** be graded. There is a Periodic Table (page 19) and a table of BDEs (page 20) 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.

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

1.	(30 pts)	Structure/NMR	______________
2.	(40 pts)	Potpourri	______________
3.	(40 pts)	Radicals	______________
4.	(30 pts)	Reactions	______________
5.	(20 pts)	Kinetics	______________
6.	(40 pts)	Structure	______________
7.	(30 pts)	Synthesis/NMR	______________
8.	(20 pts)	Mechanisms	______________

Total (250 pts)

1) *Structure/NMR:* (30 pts) The **terpene**, (R)-citronell**<u>al</u>** ($[\alpha]_D$ = +12.0°) **A**, which is a constituent of citronella oil, contains two degrees (elements) of unsaturation and it has the broad band decoupled ^{13}C NMR spectrum shown below. [Note the following: i) Examine **carefully** the "two" signals in the region between 25-30 ppm. ii) There is more than enough information in the problem to determine the molecular formula of **A**.]



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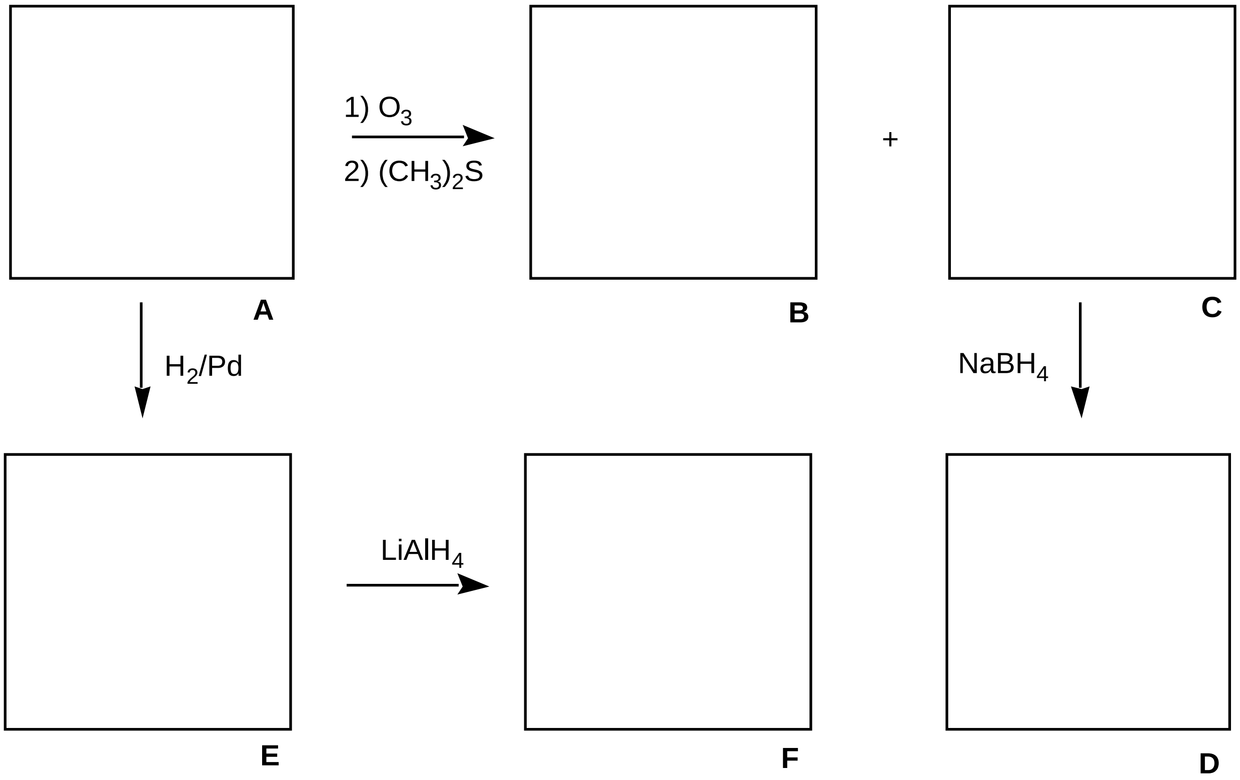
Ozonolysis of citronellal and subsequent reaction with dimethyl sulfide provides compounds **B** and **C**. The ^{1}H NMR spectrum of **B** displays a **singlet only** (δ 2.2). The ^{13}C NMR broad band decoupled spectrum of **B** displays two singlets (206 and 30 ppm). Compound **C**, ($C_7H_{12}O_2$) reacts with $NaBH_4$ to produce (R)-3-methylhexan-1,6-diol **D**. Upon reaction of citronellal with hydrogen in the presence of a palladium catalyst, compound **E** is formed. The reaction of **E** with $LiAlH_4$ affords compound **F**, (3R)-3,7-dimethyloctanol.



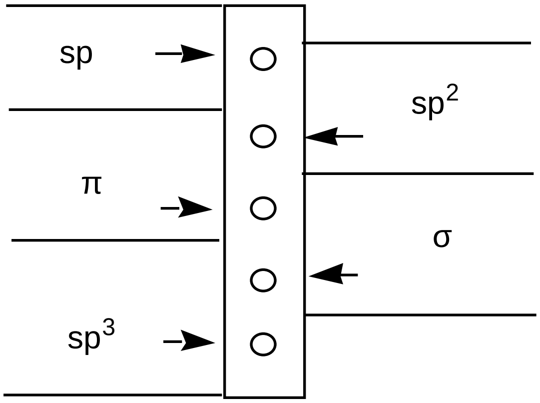
What are the structures of **A**-**F**? Place your answers in the appropriate boxes and give a brief rationale below. Pay attention to absolute stereochemistry.

2) *Potpourri:* (8 x 5 pts. = 40 pts.) **Provide** the best answer(s) in each of the following questions:

a) The value of a particular coupling constant (J) is 8 Hz at 60 MHz. What will be the value of J at 300 MHz? (**Enter** your answer.)

_______ Hz

b) The hybridization of carbons in the allene, (*S*)-2,3-pentadiene. (**Mark** your ballot. No hanging chads will be accepted.)



c) The value (kcal/mole) of $\Delta(\Delta G^{o})$ for the equilibrium between the chair conformations of trans-1,3-dimethylcyclohexane. (**Circle** your answer.)

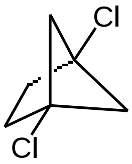
0.9   1.8   2.7   3.6   none of these

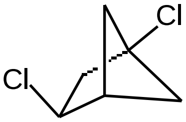
d) The acid that has the **median** pK_a. (**Circle** your answer.)

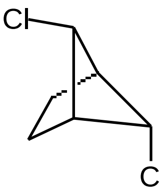
acetic acid   ethanol   *t*-butyl alcohol   ammonia   methane

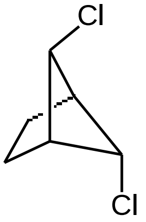
continued --->

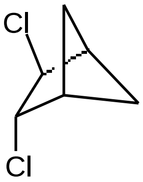
e) The dichloro bicyclo[2.1.1]hexane(s) that displays **four** singlets in its broad band decoupled ^{13}C NMR spectra. (**Circle** your answer.)











f) A sample of citronellal (problem 1) that has $[\alpha]_D = -9.0$, contains what percentage of the (*S*)-enantiomer? (**Circle** your answer.)

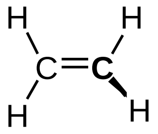
12.5 75 25 50 87.5

g) For a series of sp^3, sp^2, and sp C-H bonds, the bond dissociation energies (BDEs) and acidities are related how? (**Circle** your answer.)

linearly exponentially logarithmically inversely

h) The bond (**bold**) with the largest bond dissociation energy (BDE). (**Circle** your answer.)

$H_3\mathbf{C}-\mathbf{C}H_3$ $H_3\mathbf{C}-\mathbf{H}$ $(CH_3)_3\mathbf{C}-\mathbf{Br}$



$R\mathbf{O}-\mathbf{O}R$

3) *Radicals:* (40 pts)

a) (10 pts) For the free radical iodination of ethane, provide the propagation steps and the overall reaction for this process in the gas phase. Place the structures in the appropriate boxes below.

Propagation step 1

☐ + ☐ ⟶ ☐ + ☐ _______ kcal/mol

________ ________ ________ ________

Propagation step 2

☐ + ☐ ⟶ ☐ + ☐ _______ kcal/mol

________ ________ ________ ________

Overall reaction

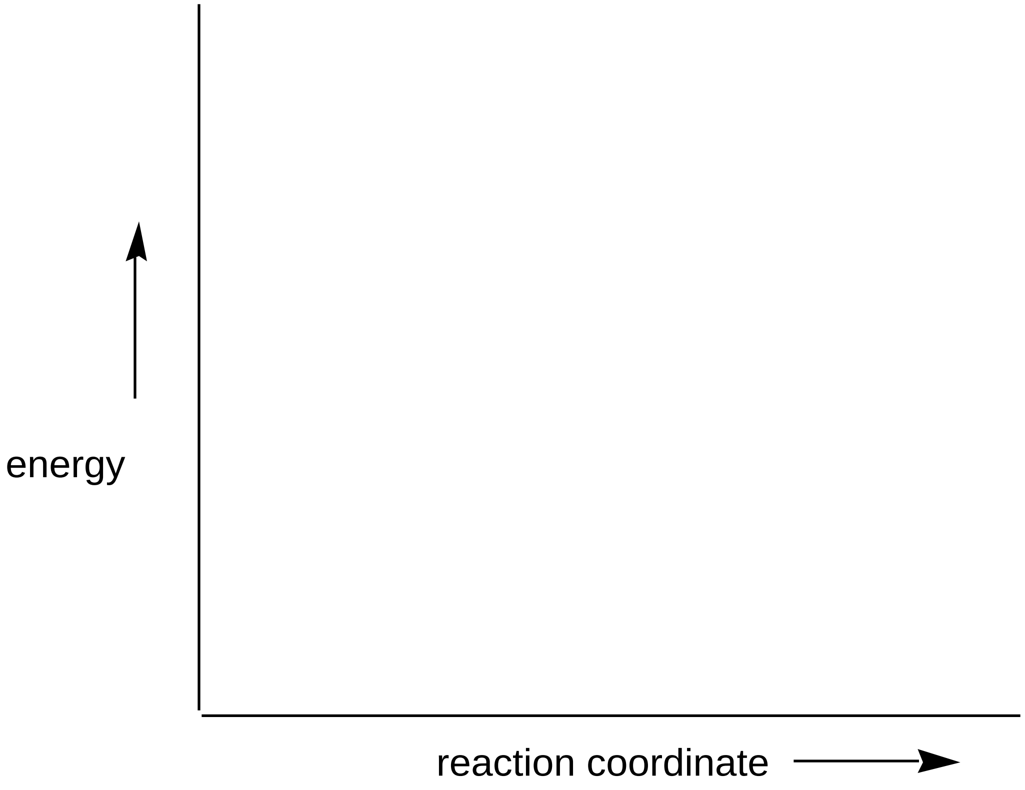
☐ + ☐ ⟶ ☐ + ☐ _______ kcal/mol

b) (10 pts) Compute the thermicity of the three reactions above placing the appropriate answers and BDEs (page 20) on the lines under the boxes. Show your work here. Why is this procedure an ineffective method for preparing alkyl halides?

continued --->

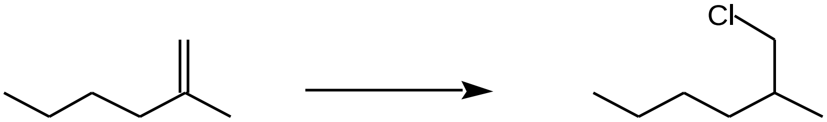
c) (10 pts) Iodine is a solid at 25 ^{o}C and 1 atm. Using the following data and your answer in (b), determine the heat of vaporization (sublimation) of I_2 at 25 ^{o}C and 1 atm: ΔH_f^o (kcal/mol); C_2H_6 = -20.0, C_2H_5I = -1.9, HI = +6.3. Show work.

d) (10 pts) Provide an energy vs. reaction coordinate diagram using the diagram below. Label the energy differences (values obtained in part b), be true to the Hammond Postulate, and the height of the transition states.



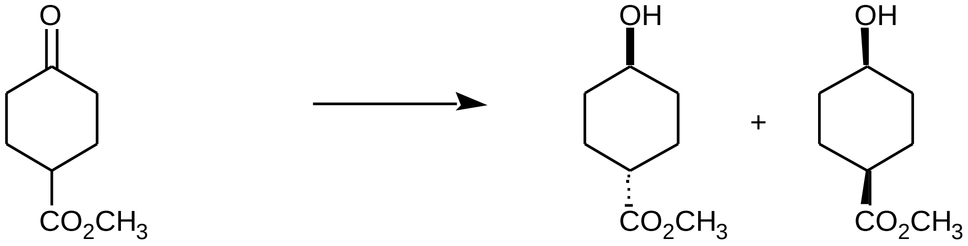
4) *Reactions* : (6 x 5 pts = 30 pts) **Do 6 of the following 7 problems**. Place an "X" through the problem that is **not** to be graded. Some questions require products; some reagents. **Pay attention to stereochemistry.**

a)

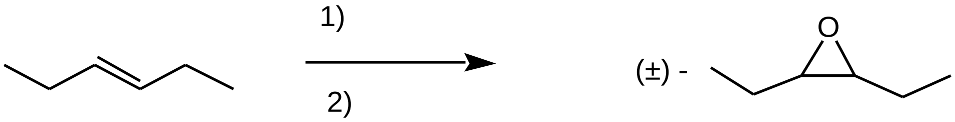


b) (R)-2-octanol $\xrightarrow[\text{dioxane}]{\text{SOCl}_2}$

c)

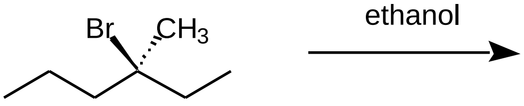


d)



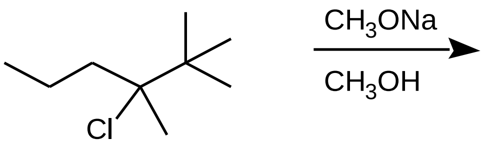
e)

f)



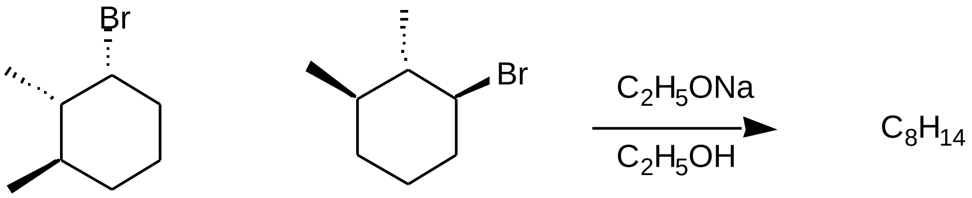
single enantiomer

g)

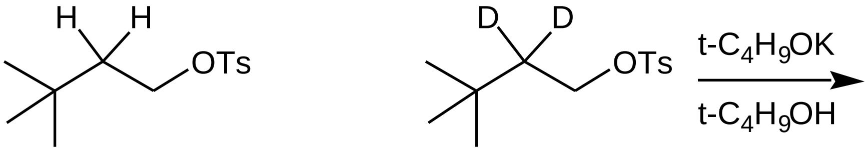


5) *Kinetics:* (4 x 5 pts = 20 pts) In each of the following problems, **circle** the compound that reacts **faster** and draw the structure of the product of the reaction. Give a **brief** explanation. [Note: If two reactants react at the same rate, circle both of them and clearly specify the product.]

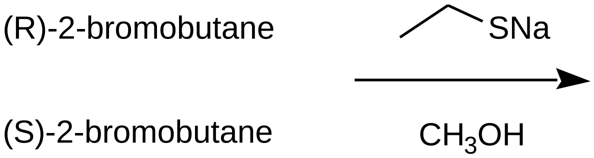
a)



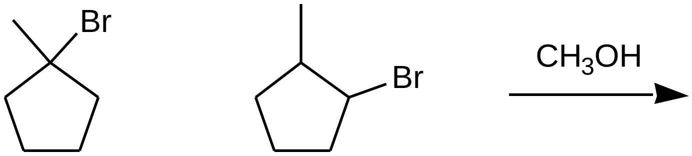
b)



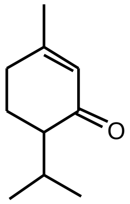
c)



d)



6) *Structure:* (40 pts) (R)-(+)- Piperitone (**1**) is a terpene with the fragrance of peppermint. The *d*-form is reported to have $[\alpha]_D = 49^{o}$ while the *l*-form is reported as $[\alpha]_D = -16^{o}$. A sample of piperitone from a bottle in the FEZ laboratory had $[\alpha]_D = -40^{o}$.



1

a) (10 pts) Assuming that enantiomerically-pure piperitone has $[\alpha]_D = 50^{o}$, calculate the %ee of the FEZ sample. Show work.

b) (10 pts) Using your knowledge of keto-enol tautomerization, briefly explain how the two *l*-forms cited above became partially racemized. Be brief and concise.

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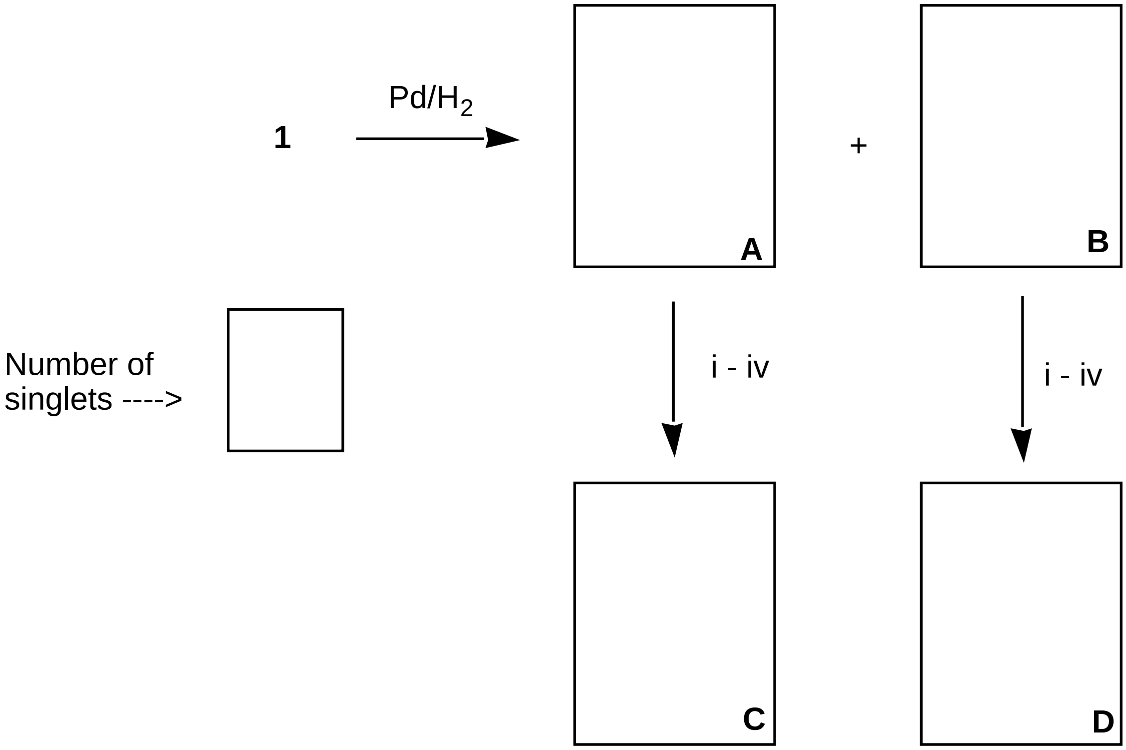
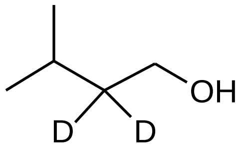
c) (20 pts) Hydrogenation of piperitone in the presence of a Pd catalyst provides ketones **A** and **B** (both $C_{10}H_{18}O$). Ketone **A** provides **C** ($C_{10}H_{20}$) and ketone **B** affords **D** ($C_{10}H_{20}$) after the following series of reactions: i) $NaBH_4$ or $LiAlH_4$; ii) PBr_3; iii) Mg in ether; iv) H_2O. Compound **C** has a $\Delta(\Delta G^o)$ = 0.3 kcal/mol between its two chair conformations while compound **D** has $\Delta(\Delta G^o)$ = 3.9 kcal/mol between its two chair conformations. Both **C** and **D** contain the same number of singlets in their respective broadband decoupled ^{13}C NMR spectra. Provide structures for **A-D** aand the number of singlets in the ^{13}C NMR spectra. Explain briefly.



7) *Synthesis/NMR:* (30 pts) A chemist requires a sample of 2,2-dideuterio-3-methyl-1-butanol (**1**). She designs a synthesis of **1** from isobutylene. She has available to her all C_1 compounds and all reagents including $NaBD_4$, $LiAlD_4$ and D_2O.



1

a) (15 pts) Show how she may have -- or you would -- accomplish this synthesis. [Note: Not all deuterium reagents are necessary for the completion of the synthesis.]

continued

b) (15 pts) Use the template below to draw the ^{1}H NMR spectrum of **1** that has the hydroxyl hydrogen exchanged with D_2O. [Note: Since deuterium bound to oxygen does not couple to vicinal hydrogens, you may make the same assumption about carbon bound deuterium.] Place the signals in their correct, relative positions (chemical shifts). Include the coupling patterns and the relative integrals.

Name: ______________________________

8) *Mechanisms:* (20 pts) Using the curved arrow formalism, provide a mechanism for **one and only one** of the following reactions.

a) 2-butyne ------> (*E*)-2-butene

b) isobutylene ------> isobutyl alcohol (2-methyl-1-propanol)

c) (Z)-2-butene ------> CH_3CHO

d) C_2H_5OH ------> CH_3CHO

Name: ______________________________

Work Sheets

Name: ______________________________

Work Sheets

Name: ______________________________

Work Sheets

Name: ______________________________

Work Sheets

Name: ______________________________

Periodic Table

Name: ______________________________

Bond Dissociation Energies

http://classes.yale.edu/chem220a/studyaids/thermo/BDE.html