

# Chemistry 210

the **Final** learning experience

**University of Missouri-Columbia**

**Dr. Rainer Glaser**

**Friday, December 18, 1992**

**12:40 - 2:40**

Name:	<i>Answer Key</i>
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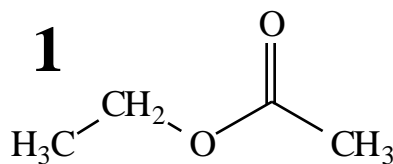
	Max.	Yours
Question 1	27	
Question 2	33	
Question 3	32	
Question 4	41	
Question 5	30	
? Question 6 ?	31	
Question 7	6	
Total	200	

***Adrenalize!***

**Do not turn the page until advised to do so.**

**Question 1.** Identification of Organic Compounds. (27 points)

(a) Molecule **1** belongs to the class of ESTERS  
because of its CARBOXYL group R-CO<sub>2</sub>-R'. **1** can be  
formed by reaction of the alcohol ETHANOL  
(give the IUPAC name) and the acid ETHANOIC ACID  
(give the IUPAC name, do not give the trivial name). (6 points)



(b) Suppose you made molecule **1** in the laboratory and your teacher asks you to take a <sup>1</sup>H-NMR spectrum to find out whether your reaction was successful. So, you need to know what to expect in the spectrum of **1**. Explain why there are only 3 signals in the spectrum while there are 8 H- atoms in **1**. What are the relative intensities of the signals? (3 points)

<p>There are three types of hydrogens as indicated. The ratio between the types is 3:2:3 and the line intensities will reflect this ratio.</p>	
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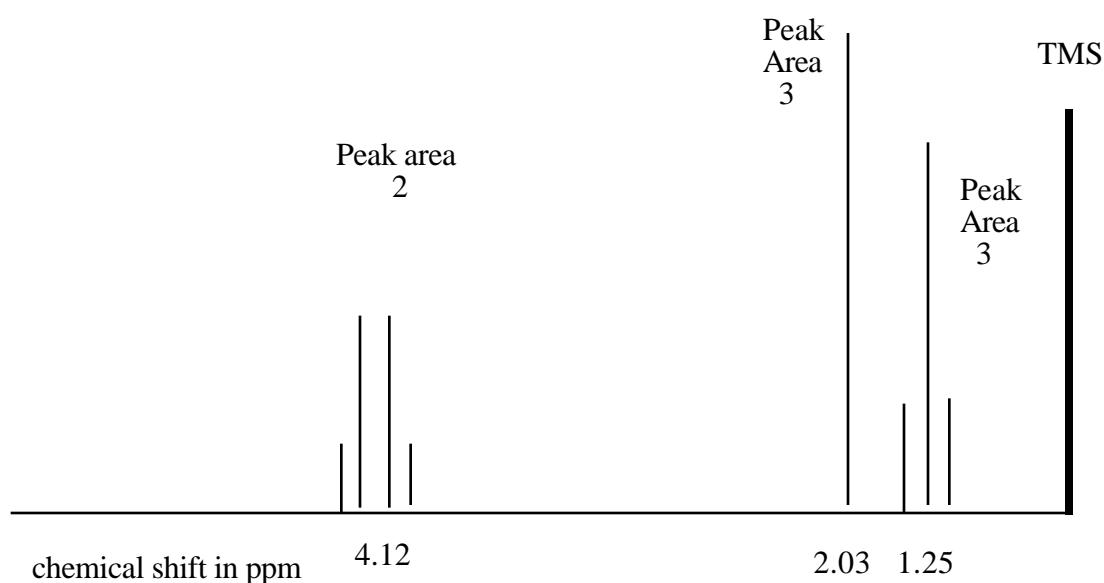
(c) On closer examination it turns out that some of the signals have a “finestructure”, that is, they are actually multiplets. For each signal indicate whether it is a singlet, a doublet, etc. For each of the multiplets, show schematically what they look like and give the relative intensities of the lines in the multiplet. Briefly explain the cause for the multiplets. (6 points)

<p>3</p>
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(d) The chemical shifts of the signals are as follows: = 1.25 ppm, 2.03 ppm, and 4.12 ppm. Draw a schematic spectrum of **1**. Label the axes. Assume that TMS was used as the internal standard. Indicate multiplets and relative intensity. Clearly indicate which types of hydrogens cause which signal and explain your assignment. (12 points)

Draw the spectrum of **1**. (6 points)

subtract 1 point for each wrong ordering, lack of multiplicity, wrong relative intensity and so forth.



Explain the chemical shifts. (6 points)

Inductive effects. (2 points)

Methyl lower than methylene. Methylene hydrogens are the most deshielded, 4.12 ppm. (2 points)  
 Of the two methyl groups, the one that is attached to the positively polarized carbonyl carbon is more deshielded. 2.03 ppm for the Me-CO and 1.25 for the Me-CH<sub>2</sub>. (2 points)

(The Me-CO also is increased a bit by the anisotropic shift caused by the CO ring current.)

**Question 2.** Preparation and Properties of Acetic Acid. (33 points)

The easiest synthesis of **1** is by reaction of an alcohol and acetic acid. So, let's take this opportunity and review some of the general principles applied to this simple molecule and review some preparations.

(a) *Preparations.* Suggest one reagent for the oxidation of ethanol to acetic acid via acetaldehyde in acidic or in alkaline medium. Show structures and give formula and name of the reagent. Also give name and formula of a reagent that will oxidize the ethanol to acetaldehyde but no further. Furthermore, show structures and give formula and name of a reagent that converts butene-2 into acetic acid. (11 points)

Oxidation of ethanol in acidic or basic medium. (3 points)

ethanol  $\implies$  acetaldehyde  $\implies$  acetic acid (show structures, 1 point)

oxidation reagents: alkaline  $\text{KMnO}_4$ , Jones reagent  $\text{CrO}_3$  in sulfuric acid, accept anything reasonable

Oxidation of ethanol to acetaldehyde. (3 points)

PCC, Pyridiniumchlorochromate which is  $\text{CrO}_3$  and pyridinium hydrochloride.

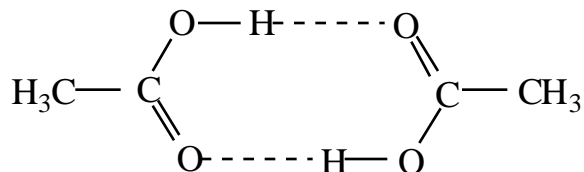
Oxidation of butene-2 to acetic acid. (5 points)

Show the structure of butene-2. Several oxidation reagents will do:

hot alkaline  $\text{KMnO}_4$  will oxidize to the acids (way to go)

ozonolysis followed by workup with hydrogenperoxide

(b) *Properties.* The melting and boiling points of acetic acid are 16.6°C and 118°C and they are thus much higher than what might be expected based on the molecular weight alone. Butane, for example, has about the same mass but you are well aware that butane is a *gas* at room temperature. It turns out that acetic acid forms “hydrogen bonded dimers” in which two acetic acid molecules aggregate. Draw the structure of such a dimer. Explain the H-bonding here, that is, what are the requirements for H bonding in general and how are these requirements met in this specific case here. (10 points)



H bonding requires strong acceptor (electronegative atom): here the carbonyl oxygen

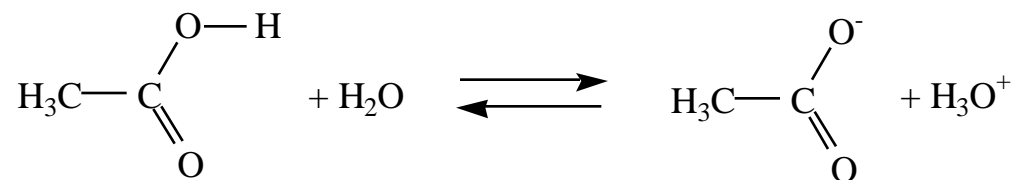
H bonding requires positively charged “acidic” H (donor) attached to electronegative atom: here HO-

(c) *Structure.* Give the CC bond length data requested. Compare these data with the values measured for the C=O and C-O bonds in formic acid. Does bond polarity increase or decrease bond lengths? Indicate the atom hybridizations in the round boxes. (12 points)

C-C single bond: 1.2	C=C double bond: 1.34	C C triple bond: 1.54
All data are in angstrom (Å) and, of course, in meters 1 Å is:		10 <sup>-10</sup> meter
(3 points)	Compare: (3 points)	
	Bond polarity greatly reduces the bond lengths. Stronger bonds.	

**Question 3.** Acidity of Acetic Acid and Resonance Forms. (32 points)

The equilibrium constant for the reaction



is the acid dissociation constant  $K_a$  with a value of  $1.8 \times 10^{-5}$  M. The related  $\text{p}K_a$  value is 4.74. The value indicates, for example, that a 0.1 M aqueous solution of acetic acid is only 1.3% dissociated.

- (a) Give the equation that relates  $K_a$  and  $\text{p}K_a$ .  
(2 points)

$$\text{p}K_a = -\log(K_a)$$

- (b) The  $K_a$  value of ethanol is about  $10^{-16}$ , that is, ethanol is only  $10^{-11}$  strong an acid as acetic acid!! Why is that? Consider the anions formed in the two acid dissociation reactions and argue why the acetic acid is so much stronger. Use resonance forms for your explanation; show all electrons in all resonance forms and show all formal and ionic charges. Be precise. (8 points)

Because the carboxylate anion is more stable compared to the methoxy anion.

The reason for that is that charge delocalization occurs in the carboxylate (via resonance as shown) and charge localization occurs in the methoxide. (4 points)

Need to show two complete resonance forms for the acetate. See any textbook. (4 points)

(c) The acidity of acetic acid can be altered greatly by substitution. The  $pK_a$  of all of the acids listed have been measured and their numerical values are given in the top line. Assign these values to the correct boxes. Provide a brief explanation of your reasoning. (12 points)

2.59	3.18	0.64	1.26	2.86	2.90	4.87	(1 p. / box)
Acid		$pK_a$		Acid		$pK_a$	
CH <sub>3</sub> -COOH		4.74		F-CH <sub>2</sub> -COOH		2.59	
CH <sub>3</sub> -CH <sub>2</sub> -COOH		4.87		Cl-CH <sub>2</sub> -COOH		2.86	
Cl <sub>2</sub> CH-COOH		1.26		Br-CH <sub>2</sub> -COOH		2.90	
Cl <sub>3</sub> C-COOH		0.64		I-CH <sub>2</sub> -COOH		3.18	

Brief explanation (5 points)

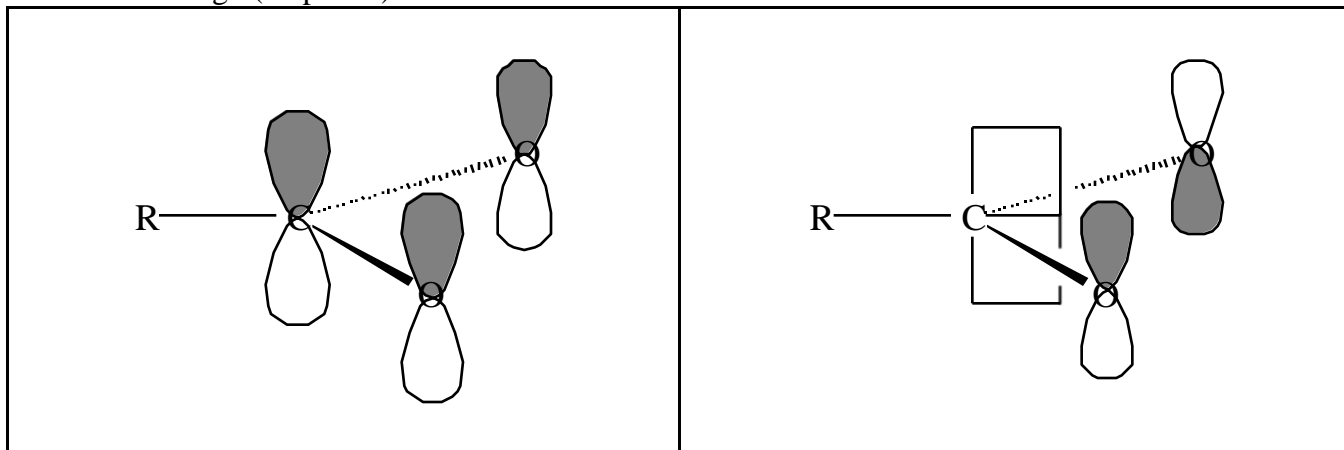
The idea is that electronegative atoms will stabilize the anion and thus reduce the  $pK_a$ .

4.87 is for Et-COOH; the only case where the substituent is donating!

0.64 clearly is the one with three chlorines, and 1.26 the one with the two chlorines.

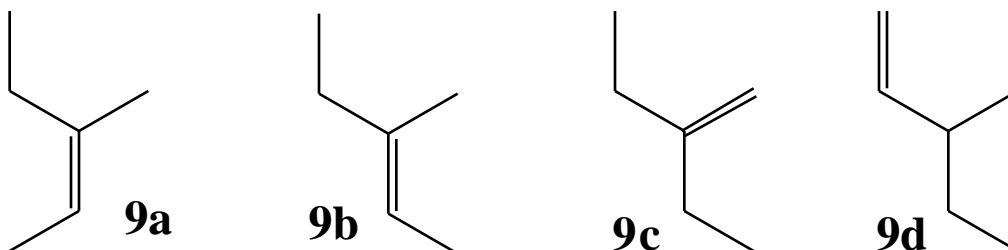
The rest of the numbers for the monosubstituted acids reflecting EN.

(d) In the acetate anion, there are four electrons involved in the  $\pi$  system. These four electrons occupy two molecular orbitals. Schematically draw these two MOs. Clearly indicate nodes. Circle that MO that is more bonding. (10 points)



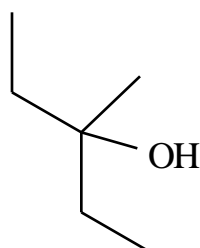
**Question 4.** Elimination Reactions. (41 points)

(a) For each of the olefines **9a-d**, state whether they are *cis* or *trans* (if applicable) E or Z (if applicable). If there are no geometrical isomers, then state “no GIs” (8 points)



	cis or trans	E or Z
<b>9a</b>	does not apply	Z
<b>9b</b>	does not apply	E
<b>9c</b>	does not apply	no GIs
<b>9d</b>	does not apply	no GIs

(b) **9a-9c** can be formed from one alcohol **10**. Draw the structure of **10**, name it, and give the reaction conditions for the elimination to occur. (5 points).



**10**

3-methyl-pentanol-3  
3-methyl-pentan-3-ol  
3-methyl-3-pentanol

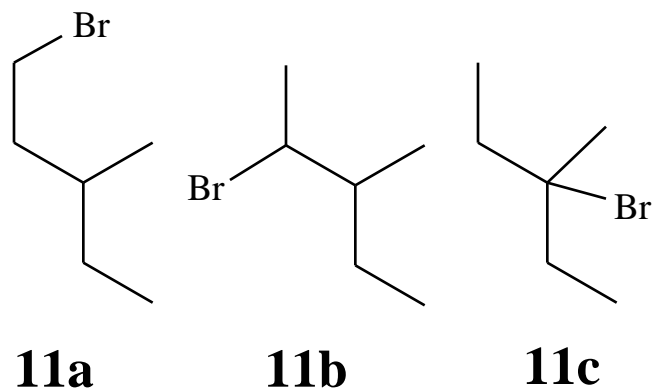
will all be accepted

Reaction conditions: Acid catalyses is required; e.g. concentrated sulfuric acid.

(c) The formation of **9c** from **10** is disfavored because it leads to the LESS substituted alkene; this product is called the HOFFMANN product. The preferred isomers **9a** and **9b** both are so-called SAYTZEF products. (6 points)



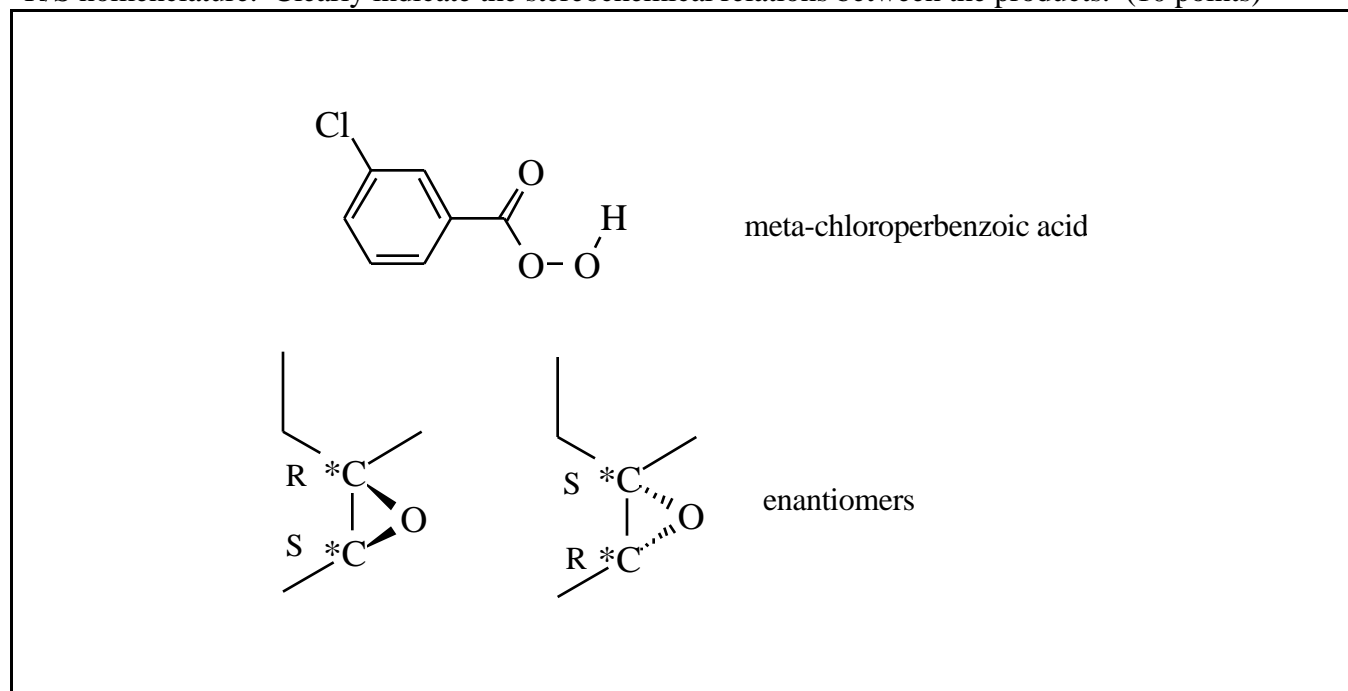
(d) Let's look into the synthesis of the olefines **9a-d** via base catalyzed elimination from the appropriate alkyl bromide. Give the reaction conditions. Indicate the head carbon type (primary etc), give the number of the major olefine formed from each bromide, indicate the most likely mechanisms of the elimination reaction (E1, E2 or E1cb), and in the last column indicate (say yes or no) whether nucleophilic substitution is very likely to compete with elimination. (12 points)



**Reaction conditions** for the elimination: Alkoxide in Alcohol solvent, high T.

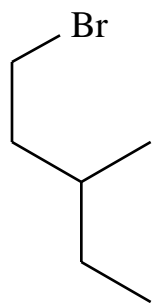
Bromide	Head Carbon Type	Product Olefine	Mechanism Type	Likely Competition from S <sub>N</sub> ?
<b>11a</b>	primary	<b>9d</b>	E2	Yes!
<b>11b</b>	secondary	<b>9a</b> and <b>9b</b>	E2	Little
<b>11c</b>	tertiary	<b>9a</b> and <b>9b</b>	E2 some E1	No

(e) Consider the epoxidation of **9a** with MCPBA. Give the structure and full name of MCPBA. Draw all stereoisomers formed in the reaction (note that the oxidation may occur from the "top" and from the "bottom"). Indicate all chiral carbons by a star. Specify the configuration of each chiral center with the R/S nomenclature. Clearly indicate the stereochemical relations between the products. (10 points)



**Question 5.** Radical Reactions. (30 points)

(a) How can we go about making the alkyl bromides **11a-c**? Well, the radical chain bromination of the alkane 3-METHYL-PENTANE (name the correct alkane) does of course come to mind. If the H abstraction was entirely random, how many products would we expect (draw them) and in what ratio (give percentages) would we expect them to occur? Circle the major product and briefly explain (just a few good words). In case it matters: 100 divided by 14 is roughly 7. (15 points)

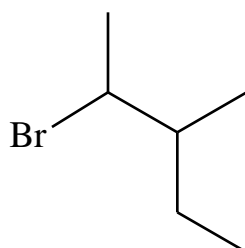


**11a**

6 Hs

$$6+4+1+3 = 14 \quad 100/14 = 7$$

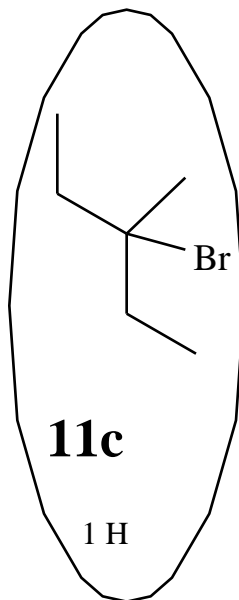
$$6*7=42\%$$



**11b**

4 Hs

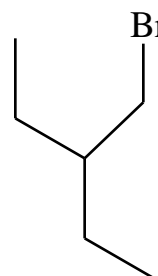
$$4*7=28\%$$



**11c**

1 H

$$7\%$$



**11d**

3 Hs

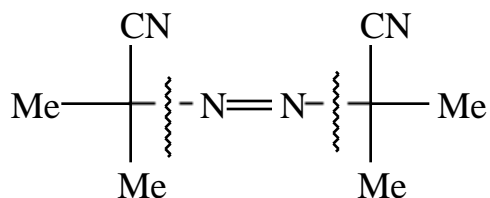
$$3*7=21\%$$

The bromination is rather selective and leads to the product that arises from the most stable intermediate radical.

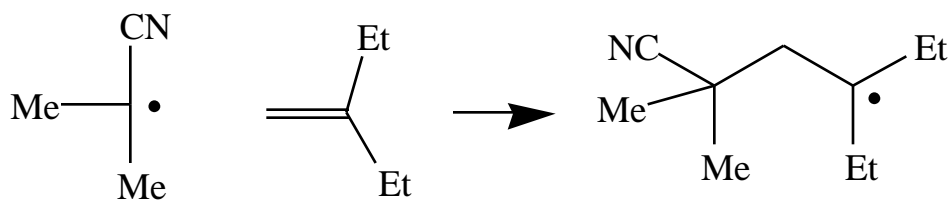
(b) Let's make a polymer from the olefine **9c**. This is done by a radical chain reaction. To start this chain reaction we need an initiation. (1) Suggest a typical radical chain reaction starter molecule and show the initiation reaction. Then show with structural formulas (2) how this starter radical adds to the olefine and (3) how the formed radical adds the second olefine molecule. Pay attention to regiochemistry in your drawings. (15 points)

(1) Typical starter and initiation reaction

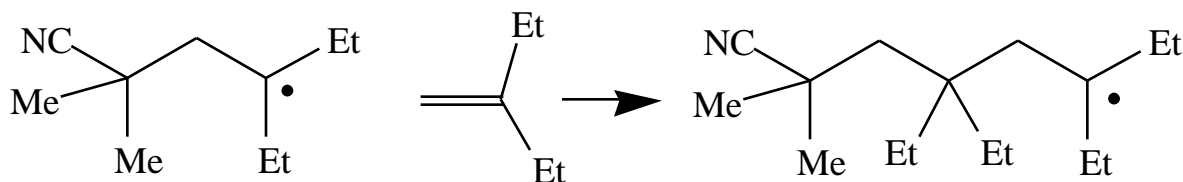
AIBN Azobisisobutyronitrile (many other appropriate starters accepted)



(2)



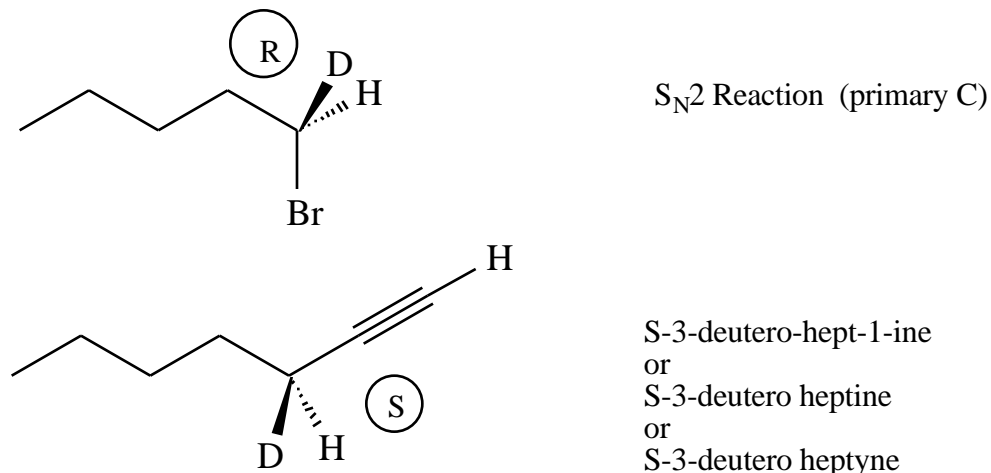
(3)



**Question 6. Substitution Reaction. (31 points)**

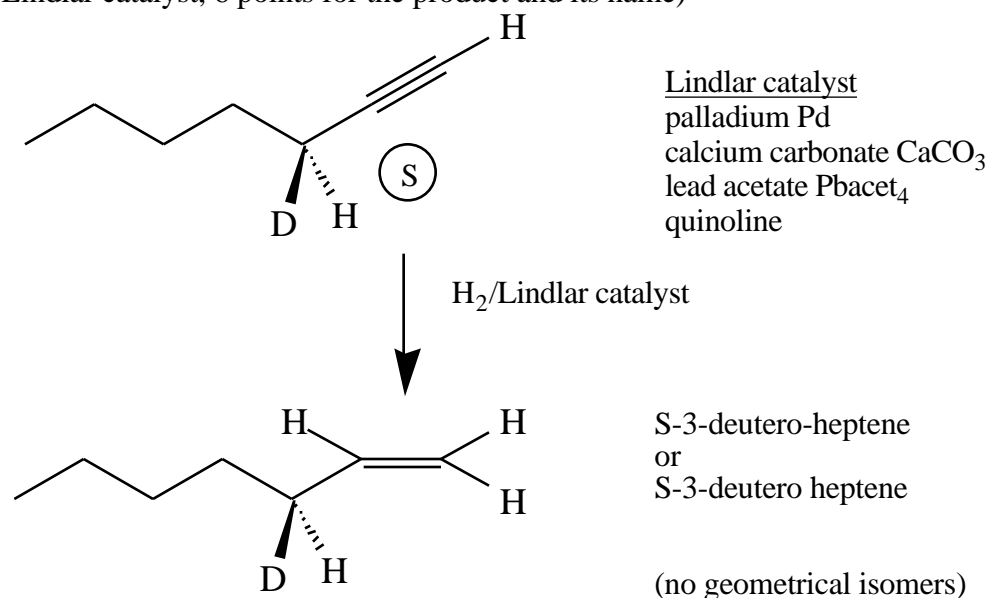
(a) Consider the substitution reaction of the pure enantiomer (R)-1-deutero-1-bromopentane by lithioacetylene,  $\text{H-C}\equiv\text{C}^- \text{Li}^+$ . Draw the substrate in a perspective drawing that clearly shows the configuration. Show the product of the reaction and its configuration. Give the full name of the product and indicate the mechanism of the substitution. (8 points)

(2 points for the substrate, 4 points for the product and its name, 2 points for the mechanism.)



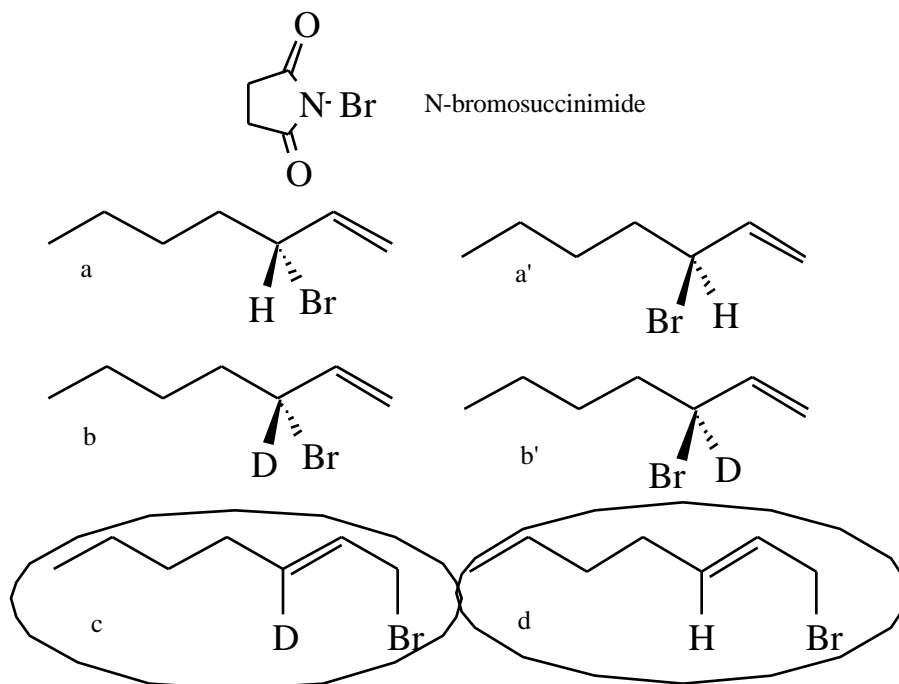
(b) Now, suppose we treat the product of the reaction in (a) with hydrogen in the presence of a Lindlar catalyst. What is a Lindlar catalyst? What is the product of that reaction; give the full name and pay attention to stereochemistry. (8 points)

(2 points for Lindlar catalyst, 6 points for the product and its name)



(c) Now, suppose we treat the product of the reaction in (b) with NBS. Show all six products that are possible. Circle the two products that are the least likely. (11 points)

(1.5 point each correct product, 2 points for circles)

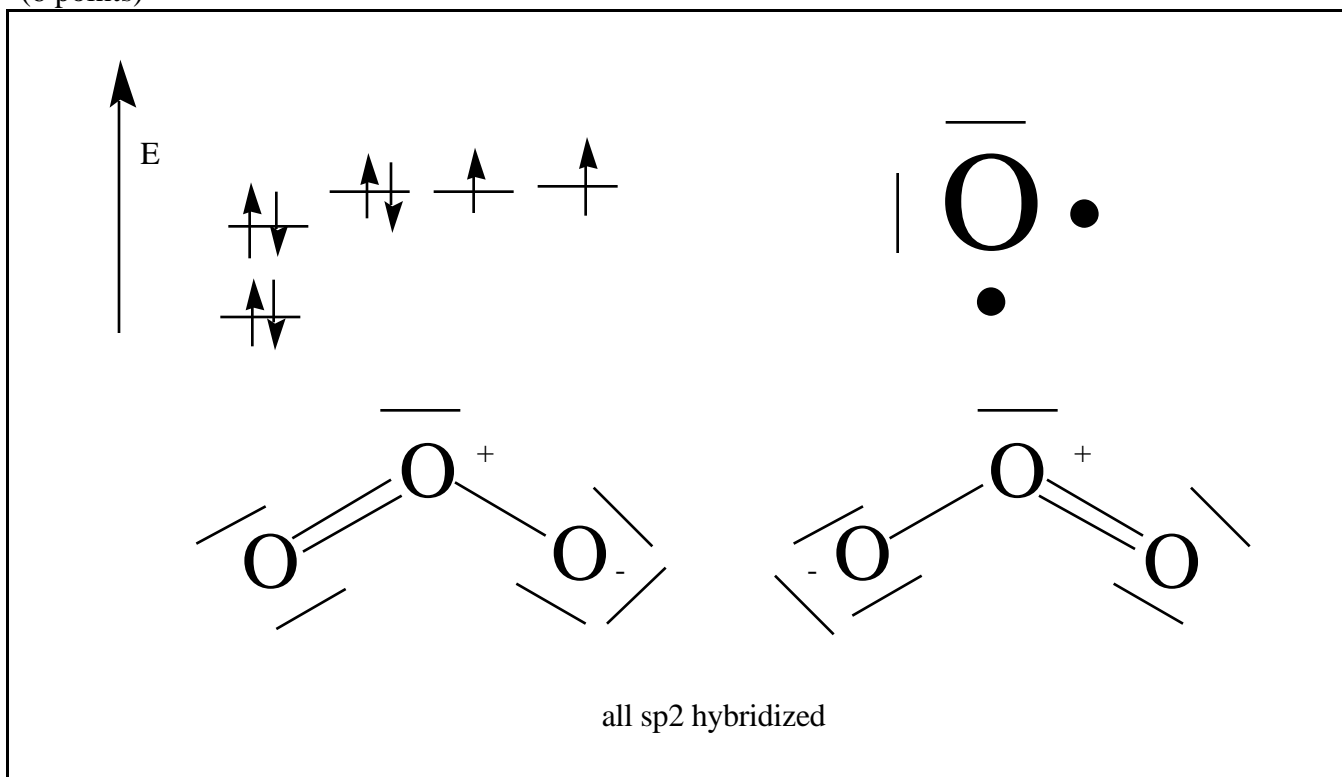


(d) Do you expect a large kinetic isotope effect in the reaction in (c)? If there is (or were) such a kinetic isotope process, which one (or two) of the products in (c) would be the major product(s)? (4 points)

Yes, the H abstraction is the slow step.  
 H is more easy to abstract than is D.  
 The enantiomers b and b' will be the major products.

**Question 7. Hybridizations.**

Draw an energy level diagram for the ground state of oxygen and label the atomic orbitals. Draw the Lewis structure of atomic oxygen. As you can see, atomic oxygen is a biradical (two unpaired electrons) and it is quite reactive. One important reaction of O is its addition to molecular oxygen, O<sub>2</sub>, to give ozone. Draw the Lewis structure of ozone and indicate hybridizations of all atoms. Show formal charges (if any). (6 points)



ZAAA AAA AAAAAA AAAAA  
 AZ Schöne Ferien. Erholt Euch gut. ZAA  
 ZAAA AAA AAAAAA AAAAA  
 Das war doch gar nicht so schwer, nicht wahr.  
 / The Very End /