CH310N Spring 2011

Anslyn

February 15, 2011

Exam 1

Please **PRINT** the first three letters of your last name in the three boxes.

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Total Sc	Score	(100 ptc)
	Score	 (100 pts)

12) _____ (10 pts)

1.

(a) (From the notes) Please give the common names for the following compounds. (2 points)

(b) (From homework, problem 16.14) Please give the IUPAC name for the following compound. (2 points)

(c) (Partially from the notes) Please draw the chemical structures for the following names. (3 points)

- In this question you are asked to distinguish whether or not hydrogens are diastereotopic.
 Then, you are requested to state the splitting pattern of a specific hydrogen (singlet, doublet, triplet, or doublet of doublet, etc.). (9 points)
 - Br Hb CI CHa₃

Are the Ha hydrogen atoms disastereotopic?

Yes or No NO

Splitting of Hb: Quartet

b) Br Hb NMe₂

Are the Ha hydrogen atoms diastereotopic?

Yes or No Yes

Splitting of Hb: Doublet of cloublets
(Possibly a triplet)

c)

Are the Ha hydrogen atoms diastereotopic?

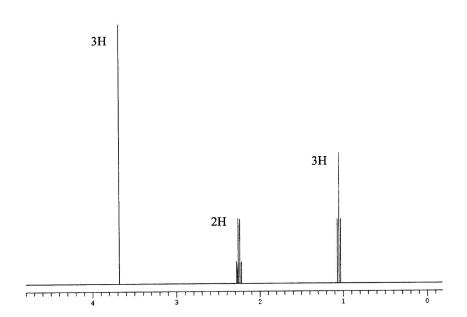
Yes or No Ve 5

Are the Hb hydrogen atoms diastereotopic?

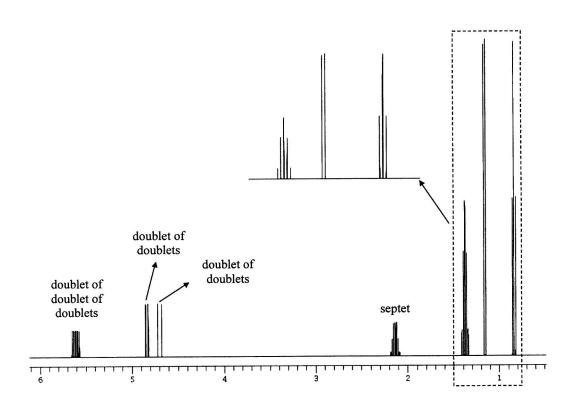
Yes or No No

Splitting of Hb: Doublet of doublets

(Possibly a triplet)



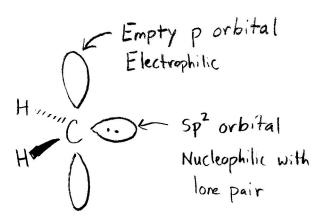
(b) Circle the molecule which represents the following ¹H-NMR spectrum. (3 points)



4. As we discussed in class, heating diazomethane generates nitrogen gas and a carbene. This question pertains to the structure and reactivity of the carbene species. (6 points)

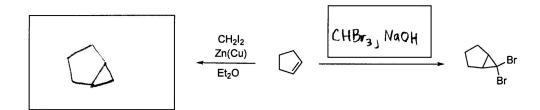
Diazomethane

a) Draw a picture describing the geometry of the carbene that is generated, showing any orbitals that contain lone pairs or are empty.



- b) On your picture from part a, indicate the types of orbitals that are present (s, p, sp³, etc).
- c) On your picture from part a, indicate in which orbital the lone pair resides.
- d) On your picture from part a, identify any orbitals having nucleophilic character. Do the same for orbitals with electrophilic character.

- 5. Fill in the box with the appropriate reactant, reagent, or product. Some boxes require more than one step. (16 points)
 - a) Partially from homework, problem 15.12c



b)

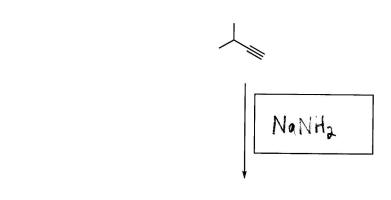
c)

d) From class notes

$$\frac{\left(H_{3}C\right)_{2}^{CuLi}}{Et_{2}O}$$

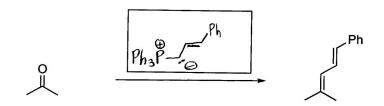
$$CH_{3}$$

e)



f) From class notes

g) From homework, problem 16.23f



h) Partially from class notes

i) From homework, problem 16.30c

j) Partially from class notes, partially from homework problem 15.7b

6. The next question pertains to the trends in reactivity of various substrates towards hydration of a carbonyl. Based on arguments presented in class, please circle the species that is most hydrated in water, and explain your answer in ONE OR TWO SENTENCES. (6 points)

Less steric hinderance makes formaldehyde more susceptible to nucleophilic addition.

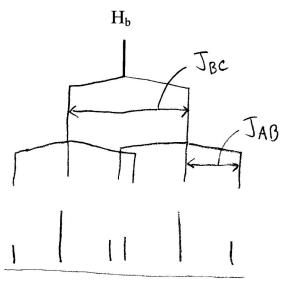
Electron withdrawing Cl atoms make the carbonyl carbon more electrophilic, promoting nucleophilic addition.

7. From homework, problem 13.28 (with a slight twist). This question pertains to the splitting between adjacent protons in the ¹H NMR spectrum of the molecule shown below. Given the various coupling constants that are shown, please draw the splitting tree that gives rise to the expected splitting of H_b. Name the pattern that is predicted in each case. (9 points)

$$H_3C$$
 CI CH_3 H_a H_b H_c

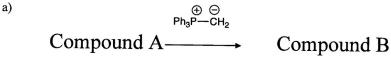
a) $J_{ab} = J_{bc} = 6 \text{ Hz}$

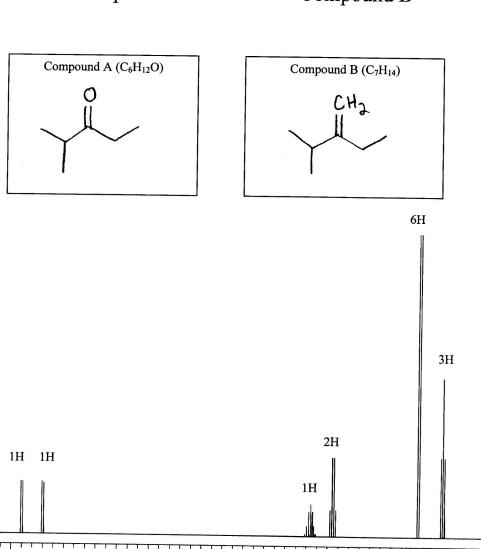
b)
$$J_{ab} = 5 \text{ Hz}, J_{bc} = 8 \text{ Hz}$$



Doublet of triplets

8. Compound A (molecular formula C₆H₁₂O) undergoes a Wittig reaction, using a methyl phosphonium ylide, to form Compound B (molecular formula C₇H₁₄). The ¹H-NMR spectrum of Compound B is shown below. Using this information given, predict the molecular structure for both compounds A and B. (8 points)





9. Hydroxyaldehydes will undergo intramolecular hemiacetal formation when a stable five- or six-membered ring can be formed, such as in the case of 4-hydroxypentanal (pictured below). This transformation is further promoted by the presence of base. Draw the mechanism for the following reaction, including all participating lone pairs, applicable formal charges, and required arrow pushing to indicate flow of electrons. (8 points)

$$H_3C$$
 H_3C
 H_3C

10. From homework, problem 16.21. The molecule pictured below, 1-phenyl-2-butanol is used in the perfume industry. Please show how to synthesize this alcohol from bromobenzene, 1-butene, and any necessary inorganic reagents. Note that you do NOT need to show arrow pushing for each step, and the starting materials may be the only source of carbon atoms in the final product. (8 points)

11. In the presence of an acid catalyst, a hemiacetal will react with an alcohol to form an acetal product. Please draw the mechanism for the following transformation, including all participating lone pairs, applicable formal charges, and required arrow pushing to indicate flow of electrons. (8 points)

OH OEt EtOH OET OET
$$H_3O^+$$
 OET $H_3O^ H_3O^ H_3O$

12. Using the starting materials given as the only source of carbon atoms in the product, show how you would bring about the following transformation. Note that you do NOT need to show arrow pushing for each step. (10 points)