Chemistry 216

Second Examination

June 17, 2010

Professor Masato Koreeda
(120 min, 120 points)

Name _____
Please Print

Signature _____

Student ID # _____

Please CHECK OFF your lab section.

sectn #	GSI
_____130	Rebecca Chota
_____131	Junsi Gu
_____132	Rui Huang
_____133	Natalie Vandeven
_____134	Deidra Gerlach
_____135	Shaoon Rahman
_____136	Soojeong Kim
_____137	Emily Nelson
_____138	Anthony Grillo
_____139	Wen Wen

This exam has 13 pages including this cover page. The last five pages include a periodic table, tables of characteristic IR frequencies, representative H-1 and C-13 NMR chemical shifts, and H-1/H-1 coupling constants and a table of pKa values for representative acids.

I	14	
II	6	
III	11	
IV	14	
V	5	
VI	25	
VII	20	
VIII	12	
IX	13	
TOTAL	**120**	

I. (14 points) The Grignard reagent C_6H_5-MgBr is prepared from bromobenzene (C_6H_5-Br) and Mg. Answer in the boxes below the following questions.

(1) (2 points) Is the carbon atom associated with the bromine atom in bromobenzene electrophilic or nucleophilic?

electrophilic nucleophilic

[circle one]

(2) (2 points) Is the carbon atom associated with magnesium in the Grignard reagent electrophilic or nucleophilic?

electrophilic nucleophilic

[circle one]

(3) (2 points) Is the magnesium atom oxidized or reduced during the formation of the Grignard reagent?

oxidized reduced

[circle one]

(4) (4 points) Explain why the Grignard reaction has to be carried out in an anhydrous solvent.

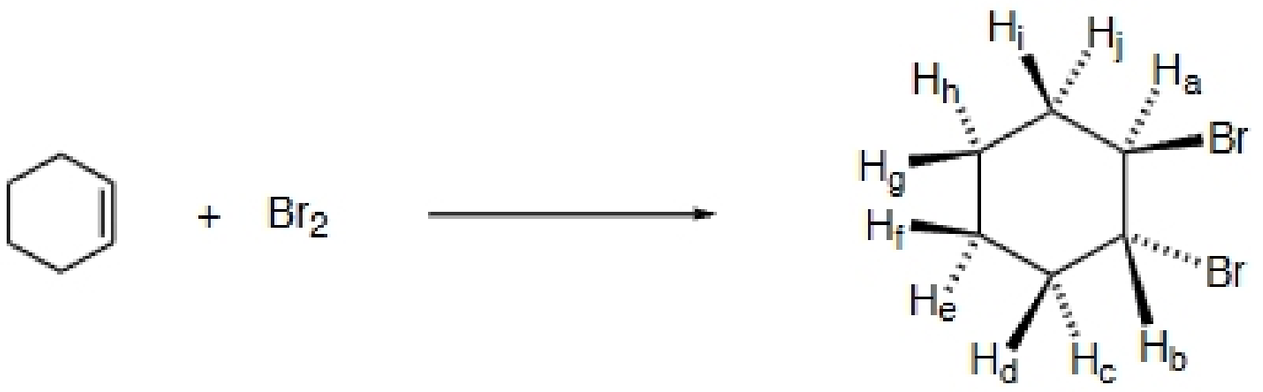
(5) (4 points) Write the conjugate carbon acid (i.e., C-H) of the C_6H_5–MgBr and explain why Grignard reagents are strong bases.

structure:	explanation:

II. (6 points) Ethanol [CH_3CH_2OH] is often present in technical-grade diethyl ether. If this grade of diethyl ether were used, what effect, if any, would the ethanol have on a Grignard reagent used? Explain through the use of a chemical equation using C_6H_5–MgBr as an example.

explanation based upon the reaction mechansim:

III. (11 points) Treatment of cyclohexene with bromine produces *trans*-1,2-dibromocyclohexane as a racemate. In spite of its simple structure, it shows quite complex spectra, particularly the ^{1}H NMR spectrum.

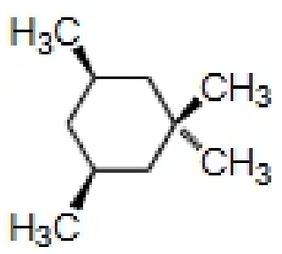


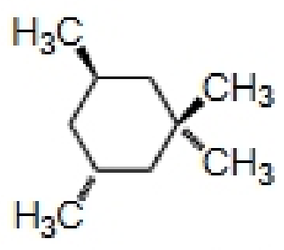
(1) (2 points) How many different ^{13}C NMR peaks would you expect from this dibromide? _____

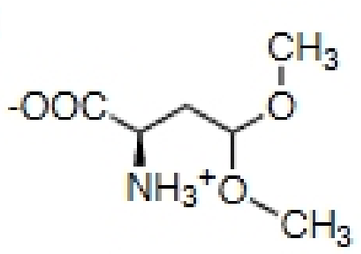
(2) (9 points) Identify the indicated pairs of hydrogens in the dibromide as (i) homotopic, (ii) enantiotopic, or (iii) diastereotopic Hs. Write the answers as (i), (ii), or (iii).

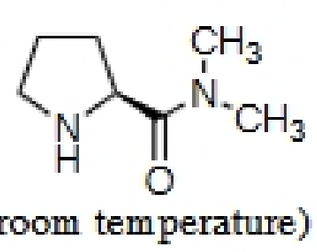
H_a and H_b _____ H_c and H_d _____ H_e and H_f _____
H_g and H_h _____ H_i and H_j _____ H_c and H_i _____
H_d and H_j _____ H_e and H_g _____ H_f and H_h _____

IV. (14 points) Show how many peaks you would expect to observe in the proton-decoupled ^{13}C NMR spectra of the following compounds. Indicate your answers in each of the boxes provided.

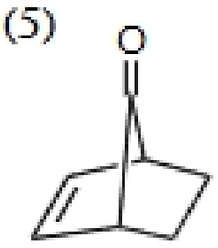
(1)


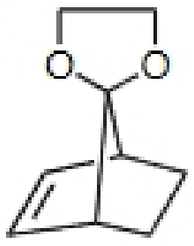
(2)


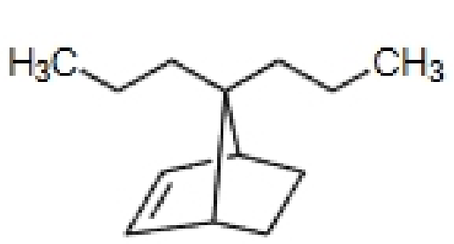
(3)


(4)


(room temperature)

(5)


(6)


(7)


V. (5 points) The pK_a value of the NH of CH_3NH_2 is about 35. In contrast, the pK_a value of NH of urea $[(H_2N)_2C{=}O]$ is about 12. Provide an explanation in the box below as to why the NH of urea is considerably more acidic than that of methylamine. If your explanation involves the resonance concept, make sure to draw a relevant resonance structure(s).

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