Chemistry 605 (Reich)

SECOND HOUR EXAM

Thur. April 12, 2012

Question/Points

R-11H ____/30
R-11J,K ____/15
R-11L,M ____/30
R-11N ____/17
R-11O ____/8

Total ____/100

Practice Exam 2

Name__________________________

If you place answers anywhere else except in the spaces provided, (e.g. on the spectra or on extra pages) clearly indicate this on the answer sheets.
Problem R-11H \( (\text{C}_{12}\text{H}_{16}\text{O}_3) \). You are provided the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of a compound. Interpret the spectra, and determine the structure or structures. Note that the signal at \(\delta\) 6.5 disappeared when D$_2$O was added.

(a) DBE ________

(b) Analyze the multiplets below. Identify the patterns (e.g., ABXYZ - underline the observed nuclei). If they are first order, report them in the standard format (\(\delta\) 0.00, dqt, \(J = 0.0, 0.0, 0.0, 2\)H). Provide part structure(s) defined by these protons.

\[ \delta 1.7-2.1 \]

\[ \delta 3.9-4.1 \]

\[ \delta 6.7-7.2 \]

(c) Identify at least 3 signals in the \(^{13}\text{C}\) NMR spectrum which provide significant structural information, and describe the part structures obtained from them.

(d) Draw the structure of R-11H below. If more than one structure fits the data, draw them, but circle your best choice.
Problem R-11H \((\text{C}_{12}\text{H}_{16}\text{O}_3)\)

300 MHz \(^1\text{H}\) NMR spectrum in CDCl\(_3\)

Source: Chris Marvin/Charlie Fry 09/32
Problem R-11H \((\text{C}_{12}\text{H}_{16}\text{O}_3)\)

75 MHz \(^{13}\text{C}\) NMR spectrum in CDCl\(_3\)

Source: Chris Marvin/Charlie Fry 09/32

DEPT-135

DEPT-90

Normal \({^1\text{H}}\)
Problem R-11J and K ($C_{19}H_{18}O$). You are given 200 MHz $^1$H NMR spectra of two stereoisomers of a compound which differ at one stereocenter only (i.e., 1 and 2, or 6 and 8), the possibilities are 1 to 8 below. Your task is to make both a structural and a stereochemical assignment. Explain the basis of your assignment below, taking care to clearly identify the signals you are using.

(a) What spectral features allow you to distinguish the two structural types (1 to 4 versus 5 to 8)?

(b) What spectral features allow you to distinguish the pair of isomers? Write the spectrum number (R-11J or R-11K) in the appropriate blank.

(c) Just to show you understand the spectra, give just the chemical shifts of the two protons at the CH$_2$ group (marked with an arrow in 1).

R-11J ______. ______

R-11K ______. ______
Problem R-11J \((C_{19}H_{18}O)\)
200 MHz \(^1\text{H} \) NMR Spectrum in CDCl\(_3\)
(Source: Drew Weber/Zimmerman 11/18)

Problem R-11K \((C_{19}H_{18}O)\)
200 MHz \(^1\text{H} \) NMR Spectrum in CDCl\(_3\)
(Source: Drew Weber/Zimmerman 11/18)
**Problem R-11L and R-11M.** From the 270 MHz $^1$H NMR spectra of two stereoisomeric bromo pentaacetoxy cyclohexanes assign stereochemistry and conformation ("interpret" means give $\delta$, $J$ and multiplicity).

![Chemical Structure]

(a) Interpret the signal at $\delta$ 4.5 in **R-11L**. Suggest possible part structures. Circle the proton at $\delta$ 4.5

![Structure Interpretation]

(b) Interpret the signal at $\delta$ 5.2 in **R-11L**. Suggest possible part structures. Circle the proton at $\delta$ 5.2.

![Structure Interpretation]

(c) Identify other significant multiplets in the expansion ($\delta$ 5.3 - 5.8) on the right (**R-11L**), draw coupling trees, and identify part structures. HINT: these are all first order

![Expansions and Coupling Trees]

(d) Complete the structure for **R-11L** below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.

![Completed Structure]
(e) What do the signals at $\delta$ 2 tell you about the structure of R-11M (compare them to the $\delta$ 2 signals of R-11L).

(f) Assign and interpret the signal at $\delta$ 4.0 in R-11M. Suggest possible part structures.

(g) Analyze the rest of the NMR spectrum of R-11M. Point out significant features of the spectrum which can be used to assign stereochemistry. HINT: there are some second-order effects in the multiplet $\delta$ 5.1 - 5.5.

(h) Complete the structure of R-11M below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.
Problem R-11L \((C_{16}H_{21}BrO_{10})\)

270 MHz \(^1H\) NMR Spectrum in CDCl\(_3\)

(Source: Ieva Reich 11/15)
Problem R-11M (C_{18}H_{21}BrO_{10})
270 MHz $^1$H NMR Spectrum in CDCl$_3$
(Source: Ieva Reich 11/15)
Problem R-11N (C₉H₁₆ClN). In this problem you are required to determine the position of a Cl substituent in a 1-aza-bicyclo[2.2.2]heptane from the ¹H NMR spectra. You are given the ¹H NMR spectra of the compound and the 7,7-dideuterated analog.

(a) Analyze the coupling system of R-11N and report your results below. For each position either give the multiplicity, J and δ values, or enter Cl if that is where you think it is. NOTES: 1. You may use first order analysis - there are no significant second order effects. 2. There are no effects detectable due to coupling between H and D.

2x ____________________________
2n ____________________________
3x ____________________________
3n ____________________________
6x ____________________________
6n ____________________________
7s ____________________________
7a ____________________________

(b) Briefly describe how you decided on the location of the chlorine

(c) Briefly describe specifically how you distinguished proton(s) at 2 from those at 3.

(d) Briefly describe how you distinguished the x and n signals at carbons 2 and 3.
Problem R-11N (C₉H₁₆ClN)
100 MHz ¹H NMR Spectrum in CDCl₃
(Source: JACS 1968, 90, 13551 4/45)

One of the H atoms at positions 2, 3 or 6 is substituted by a Cl. Which one?

100 MHz ¹H NMR Spectrum in CDCl₃
(Source: JACS 1968, 90, 13551 4/45)
Problem R-110. Identify the SH protons in the two 300 MHz $^1$H NMR spectra (CDCl$_3$) below, and explain the difference in their appearance (Source: Aldrich NMR Library).