Chemistry 605 (Hans J. Reich)

THIRD HOUR EXAM

Mon. May 14, 2012

Question/Points

R-11P _____/15
R-11Q _____/15
R-11R _____/20
R-11S _____/10
R-11T _____/20
R-11U _____/20
Total _____/100

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.

Average 74
Hi 94
Median 73
AB 80
BC 50

Distribution from grade list (average: 73.5; count: 27)
**Problem R-11P** \((\text{C}_8\text{H}_8\text{F}_2\text{Si})\). Below is a 300 MHz \(^1\text{H}\) NMR spectrum of vinyl difluorophenylsilane (source: Josh Dykstra/Burke). Analyze the spectrum, and label the spectrum with coupling trees, and label them with \(\text{H}_\text{g}\), \(\text{H}_\text{c}\) and \(\text{H}_\text{t}\). Report all coupling in the standard format (\(^n\text{J}_{X-Y} = \text{00.0 Hz}\)). Apart from intensities, the spectrum is basically first order.

![](image)

5 pts each

There are also a number of small peaks from \(^{29}\text{Si}\) coupling to the various protons. Pretty indistinct - hard to be sure which might be impurities because usually can't see both satellites.

\[2\text{J}_{\text{Ht-Hc}} = 4.5 \text{ Hz}\]
\[3\text{J}_{\text{Ht-Hg}} = 20.2 \text{ Hz}\]
\[3\text{J}_{\text{Hg-F}} = 2.9 \text{ Hz}\]
\[4\text{J}_{\text{Ht-F}} = 1.8 \text{ Hz}\]

**The strange intensities of the middle peak is confirmed by a simulation**
Problem R-11Q \((C_{11}H_{19}NO_8)\). This problem requires you to determine the stereochemistry of two isomers of sialic acid (A and B). Below is shown a portion of the 126 MHz \(^{13}\text{C}\) NMR spectrum (\(D_2O\) solvent) of a 10:1 mixture of two isomers (Hori, H.; Nakajima, T.; Nishida, Y.; Ohrui, H.; Meguro, H. *Tetrahedron Lett.* **1988**, 29, 6317).

Spectrum 1 is the fully proton decoupled. Spectrum 2 has the decoupler turned off.

(a) Which carbons of the sialic acid are being shown here? Mark the shifts on the structures.

Carbonyl peaks - amide at 177.7 and 177.9 ppm, carboxylic acid at 176.1 and 175.3 ppm

(b) Interpret the multiplicity of the signal at 177.7 ppm in the coupled spectrum (2). Estimate coupling constants, and assign them.

qd, \(J = 6, 3\) Hz

Thus this must be the amide carbonyl - coupled to \(CH_3\) (6 Hz) and the N-C-H proton (3 Hz). Coupling cannot be to N-H proton since in \(D_2O\) this would be N-D.

(c) Which is the major isomer (A or B)? **B**. Give your reasoning below. Be specific and brief.

The minor isomer (δ 175.3) has a \(^3\)J\(_{\text{CH}}\) coupling between the vicinal axial C and the axial H of 6 Hz.

The major isomer has no significant \(^3\)J coupling to either of the vicinal C-H protons - Karplus angle is ca 60°.
Problem R-11R \((C_{18}H_{22}Se_2)\) You are given the structure, and asked to interpret the spectrum (complete spectrum on next page).

(a) Analyze the multiplet at \(\delta 2.1\) and report couplings.

Septet of doublets, \(^3J_{HH} = 6.5\), 3 Hz (H_D)

No Se satellites due to \(^3J_{HD-Se}\) can be seen here (satellites of the larger inner peaks are buried under the outer ones)

(b) Analyze the multiplet at \(\delta 3.7\). Identify all peaks. Obtain exact shifts and report all shifts and couplings in the form: \(\delta 0.00, \; ^nJ_{XY} = 00 \) Hz. An enlarged copy of the multiplet is shown below. The Hz values are from TMS at 0 Hz.

Main feature is the AB quartet (H_A, H_B) of the diastereotopic Se-CH_2-Ph group.

764, 753, 749, 738 Hz (marked with • and •)

\(J_{AB} = 754-753 = 11\text{Hz}; \; 749-738 = 11 \text{Hz}\)

Solve the AB quartet:

\(\nu_{AB} = 10.2 \text{Hz}, \; \nu_{\text{center}} = 751 \text{Hz}\)

\(\nu_A = 751-5.1 = 746 \text{Hz}, \; \delta 3.73\)

\(\nu_B = 751+5.1 = 756 \text{Hz}, \; \delta 3.78\)

There are selenium satellites on both sides of each peak of the AB quartet. The \(^2J_{HSe}\) if slightly larger for H_B (13.5 Hz) than for H_A (11.5 Hz)

There is also a doublet for H_C at 735 Hz (marked with •) \(\delta 3.67, \; ^3J = 3 \text{Hz} \) (to H_D)

One satellite only is visible (double intensity because there are 2 Se). It is about 2 Hz from central peak, so \(^2J_{HC-Se} = 4 \text{Hz}\).
Problem R-11R  $\text{C}_{18}\text{H}_{22}\text{Se}_2$

200 MHz $^1\text{H}$ NMR spectrum.
Solvent CDCl$_3$.
(Source: Bob Dykstra/HJR 12/25)
Problem R-11S \((C_{16}H_{22}Fe_2O_2P_2)\). Below are the 60 MHz \(^1H\) NMR spectra of two stereoisomers (E and Z) of the iron Cp complexes shown \((J. Am. Chem. Soc 1963, 85, 3120)\).

(a) Which isomer corresponds to Spectrum 1 E, and which to Spectrum 2 Z? Explain

This is a simple symmetry argument - in the Z isomer the PMe\(_2\) group is diastereotopic, so two triplets are seen. In the E they are identical (related by a \(C_2\) axis).

(b) Explain the appearance of the multiplet at \(\delta\ 1.6\) (i.e. why does it look like this).

In the absence of other effects, the methyl groups should be coupled to one \(^{31}\)P nucleus, hence a doublet. If the 4-bond coupling to the remote P was large enough, one would expect to see a dd. One sees a triplet because there is a large \(J\) between the two \(^{31}\)P nuclei, so anything coupled to them will show “virtual coupling” effects - i.e. the methyl group appears to be coupled equally to both P.

(c) Would you expect the spectrum to look significantly different at 300 MHz (instead of the 60 MHz of the spectra shown)?

Apart from a larger separation between the two triplets in Spectrum 2, there would be no difference - the chemical shift between the P nuclei is zero at all fields, so the “virtual couplings” effect will always be there.
Problem R-11T \((C_{19}H_{25}FO_2)\). Below are part of the 60 MHz \(^1\text{H}\) NMR spectra of two stereoisomers (A and B) of the fluorinated steroids shown. To aid in your analysis, a conformational drawing is also provided \((J. \text{Am. Chem. Soc.} \textbf{1963}, \textbf{85}, \text{3038})\).

(a) Which protons are being shown here? Analyze the coupling, and report them in the standard format (give \(\delta\) and identify any couplings you found).

Spectrum 1:

6
\(\delta\) 6.05, broad s, H\(^4\)
\(J_{H^6a-F} = 48 \text{ Hz}\)
\(J_{H^6a-7a} = 11 \text{ Hz}\)
\(J_{H^6a-7e} = 6 \text{ Hz}\)
\(J_{H^6a-4} = 2 \text{ Hz}\)

7
\(\delta\) 5.89, d, \(J = 5 \text{ Hz}\)
\(J_{H^6e-F} = 51 \text{ Hz}\)
\(J_{H^6e-7a} = 3 \text{ Hz}\)
\(J_{H^6e-7e} = 3 \text{ Hz}\)
\(J_{H^6e-4} < 2 \text{ Hz}\)

(b) Which isomer corresponds to Spectrum 1 \(\textbf{A}\), which to Spectrum 2 \(\textbf{B}\). Explain briefly.

The large H-H coupling in Spectrum 1 requires that the proton at H\(^6\) be axial, to get one large ax-ax coupling \((J_{H^6a-7a} = 11 \text{ Hz})\). The vicinal couplings in Spectrum 2 are all small (3 Hz) so only eq-equ and eq-ax coupling, hence H\(^6\) must be equatorial.
Problem R-11U \((C_{2}H_{4}AsF_{7}NXe)\). This problem requires you to interpret the \(^{129}\text{Xe}\) and \(^{14}\text{N}\) spectra of \([\text{CH}_3\text{C}≡\text{N}-\text{Xe-F}]^+\text{AsF}_6^-\) (Emara, A. A. A; Schrobilgen, G. J. *Chem. Commun.* 1987, 1644).

(a) Analyze Spectrum 1 and 2. Spectrum 2 is of a compound labeled >99% with \(^{13}\text{C}\) at the CN carbon. Report coupling constants. Use the form \(^nJ_{X-Y} = 00.0\) Hz.

- \(^{129}\text{Xe}\), \(I = 1/2\), 26.3% abundant
- \(^{129}\text{Xe}\) NMR spectrum of \([\text{CH}_3\text{C}≡\text{N}-\text{Xe-F}]^+\text{AsF}_6^-\) in HF at -10 °C
- \(^{129}\text{Xe}\), \(I = 1/2\), 26.3% abundant
- \(^{129}\text{Xe}\) NMR spectrum of \([\text{CH}_3\text{C}≡\text{N}-\text{Xe-F}]^+\text{AsF}_6^-\) in HF at -10 °C

- \(^{1}J_{\text{Xe-F}} = 6020\) Hz
- \(^{1}J_{\text{Xe-14N}} = 313\) Hz
- \(^{2}J_{\text{Xe-13C}} = 79\) Hz

(b) Analyze Spectrum 3. Make sure you understand and explain the origin of all peaks. Why are the signals somewhat broadened?

- Central peak: all of the isotopes of Xe except \(^{129}\text{Xe}\)
- Outer peaks: \(^{129}\text{Xe}\) satellites due to \(^{129}\text{Xe} - ^{14}\text{N}\) coupling, \(J\) ca 300 Hz
- The signals are broadened because \(^{14}\text{N}\) \(T_1\) is quite short due to quadrupolar relaxation, so signals are broadened. There could also be broadening effects from unresolved coupling to F and \(\text{CH}_3\).