Chemistry 605 (Reich)

THIRD HOUR EXAM

Wed. May 15, 2013

Question/Points

R-12L _____ /20
R-12M _____ /15
R-12N _____ /25
R-12O _____ /10
R-12P _____ /20
Total _____ /90

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.

Distribution from grade list (average: 70.1; count: 31)

Average 70/90
Hi 88/90
Median 73
AB 70/90
BC 45/90
**Problem R-12L.** The 100 MHz $^1$H and 19.15 MHz $^{77}$Se NMR spectra of a mono-iodo selenophene are shown below. Both spectra are at the same Hz scale.

(a) Interpret the $^1$H NMR spectrum, including the various small peaks (e.g., those at $\delta$ 7.8 and 8.5). Report $\delta$ and all coupling constants in the standard format.

- $\delta$ 7.30, dd, $J = 5.5, 1.5$ Hz. Se satellites: $^3J_{\text{HSe}} = 8$ Hz
- $\delta$ 8.05, dd, $J = 5.5, 2.5$ Hz. Se satellites: $^2J_{\text{HSe}} = 46$ Hz
- $\delta$ 8.26, dd, $J = 2.5, 1.5$ Hz. Se satellites: $^2J_{\text{HSe}} = 45$ Hz

(b) Interpret the $^{77}$Se NMR spectrum. Report all coupling constants. Draw a "coupling tree" on the spectrum.

- $\delta$ 72.4, ddd, $J = 46, 45, 8$ Hz

(c) Draw the structure of R-12L below, briefly give your reasoning.

The two large Se-H couplings require I to be at the 3 position (if know that $^2J >> ^3J$ - see examples under Selenophene in HDATA). This substitution also fits the proton couplings.

Chemical shift arguments also favor this structure - the two most downfield protons have the large Se-H coupling.
Problem R-12M \((C_{10}H_{9}NO)\). You are asked to interpret the coupled \(^{13}\text{C}\) NMR spectrum of an oxazoline.

(a) Which carbon are we looking at? \(\text{C}^3\)

(b) Analyze the spectrum, report all coupling constants in the standard format \((^3J_{X-Y} = 00.0\ \text{Hz})\).

\[
\begin{align*}
\text{tdd, } J & = 146, 8, 3 \\
^1J_{\text{C-H}} & = 146 \text{ Hz} \\
^3J_{\text{C-H}} \text{ (trans)} & = 8 \text{ Hz} \\
^3J_{\text{C-H}} \text{ (cis)} & = 3 \text{ Hz}
\end{align*}
\]

(c) The spectrum below is of the same compound with one H replaced by D. Where is the deuterium? Place it on the structure, and explain briefly.

Only the small cis \(^3J_{\text{C-H}}\) remains in the deuterated compound, so the trans proton must have been replaced by deuterium. The C-D coupling would be only about 1.3 Hz, so is not detectable at this resolution.

(d) What is the proton NMR frequency of the spectrometer they were using? 497 MHz

1 ppm = 125 Hz in the \(^{13}\text{C}\) NMR spectrum, so the \(^{13}\text{C}\) frequency is 125 MHz. Thus the proton frequency is \(125 \times (100/25.14) = 497.2 \text{ MHz}\)

(a) Identify all signals in the low temperature spectrum (-75 °C), and report approximate coupling constants using the form: $\delta$, $^XJ_{1-2}$ Hz. Use the numberings shown on the structure. For each signal briefly give your reasoning for the assignment.

- $P_1$ (δ -17, $^1J_{P_1-P_2} = 502$ Hz, $^2J_{P_1-P_4/5} = 49$ Hz, $^2J_{P_1-P_3} = 20$ Hz)
  - This is the P closest to the two PEt$_3$ groups, so expect triplet splitting.
  - The dd ($J = 502, 49, 22$ Hz) at δ -17 is the only signal that shows a triplet, so this must be $P_1$, which should also be coupled to both $P_2$ and $P_3$, as observed.

- $P_2$ (δ 18, $^1J_{P_1-P_2} = 500$ Hz, $^2J_{P_1-P_3} = 40$ Hz)
  - $P_2$ should also show the large $^1J$ to $P_1$, so it must be the dd ($J = 500, 45$ Hz) at δ 18. $P_1$ and $P_2$ form an ABXY$_2$ system, would need to do an AB quartet calculation to get accurate chemical shifts.

- $P_3$ (δ 112, $^2J_{P_3-P_2} = 40$ Hz, $^2J_{P_3-P_1} = 20$ Hz)
  - $P_3$ is coupled to both $P_1$ and $P_2$ (dd, $J = 46, 25$ Hz), so it has to be the δ 112 signal.

- $P_4$, $P_5$ (δ -122, d, $J = 48$ Hz)
  - This is the signal with double area at δ -122, d, $J = 48$ Hz.

(b) Identify the process which is responsible for the changes in the NMR spectrum at the higher temperatures (-30 °C and +50 °C). The signal at -122 ppm in the +50 °C spectrum is a triplet. Draw a structure or an equation.

- The Pd migrates back and forth between $P_1$ and $P_2$, so their chemical shifts are averaged, and both $P_3$ and $P_4/P_5$ become triplets, equally coupled to both. Since the two coupling constants are fairly close (expect the $P_4/P_5$ coupling to be $(49+0)/2 = 25$, and $P_3$ coupling to be $(40+20)/2 = 30$ Hz in size, the $P_1/P_2$ signal becomes an approximate quartet.

- The exchange is intramolecular, since the coupling between $P_1/P_2$ and $P_4/P_5$ is maintained in the high temperature spectrum.

(c) What is the proton frequency (MHz) of the spectrometer which was used for these spectra?

- $32.4 \times (100/40.49) = 80$ MHz
Problem R-12N. 32.4 MHz $^{31}$P-$^1$H NMR spectra. 
Solvent toluene-$d_8$
(Source: Chem. Commun. 1988, 1615)

+50 °C

-30 °C

-75 °C

Hz scale for main spectra

$^2J_{12} = 502$ Hz

Hz scale for expansions

$J_{12} = 502$ Hz

$P^1, P^2$

$P^3$

$P^4, P^5$

Me$_3$C

Pd $\rightarrow$ Cl

P$_1$, P$_2$

$2000$ $1800$ $1600$ $1400$ $1200$ $1000$ $800$ $600$ $400$ $200$ $0$

0 $-120$ $-125$ $-130$

0 $-120$ $-125$ $-130$

0 $-120$ $-125$ $-130$

0 $-120$ $-125$ $-130$
Problem R-12O (C_{16}H_{21}ClNOPt). Shown below are partial $^1$H NMR spectra of a platinum complex at several field strengths. All three spectra are at the same Hz scale. Only the signal for H$_A$ is shown (source: *Magn. Res. Chem.* 1985, 23, 671).

(a) Explain the small outer peaks of the multiplet.

These are $^{195}$Pt satellites: $^3J_{\text{Pt-H}} = 27$ Hz

$^{195}$Pt $I = 1/2$, 33.7% abundant

$^{31}$P $I = 1/2$, 100% abundant

(b) Analyze the multiplet. Give approximate coupling constants, report them in the form $^nJ_{XY} =$ _Hz. Assign the couplings.

The central peak is a ddd, $J = 6$, 4.5, 2 Hz

6 Hz is ortho coupling ($^3J_{\text{H-H}}$)

4.5 Hz is coupling to P ($^4J_{\text{H-P}}$)

2 Hz is meta coupling ($^4J_{\text{H-H}}$)

(c) Why do the small outer peaks become broad at higher field strength? This is not a fluxional molecule, and there is no ligand exchange under these conditions.

$^{195}$Pt must be relaxing by the CSA mechanism (chemical shift anisotropy), whose effectiveness varies as $B_0^2$, so $T_1$ values become shorter at higher field, until the coupling in the satellites begins to be averaged out at 500 MHz. The central peak is not affected by this process (other Pt isotopes).
Problem R-12P ($\text{C}_8\text{H}_{12}\text{O}$). This question requires you to assign the protons of compound R-12P using the 300 MHz proton NMR spectra given. The spectrum shows the normal $^1\text{H}$ NMR, and two inserts which are difference spectra resulting from subtraction of the normal spectrum from one in which the large signal at $\delta$ 0.95 or at $\delta$ 1.4 was preirradiated for a second or so, and then the decoupler was turned off during acquisition of the FID. The assignment of these signals is shown on the structures. The integration of the insets has been expanded five times (5x) compared to the normal spectrum.

(a) What kind of experiment is being performed here? What information does this experiment provide?

Homonuclear NOE difference experiment. One proton signal is irradiated until it is saturated, increase in area of other protons tells us which ones are close in space to the one being irradiated, provided that the irradiated proton is causing DD relaxation of the observed proton.

(b) For the NMR signals below assign each to one of the protons labeled $\text{H}_a$ to $\text{H}_f$. Briefly summarize the evidence you used in making each assignment. Each of the signals corresponds to a single proton. The signals marked with an x are impurities.

\[
\begin{align*}
\delta 1.43 & \quad \text{H}_f \\
\delta 2.08 & \quad \text{H}_b \\
\delta 2.28 & \quad \text{H}_a \\
\delta 2.43 & \quad \text{H}_c \\
\delta 2.55 & \quad \text{H}_d \\
\delta 2.60 & \quad \text{H}_e
\end{align*}
\]

\[\text{Assigned by difference - just a doublet, coupled only to H}_a. \quad \text{There must be a } 90^\circ \text{ dihedral angle with H}_c \text{ and H}_d\]

\[\text{2.08 and 2.28 should be the } \alpha-\text{keto protons H}_a \text{ and H}_b. \quad \text{They are coupled to each other, and show a characteristic large geminal coupling of } 17 \text{ Hz.}\]

\[\text{This signal shows an NOE effect when the endo Me group is irradiated (}\delta 0.95), \text{ so it must be H}_a, \text{ other is H}_b\]

\[\text{2.43 and 2.55 both show NOE effect when either Me group is irradiated, so they must be the H}_c \text{ and H}_d \text{ protons. 2.55 is just a dd, so must be H}_d; \text{ H}_c \text{ is complex, since it could be coupled to H}_a, \text{ H}_b, \text{ H}_d, \text{ H}_e, \text{ and H}_f}\]

\[\text{This signal shows an NOE effect when the exo Me group is irradiated (}\delta 1.38), \text{ so it must be H}_e, \text{ other is H}_f (}\delta 1.43)\]

Are there any ambiguities in the assignments you have made?

None

(c) Comment on the chemical shift difference between the two methyl signals, as well as the protons $\text{H}_e$ and $\text{H}_f$.

The endo methyl group (δ 0.95) and $\text{H}_f$ may both be over the shielding cone above and below the C=O group, hence the unusual upfield shift.
Problem R-12P \((\text{C}_8\text{H}_{12}\text{O})\)

300 MHz \(^1\text{H} \) NMR Spectrum

Source: The XL Series NMR Spectra Collection Vol 1
Varian Associates 12/19

Difference spectrum:
Irradiate at \(\delta 1.38\)

Must be \(H_e\) - closest proton to exo Me

Difference spectrum:
Irradiate at \(\delta 0.95\)

Common to both - must be \(H_c\) and \(H_d\)

Must be \(H_a\) - closest proton to endo Me

\(J = 18\), next to ketone

These two are coupled to each other with large \(J\), thus \(a, b\) or possibly \(e, f\)

Normal spectrum

\(H_e\) 2.60, \(H_d\) 2.55, \(H_c\) 2.43, \(H_a\) 2.28, \(H_b\) 2.08, \(H_f\)