Course: CY51003: Spectroscopic Methods of Structure Determination

End-Autumn Semester Examination 2014-2015

Department of Chemistry

Total Time: 3 hours No. of Students: 59 Total Marks: 50

Answer the following **all five** questions. 5x10 = 50

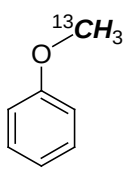
1. a) Calculate the intensity of [M+3] peaks with respect to [M] for C_2F_4BrCl (*only up to two decimal places*). [**4**]

b) Explain the McLafferty rearrangement (fragmentation) of the ketone 'octan-4-one' ($C_8H_{16}O$) and identify m/z value for the fragments which will appear in mass spectra. [**3**]

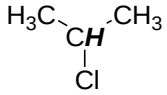
c) Whay C≡C Stretching frequency of 2-pentyne is not visible in IR but it is visible for 1-methoxybut-1-yne? [**1.5 + 1.5**]

Isotope, mass, abundance	Isotope, mass, abundance	Isotope, mass, abundance	Isotope, mass, abundance
^{1}H, 1.00783, 99.985% **^{2}H or D, 2.0141, 0.015%**	**^{12}C, 12.00, 98.90%** **^{13}C, 13.00336, 1.1%**	**^{14}N, 14.0031, 99.62%** **^{15}N, 15.0001, 0.38%**	**^{16}O, 15.9949, 99.76%** **^{17}O, 16.9991, 0.04%**
^{19}F, 18.9984, 100%	**^{35}Cl, 34.9689, 75.77%** **^{37}Cl, 36.9659, 24.23%**	**^{79}Br, 78.9183, 50.69%** **^{81}Br, 80.9163, 49.31%**	**^{31}P, 30.9738, 100%**

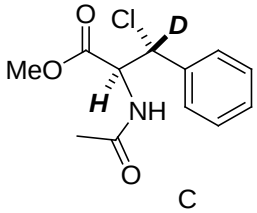
2. a) What will be splitting pattern for the nuclei shown in **bold** and *italic* (total six cases) for the following four molecules (**A**-**D**) in the respective NMR spectra? [**3**]



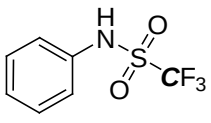
A



B



C

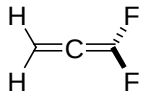


D

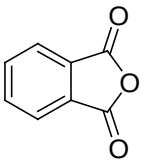
b) Why indirect spin –spin coupling constants are expressed in hertz but chemical shift in ppm? [**2**]

c) For studying reaction of proteins (molecular weight >10,000) with small organic molecules, among IR, ESI-TOF and NMR; which spectroscopic method will you prefer to understand product formation? Justify your answer briefly for your inclusion or exclusion of a particular spectroscopic method. [**3**]

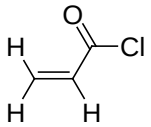
d) For ^{1}H NMR spectroscopy, identify the type of spin system following molecules (**E-H**) posses and also draw the splitting pattern you are expecting in ^{1}H NMR spectra for **E** and **G**. [**2**]



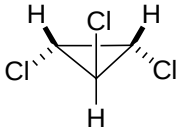
E



F



G



H

3. Answer the following questions briefly [10]

a) What is double resonance and briefly explain it by using vector model? [**2**]

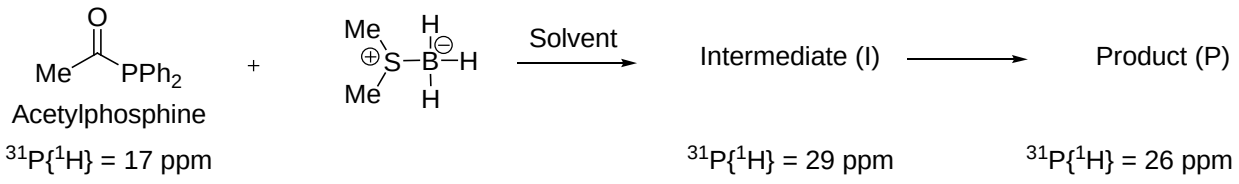
b) Why ^{1}H NMR scale is spread (mainly) over 15 ppm but for ^{13}C it is 250 ppm? [**2**]

c) Why NMR spectra obtained from 600 MHz spectrometer shows better splitting for multiplet signals having very small coupling constant than spectra recorded in 100 MHz machine? [**3**]

d) Why middle peak of a triplet correspond to the chemical shift for the triplet signal where as for doublet you need to take average value of the two splitted signals? [**3**]

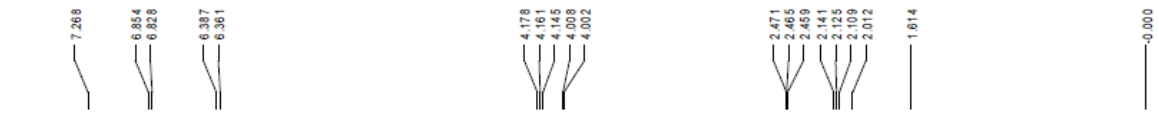
4. a) Reduction of keto-functional group of acetylphosphine to the corresponding alcohol has been followed by $^{31}P\{^{1}H\}$ NMR spectroscopy. The reaction required two equivalent of reducing agent $Me_2S{\cdot}BH_3$ and proceeds via a stepwise mechanism. *Propose* the intermediate and product structure by using $^{31}P\{^{1}H\}$NMR data of acetylphosphine (δ = 17 ppm), intermediate (δ = 29 ppm) and product (δ = 26 ppm) (see scheme in **next page**) and also *justify* three δ values. [**4**]

Hints: Acetophenone reacts completely with one equivalent of $Me_2S{\cdot}BH_3$ to provide corresponding alcohol (Ph-CH(OH)CH_3).



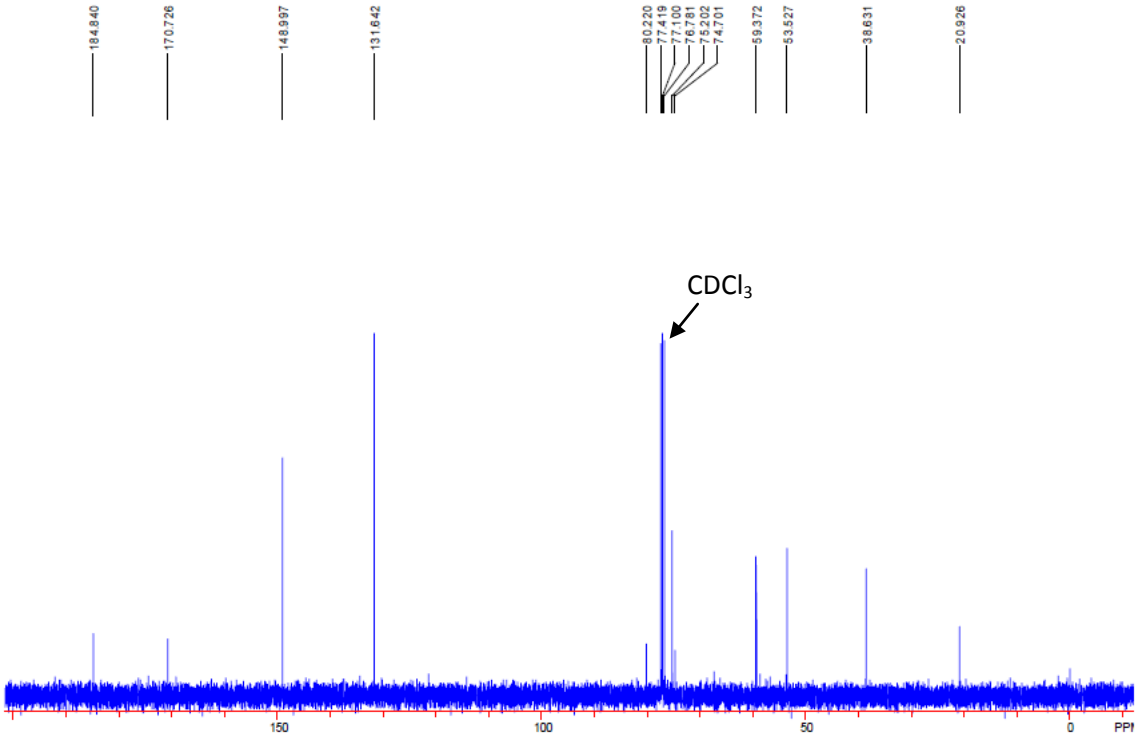
Scheme: Reduction of acetylphosphine with $Me_2S{\cdot}BH_3$ and corresponding $^{31}P\{^1H\}$ NMR data.

b) On reaction of phenol derivative with **S**, a new product is formed. Identify the product by using the spectral data as provided below: **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 6.84 (d, *J* = 10.0 Hz, 2H), 6.37 (d, *J* = 10.0 Hz, 2H), 4.16 (t, *J* = 6.4 Hz, 2H), 4.01 (d, *J* = 2.4 Hz, 2H), 2.47 (t, *J* = 2.4 Hz, 1H). 2.13 (t, *J* = 6.4 Hz, 2H), 2.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) 184.84, 170.73, 149.00, 131.64, 80.22, 75.20, 74.70, 59.37, 53.53, 38.63, 20.93; **HRMS** (FTMS-ESI): $[M+Na]^+$ calcd for $C_{13}H_{14}O_4Na^+$ 257.0784, found 257.0785; **IR** (KBr) ν (cm-1) 3270, 3046, 2965, 2925, 2863, 2119, 1738, 1670, 1633, 1607, 1436. [**6**]



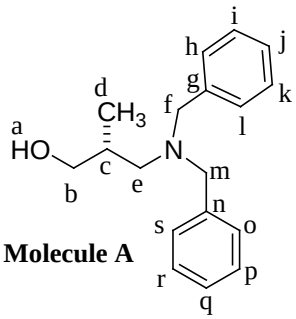
See also ^{1}H and ^{13}C NMR spectra of the product.

Question: 4. b) ^{1}H & ^{13}C NMR spectra of the **product**:



5.a) Analytical data for the compound with molecular formula C_4H_7ClO are: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.07 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.1, 44.3, 41.1, 25.0; **IR** (neat) 2962, 2831, 2728, 1724, 1439, 1411 cm^{-1}. Determine the structure of the molecule by correlating the spectral data. [**3**]

b) (i) Assign ^{1}H and ^{13}C NMR signals to the appropriate nuclei present in the molecule **A (**use **a** to **s** numbering to assign the peak**s). (ii)** Explain all ^{1}H-^{1}H coupling constant values by **only** applying proper **conformational** analysis. (Spectra are provided in the next page) [**4 + 3 = 7**]



Molecule A

Analytical data for molecule A: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 – 7.33 (m, 8H), 7.33 – 7.26 (m, 2H), 5.56 (s, 1H), 4.04 (d, *J* = 13.1 Hz, 2H), 3.64 (dd, *J* = 10.5, 3.7, 1H), 3.30 (dd, *J* = 10.5, 9.3 Hz, 1H), 3.19 (d, *J* = 13.1 Hz, 2H), 2.58 (dd, *J* = 12.6, 11.1 Hz, 1H), 2.41 (dd, *J* = 12.7, 3.5 Hz, 1H), 2.36 – 2.16 (m, 1H), 0.75 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 138.1, 129.3, 128.6, 127.4, 70.5, 61.4, 59.1, 31.6, 15.0.

Question: 5. b) ^{1}H & ^{13}C NMR spectra of **Molecule A**: