Problem Set 4 **^{13}C NMR Spectroscopy**

CHEM 393

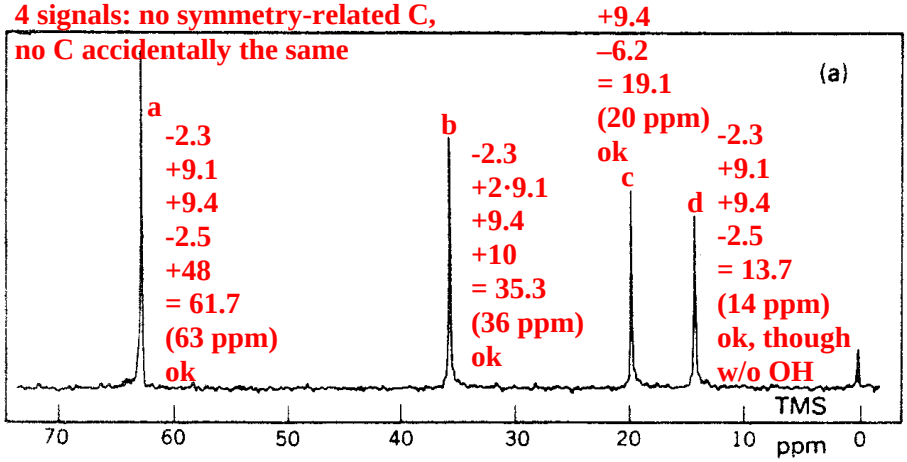
Dr. H.M. Muchall

1. (12 points) The following proton-decoupled ^{13}C NMR spectra belong to three isomeric compounds $C_4H_{10}O$. Identify the three compounds from their spectra. Support your structures by calculating the chemical shifts for each distinct carbon atom.

U = 0

alcohol or ether?

4 signals: no symmetry-related C, no C accidentally the same



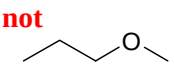
a
-2.3
+9.1
+9.4
-2.5
+48
= 61.7
(63 ppm)
ok

b
-2.3
+2·9.1
+9.4
+10
= 35.3
(36 ppm)
ok

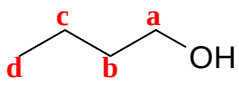
c
-2.3
+2·9.1
+9.4
–6.2
= 19.1
(20 ppm)
ok

d
-2.3
+9.1
+9.4
-2.5
= 13.7
(14 ppm)
ok, though w/o OH

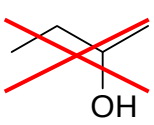
not



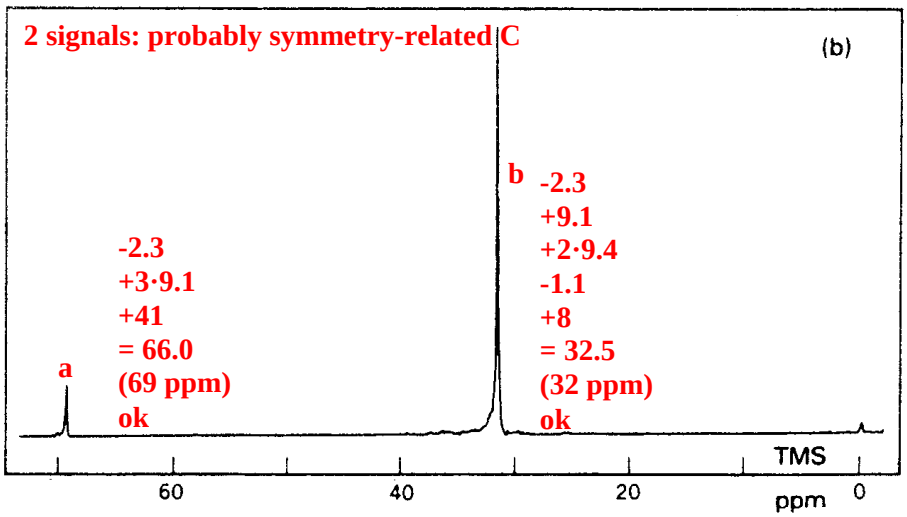
would show 2 signals near 60 ppm



8.7 ppm, too low



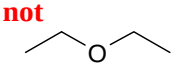
2 signals: probably symmetry-related C



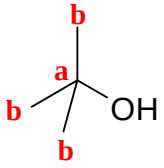
a
-2.3
+3·9.1
+41
= 66.0
(69 ppm)
ok

b
-2.3
+9.1
+2·9.4
-1.1
+8
= 32.5
(32 ppm)
ok

not

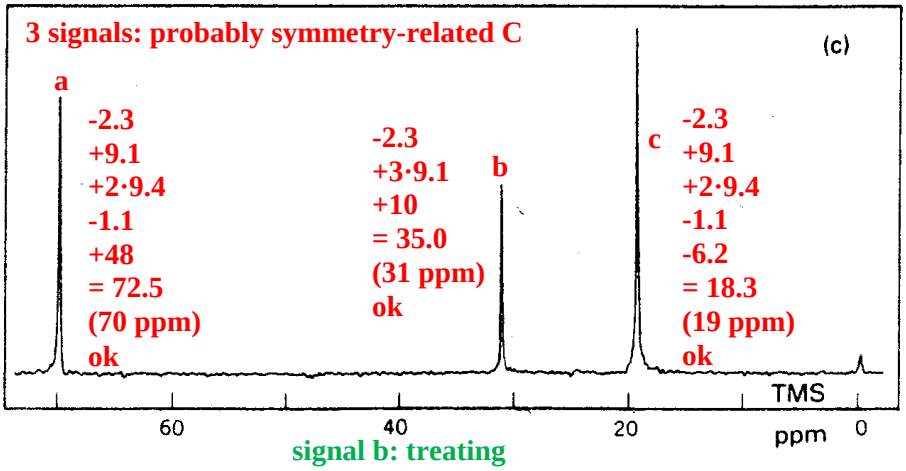


signal intensities would be closer to 1:1



carbon “a” is 3°

3 signals: probably symmetry-related C

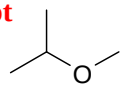


a
-2.3
+9.1
+2·9.4
-1.1
+48
= 72.5
(70 ppm)
ok

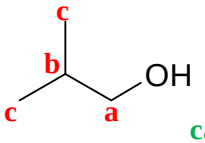
b
-2.3
+3·9.1
+10
= 35.0
(31 ppm)
ok

c
-2.3
+9.1
+2·9.4
-1.1
-6.2
= 18.3
(19 ppm)
ok

not



would show 2 signals near 60 ppm



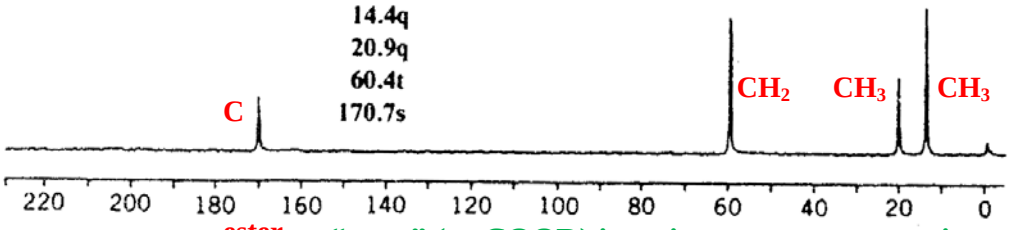
carbon “a” is 1°

signal b: treating carbon “a” as 2° would have led to a closer result here

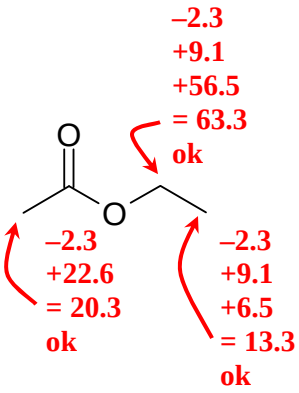
2. (7 points) Which compounds show the following ^{13}C NMR spectra? Support your structures with calculated chemical shifts.

U = 1 $C_4H_8O_2$
C=O

4 signals: no symmetry-related C, no C accidentally the same



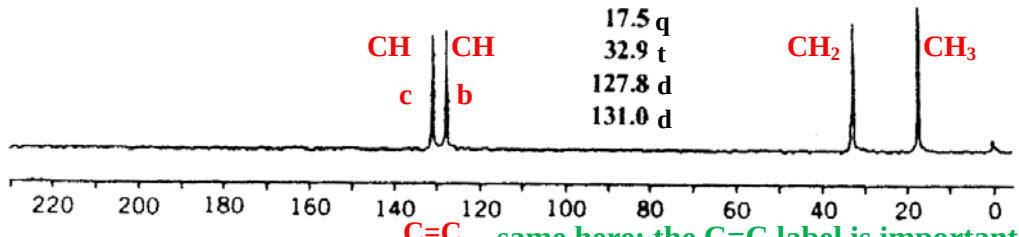
ester



"ester" (or COOR) is an important entry, as it allows you to narrow down on the final structure: it must be provided for full marks; just "C" won't get you points

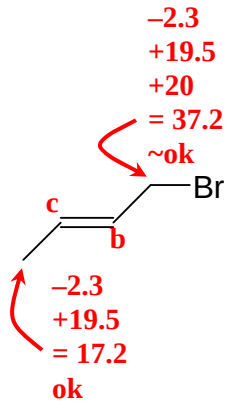
U = 1 C_4H_7Br
C=C

4 signals: no symmetry-related C, no C accidentally the same



C=C

same here: the C=C label is important!



c:
123.3
+10.6
–7.9
+2
= 128.0
ok

b:
123.3
+10.6
–7.9
= 126.0
ok

these final values for the E configuration given are already a bit too low; it is unlikely that it should be the Z configuration, where another 1.1 ppm would have to be subtracted

The signal-count observation (plus conclusions from it) is definitely important and required for full points!

Always remember not just to calculate a chemical shift, but to evaluate it against the increments available to you and/or the experimental value! An "ok" for a reasonable difference calculated with reasonable increments is fine. "Reasonable" depends on the problem: if there are multiple isomers available, even a difference of 4 ppm might be due to the fact that you've got the wrong one!