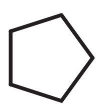
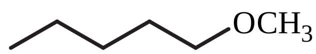
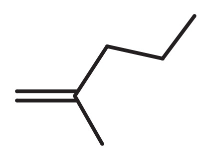
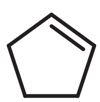
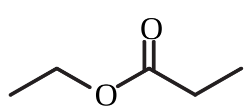
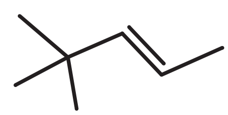
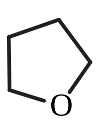
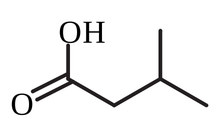
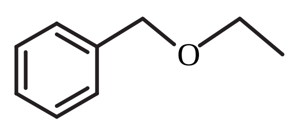
*Chem 262*
*Homework set M*

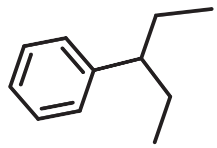
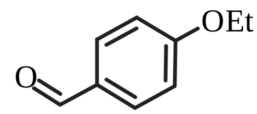
You'll know enough about NMR to work the couple of problems in this set after Wednesday's class, and the rest after Friday's. Start on the problems early — don't wait until the night before the exam to find out that you're not sure how to begin. The section on solving NMR problems in the Lecture Supplement will help you learn to figure out structures from NMR spectra.

**M-1** (a) For each compound below, (a) state how many different ${}^{1}$H NMR signals you would expect to see. In other words, how many different sets of equivalent Hs are there? (remember, Hs are either the same or different, i.e. "almost the same" = different. (b) Decide approximately where each signal would appear in an NMR spectrum — your choices are: **downfield of $\delta$ 9** (aldehyde, carbox acid), **$\delta$ 7-8** (aromatic), **$\delta$ 5-6** (vinylic), **$\delta$ 3-4** ($\alpha$ electroneg atom), **upfield of $\delta$ 2.5**. Here, Hs that are "almost the same" will show up in the same general region of the spectrum (as separate signals).

**M-2** Draw the compounds responsible for the $^{1}H$ NMR data given, and indicate which NMR signals correspond to which Hs in your structures. The ratios of the numbers of Hs contributing to each NMR absorption are given. (This information comes from integration of the spectrum.)

If you understand how to identify equivalent vs different sets of Hs, and you understand the effects of electronegative atoms, this problem is just a matter of systematic reasoning. Identify the molecule pieces, and then think about how to connect them. Don't just guess until you stumble across something that "kind-of-sort-of seems to work".

(a) Formula $\mathbf{C_5H_{12}O}$, δ 3.3 and δ 1.2 in a 1:3 ratio.

(b) Formula $\mathbf{C_4H_{10}O_2}$, δ 3.3 and δ 3.4 in a 3:2 ratio.

(c) Formula $\mathbf{C_3H_8O_2}$, δ 4.4 and δ 3.3 in a 1:3 ratio.

(d) Formula $\mathbf{C_5H_{12}O_2}$, δ 3.1 and δ 1.2 in a 1:1 ratio.

**M-3** The $^{1}$H NMR spectra of seven isomeric compounds having the formula $\mathbf{C_4H_{10}O}$ are summarized below. Identify each compound, and indicate which Hs in your structure correspond to each absorption. (All *J* values are ≈ 7 Hz). Standard abbreviations for splittings are used — s = singlet; d = doublet; t = triplet; q = quartet; br = broad)

(a) δ 2.87 (br s, 1H); δ 1.28 (s, 9H).

(b) δ 1.20 (t); δ 3.45 (q); ratio 3:2.

(c) δ 1.13 (d, 6H); δ 3.30 (s, 3H); δ 3.65 (septet, 1H).

(d) δ 0.92 (t, 3H); δ 1.18 (d, 3H); δ 1.45 (quintet, 2H); δ 1.80 (br s, 1H); δ 3.75 (sextet, 1H).

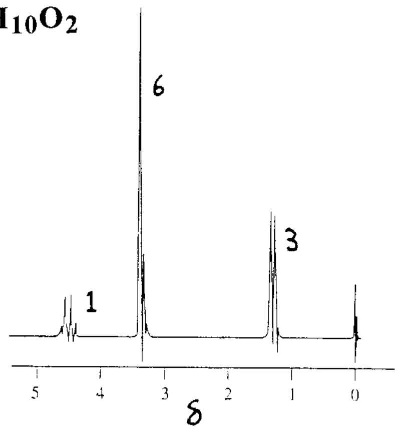
(e) δ 0.90 (d, 6H); δ 1.78 (nonet, 1H); δ 2.45 (br s, 1H); δ 3.30 (d, 2H).

(f) δ 0.95 (t, 3H); δ 1.52 (sextet, 2H); δ 3.30 (s, 3H); δ 3.40 (t, 2H).

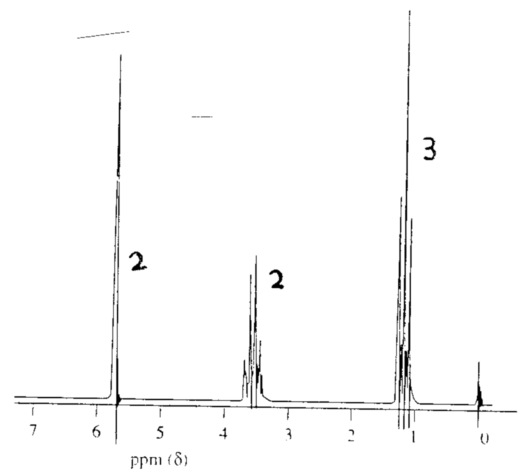
(g) δ 0.95 (t, 3H); δ 1.50 (complex abs, 4H); δ 2.20 (br s, 1H); δ 3.70 (t, 2H). ("Complex" is a polite way of saying "uninterpretable mess" (like the blob in M-4d) — that's life in the Real World — just work around it.

**M-4** For each of the next four problems, draw the compounds responsible for the corresponding NMR spectra and indicate which Hs in your structure are responsible for each absorption. (In some, the numbers of Hs contributing to each signal are given; for the others, you will have to measure the integration curves to figure it out.)

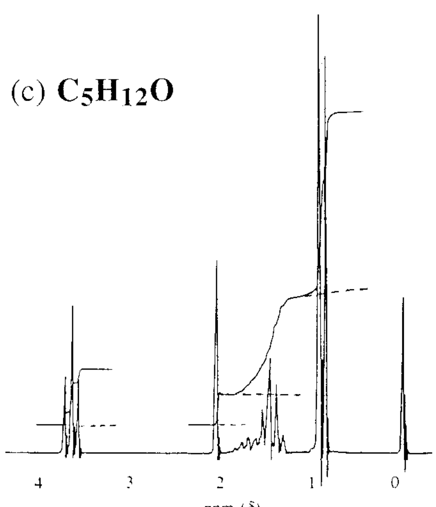
(a) $C_4H_{10}O_2$



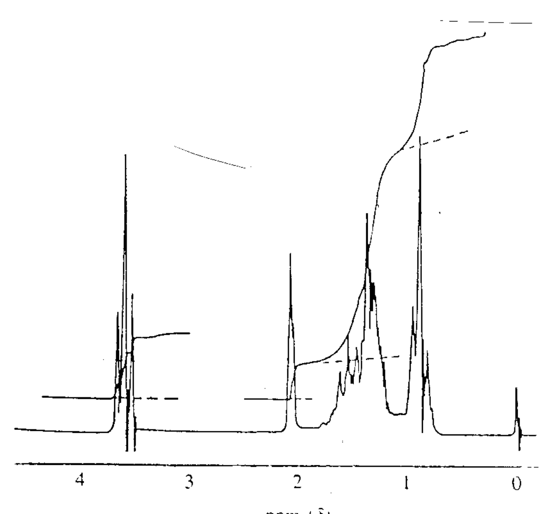

(b) $C_3H_7BrO$



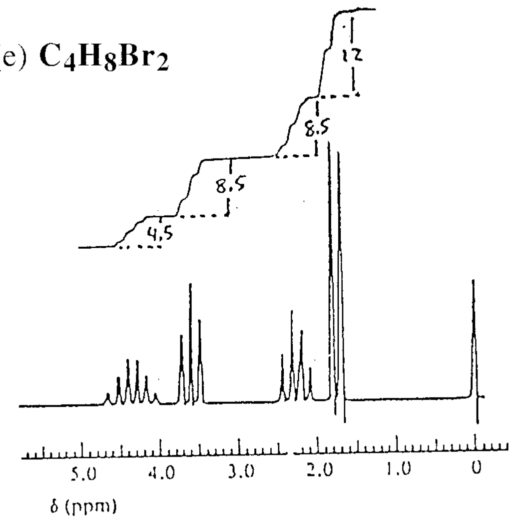

(c) $C_5H_{12}O$



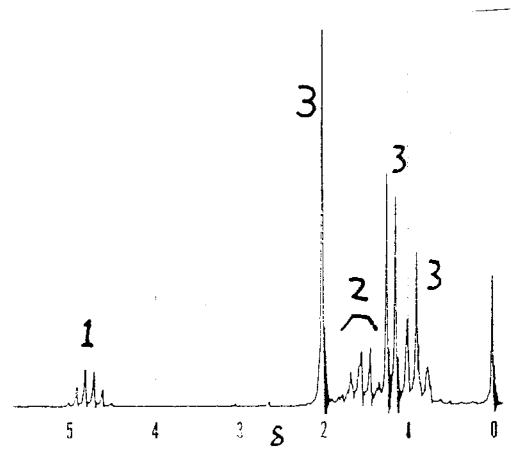

(d) $C_5H_{12}O$



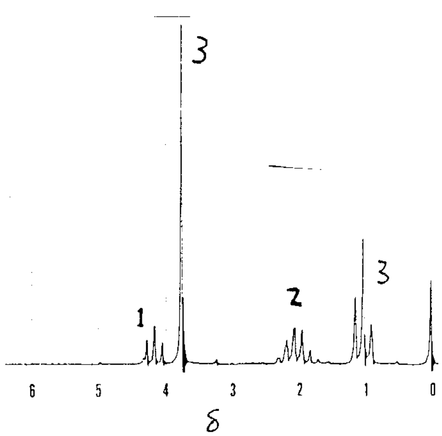
(e) **$C_4H_8Br_2$**




(f) **$C_6H_{12}O_2$**




(g) **$C_5H_9BrO_2$** (an ester)




(h) **$C_6H_{11}ClO_2$** (an ester)