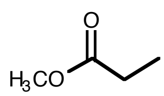
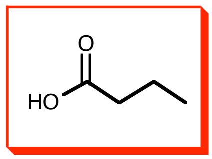
Chem. 218 Problem Set 1

Reccomended Problems from the text: 12.2, 12.5, 12.6, 12.10-12.14, 12.32, 12.34, 12.36, 14.28-15.32. 14.55-14.59, 14.63

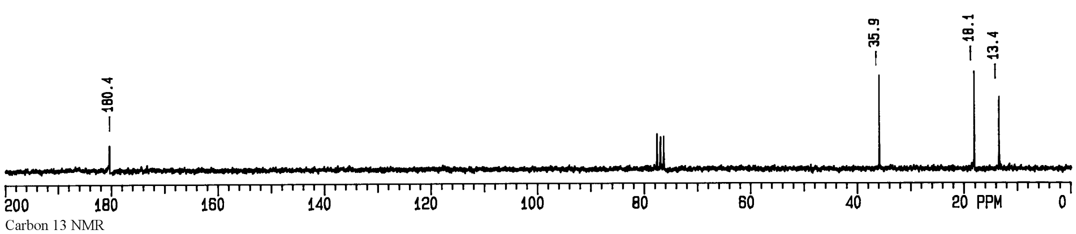
1. For each of the following, two constitutional isomers are given. Determine which one corresponds to the ^{13}C spectrum given. (A list of ^{13}C chemical shifts is on page 410).

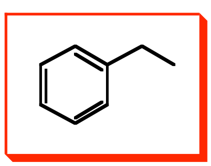


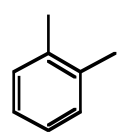


a.

Both compounds will give a spectrum with four distinct peaks. The main difference between the two molecules is that there is a carbon single bonded to an oxygen in the ester, while there are no carbons single bonded to oxygens in the acid. Carbons single bonded to oxygens appear between 50-90, and there is no peak in this range, so it must be the carboxylic acid.

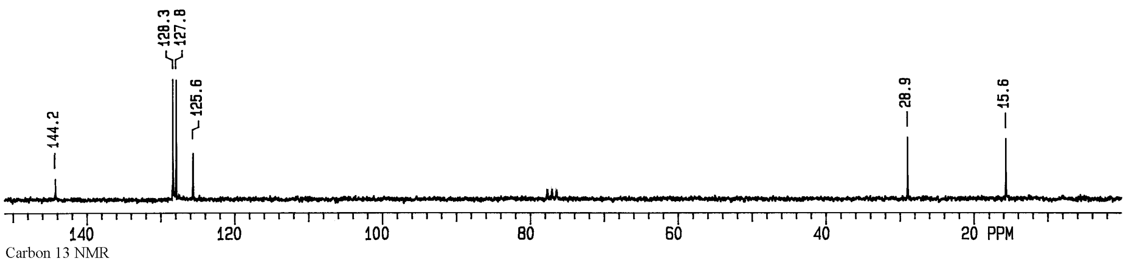


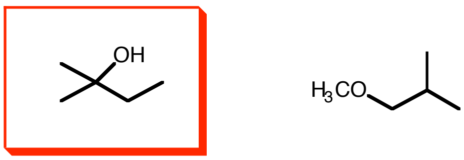




b.

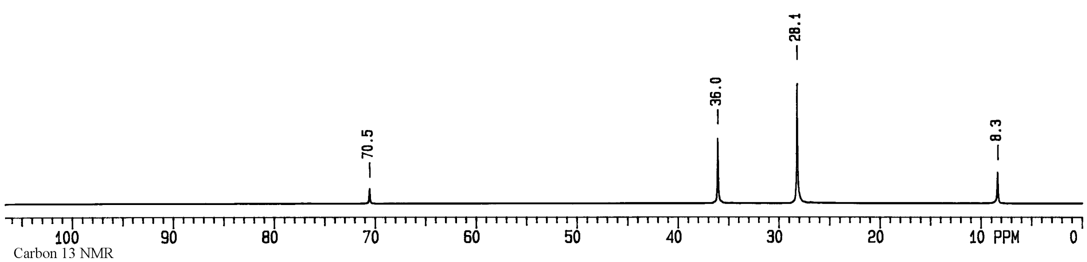
Examination of the aromatic region of the spectrum: there are four peaks. In ethylbenzene, there are four different types of carbons in the ring. In dimethyl benzene, there are only three types of carbons in the ring. If we also look at the alkyl range, there are two types of carbons in the ethyl benzene, and only one type in dimethyl benzene. There are two alkyl carbon peaks in the spectrum, so it must be ethyl benzene.



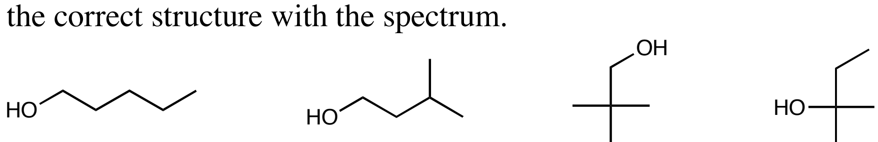


c.

Both compounds would result in four peaks. In the first compound (2-methyl-2-butanol), there will be one carbon attached to an oxygen while there are two carbons atttached to an oxygen in the second compound (isobutylmethyl ether). In the spectrum, there is only a single carbon in the 50-90 range, so it must be the alcohol.



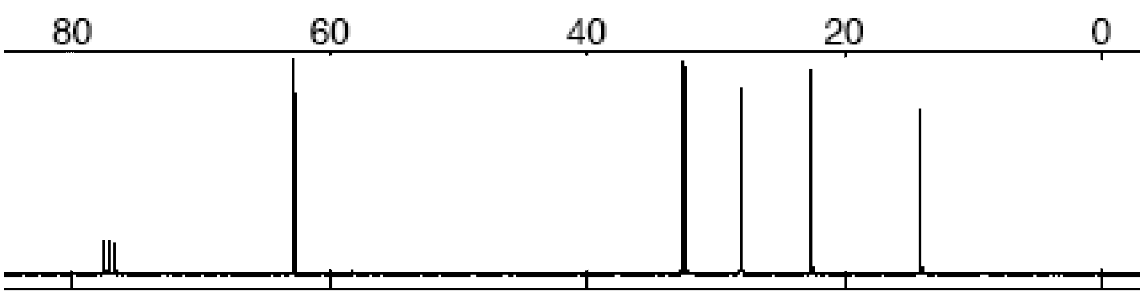
2. Match the correct structure with the spectrum.



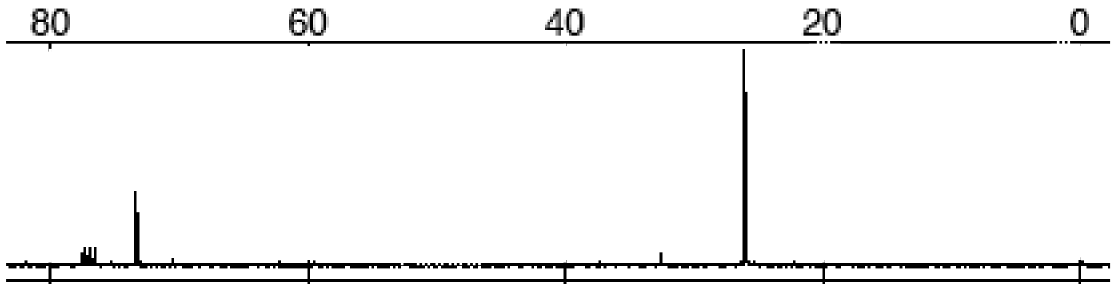
1-pentanol 3-methyl-1-butanol neopentyl alcohol tert-amylalcohol

5 types of carbon 4 types of carbon 3 types of carbon 4 types of carbon

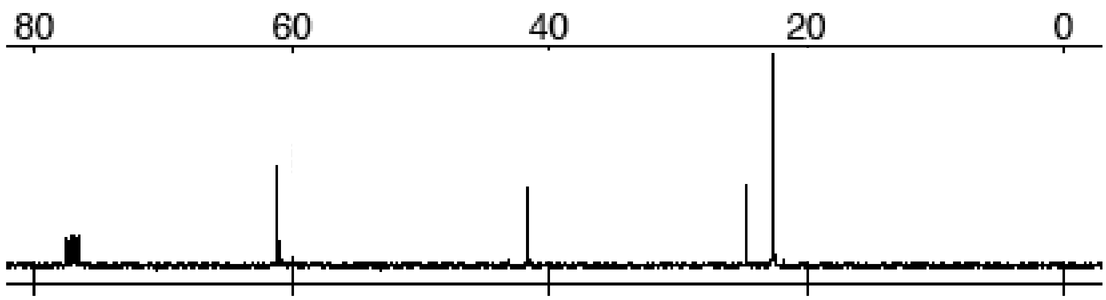
The spectrum below has five peaks, so it is 1-pentanol



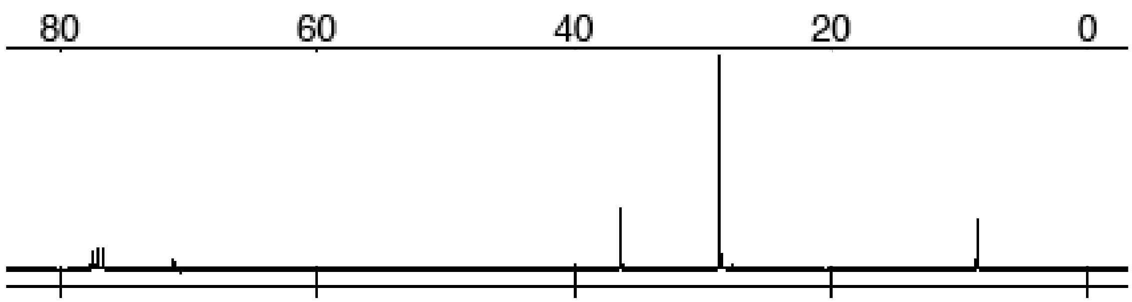
There are three peaks, so neopentyl alcohol.



There are four peaks, and the C-O is fairly large, indicating the carbon attached to the oxygen in not quartenary, so 3-methyl-1-butanol.

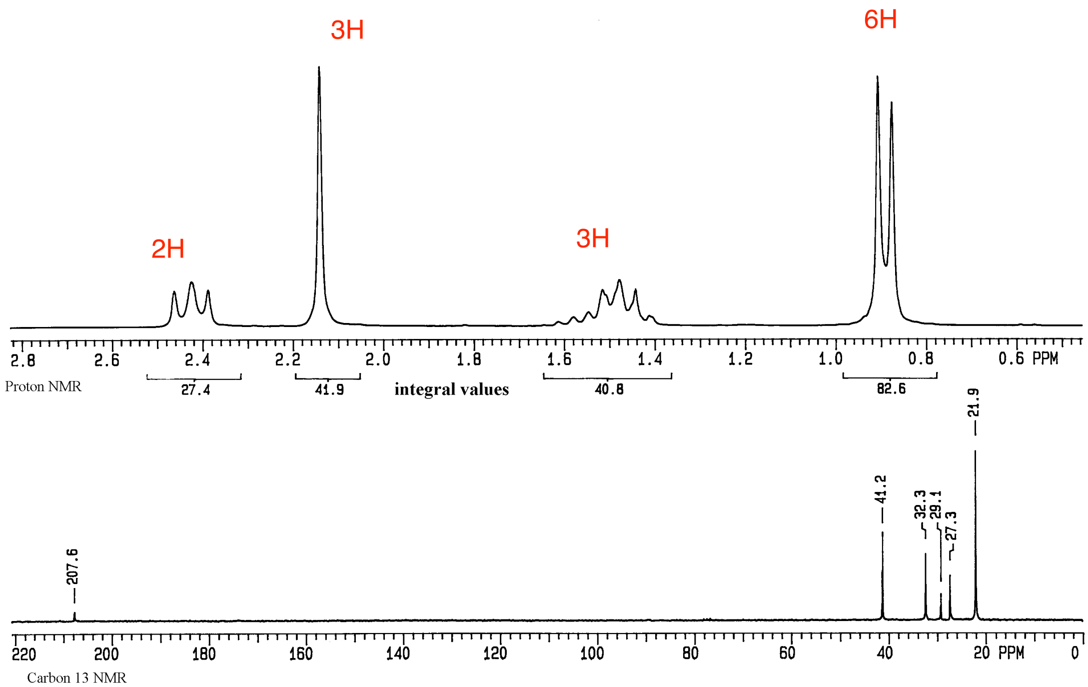


There are four peaks, and the C-O is very small, indicating the carbon attached to the oxygen is quartenary, so tert-amyl alcohol.



3. Determine the structure of the following compounds

(a) $C_7H_{14}O$



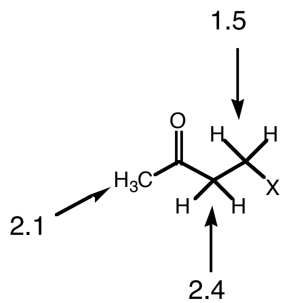
1. DOU=1 So, look for alkenes or carbonyls in ^{13}C.
2. There is a carbonyl in the ^{13}C at 208 ppm, which is the region for aldehydes and ketones. Look in the ^{1}H NMR for an aldehyde.
3. There is not an aldehyde peak in the ^{1}H, so the carbonyl must be a ketone.
4. Construct a table for ^{1}H data:

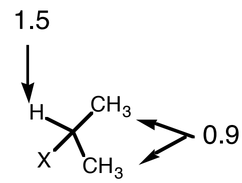
chem. shift	integration	multiplicity	possible fragment
2.4	2H	t	X-CH_2CH_2
2.1	3H	s	X-CH_3
1.5	3H	m	???
0.9	6H	d	$CH(CH_3)_2$

5. In the ^{1}H spectrum, it is unclear what the multiplet at 1.5 represents. Is this a CH_3 group or three overlapping CH groups or a CH overlapping with a CH_2? Look at the ^{13}C data: not counting the carbonyl, which does not have any hydrogens on it, there are five types of carbon. So, there must be five types of carbon in the proton spectrum.

In the proton: there is a CH_2 (at 2.4), a CH_3 (at 2.1), and two equivalent CH_3s (at 0.9). This means that there must be two more types of carbons under the peak at 1.5, which would make that multiplet a CH overlapping with a CH_2 group. This makes sense, since the triplet at 2.4 is coupled to a CH_2, and the doublet at 0.9 is coupled to a CH.

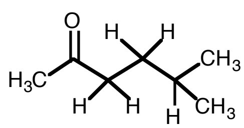
We know there is a ketone, and protons on carbons adjacent to carbonyls are in the 2.1-2.6 range, so the peaks at 2.1 and 2.4 are probably protons on carbons adjacent to the carbonyl. Starting to put together some fragments:





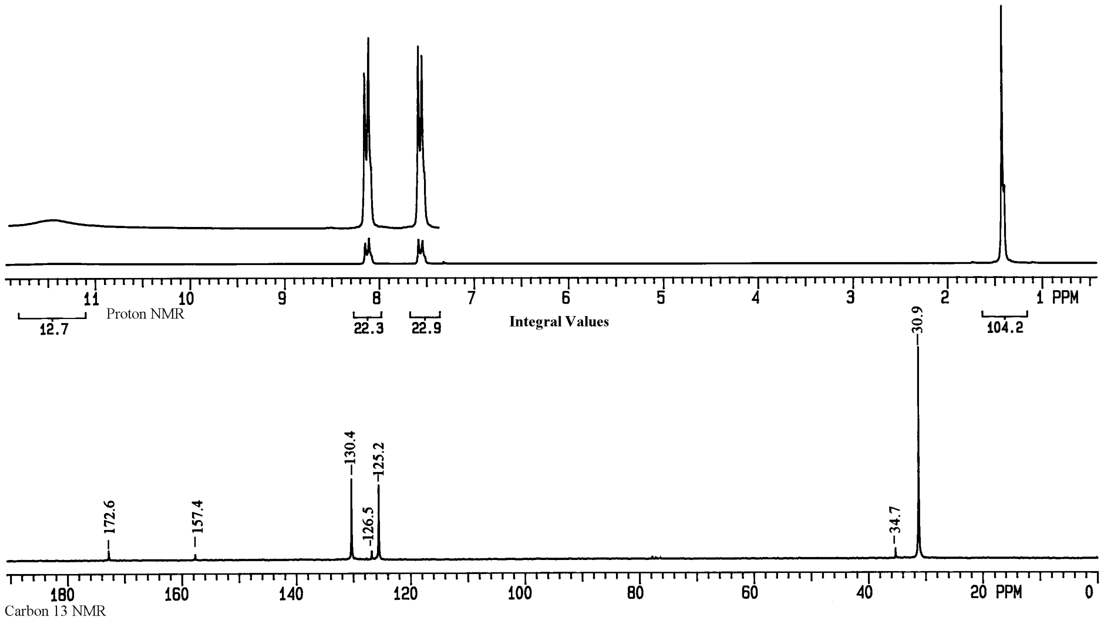
Where X=an unknown.

What if we attach the two fragments?

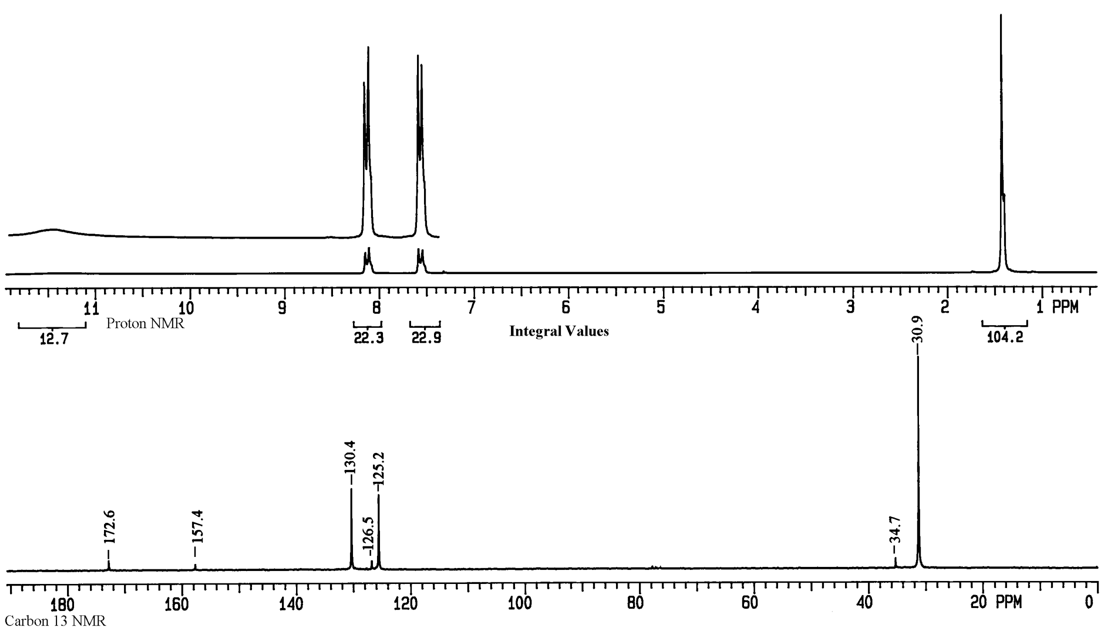


This structure fits both ^{1}H and the ^{13}C data.

(b) $C_{11}H_{14}O_2$

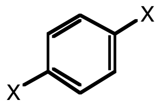


(b) $C_{11}H_{14}O_2$



1. DOU= 5, and since there are peaks in the aromatic range of both the carbon and the proton, there must be a phenyl ring.
2. There is one DOU remaining: In the proton, there is what appears to be a carboxylic acid peak around 11. This is verified by the carbonyl group at 173 in the carbon.

3. There are then, four different types of aromatic carbons, and two different types of aromatic protons, which are coupled together (they are both doublets). So, we can draw the aromatic portion:



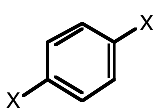
where X is two different substituents. This orientation on the ring is the only possibility to give two types of protons and four types of carbons.

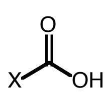
4. Construct the table:

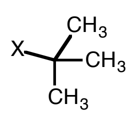
chem. shift	integration	multiplicity	possible fragment
11.5	1H	s	CO_2H
8.1	2H	d	CH_2CH_2 (aromatic)
7.5	2H	d	CH_2CH_2 (aromatic)
1.5	9H	s	X-$(CH_3)_3$

Based on the ^{13}C, there are two types of carbons, in addition to the carboxylic acid and the aromatic carbons. One is a very small peak, so may be a quaternary carbon. In the proton, there is only one other type of carbon in addition to the aromatic, which verifies our hypothesis that there may be a quaternary carbon. This quaternary carbon is probably attached to the three equivalent methyl groups as well as a carbon that does not have any protons.

5. Fragments:







6. Put the fragments together: