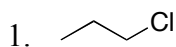
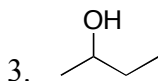
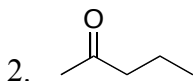


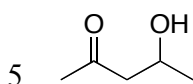
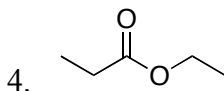
## Chem 360 Jasperse Chapter 13 Answers to in-class NMR Spectroscopy Problems



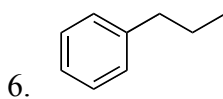
- integraton says CH<sub>2</sub> beside Cl
- splitting says Cl-CH<sub>2</sub> is beside another CH<sub>2</sub>
- splitting says CH<sub>3</sub> is beside a CH<sub>2</sub>.



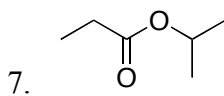
- note: this one is tricky for several reasons.
  - The alcohol carbon is a chiral center. That means the two hydrogens on the adjacent CH<sub>2</sub> carbon are **not** equivalent: one is cis and the other is trans to the OH group. This nonequivalency means that they can come at slightly offset chemical shifts, split each other, and generally mess things up a lot.
  - The methyl group, which one would expect to be a triplet, is superimposed on the CH<sub>2</sub> hydrogens. The lack of symmetry reflects the overlap situation.
  - Because the CH<sub>2</sub> hydrogens are non-equivalent, the CH<sub>3</sub> group is not a perfect triplet.
  - Because the overlapping CH<sub>2</sub> and the CH<sub>3</sub> hydrogens are so close, it also disrupts their splitting somewhat.
  - Nevertheless, this should be quite solvable from the non-complex stuff. The CH<sub>3</sub>CH(OH) half of the molecule should have been clear. With only two other carbons to spot, the messiness of the CH<sub>2</sub>CH<sub>3</sub> pile should not have prevented solution.



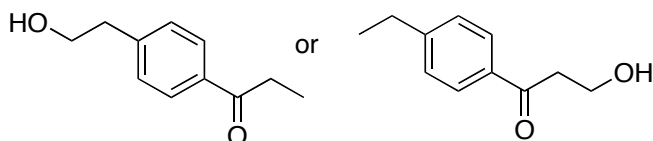
- 1H singlet tells alcohol OH
- 3H singlet in 2's is a methyl carbonyl
- 3H doublet in 1's is a CH<sub>3</sub> attached to a CH group
- Two CH<sub>3</sub> groups plus an OH provides 3 "end groups". This requires branching.
- Having a 1H multiplet also requires branching. (A carbon with only one attached hydrogen must have 3 non-H attachments. That means branching.)



- -Note: the 5H integration in the aryl region is diagnostic for a mono-substituted benzene
- A C<sub>6</sub>H<sub>5</sub> benzene provides one "end group", the CH<sub>3</sub> group provides the other.



- 6H doublet proves isopropyl group. Two symmetry equal methyls are attached to a common CH group.
- The chemical shifts prove that the isopropyl CH is attached to oxygen, and the ethyl CH<sub>2</sub> is attached to carbonyl



- -either solution would be acceptable. The splitting and integration patterns would be identical. And since carbonyl and aryl have similar impact on chemical shifts, you can't really tell which it is.
- The 4H integration in the aryl region is indicative of a disubstituted benzene
- The 2H-doublet-2H-doublet pattern in the aryl region is indicative of a para-disubstituted benzene. Ortho or meta wouldn't give such nice symmetry and splitting.
- The 1H singlet indicates an OH
- The 2H triplet in 3's must be a CH<sub>2</sub> between the oxygen and another CH<sub>2</sub>
- The 2H quartet in 2's must be between a CH<sub>3</sub> and either the carbonyl or an aryl

9. Match

- 5.30 (regular alkenyl)
- 2.40 (regular allylic type)
- 1.20 (regular non-functionalized alkyl)
- 6.73 (special alkenyl: the partial plus charge induced by electron withdrawing carbonyl causes this)
- 8.21 (special aryl: the partial plus charge induced by electron withdrawing nitro group causes this)

10. Predict

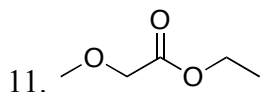
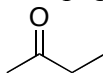
- Structure 1:

1's 3H triplet  
 2's 2H quartet  
 2's 2H triplet  
 1's 2H pentet  
 3's 2H triplet  
 anywhere 1H singlet (broad)

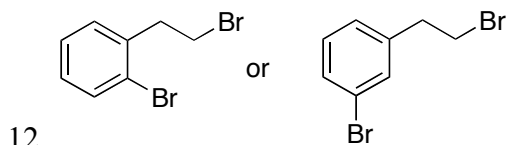
- Structure 2:

1's 3H doublet  
 3's 1H sextet  
 3's 3H singlet  
 1's 2H quartet  
 2's 2H triplet  
 7's 5H mess (all five aromatics piled on top of each other)

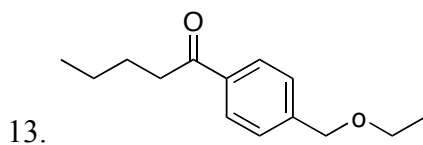
- Structure 3, page 10



- Note: this one is tricky because of the signals in the 4's. The quartet barely in the 4's is normal for an ester. But the singlet at 4.5 is being influenced by two functional groups. The oxygen alone would move it to the 3's; the additional carbonyl adds another step and pushes it down to the 4's.
- It was crucial to integrate. Many students thought the singlet at 4.5 was just an OH singlet. That it integrated for 2H proved it to be a CH<sub>2</sub> group instead.
- 3H singlet in the 3's is proof for a methyl on an oxygen

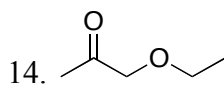


- The 4H integration in the aryl region proves a disubstituted benzene.
- The complexity in the aryl region proves it isn't para-substituted, which always gives simple, symmetric pattern. Whether it's ortho or meta (hard for you to tell), you get messy pattern and you can't really tell. In this case the actual answer is ortho.

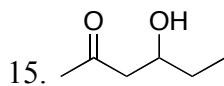


Interesting facets of this problem:

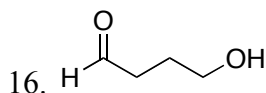
- 4H aryl means disubstituted benzene
- doublet-doublet symmetry shows para-disubstitution
- the singlet at 4.8 integrated for 2H, so it isn't an alcohol. It is down so far due to both the oxygen and the carbonyl. You can see the sum: 1's (normal) +2 (for oxygen) + 1 (for allylic) = 4's.
- the CH<sub>2</sub> in the 3's must be in between an oxygen (due to chemical shift) and a methyl (quartet splitting)
- the CH<sub>2</sub> in the 2's must be in between another CH<sub>2</sub> (splitting) and something double bonded (carbonyl or benzene were both candidates in this case, but it turned out to be the carbonyl...)
- the carbonyl is kind of "invisible", you could have explained all the NMR lines without it. In fact, some students missed the problem because they simply omitted the carbonyl altogether. This is an example where keeping track of the chemical formula was a reminder that you needed the carbonyl in there somewhere. Also, some IR support information to indicate the carbonyl would have been very helpful!



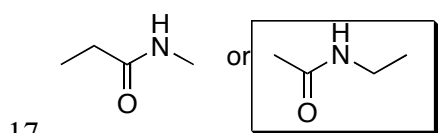
- Again, 2H singlet at 4.8 is influenced by the additive effect of two functional groups
- Distinctive 3H-singlet in the 2's for a methyl carbonyl
- Distinctive ethyl oxygen pattern: 2H quartet in the 3-4.4 range, with the 3H triplet



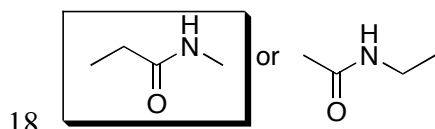
- 1H singlet means alcohol OH
- another methyl carbonyl as 3H singlet in the 2's
- messy pattern for 5H in the 1's reflects overlapping signals, again is the methyl overlapping with the CH<sub>2</sub>, further complicated by the chirality of the alcohol



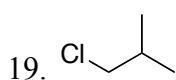
- 1H in the 9's is dead giveaway for aldehyde
- 1H singlet at 4.5 is dead giveaway for alcohol
- this is a funny one because you didn't have any nice CH<sub>3</sub>'s to work with. Absence of a methyl end-group with a clean 3H integral means the ends are both functionalized.
- The aldehyde has crummy splitting. Aldehyde splitting is always very, very small; a little bit, but not much. You can vaguely see some triplet form in the aldehyd hydrogen, and you can see the lines in the 2's which are in between a CH<sub>2</sub> (thus the triplet) and the aldehyde are like little double lines (due to aldehyde splitting) for each line of the triplet.
- another methyl carbonyl as 3H singlet in the 2's
- messy pattern for 5H in the 1's reflects overlapping signals, again is the methyl overlapping with the CH<sub>2</sub>, further complicated by the chirality of the alcohol



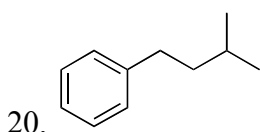
- 1H singlet goes for NH just as for OH
- clear ethyl group
- the chemical shift influence of a nitrogen is similar to a carbonyl. Not obvious whether the methyl group is on carbonyl and ethyl on nitrogen, or the ethyl on the carbonyl and the methyl on the nitrogen. In this case, the real answer has the methyl carbonyl



- 1H singlet goes for NH just as for OH
- there is a confusing ethyl group and methyl group in this case.
- The non-symmetry and the unusual 5H integraton at 2.5 are indications that you have two separate signal sets superimposed.
- the chemical shift influence of a nitrogen is similar to a carbonyl. Not obvious whether the methyl group is on carbonyl and ethyl on nitrogen, or the ethyl on the carbonyl and the methyl on the nitrogen. In this case, the real answer has the methyl on nitrogen and the ethyl on the carbonyl

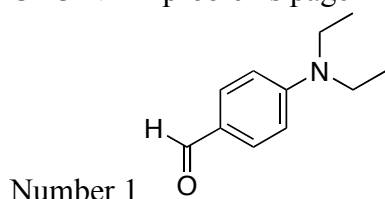


- 6H doublet combined with a 1H multiplet indicate an isopropyl group, with symmetry-duplicate methyls

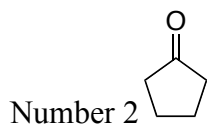


- 5H integral in 7's proves mono-substituted benzene
- 6H doublet in the 1's proves an isopropyl group
- 2H triplet in 2's shows CH2 between benzene and another CH2
- 3H mess at 1.8 is an overlap of a CH2 and CH group

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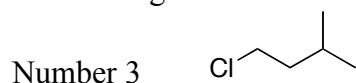


- 4 lines in aryl region, two doublets and two singlets, proves para-disubstituted symmetry
- carbonyl doublet at 190 proves aldehyde (only way for carbonyl to have an attached H)
- only two lines in the alkyl region proves more symmetry
- triplet/quartet splitting proves CH2 and CH3 groups.

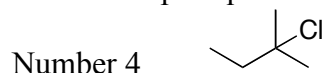


- carbonyl singlet proves ketone
- only 3 lines for a 5-carbon molecule proves symmetry
- with both alkyls as triplets (CH2), there are no "end groups". Must involve a ring

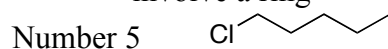
## 22. C-13 Problems Page 22



- 4 lines in aryl region proves para-disubstituted symmetry
- carbonyl doublet at 190 proves aldehyde (only way for carbonyl to have an attached H)
- only two lines in the alkyl region proves more symmetry
- triplet/quartet splitting proves CH<sub>2</sub> and CH<sub>3</sub> groups.

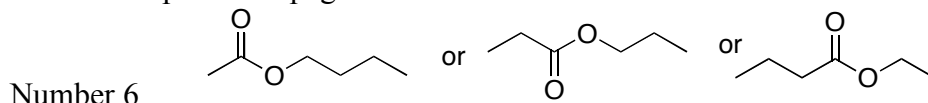


- carbonyl singlet proves ketone
- only 3 lines for a 5-carbon molecule proves symmetry
- with both alkyls as triplets (CH<sub>2</sub>), there are no “end groups”. Must involve a ring

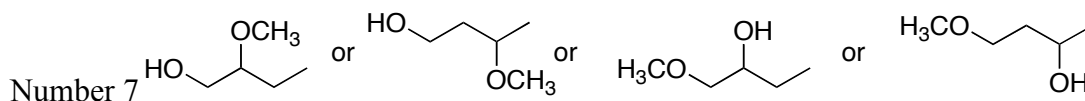


- carbonyl singlet proves ketone
- only 3 lines for a 5-carbon molecule proves symmetry
- with both alkyls as triplets (CH<sub>2</sub>), there are no “end groups”. Must involve a ring

## 23. C-13 NMR problems page 23.

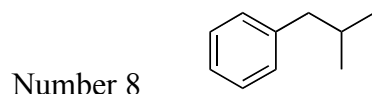


- carbonyl shift proves ester
- triplet in 50-100 proves one CH<sub>2</sub> group attached to oxygen
- two quartets prove two CH<sub>3</sub> end groups
- any of the solutions that has two end groups, an ester, and a CH<sub>2</sub> on the ester oxygen are satisfactory

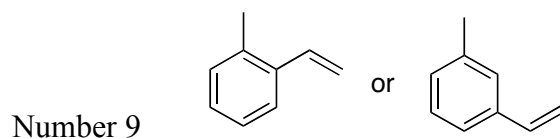


- no elements of unsaturation, so oxygens must be alcohols and/or ethers
- 5 carbons, 5 lines, so no symmetry
- three lines in the 50-100 range, so three of the carbons must be attached to oxygens. Since an ether has two and an alcohol has one, having one ether and one alcohol fits.
- The H-count based on carbon splitting indicates only 11 hydrogens. The 12<sup>th</sup> is therefore an alcohol OH
- With two methyl quartets and an OH, that gives three “end groups”, requiring branching.
- The doublet at 56 also requires the presence of a CH group, which has three other attachments. That means branching.
- As shown, many solutions can account for having a CH doublet with either an alcohol or ether oxygen attached.
- The quartet in the oxygen zone requires the presence of an OCH<sub>3</sub> group.

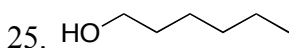
## 24. C-13 NMR problems page 24.



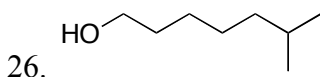
- monosubstituted benzene, based on 4-line aryl symmetry with three doublets but only one singlet
- symmetry required in the alkyl region



- No symmetry whatsoever
- The eight lines in the aryl region, two of them singlets, prove a disubstituted, non-symmetric benzene plus an alkene. The aromatic could be either ortho or meta, but not para.
- The formula requires 5 elements of unsaturation, which also demands an alkene
- The alkene must have a =CH<sub>2</sub> group, based on the triplet splitting at 114.
- One solitary methyl group, based on just a quarter in the alkyl zone.



- 1H singlet says alcohol
- 2H triplet in the 3's says a CH<sub>2</sub> is in between the oxygen and another CH<sub>2</sub> group
- 3H triplet in the 1's shows there is a CH<sub>3</sub> at an end, connected to a CH<sub>2</sub> group
- this problem is representative of many long-chain molecules. Many of the hydrogens in the middle but neither at the end nor really close to a functional group tend to lie on top of each other and make a mess. Often integration can tell you how many are in there. But normally, try to work from the ends, then use formula and integration to figure how many are in the messy pile.



- another long chain with lots of superimposed pileup hydrogens. Integration indicates 9 hydrogens in the messy pile
- The strong 6H doublet proves you have an isopropyl group at one end
- The 1H singlet again proves alcohol
- The 2H triplet in the 3's again proves the alcohol is primary (OH attached to a CH<sub>2</sub> group as opposed to a CH group..), and the OH-bearing CH<sub>2</sub> group has a CH<sub>2</sub> on the other side.