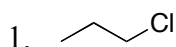
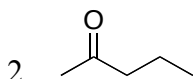


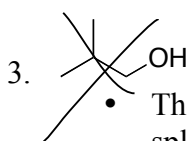
Chem 360 Jasperse Chapter 13 Answers to in-class NMR Spectroscopy Problems



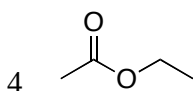
- integraton says CH₂ beside Cl
- splitting says Cl-CH₂ is beside another CH₂
- splitting says CH₃ is beside a CH₂.



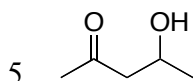
- integraton shows 2H:3H:2H:3H
- Two sets in the 2's are consistent with two allylic sets, i.e. a ketone
- The 3H triplet at 0.9 proves that it's beside a CH₂ (due to splitting)
- The CH₂ must be the one at 1.6 (the CH₂ at 2.4 can't be next to the methyl, or it would split for at least 4 lines)
- The 3H singlet at 2.1 must be a methyl group (integration) beside a carbonyl (chemical shift) with no hydrogen neighbors (splitting).



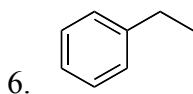
- The rounded 1H peak is the OH peak, which in this case does not runner split/couple the CH₂ group to which it is attached
- The 6H doublet at 0.9, combined with a 1H multiplet (at 1.8) is diagnostic for an isopropyl group. The two methyl groups are symmetry equivalent.
- Note: The CH group has 8 neighbors, so it would formally have 9 lines. But notice that the 8th and 9th lines are so small that you would hardly notice them if you weren't looking for them. This is common: for many-line sets, the outside ones get smaller and smaller. So you can assume a minimum number of neighbors (I see at least 7 lines so I must have at least 6 neighbor hydrogens), but you shouldn't preclude the possibility of even more neighbor H's.



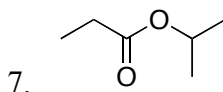
- Classic ester, with one set in the 2's and another in the low 4's.
- The ester oxygen typically puts the attached CH set in the low 4's rather than just the high 3's.
- The 3H singlet in the 2's is characteristic for a methyl group attached to a carbonyl or to a benzene
- This NMR shows a class ethyl group, with it's 3H triplet, 2H quarter.



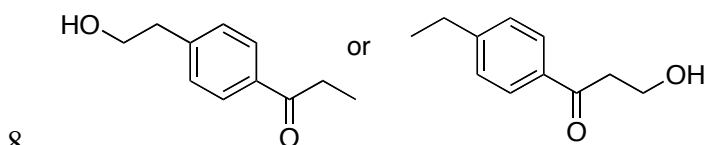
- 1H singlet tells alcohol OH
- 3H singlet in 2's is a methyl carbonyl
- 3H doublet in 1's is a CH₃ attached to a CH group
- Two CH₃ groups plus an OH provides 3 "end groups". This requires branching.
- Having a 1H multiplet also requires branching. (A carbon with only one attached hydrogen must have 3 non-H attachments. That means branching.)



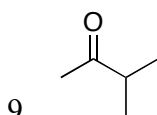
- Classic ethyl group, with the 3H triplet and 2H quartet
- The 5H integration in the aromatic region tells that it's a monosubstituted benzene.
- The complex splitting and messy look in the 7's result from overlapping of ortho, meta, and para hydrogens.
- If you see 5H in the 7's, that tells it's a monosubstituted benzene. There is no purpose in analyzing any further than that.



- 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 CH2 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 CH2 between the oxygen and another CH2
- The 2H quartet in 2's must be between a CH3 and either the carbonyl or an aryl



- Classic methyl carbonyl
- Classic isopropyl, with the 6H doublet and the multiplet at 2.6
- Notice: Even though the 1H group at 2.6 has 6 neighbor hydrogens and should be 7 lines, the 6th and 7th lines are really small and you might not recognize them. Imagine if it had 8th and 9th lines as well! For hydrogens with a lot of neighbors, it is best to reason that it has "at least 5 lines and 4 neighbors, but it could have more..."

10. Predict

- Structure 1:

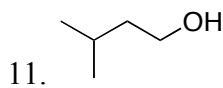
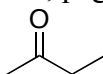
1's 3H triplet
 2's 2H quartet
 2's 2H triplet
 1's 2H pentet
 3's 2H triplet
 anywhere 1H singlet (broad)

- Structure 2:

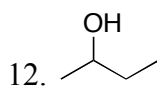
1's 6H doublet
 1's 1H multiple (9 lines)

 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

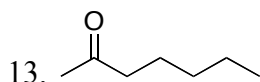


- Isopropyl group (6H doublet and 1H multiplet)
- The methane hydrogen has 8 neighbors, but notice how unnoticeably small the 8th and 9th lines are
- The formula has no elements of unsaturation, and with an oxygen that requires an alcohol or an ether. Ether doesn't fit, since there aren't two sets in the 3's. But where is the OH hydrogen?
- The OH is overlapping with a CH₂ quartet at 1.5. That's how the integration gets to three.
- Notice that the CH₂ quartet is not explained by a CH₃ neighbor. Often a CH₂ quartet is explained as part of an ethyl group, but not in this case.
- Notice that the oxygenated CH₂ is broadened; the OH is causing some broadening.

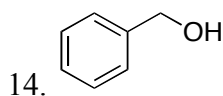


- The correct formula is C₄H₁₀O, not C₅H₁₂O. My error.
- The broad 1H bump is an OH.
- Notice that the methyl doublet at 1.2 is a 3H, not a 6H. So it's a methyl beside a CH, but is not an isopropyl.
- The splitting looks weird at 1.5 because the alcohol carbon is a chiral center. That means the two hydrogens on the adjacent CH₂ 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.

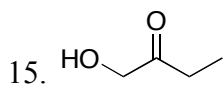
- Nevertheless, this should be quite solvable from the non-complex stuff. The $\text{CH}_3\text{CH}(\text{OH})$ half of the molecule should have been clear. With only two other carbons to spot, the messiness of the CH_2CH_3 pile should not have prevented solution.



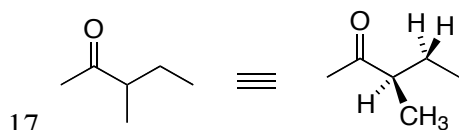
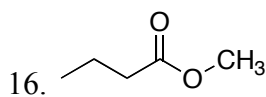
- The integration of 1:1.5:1:2:1.5 doesn't make sense; doubling them all to 2:3:2:4:3 makes it work so that there are no "half" hydrogens and so that the integrals sum up to 14H
- One element of unsaturation and two "allylic" sets suggests a carbonyl
- 3H singlet in 2's suggests methyl carbonyl
- Two 3H methyl end groups and no obvious 1H signals suggests no branching
- The 4H mess thing at 1.3 lacks the normal symmetry, and indicates overlapping signals. In this case, two CH_2 groups (each of which is too far distant from the carbonyl to be significantly influenced).
- This overlap of CH_2 signals is common for straight chains.
- The use of integration can help to show how many CH_2 's are stacked up.



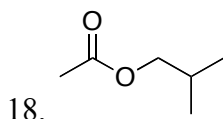
- CH_2 at 4.7 reflects the influence of two functional groups.
- $\text{EU}=4$ fits with a benzene
- 5H integral proves monosubstituted benzene.
- The weird overlapping mess of ortho/meta/para hydrogens is not worth analyzing.
- No 3H groups, the "end groups" are the monosubstituted benzene and an OH.



- The 2H singlet is at 4.3 because it is influenced by both the OH and the carbonyl.
- Many two-oxygen one-element-of-unsaturation formulas are esters, but not here.
- Many singlets are either methyls or OH groups, but the 2H set at 4.3 is a CH_2 with no hydrogen neighbors.



- The impact of a chiral center. The two H's on the CH_2 group are not equivalent, resulting in funny splitting and different chemical shifts (1.4 and 1.7).

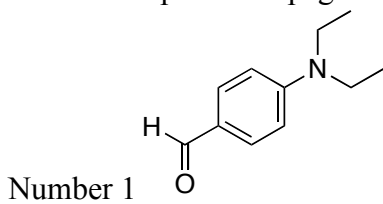


- Isopropyl group
- Again notice that the CH hydrogen at 1.9, which has 8 neighbors, shows barely seven lines with the 8th and 9th lines lost in the baseline.
- The CH group starts out relatively high in the 1's to start with (CH groups start at 1.55), and then being close if not directly connected to the ester oxygen pulls it even higher into the 1's.

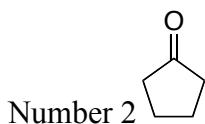
19. Each of these integrates with 4H in the aromatic region, indicating disubstituted benzenes. For disubbed benzenes, para should be easy to recognize because it has symmetry. That's what you see in spectrum one. Ortho and ~~para~~ ^{meta} do not have symmetry, so they are difficult to identify, and their distinction is beyond our scope. The meta substrate is in the middle (meta has a singlet, doublet, triplet, and doublet). The ortho substrate is on the bottom (doublet, doublet, triplet, and triplet.)

20. The difference between decoupled, coupled, and a DEPT135 is illustrated. In the DEPT135, CH₂ carbons point in the opposite direction from CH and CH₃ carbons, and carbons without hydrogens don't show at all.

21. C-13 NMR problems page 21.

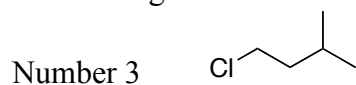


- 4 lines in aryl region, two doublets and two singlets, proves para-disubstituted symmetry
- carbonyl doublet at 190 proves aldehyde (only way for carbonyl to have an attached H)
- only two lines in the alkyl region proves more symmetry
- triplet/quartet splitting proves CH₂ and CH₃ groups.



- 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



- 1. 5 C's, 4 lines, so symmetry
- 2. t, t, d, q shows CH₂, CH₂, CH, and CH₃
- 3. CH₃ is duplicate, based on tallness of q and need another CH₃ to get 10 H's
- 4. To symmetrize the CH₃'s, probably connected to same carbon, the CH
- 5. The line at 0 is the reference line.
-

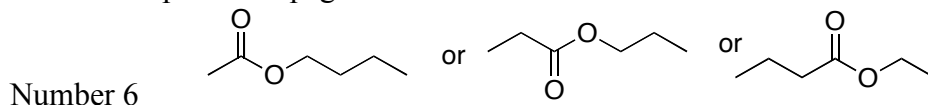


- 1. The line at 0 is the reference line.
- 2. 5 C's, 4 lines, so symmetry
- 3. s, t, q, q shows C, CH₂, CH₃, and CH₃
- 4. The C at 70 must have Cl, and the duplicate methyls

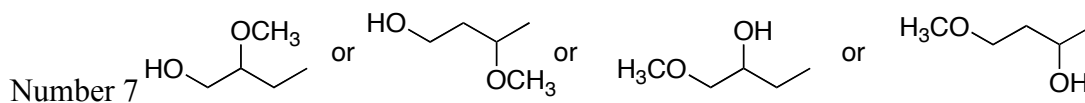


- 1. 5 C's, 5 lines, so no symmetry
- 2. The most downfield C probably has the Cl
- 3. Four t's and one q suggest four CH₂'s and a methyl

23. C-13 NMR problems page 23.

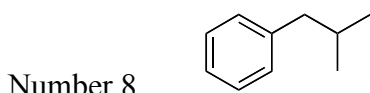


- carbonyl shift proves ester
- triplet in 50-100 proves one CH₂ group attached to oxygen
- two quartets prove two CH₃ end groups
- any of the solutions that has two end groups, an ester, and a CH₂ on the ester oxygen are satisfactory

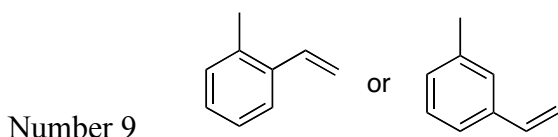


- no elements of unsaturation, so oxygens must be alcohols and/or ethers
- 5 carbons, 5 lines, so no symmetry
- three lines in the 50-100 range, so three of the carbons must be attached to oxygens. Since an ether has two and an alcohol has one, having one ether and one alcohol fits.
- The H-count based on carbon splitting indicates only 11 hydrogens. The 12th 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 OCH₃ group.

24. C-13 NMR problems page 24.

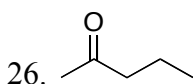


- monosubstituted benzene, based on 4-line aryl symmetry with three doublets but only one singlet
- symmetry required in the alkyl region

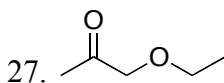


- No symmetry whatsoever
- The eight lines in the aryl region, two of them singlets, prove a disubstituted, non-symmetric benzene plus an alkene. The aromatic could be either ortho or meta, but not para.
- The formula requires 5 elements of unsaturation, which also demands an alkene
- The alkene must have a =CH₂ group, based on the triplet splitting at 114.
- One solitary methyl group, based on just a quarter in the alkyl zone.

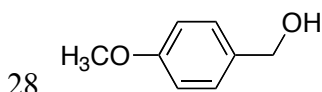
25. An illustration of two-dimensional C-H and H-H correlation spectra. In the C-H spectra, you can see which hydrogens belong to which carbon. In the H-H, you can see which hydrogens are coupled to which other hydrogens, in other words to find out what is connected to what.



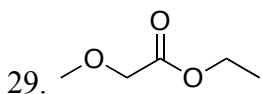
- Another illustration of two-dimensional C-H and H-H correlation spectra. In the C-H spectra, you can see which hydrogens belong to which carbon. The carbonyl carbon doesn't show because it doesn't have any hydrogens attached. In the H-H, you can see that the set at 1.6 is coupled to both the peaks at 1.0 and at 2.4.



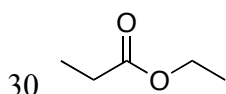
- Again, 2H singlet at 4.8 is influenced by the additive effect of two functional groups
- Distinctive 3H-singlet in the 2's for a methyl carbonyl
- Distinctive ethyl oxygen pattern: 2H quartet in the 3-4.4 range, with the 3H triplet



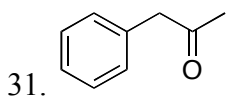
- 4H in the aromatic proves disubbed.
- Symmetry proves para-disubbed.
- The 2H singlet at 4.6 is influenced by both the OH group and the benzene.
- Broad 1H is an alcohol.



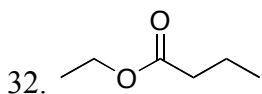
- Note: this one is tricky because of the signals in the 4's. The quartet barely in the 4's is normal for an ester. But the singlet at 4.5 is being influenced by two functional groups. The oxygen alone would move it to the 3's; the additional carbonyl adds another step and pushes it down to the 4's.
- 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 CH₂ group instead.
- 3H singlet in the 3's is proof for a methyl on an oxygen



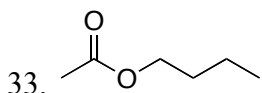
- Two ethyl groups, with the distinctive 3H triplet/2H quarter.
- You can tell which CH₂ is which, based on chemical shift. But you have no way to know which CH₃ is which. (If you ran a two-dimensional H-H correlation experiment, you could determine that very easily. But not from the simple proton NMR.)



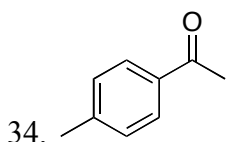
- 5H integration in the 7's proves monosubstituted benzene
- Formula requires 5 elements of unsaturation, 4 of which come from the benzene, but the 5th comes from a carbonyl.
- The signal in the 3's at first looks like an oxygenated methyl group, but that can't be correct because it integrates for 2H rather than 3H.
- Instead, it is doubly allylic.



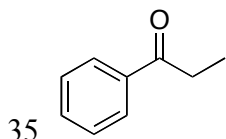
- Ester indicated by a set in the 2's and the low 4's
- The signature ethyl group is on the ester oxygen, based on chemical shift, with the propyl group on the carbonyl, again based on chemical shift



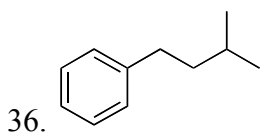
- Another ester
- Signature methyl carbonyl
- Notice the imperfect splitting in the CH₂ groups at 1.6 and 1.4. When a set is being split by non-equal neighbors, sometimes the splittings get increasingly imperfect and the N+1 rule becomes unreliable.



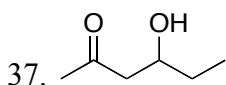
- Another para-disubstituted benzene, based on the 4H in the aromatic area and the symmetry
- Often aromatic hydrogens get somewhat split by meta or para hydrogens. Notice how the doublets are not perfectly sharp and clean as a result.
- You can't tell which of the methyl CH₃'s in the 2's is next to the carbonyl and which is next to the benzene.



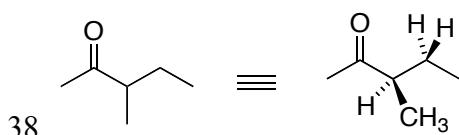
- The aromatic hydrogens sum up to 5H, which proves monosubstituted benzene. While you can see more logical details (the 2H doublet at 8.0 are the two ortho hydrogens; the 1H triplet at 7.6 is the one para hydrogen; and the 2H triplet at 7.4 are the meta hydrogens), you don't really need to use anything beyond that it's monosubstituted.
- The ethyl quartet is at 3.0, because it is directly influenced by the carbonyl but also is close to the benzene as well.



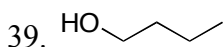
- 5H integral in 7's proves mono-substituted benzene
- 6H doublet in the 1's proves an isopropyl group
- 2H triplet in 2's shows CH₂ between benzene and another CH₂
- 3H mess at 1.8 is an overlap of a CH₂ and CH group



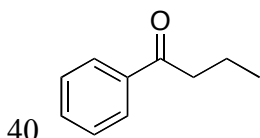
- 1H singlet means alcohol OH
- another methyl carbonyl as 3H singlet in the 2's
- messy pattern for 5H in the 1's reflects overlapping signals, the methyl overlapping with the CH₂, further complicated by the chirality of the alcohol



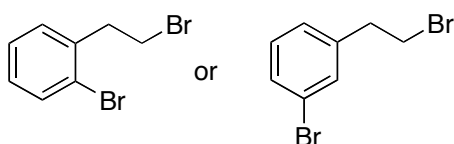
- The impact of a chiral center. The two H's on the CH₂ group are not equivalent, resulting in funny splitting and different chemical shifts (1.4 and 1.7).



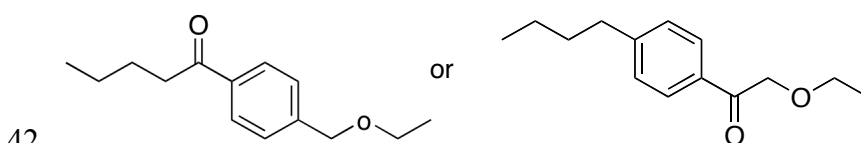
- Signature 1H singlet for OH
- The CH₂ groups at 1.55 and 1.4 are somewhat rough because when flanked by nonequivalent hydrogens, the N+1 rule doesn't work perfectly.



- The aromatic hydrogens sum up to 5H, which proves monosubstituted benzene. While you can see more logical details (the 2H doublet at 8.0 are the two ortho hydrogens; the 1H triplet at 7.6 is the one para hydrogen; and the 2H triplet at 7.4 are the meta hydrogens), you don't really need to use anything beyond that it's monosubstituted.
- The propyl CH₂ is at 3.0, because it is directly influenced by the carbonyl but also is close to the benzene as well.



- 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.



Both answers have an extra carbon in the alkyl chain. Where the butyl groups are shown, there should only be propyl groups.

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 either a carbonyl or a benzene. You can see the sum: 1's (normal) +2 (for oxygen) + 1 (for allylic) = 4's.
- A two-dimensional H-H correlation spectrum might help in a case like this.