

Homework 7 – 2017/05/15

1) Analysis of an unknown compound gives the following data:

Strong IR absorption at 1696 cm^{-1} , also absorbs in the $2700\text{--}3100\text{ cm}^{-1}$ region.

Information: it looks like there is a C=O group (1696 cm^{-1}), the $2700\text{--}3100$ can be a lot of things, we'll see what it's consistent with in the other data.

m/z at m/z : 106.0419 (100.0%), 107.0452 (7.6%)

Information: I should have been a bit more careful with these data. Most of the analysis we do these days gives us the molecule weight (M^+) or the protonated/deprotonated molecule's weight (so $[M+H]^+$ or $[M-H]^-$). Here I meant M^+ . **We have something with a molecule weight of 106.**

The compound contains 79.23% C; 5.70% H; 15.08% O (weight % for all)

From this weight ratio, the stoichiometric ratio ('moles') of these elements is 79.23/12 (C) : 5.70/1 (H) : 15.08/16 (O)

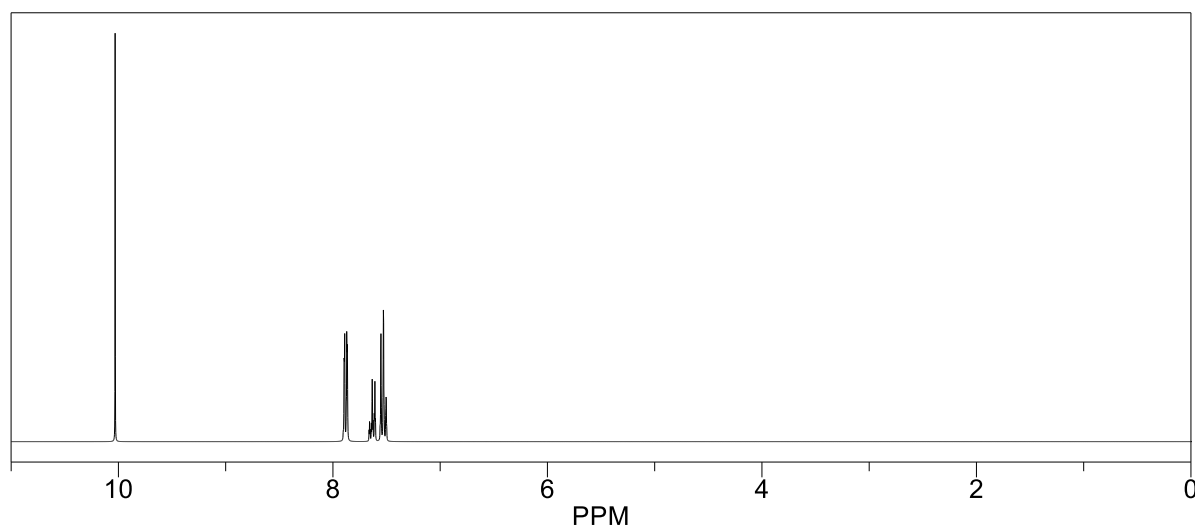
This corresponds to $6.6:5.7:0.94 = \mathbf{7:6:1}$ (or 14:12:2, 21:18:3, etc)

From the M and the atoms' stoichiometric ratio we can get the following:

$$n \cdot (7 \cdot 12 + 6 \cdot 1 + 1 \cdot 16) = 106$$

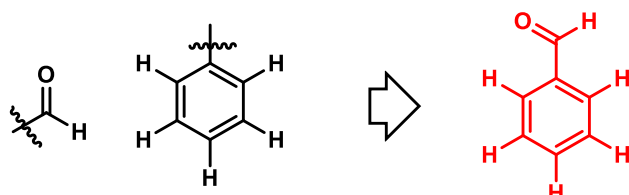
$n \cdot (106) = 106$, $n = 6$. Which means that our molecule contains 7 carbon atoms, 1 oxygen atom, and 7 hydrogen atoms.

^1H NMR spectrum:

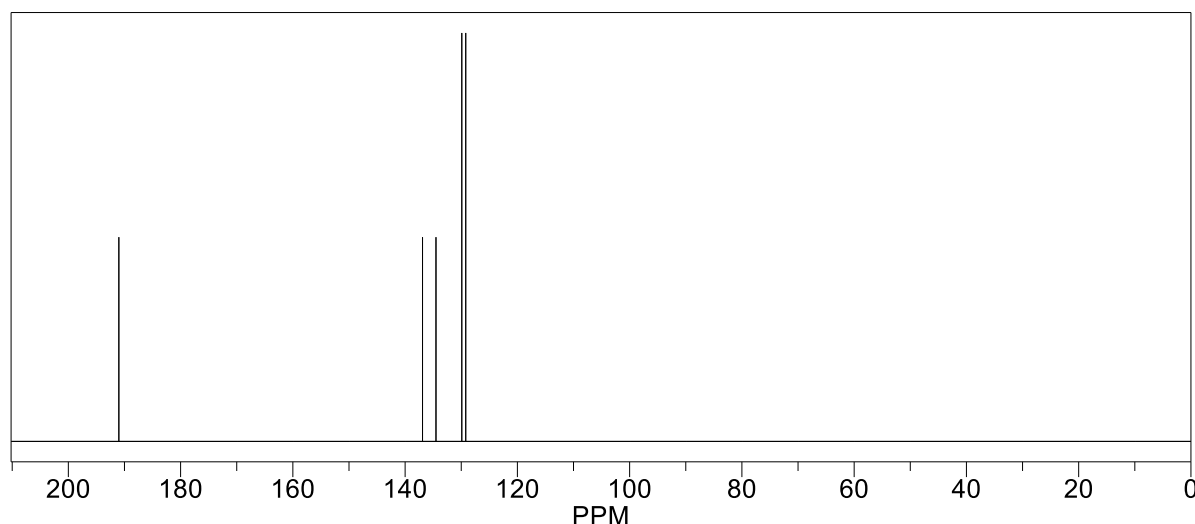


The ^1N NMR spectrum shows 1 peak around 10 ppm. This is very characteristic of aldehydes: we have a **CHO**-group. This also explains the $2700\text{--}3100\text{ cm}^{-1}$ absorption in the IR, it is the aldehyde's C-H.

There are also signals in the aromatic region. As we have 6 carbons and 5 hydrogens unaccounted for, this is very easy: it's a phenyl group (no other combination that is both aromatic, and we have enough atoms for it). These two groups can be combined in one way only, as **benzaldehyde**.



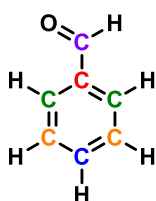
^{13}C NMR spectrum:



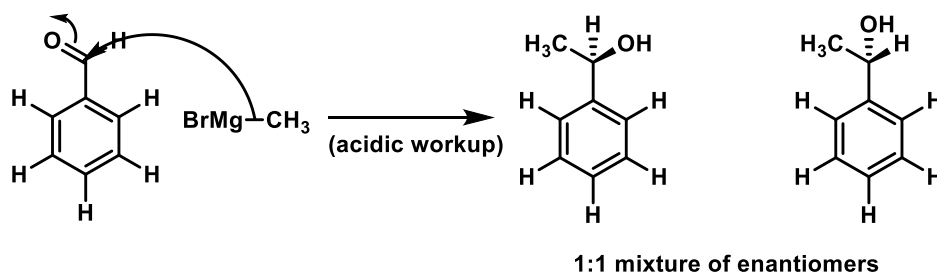
While we could solve the structure without the carbon spectrum, it's a good idea to check if it's consistent with our proposal.

We expect to see 1 carbon in the $\text{C}=\text{O}$ (aldehyde/ketone) region (around 200 ppm) – check

The aromatic ring is symmetric. There should be a separate peak for the carbon carrying the aldehyde, and one furthest away from that. Of the other four carbons the two nearest the aldehyde-carrying C are identical, and the two next to them are identical to each other. This means 4 aromatic carbon signals – check.

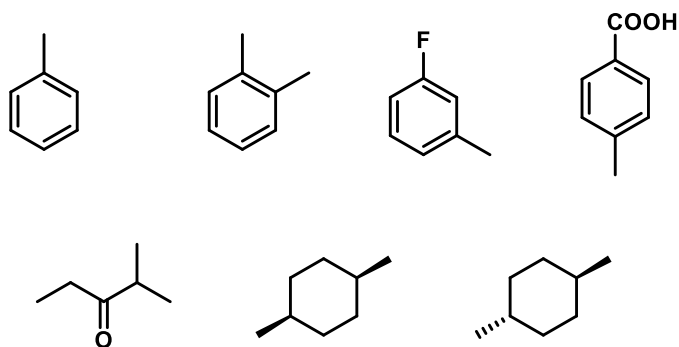


2) Draw the reaction of the mystery compound from question 1) with methylmagnesium bromide (mechanism, too)! How many products do you get?

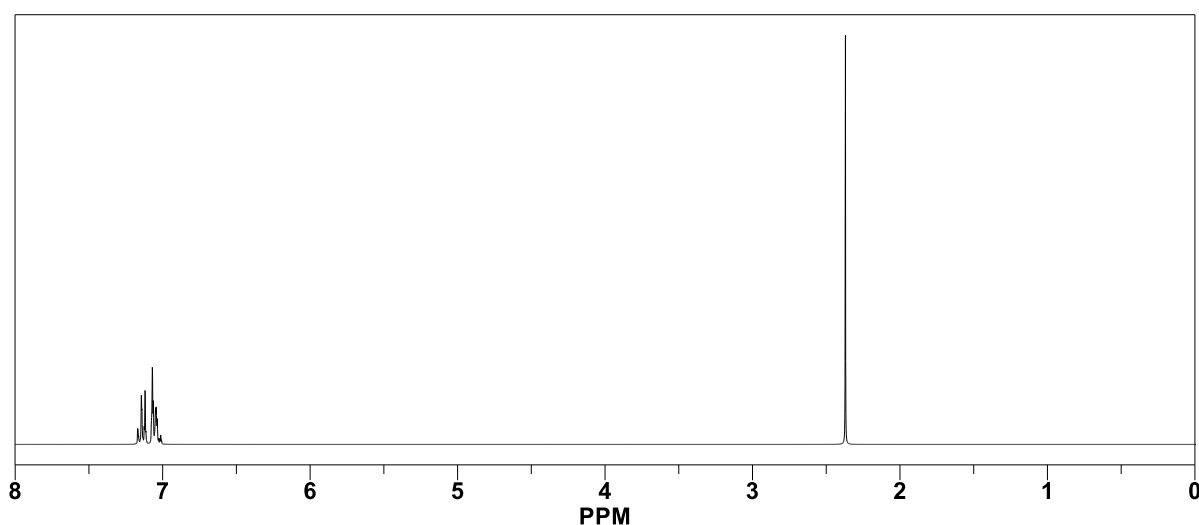
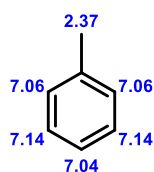


A straightforward Grignard reaction. The product is chiral, and you get a racemate.

3) Predict the ^1H NMR spectra of the following compounds (number of signals and approximate places – use the SI-data):



Some of these were a bit crazy (sorry ☹), but here we go:

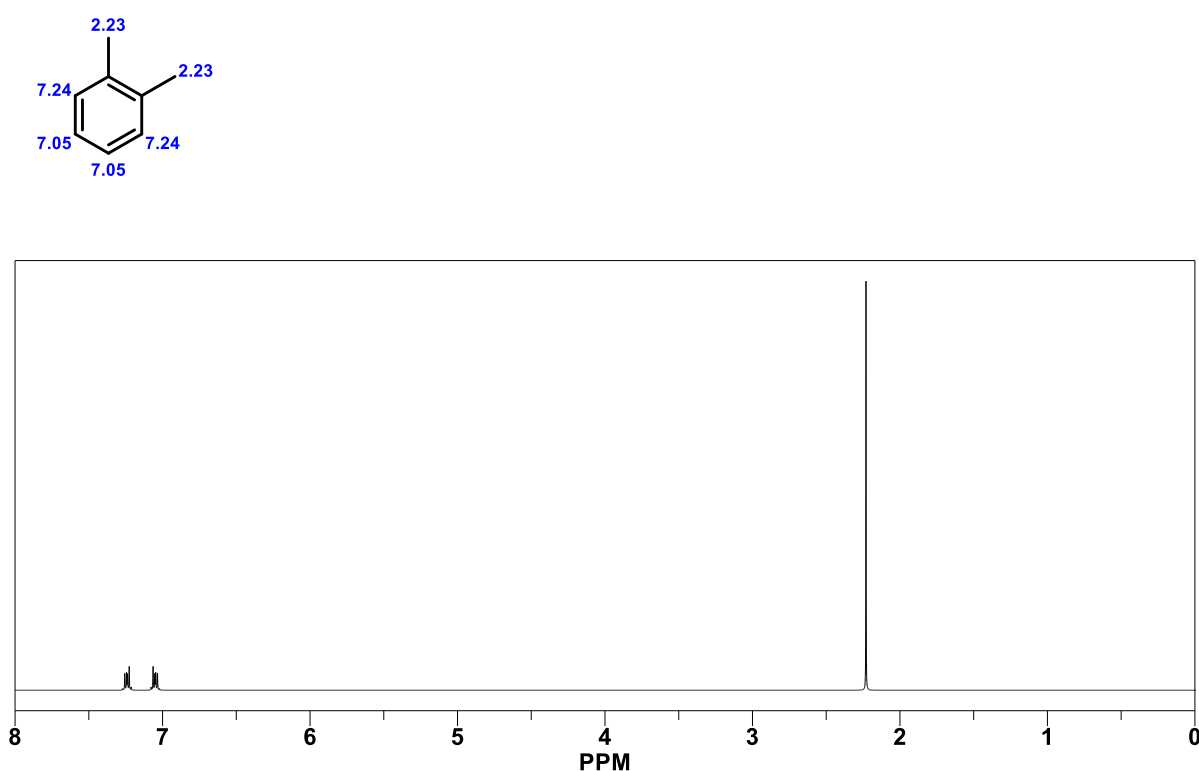


The spectrum contains a singlet for the CH₃ (around 2 ppm, CH₃ linked to aromatic).

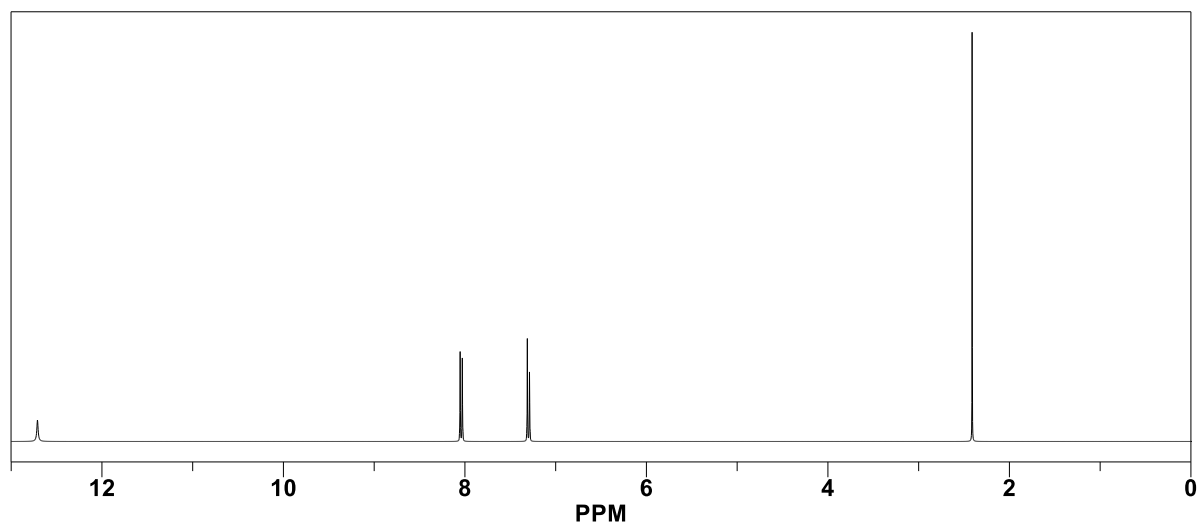
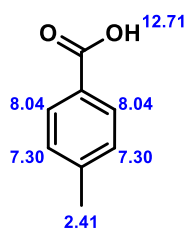
You also have signals with integration in total 5, corresponding to the aromatic C-H's. There are three individual signals with integrations 2, 2, 1. The C-H closest to the methyl is a doublet (one neighbor), the one next to it is a doublet of doublets (dd). The signal is first split by one neighbor, then by the other neighbor. Because **these neighbors are not identical**, they split one after the other, giving a dd.

The C-H furthest from the methyl (on the *para*-carbon, not sure if you went through the ortho/meta/para notation) is a triplet. It has **two identical neighbors**, which split it into three (N + 1).

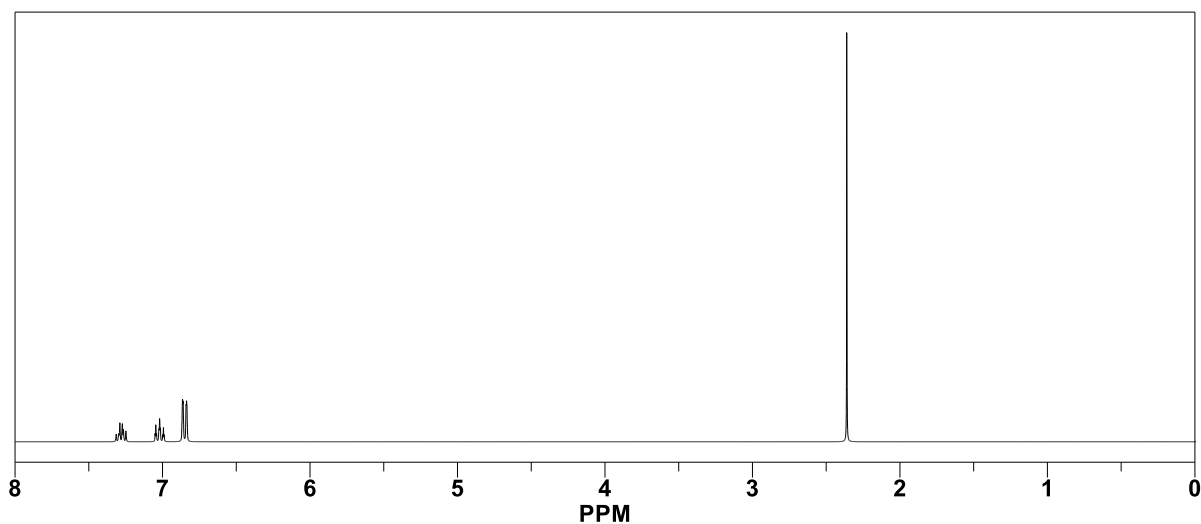
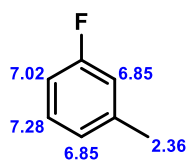
You are unlikely to see separate signals for all the aromatic C-H's, they all come in the same region.



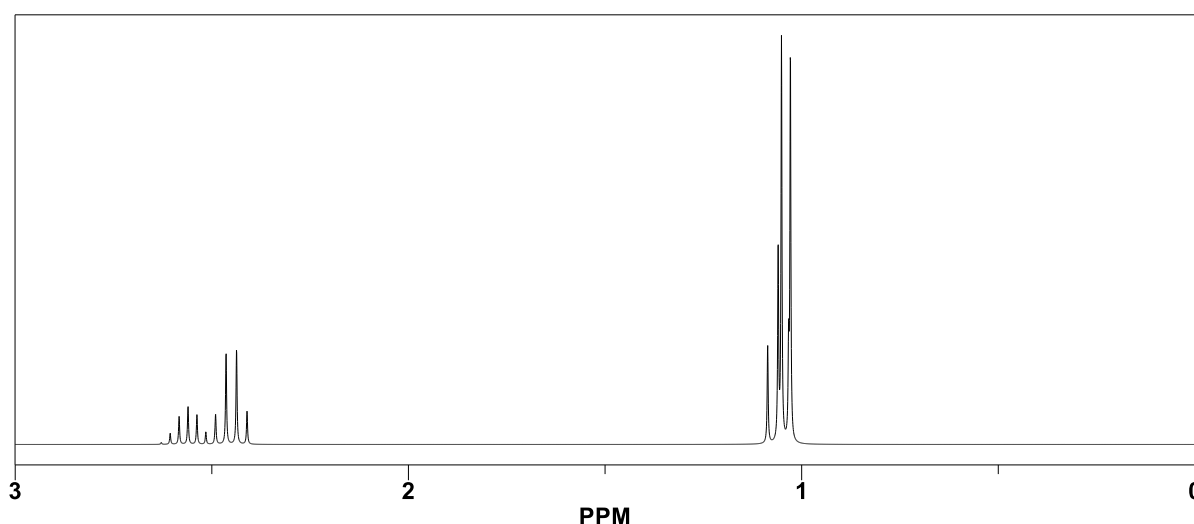
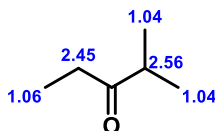
The compound is symmetric, so there is one signal for the methyls (integration 3 (or 6)), one for the aromatic C-H's next to the methyl (7.24 ppm, doublet integration 1 (or 2)), and one for the aromatic C-H further from the CH₃ (7.05 ppm, doublet, integration 1 (or 2) – this is only split by the non-identical hydrogen, and not the one that is identical to itself!).



The compound is symmetric. It has a COOH signal, which is usually around 11-12 ppm. You might also see that it is a bit broader than the other signals, which is typical of OH, NH, SH-signals. The aromatic region contains two signals, each of integration 2 (doublets, have 1 neighbor each that is not identical to them). Finally, there is a singlet for the aromatic-linked CH_3 group.

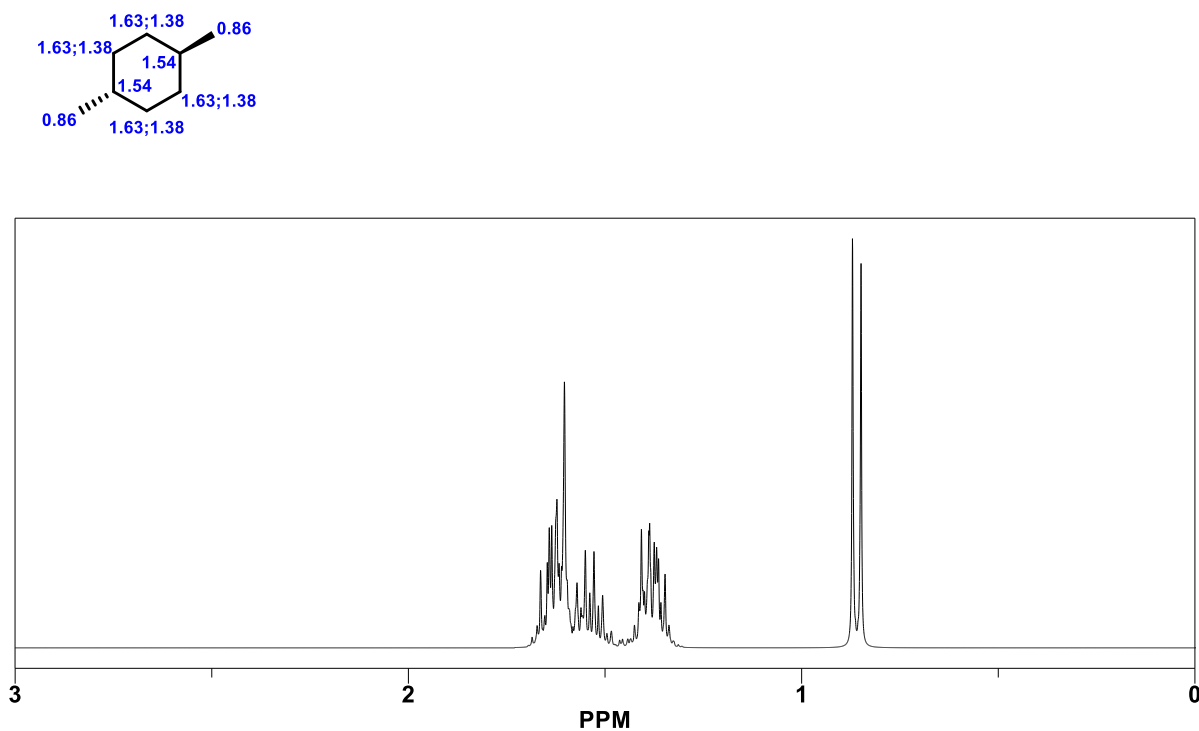
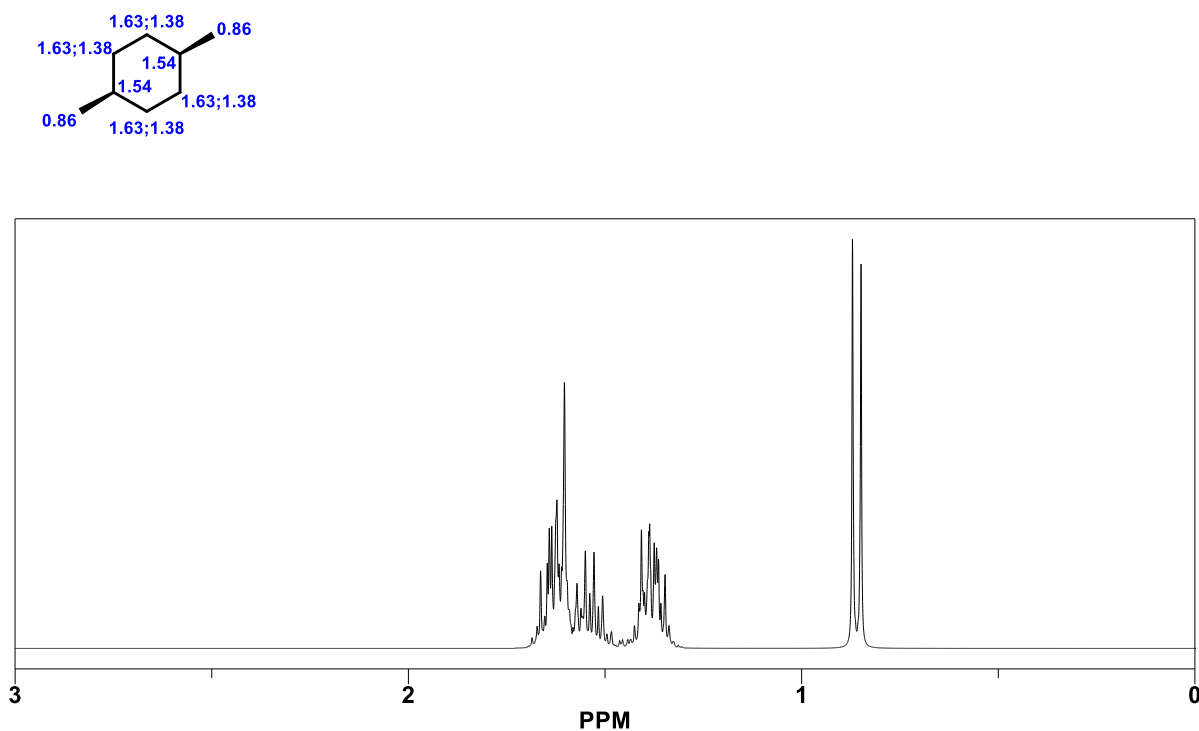


There are a couple of things about this one. First of all, hydrogens can couple to fluorines (don't think it came up in the lectures), so the C-H signals of the H neighboring the C-F are split by the F. Also, it is only a coincidence that there are two signals that are both at 6.85 ppm, because the hydrogens that give rise to them are obviously not identical. One is between a methyl and a C-F, the other between a methyl and a C-H.



The methyls of the isopropyl group are identical, integrating to 6. They are split to a doublet by the C-H. The C-H itself is integration 1, split to a septet by the 6 identical hydrogens in the two methyl groups.

The other side of the ketone is a classic ethyl group, with a triplet + quartet pattern. The signal at 1.06 ppm is an integral = 3 triplet from the CH₃ (hard to see, as it overlaps with the doublet of the two methyl groups). The 2.45 ppm-signal is an integral = 2 quartet, corresponding to the CH₂, which is split to 4 by the neighboring CH₃-group.

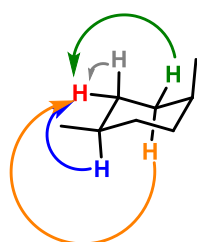
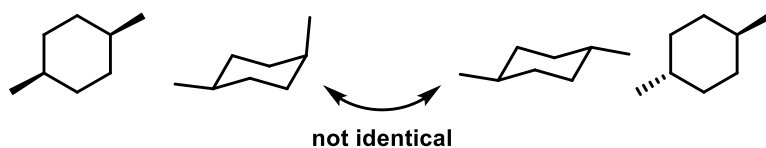


There does not seem to be much of a difference between these two spectra. However, notice that the compounds are diastereomers (see below), and as such, you should not expect the spectra to be perfectly superimposable.

The CH₂-signals are very complex, as the two H-atoms sitting on the same carbon are not identical (see below for an analysis of one H), so they split each other, as well as get split by the two, similarly not-identical H-atoms on the neighboring carbons. In theory, for the CH₂-hydrogens this means a doublet of doublet of doublet of doublets, with a lot of signals coming

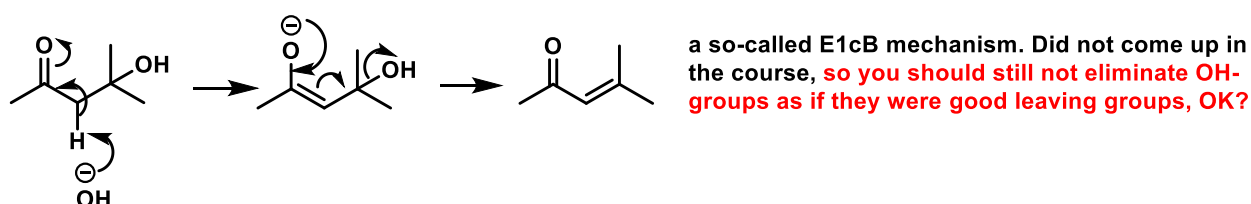
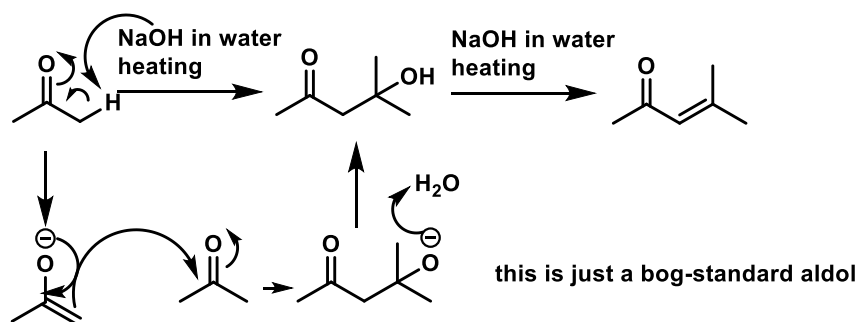
the same region of the spectrum, so mostly overlapping – but not completely. A mighty mess, in short.

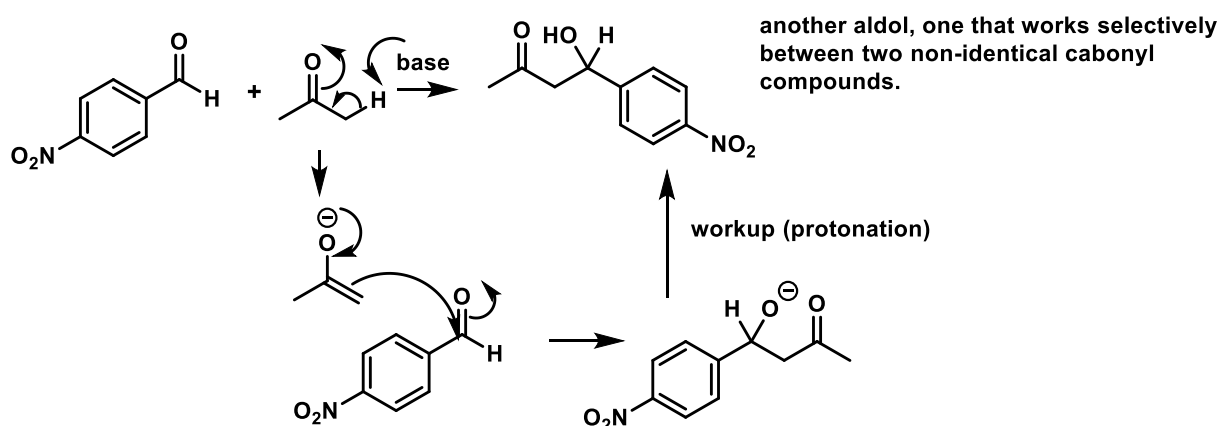
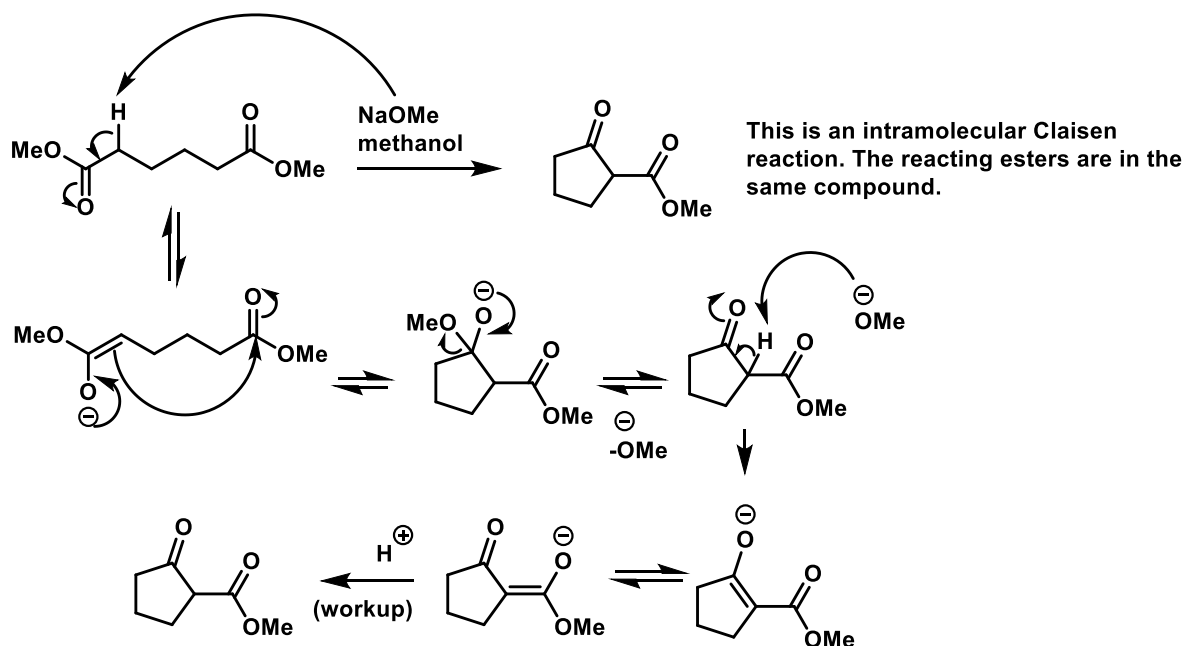
The methyls are nice and clean, a doublet below 1 ppm (split by the C-H), integrates to 6.



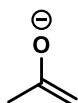
all the hydrogens with different colors are different - will have slightly different chemical shifts. As all the others are neighbors (on the same carbon, or on a neighboring carbon) to H, H will be split in turn by H, H, H and H.

4) Suggest mechanisms for the two steps of the following reactions:





are there any other possible products?
why is this one the major product?



could attack a non-deprotonated acetone too, instead of the nitrobenzaldehyde. However, the aldehyde is much more electrophilic (it's an aldehyde, less hindered, also the nitrophenyl is a strongly electron-withdrawing group), so attack on the acetone is very slow compared to attack on the aldehyde.

The other crucial thing for selectivity is that the aldehyde does not have any α -protons, so it cannot make a competing nucleophile (i.e. a different enolate)