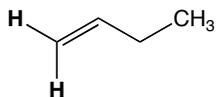


Answers to Problem Set 9b

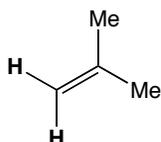
Question 1. Label the indicated hydrogen atoms as homotopic, enantiotopic, or diastereotopic.



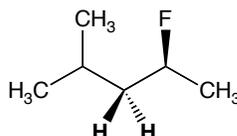
homotopic



diastereotopic

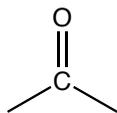


homotopic

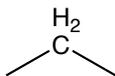


diastereotopic

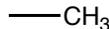
2. For this question we have been given the molecular formula, C_3H_5ClO . Looking at the IR, the strong signal at 1720 cm^{-1} tells us that we have a carbonyl (we can't have two – because we only have one oxygen atom in the molecular formula). In addition, all of the C–H absorbances are below 3000 cm^{-1} , so there are no olefinic hydrogens. The 1H NMR shows two signals – both singlets in a 2:3 ratio. That suggests we have a $-CH_2-$ (that is rather electron-poor – near the oxygen or chlorine?) and a $-CH_3$, but they are not adjacent (because there is no splitting of the signals). Let's put it all together:



(From the IR)



(From the NMR)

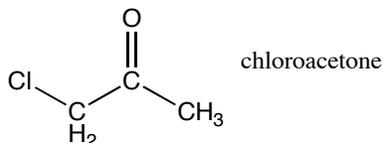


(From the NMR)

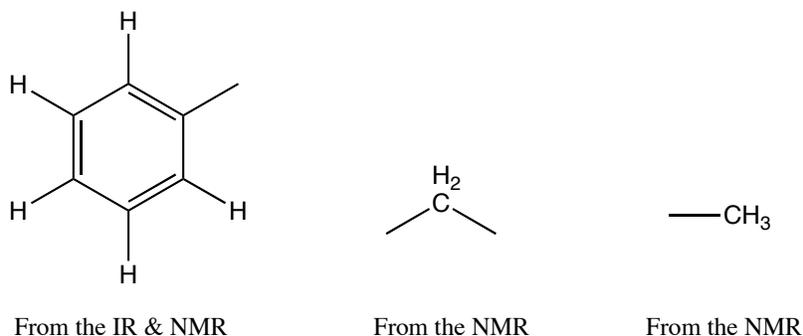


(From the mol. formula)

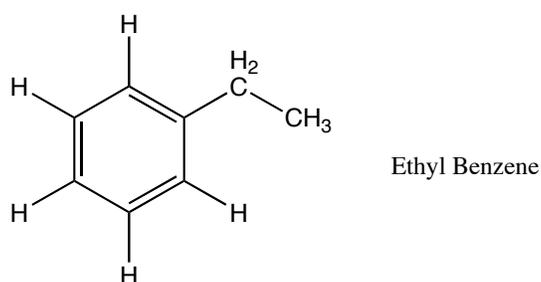
There is only one way to assemble these pieces and not have any splitting in the NMR:



3. Again, we have been given the molecular formula, C_8H_{10} . The IR shows both alkyl and olefinic C–H bonds (signals above and below 3000 cm^{-1}). In addition, there is a signal at 1600 cm^{-1} indicative of a benzene ring (the overtones are also visible). The 1H NMR has five hydrogens at $\delta 7.3$, so our benzene ring is monosubstituted (it must have 5 hydrogens on it). We also have two signals in a 2:3 ratio in the alkyl region – a quartet and a triplet. So far we have:



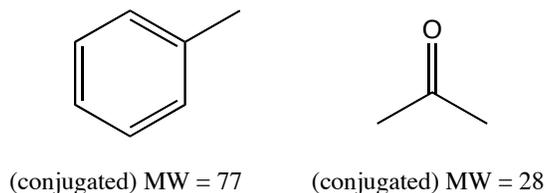
Because of the splitting pattern, the $-\text{CH}_2-$ is next to 3 equivalent hydrogens and the $-\text{CH}_3$ is next to two equivalent hydrogens. Our compound is:



4. This time we have been given the MS, not the molecular formula. The molecular ion peak is very likely at 182.

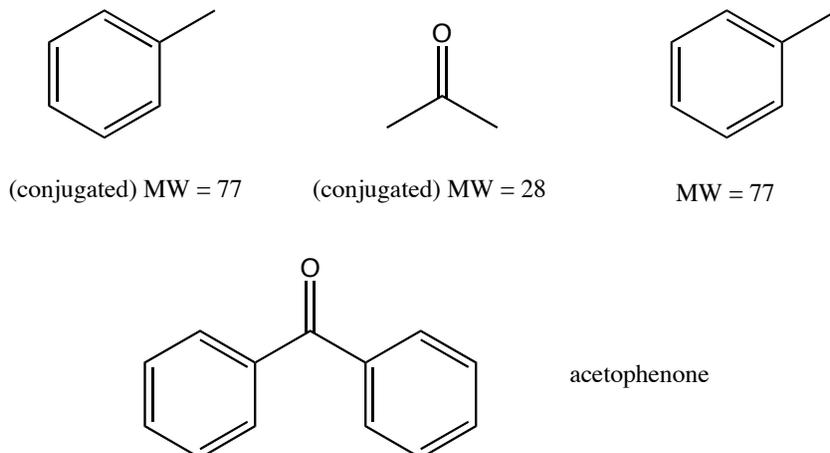
The IR: The IR has a strong signal at 1670 cm^{-1} . This is a carbonyl of some sort, but it is absorbing at lower energy than expected. We might have an amide, or a ketone [*why not an acid or aldehyde? You should be able to answer that!*] that is strongly conjugated (remember, conjugation will lower the absorption frequency of multiple bonds). There is also a signal at 1580 cm^{-1} . This looks like a benzene ring (again, probably conjugated), and the overtones are visible. Finally, the C-H stretches are all above 3000 cm^{-1} , so there are no alkyl hydrogens in the molecule.

The ^1H NMR: All the signals in the NMR are between δ 7.0-8.0. This is the region for benzene (aromatic) hydrogens. So far we have:



$77 + 28 = 105$ mass units, and our molecular formula is 182 mass units. What's missing? $182 - 105 = 77$ mass units remaining. This is the mass of another benzene ring! Our integration ratios in the NMR were misleading (remember that they are just ratios, not

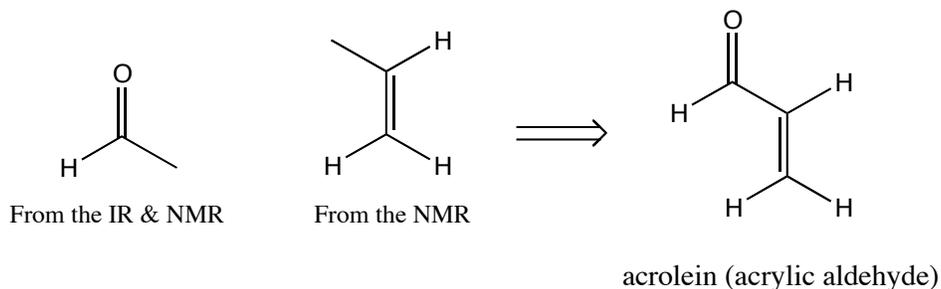
absolute numbers of hydrogen atoms), because we really have ten total hydrogen atoms. Now we can solve the identity:



5. The molecular formula is C_3H_4O .

The IR: There is a strong carbonyl stretch at 1695 cm^{-1} , and there are signals at 2750 and 2850 cm^{-1} . These strongly suggest that we have an aldehyde. There might be other signals in the 1600 cm^{-1} region (it can't be a benzene ring, we only have 3 carbons in the molecular formula!), but the IR is really ugly and we don't want to trust those little signals – yet.

The ^1H NMR: There are no signals below $\delta 6.0$. This means no alkyl hydrogens. We know we have an aldehyde, and the signal at $\delta 9.5$ confirms it. That signal is a doublet, so the aldehyde hydrogen atom signal is split by one neighboring hydrogen atom. There are 3 more hydrogen signals present, and they are all in the olefinic region. Since we only have 2 more carbons in the molecule, they all must be part of the same double bond. They appear to all be split, but the patterns are rather complex and not necessary to solve the structure. So far we have:

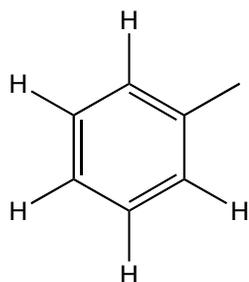


Note: This compound is very unstable and needs to be stabilized with hydroquinone to obtain an IR spectrum. That's why the IR looks "ugly" and there are peaks at 3300 cm^{-1} and 1600 cm^{-1} (from the hydroquinone).

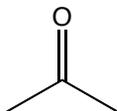
6. The MS: The molecular ion is at 162. The M+1 peak tells us that we have approximately 8-9 carbons.

The IR: We have a carbonyl stretch at 1715 cm^{-1} – most likely a ketone. We have a C=C stretch at about 1620 cm^{-1} , most likely a conjugated C=C. We have both alkyl and olefinic hydrogen signals.

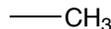
The ^1H NMR shows that we have ten hydrogens. A methyl group appears at δ 3.7 (singlet). This methyl group is likely near an electronegative atom. The five hydrogens at δ 7.4 or so appear to be benzene hydrogens. There are also two other hydrogens - both doublets (they are each split by a single hydrogen) with the same coupling constant (*this means that they are splitting each other*). The signals are at δ 6.4 and δ 7.8. This is the olefin/aromatic hydrogen region. Because of the number of signals (only two) and the *magnitude of the coupling constant* (more on this below), we can guess that these are olefinic hydrogens.



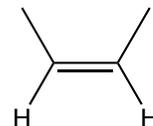
From the NMR



From the IR

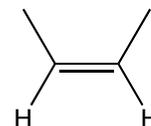
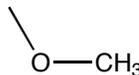
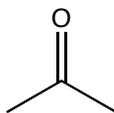
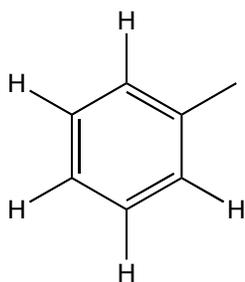


From the NMR



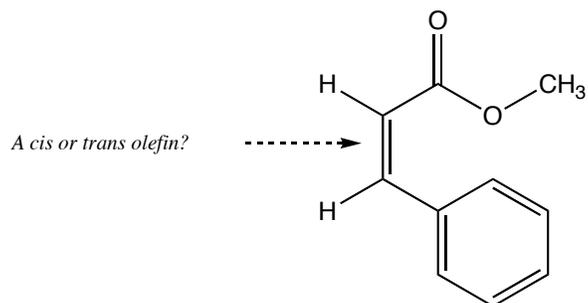
From the NMR/IR

If we total up the mass of our fragments so far ($77+28+15+26$) we get 146. That is 16 mass units too few. An oxygen atom perhaps? We have two other clues that something is wrong: a conjugated ketone will absorb around 1695 cm^{-1} , not 1715 cm^{-1} , and the methyl group signal in the NMR is too far downfield to be attached to any of our groups above (remember: electronegative groups withdraw electron density from the hydrogen and the shift the signal downfield [to the left]). This means that our methyl group is probably attached to our missing oxygen atom:



How do we assemble the fragments? Well, remember that our carbonyl absorbed around 1715 cm^{-1} in the IR **and** it must be conjugated (because of our fragments). What type of

carbonyl might this be? An ester. Esters normally absorb around 1745 cm^{-1} but conjugation will lower the frequency. Our unknown is:



But we still haven't solved the whole problem – what is the olefin geometry (*i.e.* is the double bond *cis* or *trans*)? We can only tell by looking at the ^1H NMR coupling constants between the olefinic hydrogens. The constant is $J = 16.8\text{ Hz}$. This is indicative of a *trans* disubstituted olefin. Therefore, our complete answer is:

