Lab 13B • 03/08/12

[Kinetic versus thermodynamic lab][A − cyclohexanone; B − furaldehyde][furaldehyde aromatic, deactivator][crossed reaction coordinate diagram][part A − 166 °C; part B − 202 °C]
[melting point depression][part C − multitemp experiment to determine whether A' or B' is thermo vs kinetic product][part E − competitive reversible formation]

NMR

Let's do an alkyl halide example. When we have a chlorine right next door, average chemical shift is 3.5. Hydrogen one more position away, for a bromide it's 1.7 [what exactly is it for a chloride?]. What's the structure of this compound? Start with degree of unsaturation first. What is the degree of unsaturation in this compound? How many hydrogens should this compound have if all it had was carbon and hydrogen? 12. 5 * 2 + 2 is 12. It only has 11, though, but that makes sense, because remember if you put a halogen onto a carbon, there is the effective removal of the hydrogen from that place. This has zero degrees of unsaturation, which means no rings, no double bonds; that's good to know.

What does the chemical shift information tell you? This is going to be the first approach I use to solving the problem. Does it appear that we have any hydrogens on a carbon that is the same carbon the chlorine is attached to? It doesn't look like it, does it. Look at the chemical shift pieces of information there: on the carbon right where the chlorine is, it should be more like 3.5, somewhere between 3 and 4, more generally we could say. One more position away, then we get something like 1.7, which is what we've got. The chemical shift appears to indicate there are no hydrogens on the same carbon as the chlorine − which means there's only one answer possible for this compound. Why? Because there has to be the carbon where the chlorine is located. If there's no hydrogens where that chlorine is, that in all directions, there must only be carbons. The carbon the chlorine is attached to must be [tertiary], because that's the only way to make it with no hydrogens. How many carbons have I used up so far? Four, total − the center one, plus the three others. There's only one other carbon in this compound; it doesn't matter which one of those groups I put it on, you'd get the same compound. There's the answer.

Chemical shift, nothing about 2, even, which seems to mean that there's no carbon that has the hydrogen on the same carbon as the chlorine. If that's true, then structurally, there can't be any hydrogens there, and the only way to prevent that then is to have carbons at ever position where you could have something next door. Those carbons are going to have hydrogens, which is fine, but they're at lower chemical shift, cause they're further away from chlorine. That matches the data that we're given. Based on the size of the molecule, the fact that we only have five carbons to begin with, once we knew that the point of attachment for chlorine had to have three other carbons around it, which means we've used up four of the five carbons. Since at that point, the molecule would have been symmetric, it wouldn't have matter where I attached the fifth carbon, the result would have been the same. Therefore, this is the only possible answer.

What if we took a different approach? Symmetry ended up being an issue [in a previous problem]. We had an integration of six, which means there's two possibilities, as far as what the structure might look like; what are those two possibilities? Two of them are methyl groups; two carbons that have three hydrogens that are equivalent. Or, what technically would be the other possibility? If you had two times three, could't you have three time two? You could, in theory, have three carbons, each of which having two hydrogens that are all equivalent. In a molecule with only five carbons, is that likely to be the case? Probably not. Given the small number of atoms in the compound, much more likely it's two carbons, each with three hydrogens, so two methyl groups. If we had two methyl groups that were attached to the same place, then we could have this much of the structure be true: a carbon with two methyl groups coming off of it. Now, let's use just one of the pieces of information that's given to us. We have something that integrates to 6; what's it's splitting? A singlet. How many neighbors do those six hydrogens have? None. The peak that integrates to six is also a singlet, so those hydrogens have no neighbors − which means what? Which means we have a structure where it's shown us we have a [tertiary carbon], a carbon that has no hydrogens on it. There's only two possible structures that could result. I could leave it like this and have just carbons attached all to that one position, and put the chlorine here; or, have something besides hydrogen attached to all positions, but have the chlorine to where those six hydrogens are. How many different types of hydrogens are there in the first of these possibilities? How many unique NMR signals would be generated? Two. In the second compound, how many different types of hydrogens are there? Three. The first one only has two signals, which means it's the wrong one. The second one has three signals, which means it's the correct compound. It's a different approach, where we started with the idea of symmetry. We started with the idea that we have something that integrates to 6, which means we have to have some kind of symmetry in there somewhere.

There's another way we could have done this, which is to focus on the splitting patterns that we have. For example, we could look at the fact there's a triplet that integrates to three. The fact that it integrates to three is separate from the fact it's a triplet; we have the number three showing up in two places, but it's for two different reasons. If we have an integration of three, that means we have a methyl group. What does the triplet mean? There's only two neighbors. What is the splitting for the only peak that integrates to two? Quartet. Not a quartet of doublets or a quartet of anything, just a quartet. If you look at those two hydrogens that were causing the triplet, how many neighbors can be to the right of that position?

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To the left, we already have three neighbors, that's what causes the quartet; so to the right, how many neighbors can we have? Zero, which means there's only one way we can make this compound: we have to put the other three connections to that point, make them carbons or chlorines, because it's the only way to avoid hydrogen. When we do that, we use up all the carbons and chlorines, and we've solved the structure of the compound. Those two hydrogens cause a triplet. These hydrogens are only split into a quartet, so they only have neighbors on one side, which means we can't have hydrogens at that end position, which again means there's only one possible structure for this compound.

I've got one more example. This compound has the formula C_8H_{10}, and only has two absorbances: 7.04, s, 4H; 2.296, s, 6H. Let's see if we might guess something about the structure, cause what's the degree of unsaturation? Four. That's pretty high. Can we think of any kind of molecule that we've studied so far that would have such a high degree of unsaturation? We can't have an aldehyde, cause we don't have an oxygen. How about benzene itself, as far as a degree of unsaturation of four, because you have three double bonds (at least on paper) and it's a ring. Remember that the ring itself counts as a degree of unsaturation. Benzene compounds have protons that show up generally between 7 and 8, sometimes little lower than that for some functional groups. The minimum degree of unsaturation you have to have to have a benzene-based compound is four. Why is this true [that the chemical shift is between 7 & 8]? If I have a loop, a ring, and I have a magnetic field that is passing through that ring, and let's say that I had an electric current that gets generated by the magnetic field passing through the ring – which way is the current going to go? But if I already have the magnetic field, then we use the right hand rule to say that you point your thumb in the direction of the field and you fingers tell you which way the current's going to go. Doesn't that cause a countercurrent to be generated as well, that if we're pointing along the direction of the current, then that's going to cause a magnetic field that's going to counter it somehow, induced by the fact that you're in the magnetic field. When it does, on the outside of the compound, then the magnetic field adds to the external magnetic field. On the inside, that magnetic field is in opposition. [need to figure out which way fields and currents go] There is what is known as a ring current that gets generated in benzene, because benzene is this conjugated system, so it's like an itty-bitty molecular wire of electrons that, because they're in a circuit, can be made to flow around. Once you put benzene into a magnetic field, it does cause a ring current, but the ring current causes its own magnetic field which, on the outside fo the compound, adds to the magnetic field that the hydrogens are already experiencing. If you have that occurring, where you have your own magnetic field that is adding to the external magnetic field, then that's going to cause a higher chemical shift, because an increased magnetic field causes an increased energy gap, causes an increased frequency of absorbance, which is chemical shift. That's why benzene has hydrogens that are in the 7 - 8 region, because of this effect of the fact that it's got a ring.

When benzene is placed in a magnetic field, a ring current is generated which causes a local magnetic field to form that opposes the external field on the interior of the benzene ring, but adds to the external field on the exterior of the benzene ring. This means the hydrogens, which are on the exterior of the ring, experience a greater overall magnetic field, so they have higher chemical shift.

Now that we've established that there's a benzene ring present, what's the structure of the compound? Benzene with an ethyl group, that's one suggestion. There's ortho-xylene, and there's only two other possibilities: meta-xylene and para-xylene. That's the only way you could put two carbons on a benzene ring: either not on the same place, so not an ethyl group, which means the only other possibility is two methyl groups. If you have two methyl groups, then it could be ortho, meta, or para to each other. Or, the last possibility is to have both carbons in a chain on just one position of the ring. Let's look at those four possibilities. We have ortho-, meta-, para-, and ethyl. How many types of hydrogens do we have on the first compound? Three. What about the second compound? Four. [Next, two] Last compound, what would be the splitting for the methyl group? It'd be a triplet. What would be the splitting for the methylene group? Quartet. There are only singlets in the compound, so that means it has to be para-xylene. Why? Because since the last molecule is complete symmetric, all four of the hydrogens on benzene are identical, [and] the two methyl group, because of symmetry, are identical. That last compound, there would be five signals that would be generated. For benzene, we could use the number of signals and the splitting to try to figure out what the substitution pattern is. If you see a problem with stuff in the 7 to 8 range with a high degree of unsaturation, normally, a very safe guess is to jump and say benzene.

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*There is no connection between the magnitude of the melting point & which product is the thermodynamic vs kinetic product.

Part C – When the rxn is conducted @ low T, the kinetic product should predominate, while @ high T, the thermodynamic product should predominate. Whichever of the two reference compound (made in parts A & B) most closely matches the MP obtained from the mixture formed @ low T is the kinetic product, and whichever matches the MP for the mixture formed @ high T is the thermodynamic product.

Part E – In these competition reactions, whichever rxn involves the thermodynamic product should not occur, since the thermodynamic product is unlikely to reverse.

$C_5H_{11}Cl$ – delta 1.764, q, 2H; 1.556, s, 6H; 1.36, t, 3H
0 D.O.U., so no rings and no double bonds

Method #1: delta analysis
The delta data provided appear to indicate there are no H on the same carbon as the chlorine. This means the carbon chlorine is attached to must be quaternary.

Method #2: delta symmetry
With an integration of 6, there must be two equivalent carbons each with three hydrogens or 3 carbons with two hydrogens. Given the small size of the compound, it is much more likely to be 2 methyl groups. The peak that integrates to 6 is also a singlet, so those hydrogens have no neighbors.

Method #3: splitting
– There is a triplet that integrates to 3. These hydrogens are only split into a quartet, so they only have neighbors on one side.

C_8H_{10} – delta 7.04, s, 4H; 2.296, s, 6H – DOU –> 4; benzene has 4 D.O.U. and 7 ≤ delta ≤ 8.
When benzene is placed in a magnetic field, a ring current is generated which causes a local magnetic field to form that opposes the external field on the interior of the benzene ring but adds to the magnetic field on the exterior of the magnetic field. This means benzene hydrogens experience a higher magnetic field and therefore have a higher chemical shift.
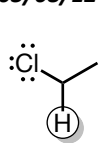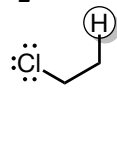
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Structures

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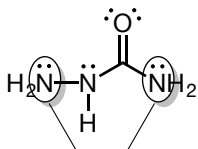
These lone pairs are heavily delocalized with the carbonyl so they are less reactive.
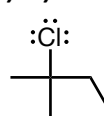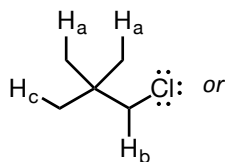
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δ 3.5 δ 1.7

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03/08/12 lab • 4

or

2 signals

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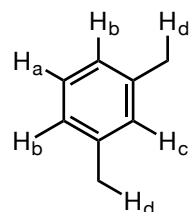only two neighbors; causes triplet
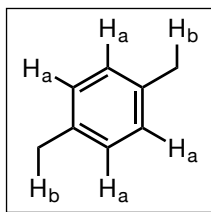
no H; must be carbon
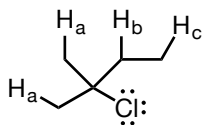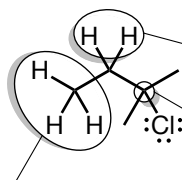
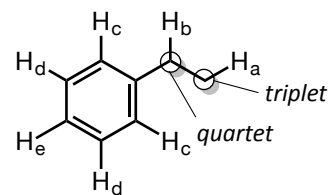integration of 3

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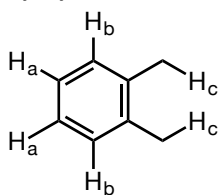
3 signals

4 signals

2 signals

5 signals
will not have
integration of six

triplet

quartet