Lab 7B • 02/14/12

[lab exam review]
[experiment 1]

Two mechanisms for bleach oxidation of an alcohol

Your text indicate that the beginning of this reaction occurs when an alcohol attacks the chloride of hypochlorous acid. [review of ion names] Hypochlorite is the active component of bleach; when we say bleach oxidation, we mean oxidation using the hypochlorite ion. From hypochlorite, we get hypochlorous acid, which we're going to have some of, along with beach, you also have acetic acid in solution. The first step would be the oxygen of the alcohol attacking the chlorine. There's two reasons this seems a little strange to me: one, you produce hydroxide. We have had another reaction where hydroxide is a "leaving group" – specifically, hydroboration-oxidation, we saw a case where there was an alkyl shift that ended up with hydroxide being kicked out. It's not the last time we're going to see that either; we'll see a variation of the E1 mechanism where hydroxide effectively ends up a leaving group. Aside from that, there's no huge driving force for this reaction, it appears, because chlorine starts out connected to an oxygen in the beginning of this reaction and ends up connected to an oxygen, so there's no change in oxidation state; there's really no change in the environment. The only thing that seems to be happening here is producing hydroxide. Maybe, overall, it could be that this is a thermodynamically favorable process and that might explain why this might be an acceptable mechanism. But let me show you an alternate one that seems a little bit more – believable. Instead, that alcohol itself gets protonated first. Since acetic acid is a weak acid, so you're not necessarily going to have a flood of H+ in solution, and since hypochlorite is a weak basse, it seems acceptable to me that you could have some hypochlorite ion, even in the presence of acetic acid. That could come along and kick off the water to give us a hypochlorite.

One way or another, the last step of the reaction is for some something like water to come along, pull off a proton at the same position where the hypochlorite is. That bond collapses towards the oxygen and kicks out chlorine, so we end up with our oxidized compound and chloride as a by-product. This part makes sense to me because what is the oxidation state of chloride before it gets eliminated; before that last step occurs, what is the oxidation state of chlorine? The automatic answer that [might come] is -1, because that's the normal rule for chlorine. But, chloride is -1, unless it's in the presence of oxygen and fluorine. That's because oxygen and fluorine are more electronegative than chlorine. If you were to look at that, if we were to analyze it the way we did for oxidation state, the oxygen chlorine bond would effectively be owned by oxygen. Only the six lone electrons would belong to chlorine; that's versus the seven electrons it would want to have in an unreacted state. So six electrons verus seven, that means that chlorine has a +1 oxidation state, at least to begin with. By the time the reaction's over, we have chloride minus, which automatically means it has a -1 oxidation state. Chloride gets reduced, because hypochlorite is the oxidizing agent. Carbon gets oxidized in response. Chloride has an oxidation state of +1; here, it's -1. The carbon, before the elimination, has an oxidation state of zero, because it has two neighboring alkyl groups, two carbons; remember that any time you have carbon connected to carbon, each atom gets one electron, which effectively means there's no change in the oxidation state by having a neighboring carbon. If we have a hydrogen next door, like we have here, that's going to cause a -1 on the carbon, because carbon's more electronegative than hydrogen; oxygen, the reverse – it would effectively take electrons in this counting process, so it would generate a +1. So, a zero, a zero, a -1, a +1, gives an oxidation state of zero, and at the end, the carbon has an oxidation state of +2. This second version of the mechanism is what I'm going to declare as the mechanism.

[experiment 1 procedure – washes: HSO3- reduces out any excess bleach, Na2CO3 neutralizes excess acid]

Why do we use something like bicarbonate instead of sodium hydroxide? Because one of the products you get from bicarbonate is carbon dioxide, so there's not much left in solution after that reaction. Bicarbonate's a weak base, so supposed you flood your solution with it as you [often] would in a wash; it's unlikely some form of side reaction's going to occur. If you use sodium hydroxide, that's really basic, you could potentially cause a reaction. Think, for example, if you had an alkyl halide. If you were going to do substitution of elimination, a lot of times you actually have to add heat to get the reaction to work, but still, you might not want to risk putting something that's a more powerful base like hydroxide in, when all you're wanting to do is neutralize the solution. Even beyond that, because bicarbonate's a weaker base, even besides the fact that it's not necessarily going to react with anything, you'll end up with a not-so-basic solution. If you use hydroxide, you might be stuck in the problem where your solution's too basic, if not for what you're trying to isolate, then maybe you're trying to do another step of the reaction. Bicarbonate is usually the best thing to use if you're trying to get rid of excess acid

[salt wash forces out ionic impurities; IR analysis – reactant has identifiable round peak; carbonyl has identifiable sharp peak; residual alcohol peak indicates either partially or fully unsuccessful reaction or wet product]
[experiment 2 – mechanism of reduction; difference in reactivity of NaBH4 and LiAlH4; practical lab consequences of difference in reactivity; IR interpretation – start with carbonyl, end up with alcohol peak, which without further characterization can't unequivocally prove alcohol exists since water could be present]
[experiment 3 – Wittig; IR directions; mechanism; unusual acidity of benzyltriphenylphosphonium salts; ylide; washes – NaHSO3 reduces triphenylphosphine oxide]

[experiment 4 – Grignard]

The start of the Girgnard reaction is like what you had seen before. We started with bromobenzene, reacted that with magnesium and ether. Even though we had covered the mechanism for forming the Grignard reagent, it's fine if I asked for a mechanism that you don't show this part, that you just show that the Grignard reagent forms. To reduce the number of steps needed when writing a Grignard reaction, there's a shorthand, which is instead of taking the time to show the magnesium bromide formally dissociating, making the anion, you could just draw an arrow from the carbon-magnesium bond itself pointing towards the carbonyl. It would be understood that it's not the magnesium that ends up attached, it is the carbon that ends up attached. The unusual part of this reaction, at least from what we've learned so far, is due to what functional group we have. What functional group is this? It's an ester. A carboxylic acid is a functional group that has a carbonyl with an –OH group attached to it. Take that hydrogen off, put an alkyl group on, and that's where you get an ester from. We did talk about esters when I brought up the term chromate ester, or I might have also used the term sulfonyl ester to mean some kind of double bond-containing functional group that has an –OR group attached to it.

The reason this leads to different reactivity can be seen in the intermediate that we get. We get an alkoxide, like we normally have, but normally, attached to that same carbon as the alkoxide, we only have carbon or hydrogen attached – hydrogen if we've got an aldehyde. Here, we have another alkoxide attached, or what could become an alkoxide if it got kicked off. Normally, when you form the alkoxide, nothing further happens to it until it gets acidified. In this case, it is possible – in fact it will happen – that the negative charge can collapse back down and make a carbonyl, kicking off the alkoxide, because the basicity of what is being kicked off here – I know this is not a good leaving group, but recognize that you start with something that itself is pretty basic. It may only be a difference in 2 pKa units or so between methoxide and this anion. You could argue that maybe there's an equilibrium between the two, but it's not that difficult to transition from one to the other. But if you did do this elimination the way I've shown it, you end up with a ketone, which since you've got a Grignard reagent around, as soon as the ketone forms, then a second equivalent of the Grignard reagent can add in. This time, you really do end up with an anion that can't go anywhere, you could say, because this time you really do only have carbon groups attached and the oxygen is not going to collapse back down to kick benzene off. Now, nothing happens until acidification, and we end up with our product, which is triphenylmethanol. Pretty much the standard Grignard mechanism, other than the fact you haven't seen it used on esters before.

[water, carbon dioxide, and oxygen can decompose Grignard reagents; reason for flame-dried glassware]
[lab directions]

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OCl-   hypochlorite

washes: NaHSO3 (sodium disulfite) – reduces excess bleach
          NaHCO3 – neutralizes excess acid
          NaCl – forces out ionic impurities

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Structures *(remaining structures identical to lab 8A)*

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Cl is O.S. +1

C: O.S. 0

C: O.S. +2

O.S. -1