Lecture 25B • 03/23/12

[studying for the final]

[nomenclature of alcohols, alkoxides, alkenes, aldehydes and ketones, benzene]
[conversion of alcohols into leaving groups: tosyl chloride, thionyl chlroide, PBr3; stereochemical differences]
[hydration and dehydration; oxidation – PCC vs CrO3; POAD; formation of alkoxides with Na or NaH; Williamson ether synthesis]
[reactivity of aldehydes vs ketones]
[formation of epoxides by Br2/H2O and NaH vs MCPBA]
[cationic versus anionic epoxide ring opening]
[acetals, ketals, hemiacetals, hemiketals, imines, enamines, cyanohydrins, oximes, hydrazones]
[reduction – LiAlH4 versus NaBH4; alkylation – Grignard, Wittig; protecting groups – DHP, TBDMSCl]
[Wolff-Kishner reduction]
[conjugation – (no) kinetic versus thermodynamic control, MO description of allyl and buta-1,3-diene, bonding/non-bonding/anti-bonding; cumulated dienes]
[aromaticity – aromatic, non-aromatic, antiaromatic; MO for cyclobutadiene and benzene; cyclopentadienyl anion; tropylium ion; pyridine; pyrrole; COT; cyclodeca-1,3,5,7,9-pentaene; Frost circle]
[benzene – nitration, sulfonation, alkylation, acylation, halogenation; ortho/para versus meta directors; activators vs deactivators; halogens' crossed behavior]
[pericyclic reactions – HOMO/LUMO interactions; ground versus excited states; conrotatory and disrotatory cyclization]
[Diels-Alder rxn – diene and dienophile; s-cis and s-trans; endo versus exo; secondary orbital overlap]

Mechanism for Jone's reagent

Start with the chromium trioxide. Generally, this is in aqueous acidic conditions, so you could show one of the chromonyls getting protonated; that can open up, which then puts a positive charge on chromium, which is what could be attacked by an alcohol. Notice that at this point, everything looks the same as a PCC reaction, it's just that instead of having O- with a pyridin[ium] at the end, it's just an –OH group. From here, other than that one structural difference, the mechanism would be identical to that of PCC.

[Frost circle for azulene – decagon]

[ether nomenclature]

If you had a compound like this: four carbons and two carbons. You take the longer chain and make that the main chain. For the short chain, you take whatever name you have like methyl, ethyl, propyl, butyl and just take the first portion of that. You end up making what are called concatenated names, shortened names. Instead of saying methyloxy or ethyloxy, we say methoxy, ethoxy, propoxy, butoxy – so take the -ane ending and just put -oxy on it. Ethane minus -ane plus -oxy gives us ethoxy. So, this compound would be 1-ethoxybutane.

Exams 3

Imidazole is this five member ring compound. You were told that it appears to have 8 electrons which might participate in the ring; that would make it look like it's antiaromatic. But, I tell you that it is aromatic, and it's easily synthesized and isolated. You're asked to draw a SMOG diagram to explain why it is aromatic. What is the hybridization of every atom on the ring? Sp2, because even the nitrogen that looks like it's sp3, it's sp2 because that lone pair in real life, even if it were just on a plain amine, that lone pair would be bouncing back and forth between two different directions. As it bounces back and forth, if you imagine it being in the middle – which it wouldn't be in the middle of the nucleus – but it's as if there's a p orbital there. If it was, there the other p orbitals that are part of the ring that it could join with and that would make it aromatic. Why? For brevity's sake, I won't fill all of these in. Let me at least indicate where my nitrogens are. I'll put my hydrogens in. As you can see, for one of the nitrogens, there is a hydrogen, and it's on an sp2 orbital, because the lone pair wants to become part of that pi system. The lone pair would be here. The other nitrogen, though, it's the lone pair that must be pointed off to the side, because that nitrogen already has a double bond. You can't have a pi bond and a lone pair in the same place. We have the two pi bonds and one lone pair; that's six electrons, that means it's aromatic.

The other question was about this compound: 2-ethylcyclopenta-1,3-diene. You're told it's unusually acidic; it has a pKa of 15. But the molecule is not aromatic. Explain why it is so acidic. It's not aromatic, but it wants to be; that's why it looses its hydrogen, because once it does lose its hydrogen, the lone pair there can delocalize. Since it delocalizes, you've got six electrons in the ring again. It's cyclic, planar, conjugated, has the right number of electrons, so it's aromatic.

To help demonstrate that, you were asked to construct a Frost circle and to briefly explain the rules for a Frost circle, including how do you determine how many orbitals there are, which ones are antibonding, non-bonding, and bonding, and then how many electrons do you throw in there. You look at what's in the ring itself to determine the number of electrons. We have two pi bonding pairs of electrons plus the lone pair, so that's six. How many orbitals do we have? It's equal to the number of atoms in the ring. The reason I put the ethyl group there was to see if I threw any of you off. The ethyl group has nothing to do with this question; it's just the ring. There's five atoms in the ring, so the Frost circle's going to [have] a five-sided figure in it. You have to put one point down at the very bottom of the ring, because it corresponds to an orbital with p orbitals that all have the same phase. As far as which orbitals are bonding, non-bonding, and antibonding, we draw a line which would be parallel to the tangent of where that lowest point would be; once you draw that lowest point, that line has to be parallel to the bottom of that circle. Anything below the lone is bonding; anything above it is antibonding; anything on the line is non-bonding. In this specific case, we end up with 5 molecular orbitals – three of them bonding, two of them antibonding. With the six electrons we have, they only go in the bonding orbitals, which confirms it's aromatic, which is why it loses the hydrogen, cause it's not aromatic until it looses the hydrogen.

Quiz

For buta-1,3-diene, there were four orbitals, and they were each different energy. Remember, for the linear system, each orbital has one more node, so we have 0, 1, 2, and 3 nodes. For the cyclic system, we still have four orbitals, but there's only one bonding orbital, two non-bonding, and then one antibonding orbital. In the question, you were told that for the butadiene, the linear one, the single bond that's there is shorter than normal, and you were told that for cyclobutadiene, the single bond there was longer than normal. Why? Just to flash up one of the orbitals here for the butadiene case. That lowest-energy orbital is one in which all the p orbitals used to represent it have the same phase, which means electrons are spread out over the whole molecule, which helps bring the molecule closer together. To put it shortly, conjugation is what brings the double bonds together, which is why the single bond there is shorter than it normally should be. That's explained, one, by the fact that we have this distributed orbital, and we only have electrons in bonding orbitals.

Where do things go wrong with the cyclobutadiene case? Because of the type of node structure that we have in these orbitals, two of the orbitals end up non-bonding. But, we still have the same number of atoms and the same number of electrons. So, whereas we had two double bonds previously, effectively we only have one in the cyclic case. You pushed electrons that would otherwise be bond into being non-bonding, which is not favorable. The compound responds by trying to stretch apart, because the further it stretched, the more those double bonds act like individual double bonds. That's why the bond is longer. There was a sub-part of the question that asked to explain how did you know which orbitals were bonding, non-bonding, and antibonding. The answer that I was looking for is that bonding is whenever your representations have more favorable overlaps between p orbitals than unfavorable ones. That's where the happy and the sad faces came from. For antibonding, it would be more unfavorable versus favorable, and for non-bonding it would be equal. But, it is true that bonding orbitals are ones that are lower in energy compared to unbonded atoms; that antibonding is higher in energy compared to unbonded atoms; and that non-bonding is equal in energy to non-bonded atoms.

[names of molecules]

Exam 3 last question

Let's do a mechanism. Toluene reacting with aluminum trichloride and propyl chloride. It's going to be the chloride that reacts first with the aluminum trichloride to make a complex. That's what effectively makes our electrophile. After it substitutes, chloride can come off of carbon, which makes a carbocation, which makes an unfavorable carbocation, which hydride shifts. A hydride shift will occur here. Now, we have a single carbocation that gets attacked by toluene. It is technically true that you're going to get two [products]: ortho and para. At this point, chloride would remove a hydrogen, which would cause benzene to be reformed.

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Structures – Identical to those from lecture 24A (03/23/12)