

## Lecture 28B • 12/09/11

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[final review]

[line structures; atomic and molecular orbital theory – bonding and antibonding; hybridization – methane; sigma and pi bonds; VSEPR shapes]

[acids and bases – effects of electronegativity, hybridization, and resonance; pKa – ethane, ethanol, propyne, acetic acid]

[nomenclature – alkanes, alkyl halides, alkenes, alkynes, alcohols, alkenols]

[physical properties – in lab]

[rotomers – syn(periplanar), anti, gauche, butane, Newmann projections]

[cyclohexane – chair and boat forms; equatorial and axial; conversion between chair and line structures; eclipsed and staggered]

[alkenes – cis/trans vs E/Z vs neither; Cahn-Ingold-Prelog rules; kinetics – rate-limiting step; thermodynamics – reaction coordinate diagram; equilibrium]

[reactions of alkenes – simple electrophilic addition; hydration; acid catalysts; solvolysis; vicinal halide formation; oxymercuration-demercuration; hydroboration-oxidation; halohydrin formation; hydrogenation; epoxidation]

[stereochemistry – R/S; phantom atoms; chiral; enantiomers, diastereomers, epimers; optical rotation; racemic mixtures; meso]

[alkynes – acetylides and alkylation; modified hydroboration [review of mechanism]; hydrogenations: full, cis (Lindlar's), trans (Na, NH<sub>3</sub>); tautomerization – base and acid]

[delocalization – resonance; SMOGs; conjugation & hyperconjugation]

[Sn1/Sn2/E1/E2 – structural effects – substrate, nucleophile, leaving group, solvent; six aspects; knowing which one occurs]

[abbreviations – DMSO, DMF, MCPBA]

[free-radical halogenation – relative reactivity ratios for Cl and Br and cause of difference; initiation, propagation, termination]

### Hydration

It turns out that the reactivity of alkynes is a bit different than alkenes because of having two pi bonds versus one. It turns out that, using tosic acid or sulfuric acid or some other acid catalyst is just not quite strong enough in order to get an alkyne to react in simple electrophilic addition the same way that an alkene can react. This reaction is not going to involve necessarily [mercury] acetate, it's not exactly the same kind of oxymercuration reaction we've seen previously, but the mercury ion is going to end up being the initiating electrophile in this reaction. Let me show you this last type of reaction you need to know.

Let's say you have a terminal alkyne like but-1-yne, and that we react it in a mixture of sulfuric acid in water, and then mercury(II) sulfate. Mercury is still the big, squishy kind of atom that we had talked about in the past, so with the alkyne, it's still going to form a cyclic-style intermediate. The mechanism for this is going to look similar to what we've covered in the past, but because this is more of an ionic compound, it's going to look very plain compared to the oxymercuration-demercuration. I'll show the reaction in the same way I did before, which is where we have the pi bond attacking the mercury, and then a pair of electrons from mercury back-attacking towards the alkyne, forming a cyclic intermediate. Notice that the mercury was +2 charged when this began, so even at the end, it's still gonna have a +2 charge. That ring is very unstable, but one of the bonds is more unstable than the other, for exactly the same reasons as we've covered previously – that it is going to be more favorable to generate a positive charge on the secondary versus primary position, which means the bond to the secondary positions going to be longer and weaker than the one to the primary, so the bond at the secondary position is going to be the one that breaks. If there is water in solution, it can attack, pushing the mercury [ring] open. Initially, we're going to have an oxonium ion, which will deprotonate, and we end up with our first stopping-off point – the formation of an enol.

But it is an enol, which means it's not thermodynamically stable; because you're in acidic solution, it's going to rearrange. This is going to be acid-catalyzed tautomerization. First thing that happens is the double bond's going to attack H<sup>+</sup>. For Markovnikov addition, we would expect that the carbocation's going to form on the more substituted position anyways. Besides the fact that you would have hyperconjugation possible, realize you've got a pair of electrons on the oxygen right next door as well, which could undergo resonance and therefore stabilize that positive charge. For both of those reasons combined, the carbocation's going to form where the alcohol is located. Technically, we could write that as a reversible mechanism. Hydrogen adds in; we form a carbocation, which is delocalized, and we form a carbonyl. The reason this happens is thermodynamics. It can deprotonate, but as soon as it does, it could get reprotonated again. At the same time that it occurs, the mercury, to become neutrally charged, can lose its connection to carbon. If that bond collapse occurs, it's going to push the carbonyl back open again. It could then grab a hydrogen, which means you have gotten rid of the mercury, but you yet one more time made an enol, so it tautomerizes one last time, and we end up with a ketone.

Let me walk through the reaction one last time. You're going to have mercury involved, somewhat similar to the oxymercuration-demercuration reaction. If you can get through that much of it, you can get to the enol, which then, it's tautomerization. This is acid tautomerization. The one last unusual thing about this reaction compared to oxymercuration-demercuration is this loss of mercury at the end, which forms an enol which tautomerizes.

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Structures

Identical to those from lecture 26A (12/07/11)