## Lecture 28A • 12/12/11

[final review]
[atomic and molecular orbital theory – bonding and antibonding; sigma and pi bonds; molecular geometry; hybridization; methane]
[acids and bases – effects of hybridization, induction, and resonance; pKa]
[nomenclature – common names: isopropyl, isobutyl, sec-butyl, tert-butyl, neo-pentyl, allyl, benzyl, aspargyl; alkanes, alkenes, alkynes, alcohols, alkyl halides, alkenols; Cahn-Ingold-Prelog rules]
[physical properties – in lab]
[rotomers – syn(periplanar), anti, gauche, eclipsed, staggered, butane, Newmann projections]
[cyclohexane – ring and angle strain; equatorial and axial; chair and boat forms; ring inversions]
[alkenes – E/Z vs cis/trans; kinetics – rate-limiting step; thermodynamics – reaction coordinate diagram, Hess's law; equilibrium]
[reactions of alkenes – Markovnikov addition; simple electrophilic addition; hydration; acid catalysts; oxymercuration-demercuration; hydroboration-oxidation; halohydrin formation; vicinal halide formation; epoxidation; reduction (hydrogenation)]
[stereochemistry – R/S; phantom atoms; enantiomer, diastereomer, epimer; optical rotation; racemic mixtures; meso]
[alkynes – hydrogenations: full, cis (Lindlar's), trans (Na, NH3); modified hydroboration; tautomerization – base and acid; alkylation (acetylide)]

acid tautomerization – First, the double bond attacks an H+. You form a carbocation, which is going to form where the oxygen is, because there's so much stabilization from that oxygen exactly because it's able to undergo resonance. Once it undergoes that resonance, we now have a carbonyl that can get deprotonated. We switched a carbon-carbon double bond for a carbon-oxygen double bond.

[six aspects of hydroboration of alkynes]

The utility would be to convert an alkyne into either an aldehyde or a ketone. Remember that this is different because, right after hydroboration, you put an –OH group on an alkene; that's not thermodynamically stable, that's why we saw that base version of the tautomerization mechanism. The –OH group ends up at the end of the molecule, so if you have a terminal alkyne, that's when you're going to get the aldehyde. If the alkyne's internal, then even if it's the less substituted position, you're still going to end up with a carbonyl internal, which is when you'd get a ketone. The synthetic utility is to go from an alkyne to either an aldehyde or a ketone. As far as reagents, it's this modified borane, followed by hydrogen peroxide and sodium hydroxide. As far as conditions, no water, just like we had for regular hydroboration. In terms of mechanism, we did go through the mechanism for that one. For regiochemistry, it's anti-Markovnikov because it's borane. For stereochemistry, there is none, because you don't end up with stereocenters [unless deuterated borane used].

[delocalization – hyperconjugation; resonance and conjugation; SMOGs]
[Sn1/Sn2/E1/E2 – mechanisms; knowing which one occurs; structural effects – substrate, nucleophile, leaving group, solvent]
[abbreviations – DMSO, DMF, MCPBA]
[free-radical halogenation – relative reactivity ratios for Cl and Br and cause of diference]

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**Structures** *(remaining structures identical to lecture 26B)*

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