Do CH 9 first!!!

1. Mechanism of electrophilic addition



* 1. product maybe syn or anti depending on conditions or reagent
     1. bridging electrophiles will force anti addition
     2. ion pair formation favors syn addition, show on board
     3. free ions give mixture (stablized carbocation or polar solvents)
  2. Bromination
     1. anti Br2 addition for almost all alkyl (I2 favored)



* + 1. anti product supports bridged intermediate
    2. ion detected in superacid



* + 1. for alkyl substituted alkenes, nearly 100% anti
    2. less stereospecific for aromatic substitutents (favored)

?

* + 1. less stereospecific in polar solvents (favored)

?

* 1. substituent effects - electron donation and delocalization accelates



* 1. Chlorination
     1. similar to bromination but bridged species less stable
     2. more syn formation
  2. Fluorination – to violent
  3. Iodination - product unstable
  4. Mixed halogenations: BrCl > BrBr > ICl > IBr > I-I: order?
     1. Least electronegative atom adds
     2. Faster for more electron deficient electrophile and more electronegative leaving group

1. HX addition: Markovnikov's rule: what is it?
   1. HI, HBr, HCl, H2SO4, H2O, ROH, RSH, RCOOH all add to alkenes in acid conditions
   2. H+ does not bridge
   3. AdE2 bimolecular stepwise addition: RDS is H+ addition



* 1. Markovnikov addition is preferred- proton adds to least substuted carbon (form most stable cation



* 1. Carbon cation rearrangements can occur



* 1. HX adds H+ in non-polar solvents
  2. Protonated solvent adds in protic solvent, i.e. H3O+
  3. HI > HBr > HCl >> HF
  4. Concerted addition, AdE3, termolecular concerted addition, reverse of E2
     1. break  bond, make 2  bonds
     2. addition is anti, favored for unreaction olefins, (unstable cation formation)
     3. mechanism favored when solvent participates (HBr in HOAc)

 

* 1. Stepwise addition(AdE2) is favored by strong acids (CF3SO3H in HOAc)

1. Hydration
   1. Acid catalyzed



* 1. Reverse of dehydration of alcohols
  2. Need strong acid with poor nucleophile/conjugate base,HBr/water?
  3. Dilute sulfuric acid common, concentrated sulfuric acid for reverse

1. Hydroboration-oxidation – convert alkene to alcohol (water addition – hydration)
   1. Hydroborane – equilibrium with diborane
      1. BH3 has empty orbital and BH bond is polar (H more electronegative)
      2. B accepts  electrons! BH3 is a Lewis acid and hydride donor?
      3. Only 4 electrons total in two bridge, low barrier for dissociation



* 1. Borane addition to C=C
     1. Boron accepts  electrons
     2. attaches to least substituted carbon (Markovnikov)
     3. H migration to electron deficient center
     4. often concerted- no C-C rotation, stereochemistry is preserved



* + 1. Two more equivalents of hydride: trialkylborane



* 1. Hydro oxidation- transfer to oxygen
     1. Trialkylborane, equivalent to carbon cation without charge
     2. Hydroperoxide anion very good nucleophile, adds to electron deficient center
     3. R migration to electron deficient O center



* 1. Base hydrolysis
     1. Hydroxide adds to alkyl borate
     2. Form tetrahedral intermediate from trigonal intermediate common process
     3. substitution of OR by OH, addition-elimination, not an SN2
     4. three equivalent of alcohols



* 1. why not just use regular water addition?
     1. Avoid rearrangement of cations
     2. Stereospecific – retain stereochemistry during addition and migrations
     3. Complementary regeochemistry to acid catalyzed hydration- anti-Markovnikov



* + 1. H. C. Brown

1. Carbon cation addition to alkene
   * 1. Dimer/trimer/polymerization
     2. Potonate  electrons/cation adds to  electrons



* + 1. Further addition can occur but steric inhibition slowes down reaction
    2. Dissociation of proton forms new alkene



* + 1. Hydrogenation yields isooctane: 100 % octane rating



1. Oxidative hydroxylation- **skip Osmium tetroxide and permanganate**
   1. Peracid is self activating, electron deficient center
   2. Oxygen adds to both carbons simultaneously, form epoxide
   3. No rotation about CC bond, preserve stereochemistry
   4. Similar chemistry to bromonium but epoxide is stable product



* 1. Acid or base catalyzed hydrolysis yields diol: anti addition



* 1. Asymmetric epoxides have different products for acid and base catalyzed reactions
     1. Base conditions favor nucleophile attack least substituted carbon (question)



* + 1. Acid conditions create positive charge at more substituted carbon



1. **Skip Hydrogenation and Ozonolysis (later in cycloaddition)**
2. Addition to dienes
   1. 1,2 versus 1,4 addition (aprotic v. protic)



* 1. HCl addition
     1. at – 60 oC 75% 1,2 addition, 20-25% 1,4 addition
     2. 20 oC? 25% 1,2 addition, 75% 1,4 addition
     3. Ion pairing keeps Cl from roaming and 1,2 is favored
     4. Higher temperature 1,4 is favored
     5. Heating pure 1,2 or 1,4 get the same mixture at high temperature, why?



1. **Skip Diels Alder (chapter 12)**
2. Nucleophilic addition
   1. Electron withdrawing group stabilze negative charge



* 1. Michael reaction with carbon nulceophiles
     1. 1,2 addition favored for more reactive group without steric hindrance
     2. 1,4 addition favored for strerically unhindered 4 position if 2 position is blocked?





* 1. Enolates prefer conjugate addition (less ion pairing) set up catalytic conditions

