January 19, 2005
Lecture 2: Structure and Bonding in Organic Chemistry II
Sections 22.3-22.4  Exercises 51-70
Reading: Sections 21.1-2

Keywords: conjugation/aromaticity; functionalization; alcohols, ethers, aldehydes, carboxylic acids, esters, amines; peptide bond

Z=H – family of hydrocarbons – continue with unsaturated hydrocarbons
add one or more sp² or sp C atoms C=C, C-H, C≡C bonds ⇒ alkenes and alkynes (alternative hybridizations)
→ simplest examples are the ethylene, ethyne (acetylene)
→ geometric isomerism: cis/trans or Z/E but-2-ene (need to break the π bond to change conformation)
→ compare
cyclohexane  cyclohexene  cyclohexadiene  cyclohexatriene  benzene
boat/chair only cis exists only cis conjugation resonance structure aromatic

How do we know the differences? ⇒ Chemical reactivity toward X₂ (X = H, Cl, Br)
for C-H substitution addition reaction addition reaction substitution with
with C-X forming two C-X forming two C-X H-X formation
in 1 and 4 positions

Z=F,Cl,Br,I – family of halocarbons: σ bond formation between C sp³ and X sp³ (note hypervalency for Cl,Br,I)

Z=O,N – hybridizations can be sp³ or sp² (sp for N): σ and/or π bond(s) formation between C and O, N

HO- alcohols O sp³ – to C sp³ ⇒ aliphatic
- to C sp² ⇒ vinyl/allyl
to aromatic C ⇒ phenyl/benzyl

-O- ethers O sp³
-C(=O)H aldehydes O sp²
-C(=O)- ketons O sp²
-C(=O)OH carboxylic acids O sp³/O sp³; carboxylate anion

Properties of functionalized hydrocarbons strongly influenced by the electronegativity of Z:
O,N,F,Cl,Br more I equal H less electronegative that C
more electronegative Z ⇒ more electron density on Z ⇒ more nucleophilic (positive charge liking)
less electronegative Z ⇒ less electron density on Z ⇒ more electrophilic (negative charge liking)
lone pairs, anions, δ⁻ approach ⇒ C (δ⁻) - O,N,F (δ⁻) ← H⁺, cations, δ⁺ approach
also C sp³ < C sp² < C aromatic < C sp – changes in electronegativity

alcohols: hydrogen bonding (compare boiling points of hydrocarbons and alcohols); how to make the OH proton acidic → change C sp³ to C sp² – note that vinyl alcohol is unstable; change to aromatic C, phenols are weak acids

aldehydes/ketones: oxidation product of primary/secondary alcohols; δ⁻ oxygen can be readily protonated (base)
carboxylic acids: oxidation product of aldehydes; weak acids (stronger than the phenols), O sp² δ⁻, C sp³ δ⁻⁺, O sp³ δ⁻, H s δ⁺
esters: alcohol+carboxylic acids ⇒ ester formation with water elimination (condensation)

amines: importance in biology as a functional group of amino acids: most simple: glycine, in zwitter ionic form H₃N⁺CH₂COO⁻; oligomerization ⇒ formation of peptide bond by water elimination