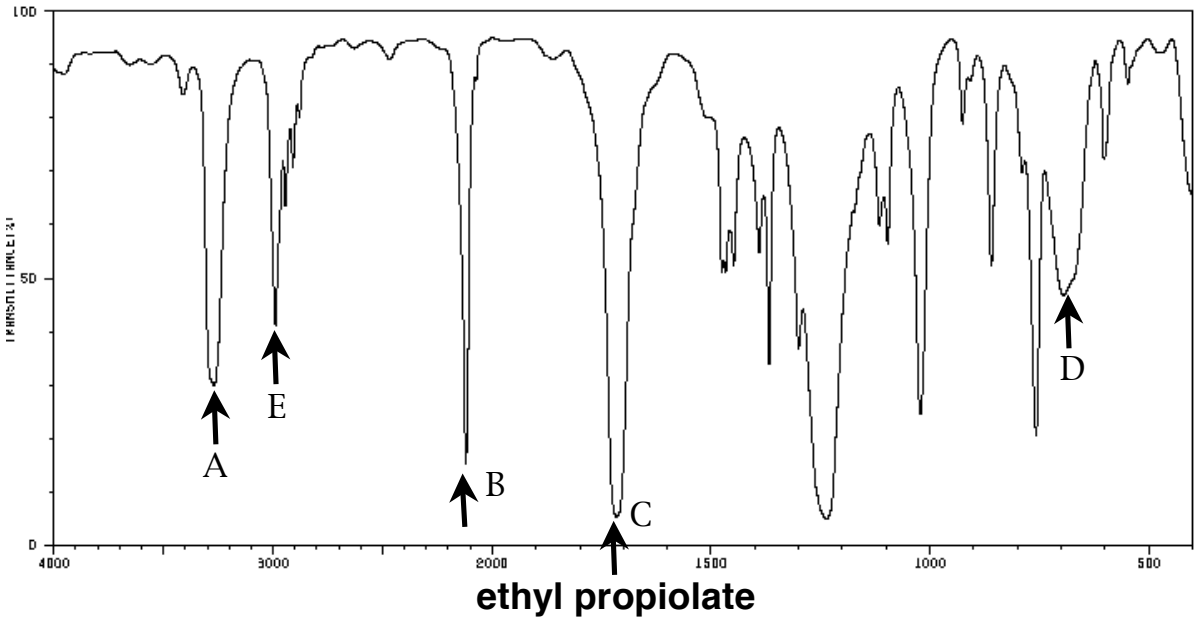
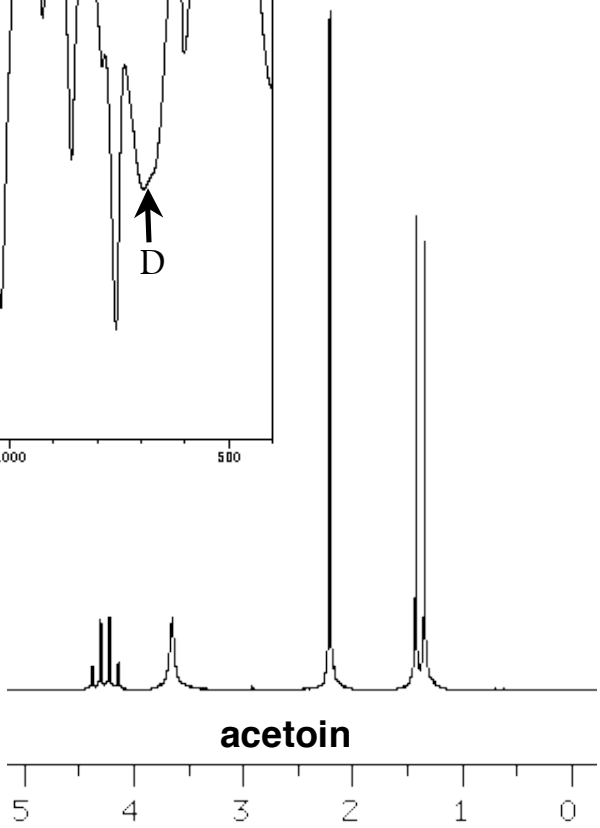
Chemistry 125 Seventh Examination Answers **April 13, 2007**

This Exam Average 66.3 1/3 of scores > 74 2/3 > 64 A > 230 A- > 205 B+ > 180
Three Exams Average 195.6 1/3 of scores > 228 2/3 > 181 B > 150 B- > 125 C+ > 105

1. (12 min) One of spectra below is for ethyl propiolate, H-C≡C-C(=O)-O-CH_2-CH_3, the other for acetoin, CH_3-C(=O)-CH(OH)-CH_3. ***Label*** each spectrum with the compound name ***and explain*** with just a few words ***every*** significant PMR peak and the four IR peaks labeled **A-D**. (**E**) is given as an example.



ethyl propiolate



acetoin

(E) alkane C-H stretch, high frequency because H is so light

(A) acetylene C-H stretch, high frequency because sp hybridization gives strong bond, and H is so light.

(B) acetylene C≡C stretch, high frequency because of triple bond, but not as high a low-mass H-X stretch. Intense because the acetylene is unsymmetrical (terminal).

(C) ester C=O stretch, high frequency because of double bond, very high intensity because of high dipole moment

(D) Bending of C≡C-H. Bending is easier (lower frequency) than stretching. Most bending involving C-H bonds is at somewhat higher frequency, but terminal acetylene is especially low, perhaps because H has nothing to run into.

δ 4.3 C-H (area 1) adjacent to both O and carbonyl, both e-withdrawing, hence far downfield. 1:3:3:1 quartet from splitting by 3 H atoms of adjacent CH_3 group. No splitting by OH because of rapid exchange.

δ 3.7 O-H (area 1) Chemical shift difficult to predict because of variable H-bonding. No splitting by adjacent CH because of rapid exchange.

δ 2.2 CH_3 (area 3) adjacent to C=O, thus shifted downfield by electron withdrawal (and perhaps by diamagnetic anisotropy of C=O. No splitting because there are no H atoms on adjacent carbon.

δ 1.4 CH_3 (area 3) adjacent to C-H. Highest field because there are no electronegative groups attached to this C atom. Split into a 1:1 doublet by the lone H on the adjacent carbon.

2. (3 min) Explain what a "normal mode" means in the context of the "fingerprint region" of IR spectra.

A normal mode is a pattern of molecular vibration in which all atoms are vibrating at the same frequency (so as to stay in phase with a fixed frequency of IR light). Normal modes in the fingerprint region involve complicated mixing of many C-C, C-N, C-O stretches and various bends which have similar individual frequencies (analogous to good energy match) and are coupled together by sharing common atoms (analogous to strong overlap).

3. (9 min) Suggest reagent(s) to achieve each of the following purposes: [Just list reagent(s) - NO mechanism required]

a) converting an internal alkyne into a *cis* double bond H_2 / Pd or Pt catalyst poisoned (e.g. with quinoline).

b) converting an internal alkyne to a terminal alkyne strong amide base (RNH^-), then quench terminal anion quickly with acid so equilibration stops at "anion" position.

c) converting a terminal alkyne into a ketone Hg^{++} / H_2O / H_2SO_4

d) converting a terminal alkyne into an aldehyde B_2H_6 (or BH_3), then HOOH/OH^-

e) converting a C=C double bond into a C=O double bond O_3 then H_2O/Zn (or another reducing agent to destroy HOOH)

f) converting a C=O double bond into a C=C double bond Ph_3P=CHR (Wittig reagent)

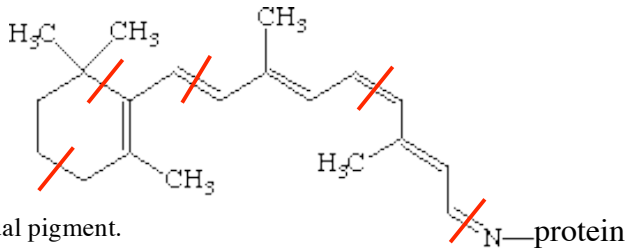
4. (4 min) Explain ***why*** different kinds of magnetic fields are appropriate for chemical NMR and medical MRI.

For medical MRI it is important that the applied magnetic field vary substantially from place to place, so that it is possible from the precession frequency to tell where in the sample the signal originates. [In BOLD imaging nearby magnetic O_2 molecules make proton signals stronger by facilitating "relaxation." Thus seeing ***where*** the signals become stronger, one sees where O_2 concentration increases because of neuronal activity.]

For chemical NMR it is important that the applied field be as uniform as possible (varying only within a very small fraction of a part per million), so that differences in local fields are attributable to different locations within molecules (due to chemical shift and spin-spin splitting), rather that to the location of molecules in the sample.

5. (5 min) Answer A **OR** B, ***NOT BOTH***

(A) In studying the mechanism of lanosterol biosynthesis using NMR and ^{13}C double-labeled isopentenyl pyrophosphate, why is it crucial that most of the isopentenyl pyrophosphate not be labeled at all? That is, ***why*** was ***dilute*** double labeling used?



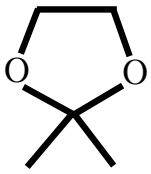
(B) Explain why this molecule on the right is well suited to be the visual pigment.

(A) When the double labeling is dilute, two ^{13}C atoms in the same individual product molecule must have come from the same starting material molecule. Thus if a signal appears as a doublet due to ^{13}C-^{13}C splitting, ^{13}C atoms that were adjacent in a starting material molecule must have been incorporated together so as to remain adjacent to one another in the product. In the case of lanosterol two pairs of ^{13}C signals appear as singlets, because the ^{13}C atoms were separated by methide shifts. The other 8 ^{13}C signals appear as doublets because there was no such rearrangement.

(B) Rhodopsin is a good visual pigment because the *n* to π* transition from the unshared pair of the nitrogen to the conjugated π system occurs at unusually low energy (in the visible part of the electromagnetic spectrum). This is because favorable mixing of the many localized π* orbitals in the conjugated chain lowers the energy of the LUMO to approach the energy of an isolated p orbital. [In grading I required mention of the *n* electrons, as discussed in class, although in truth the N unshared pair is protonated in rhodopsin, so the transition is probably π to π* rather than *n* to π*.]

[Coincidentally, the molecule in B is made from four isopentenyl pyrophosphates linked together – see red cuts]

6. (7 min) Show the mechanism for acid-catalyzed hydrolysis of the following molecule to 1,2-ethanediol and acetone. **Use curved arrows**. Several steps are required



This mechanism is shown in detail in slide 16 of the lecture of 3/9/07 and again in slide 2 of the lecture of 4/11/07. The only difference is that instead of releasing two independent alcohol molecules, the cyclic ketal releases a diol in two stages (first by opening the ring to give the hemiketal, then by releasing the diol altogether in the second stage.

7. (10 min) Historically organic chemists speak of "electrophilic" addition of CCl_2 to the C=C group of an alkene and "nucleophilic" addition of CH_3Li to the C=O group of a ketone. Draw pictures to explain in terms of the ***shapes*** of ***reagent*** HOMOs and LUMOs, and ***transition state structures***, how these processes are fundamentally similar.

The appropriate HOMOs and LUMOs and the transitions state geometries are shown in slides 6 and 30 of the lecture of 3/7/07. Of course they can be simplified from the computer-drawn versions to something more like what is shown for Cl_2C: in slide 4 of the same lecture.

In both cases a low LUMO (*2p* orbital of C or Li) is mixing with the π orbital of the alkene, while a high HOMO (unshared sp^2 hybrid pair of C or Li-CH_3 sigma bond) is mixing with the π* orbital of the alkene.