

Chemistry 125
December 18, 2009

First Semester
Final Examination

Name _____

This exam is budgeted for 150 minutes, but you may have 180 minutes to finish it. Good Luck.

1. (20 minutes) Give a brief **definition** for **one** member from each the following 8 pairs of terms used in the Chem 125 this semester. In some cases it might help to give an example. **Circle the One Member from each Pair that you are defining.**

a) Correlation energy / SCF

b) Stereogenic / Epimer

c) Conglomerate / Racemate

d) Synclinal / Enantiotopic

e) Orbital / LCAO

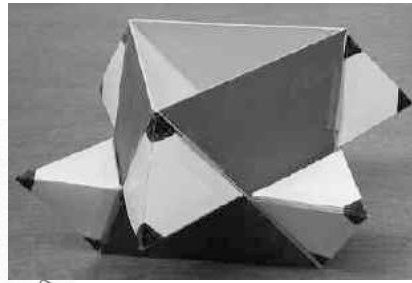
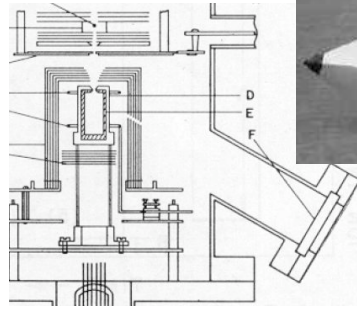
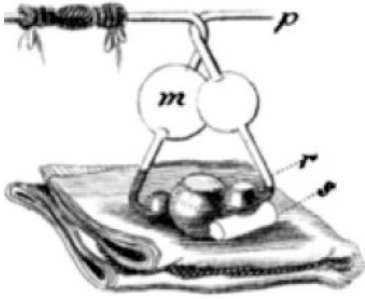
f) Earnshaw's Theorem / Cubic Octet

g) Difference Density Map / 3-Center-2-Electron Bond

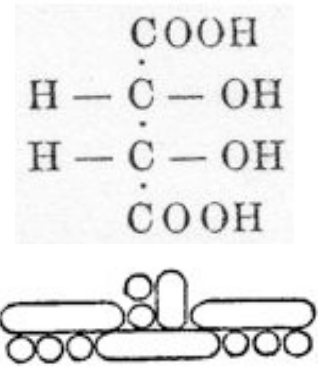
h) Zero-Point Energy / Tunneling

2. (6 min) Draw unambiguous lines to connect each device, model, formula, or notation with its inventor.

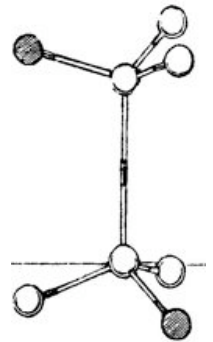
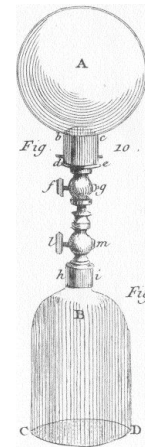
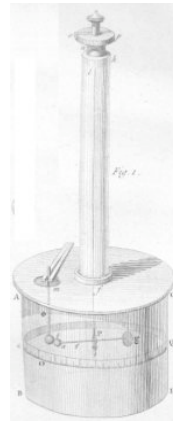
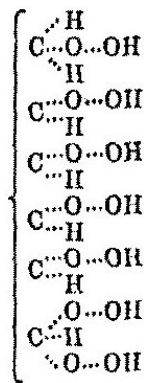
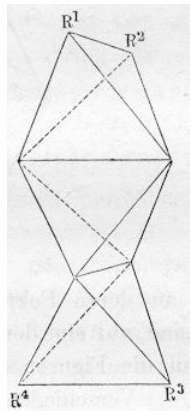
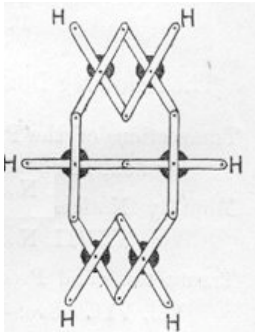
[Note: 12 items – 11 people]



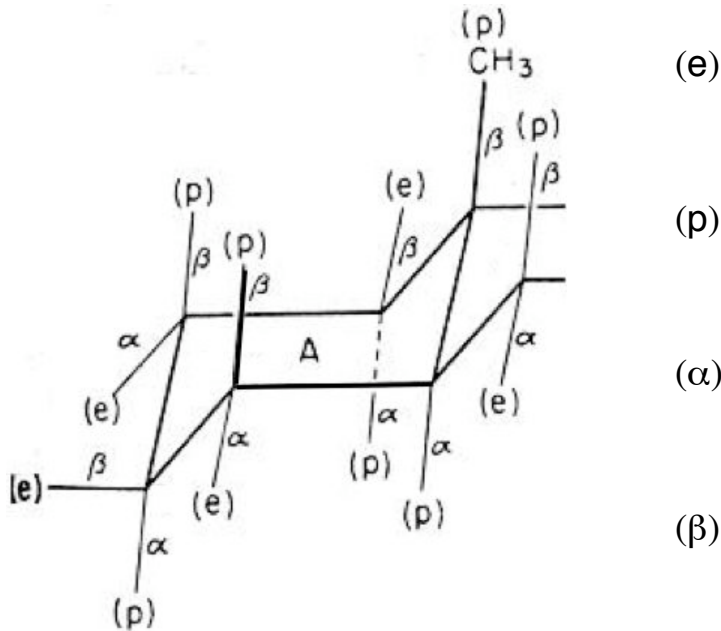
(D)-glyceraldehyde



Chupka Coulomb Couper Dewar Fischer Kekulé Lavoisier Liebig Paternó Sachse van't Hoff

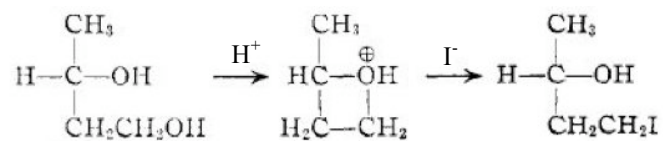


3. (5 min) Correct this picture of ring "A" of a steroid from a 1950 paper, and interpret each of the labels:



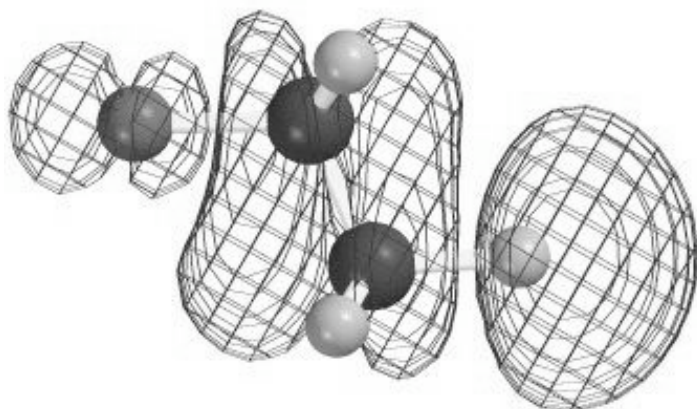
4. (12 min) Tell briefly how **tartaric acid** played an important role in developing the theory or practice of organic chemistry in each of 4 (**FOUR ONLY**) of the following 6 years: **1769, 1830, 1848, 1874, 1949, 1980**.

5. (6 minutes) Explain how the likely formation of a 4-membered ring intermediate by alternative “make as you break” processes rendered the stereochemical course of Levene’s conversion of (-)-1,3-butanediol to (-)-4-iodo-2-butanol problematic.



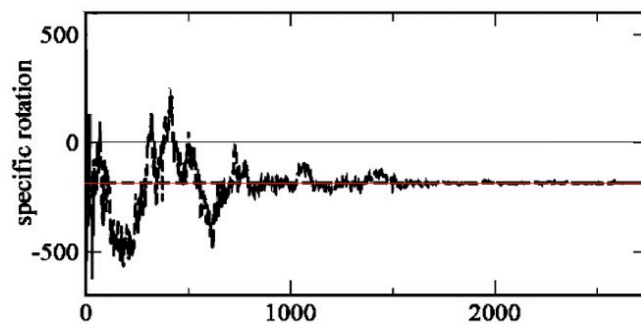
6. (5 min) Where does “overlap” crop up in a quantum mechanical calculation? [Show a mathematical formula.]

7. (6 min) Explain how the LUMO of ethyl fluoride would function during an “E2” elimination reaction with hydroxide.



8. (3 min) Rationalize briefly why, even at high temperature, the most likely energy for a molecular “degree of freedom” is zero.

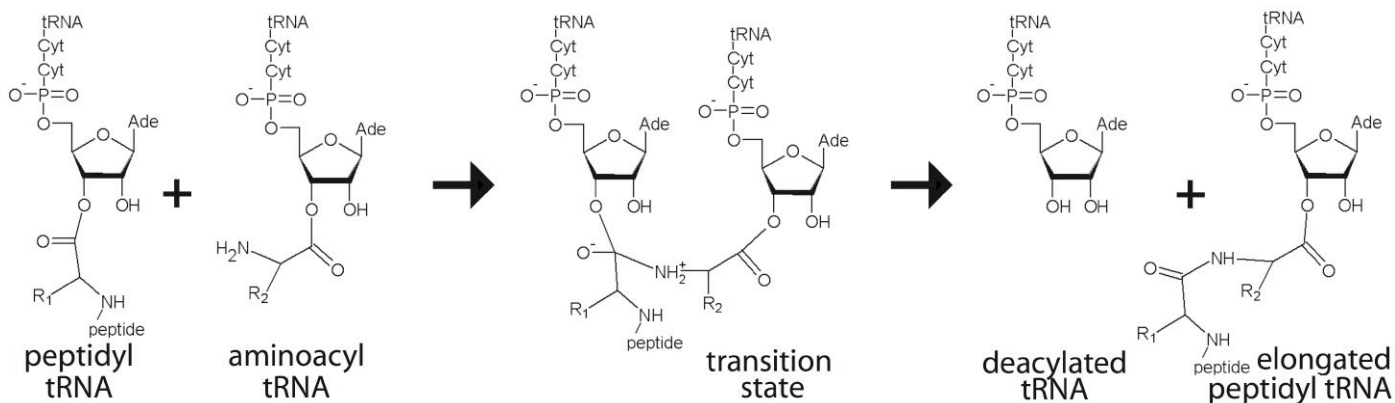
9. (3 min) Explain in a few sentences why compounds that inhibit crystal nucleation help treat malaria.
10. (4 min) Explain why there was reason to suppose that a chiral switch might not work for the sulfoxide omeprazole (Prilosec).
[Words alone will do; you need not draw molecular structures.]
11. (3 min) Explain this graph and what it says about calculating the optical rotation of an organic compound.



12. (6 min) Explain in terms of the factors influencing hybridization whether H_3O^+ should be planar or pyramidal.

- 12.** Big news in the Chemistry and MB&B Departments at Yale this semester was the Nobel Prize awarded to Prof. Steitz for his X-ray studies of the ribosome (together with Profs. Moore and Strobel and their coworkers). The remainder of the exam consists of questions on this theme.

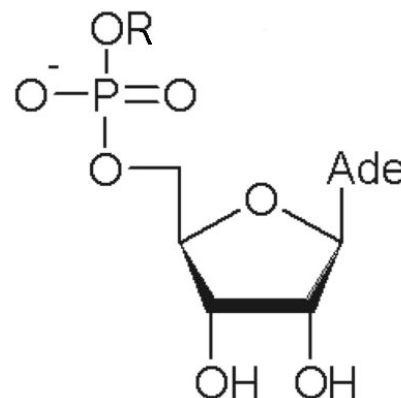
The crucial steps in the programmed biosynthesis of proteins catalyzed by the ribosome are shown in this figure from a 2005 Steitz-Strobel paper:



- A.** (3 min) In the starting materials and products of the scheme above (neglecting the “transition state”) **CIRCLE** and **NAME** the **four functional groups** whose bonding changes or has changed during the process.
- B.** (7 min) Many of the names in this scheme include the **suffix “yl”**. Tell how this suffix was first used in a publication in 1832, what it was used to name, and how it related to the general theory of organic chemistry that was proposed in that paper.

- C.** (5 min) Notice that all compounds in the scheme include this structure, where “Ade” stands for adenine, a group with a nitrogen atom that links to the 5-membered ring. **Add H atoms** to the C atoms where they have been omitted being careful to **show the configuration at each carbon unambiguously**.

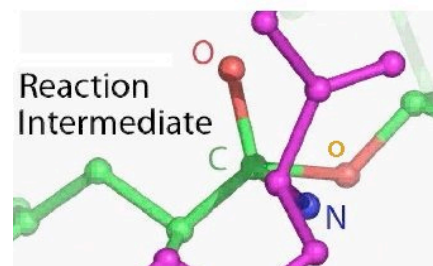
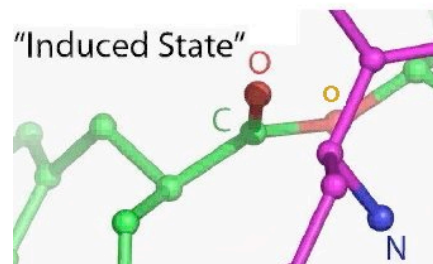
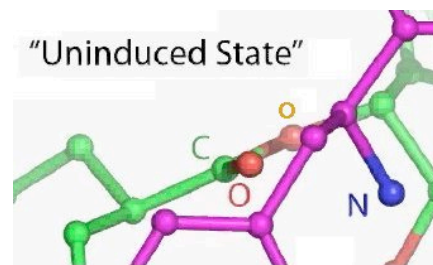
Label the **two carbons bonded to the ring oxygen** with the proper **CIP** designator of their absolute configuration.



- D.** (8 min) **Explain whether or not you would expect the ring in Question C to be planar.**
In your explanation mention at least **3 molecular mechanics factors** that should influence the ring shape **and** mention the **analogy to another familiar five-atom ring.** (You might include a sketch to illustrate your thinking)
- E.** (3 min) Discuss briefly whether the force between the **OH groups** on the ring in Question C should be attractive or repulsive.
- F.** (4 min) Suppose the $\text{CH}_2\text{-OPO}_2\text{-OR}$ group in the compound of Question C is similar in shape and size to $\text{CH}_2\text{-CH}_2\text{-C}(\text{CH}_3)_3$. Would you expect this group to have a larger or smaller **A-value** than the t-butyl group when it is a substituent on **cyclohexane**? Explain your thinking.

In his Nobel address ten days ago Prof. Steitz showed a movie illustrating how the ribosome changes shape when the appropriate aminoacyl-t-RNA comes along, pushing around the reagents and thus facilitating the reaction shown in the scheme on page 6.

The movie was based on his **x-ray studies of a number of complexes** of different relevant molecules with the ribosome. Three key x-ray structures are summarized in these figures, where important atoms of the reacting groups are labeled as N, C, O. [H atoms are omitted.] The “Uninduced State” has an erroneous aminoacyl-t-RNA; the “Induced State” has the correct t-RNA; and the “Reaction Intermediate” corresponds to what they labeled “transition state” in the scheme above.

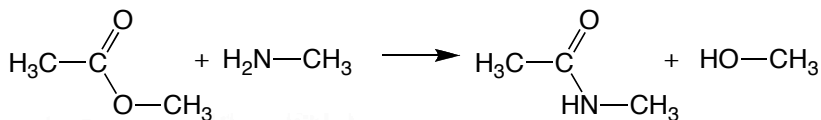


- G.** (5 min) **Name** the molecular orbital that makes the CO group reactive in this process. Also **draw it**, explaining the **size** and **sign** of its atomic orbital components.
- H.** (4 min) Explain how you would expect the adjacent oxygen atom to influence the reactivity of the CO orbital you drew in Question G.
- I.** (4 min) Explain in terms of **overlap** why the “Induced State” structure is so much more favorable for reaction than the “Uninduced State”.

- J.** (8 min) In the 2005 paper describing this work Steitz wrote, "Small-molecule studies¹⁵ show that that the optimal angle for nucleophilic attack is about 105° from the plane..." His reference 15 is to work by Swiss chemists in 1973. Explain how those workers (with initials B and D) determined this angle, and how their work with small-molecule was analogous to this work with the enormous ribosome.

- K.** (5 min) Here is a simplistic model for the chemical transformation catalyzed by the ribosome:

Show how to use the following table of average bond energies (naively - appropriate or not) to estimate the change in energy for this reaction.



Average Bond Energies, kcal mole⁻¹

H	C	N	O	F	Si	S	Cl	Br	I	H	C
104	99	93	111	135	76	83	103	87	71	H	C
	83 ^a	73 ^b	86 ^c	116	72	65	81	68	52		

^a C=C 146, C≡C 200.

^b C=N 147, C≡N 213.

^c C=O 176 (aldehydes), 179 (ketones).

- L.** (4 min) Actual data for the compounds in Question K (from <http://webbook.nist.gov/chemistry/>) suggest that the transformation is favorable by 14 kcal/mole. **What values would you look for** on such a website in order to calculate the energy change? Use this value to **estimate an approximate equilibrium constant** at room temperature,
- M.** (5 min) Propose an explanation for the discrepancy between the actual value of the energy change given in Question L and your estimate from Question K.
- N.** (6 min) The larger product molecule in Question K much more **strongly prefers to have a planar conformation** than does the larger starting material molecule. **Explain** how this preference relates to your answer to Question M **AND explain** a second way in which this preference should influence the free energy change for the reaction.