

Chemistry 125 Final Examination
May 7, 2004

Name _____

This exam is budgeted for 150 minutes, but you may have a full 180 minutes to complete it.

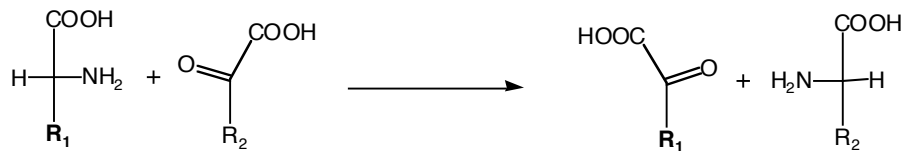
I. (30 min) Provide **as specific an example as you can** (real experimental results, not just theory) to illustrate **5 (five only)** of the following 7 assertions:

- a) A process which appears “fast” when using one type of spectroscopy can appear “slow” when using another.
- b) “Electrophilic” addition to an alkene can involve an important nucleophilic component.
- c) An reaction with a cation intermediate can involve rearrangement of the carbon skeleton.
- d) There can be a difference between “kinetic” and “equilibrium” product distributions.
- e) Nature makes good use of the Claisen condensation.
- f) Special transition-state stabilization can circumvent the Hammond Postulate.
- g) Dilute double labelling with a ^{13}C can give mechanistic information unavailable from single labelling.

II. (11 min) Answer **EITHER a or b.**

- a) Describe the analogy between why one uses a very strong base to obtain a terminal alkyne by isomerization, and why one uses base, rather than acid, to saponify fats.
- b) In a process called “transamination” two molecules can react to interchange amino and ketone functionality. Propose a mechanism for this conversion. (No curved arrows are necessary; just draw at least two intermediate molecules)

[Hint: imine formation and allylic rearrangement are involved.]



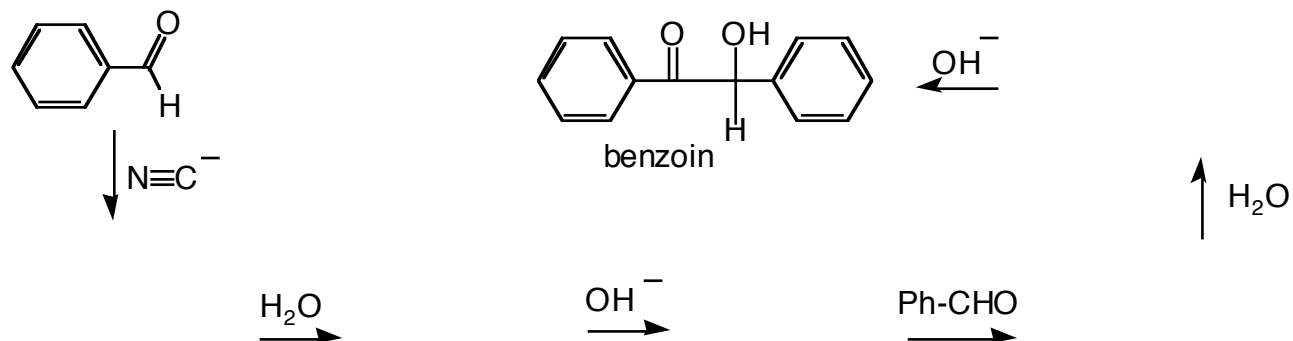
III. Benzaldehyde, Ph-CHO, the “oil of bitter almonds”, played an important early role in the development of organic chemistry, in part because of its easy oxidation to benzoic acid by molecular oxygen, but also because of the reaction in which it reacts with itself to form “benzoin”, an α -hydroxy ketone, and because of its ability to participate in reactions that form β -hydroxy ketones.

- A. (16 min) The oxidation of benzaldehyde to benzoic acid in the presence of air involves two reactions with very different mechanisms. The only reagent required for the transformation is molecular oxygen, whose oxygen atoms change oxidation state from 0 to -1 in the first reaction, and from -1 to -2 in the second.

Write mechanisms for **both reactions** involved in converting benzaldehyde to benzoic acid. Use **curved arrows** to show electron pair motion **in the second reaction** (not necessary for the first).

B. Cyanide is an important catalyst for the benzoin condensation.

- 1) (10 min) See if you can figure out how the reaction works by drawing the five intermediates in this scheme.
(No curved arrows necessary, just **draw the five intermediate structures.**)



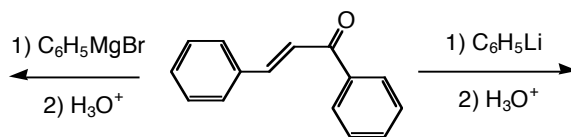
- 2) (5 min) Cyanide is uniquely suitable for catalyzing this reaction because of its influence on the third step (reaction with hydroxide). **Explain this influence.** [Hint: to help figure out the structure of this intermediate consider what must happen in the fourth step in order to proceed toward the ultimate product]

- C. 1) (6 min) Suggest reagents for converting benzaldehyde to the following molecule. (No mechanism, just reagents)
[Hint: only one of the phenyl groups comes from benzaldehyde.]



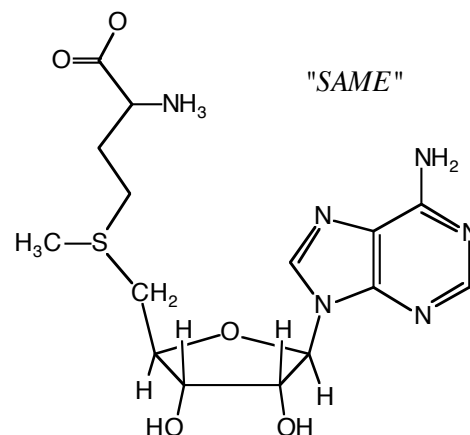
- 2) (6 min) What strong peaks in the **IR** would allow you to differentiate between benzaldehyde and the product of the previous reaction. **Why** are they **strong** and **why** do they have **different frequencies**?

- 3) (6 min) The product from the previous question is converted into different products by reacting with the following organometallic compounds. **Draw these two products.**



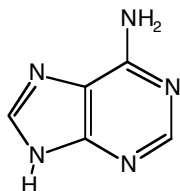
IV. Although we didn't spend time on the more biological molecules near the end of the text, you should be able to explain much of the chemistry involved in their reactions. For example, we can consider **S-adenosyl-methionine** ("**SAME**"), shown on the right, which Nature often uses to add a methyl group to a nucleophilic atom.

- A.** (1.5 min) The drawing shows all of the nuclei of *SAME* (most carbons and the hydrogens attached to them are implicit, of course), but no atomic charges are indicated. **Draw + or - as needed** on appropriate atoms to complete the formula.
- B.** (5.5 min) **Circle** the carbon in *SAME* that a nucleophile should attack most easily. Point out **as many factors as you can** to explain why this carbon should be attacked more easily than any other carbon.

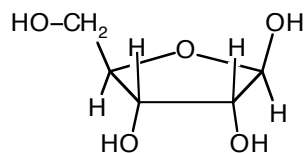


The **SAME** molecule is made up of 3 simpler biomolecules:

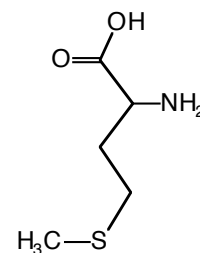
adenine, an "aromatic purine base"



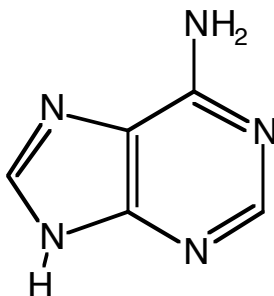
ribose, an aldopentose;



and the amino acid
methionine



- C. (8 min) Although adenine is called a “base” and has five nitrogen atoms, not one of these five nitrogens is drawn protonated in the picture of *SAME*, unlike its methionine nitrogen. On this picture of **adenine** draw clearly the atomic orbital for each of the five N lone pairs (use a few words, if necessary), and **explain** why **each** of these nitrogens should be **less basic** than the nitrogen atom of methionine (bottom of p. 5)



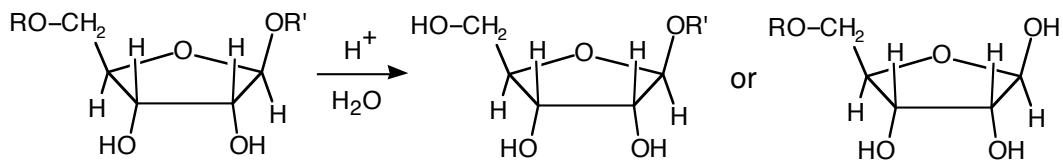
- D. (6 min) **Explain** which of the following features might class adenine as “**aromatic**”:

the **5-membered ring** on the left,

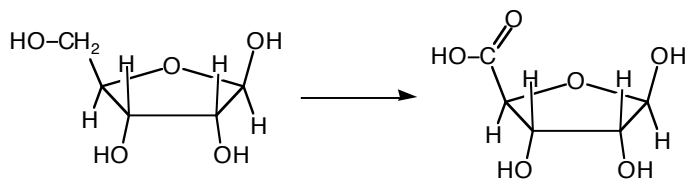
the **6-membered ring** on the right,

the **9-membered ring** of the overall periphery.

- E. (8 min) Which of the following hydrolysis reactions would you expect to be faster for the ribose diether below (an analogue of SAME)? **Explain** your choice in terms of the mechanism.

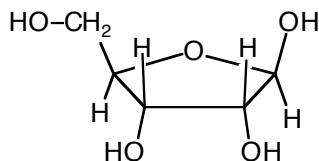


- F. (2 min) What would be the most difficult problem one would face in trying to achieve the following oxidation?

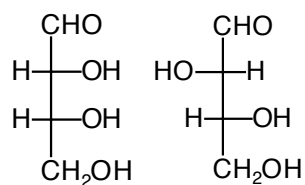


- G. (7 min) Explain how the following protocol might help in achieving the transformation in Question F.
 1) Treat with acid, acetone, and methanol; 2) oxidize with a basic oxidizing agent; 3) treat with acid and water.

- H.** (5 min) **Draw a Fischer Projection** for the **open chain form** of the aldopentose **ribose** (Note carefully which carbon in its closed-ring structure below would be the aldehyde carbon, and be careful about stereochemistry, especially at the next-to-bottom carbon).



- I.** (10 min) Explain how Emil Fischer might have experimentally confirmed the configuration you drew for ribose in Question H, if he had two **UNLABELLED** vials containing pure samples of the aldotetroses shown below, and the ability to conduct necessary reactions and observations.



- J.** (7 min) Guess a **pK_a value** involved in protonating of the **carboxylate** group in **SAME** (p.5).
Explain your thinking (perhaps citing other pK_a values for comparison).