

# Chemistry 125 Second Semester Final Examination Name \_\_\_\_\_

**May 4, 2000**

The exam budgets 150 minutes, but you may have 180 minutes to finish it. Good answers can fit in the space provided.

- 1.** (11 minutes) Give as specific an example as you can for **2 of the following 4** items. Make your answers as brief and clear as possible, but try to make them **specific** - e.g. real molecules, real numbers.

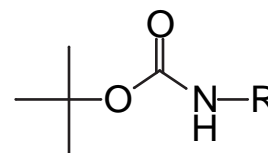
**OMIT 2 items. ONLY YOUR FIRST 2 ANSWERS WILL BE GRADED**

- |                                 |   |
|---------------------------------|---|
| a) An aldol condensation        | c) Use of Isotopes in a Mechanism Study                                 |
| b) <del>A Perkin Reaction</del> | d) <del>Name, Code, &amp; Structure for Three Natural Amino Acids</del> |

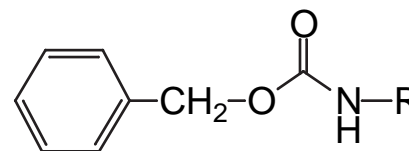
**2. Protecting Groups**

- A)** (5 min) In the synthesis of Palytoxin a diol was protected as an "acetonide". **Draw** the structure of a generic **acetonide** and **explain** why the protecting group is particularly easy to remove.

- B)** (4 min) A common protecting group for  $\text{H}_2\text{NR}$  in polypeptide synthesis is Boc, or t-butoxycarbonyl. **Explain** why it is easily removed to reveal the amine by an acid like  $\text{CF}_3\text{COOH}$ .

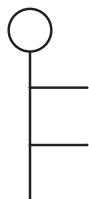


- C)** (4 min) Another protecting group for  $\text{H}_2\text{NR}$  in polypeptide synthesis is Cbz, or carbobenzyloxy. **Explain** (an analogy will do) why it is selectively removed by catalytic hydrogenation, which does not remove the Boc protecting group.

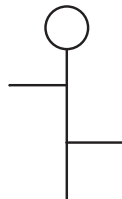


3. (9 minutes) Give **three examples** of compounds whose special stability is predicted by Hückel's rule, and provide **specific experimental data** that establish the stability of **each** of them. The examples must be substantially different (NOT just differently substituted benzenes).
4. (6 minutes) Show the HOMO/LUMO mixing that occurs during conversion of cyclobutene to butadiene. Draw both orbital shape and orbital energy diagrams.

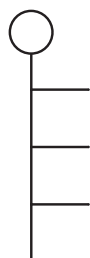
5. The mnemonic device for aldohexoses is *All altruists gladly make gum in gallon tanks*. The nonsensical one for aldopentoses is **RAXL** (rhymes with *axle*) and the one for aldotetroses is **ET** (as in extraterrestrial). In all three cases the mnemonic assumes that the structures are drawn in order with the OH on the lowest asymmetric center to the right and the successive OHs alternating with increasing frequency.



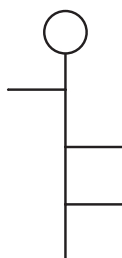
Erythrose



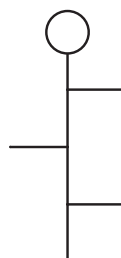
Threose



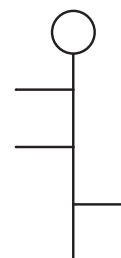
Ribose



Arabinose



Xylose



Lyxose

- A. (1 minute) Explain the source of **one "real"** name and **one "artificial"** name among the six sugars above.

- B. (10 minutes) Suppose you have one bottle with a pure samples of an aldopentose, but labeled only "an aldopentose", and one bottle with a pure sample of an aldotetrose, but labeled only "an aldotetrose". Your intuition that **the aldopentose is Arabinose** is correct, **but you have to prove it** to Emil Fischer's satisfaction by using his chemical methods (and/or Heinrich Kiliani's).

Describe the reactions or other **experiments** you would do, their **results**, and their logical **implications**. You have no other sugars for comparison, only the two mentioned above.

*Don't suggest more experiments than necessary.*

*Assume that, after a year in Chem 126L, you can be confident of your results and don't need redundancy.*

*You may continue your answer on the back of this page.*

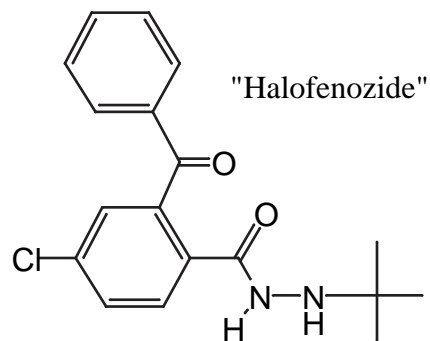
6. (16 minutes) My office neighbor is having a problem with grubs in his lawn, so he has availed himself of a Monsanto product *Grub-B-Gon*, or Halofenozide. (Happily this insecticide does not harm the Spring Tiphia, a wasp whose parasitism on grubs of the Japanese beetle is one hope for controlling this insidious invader.)

Devise a practical **synthesis** of Halofenozide in which **all the carbon atoms must come from** two cheap sources, **toluene** (methylbenzene) **and isobutylene** (2-methylpropene).

You may use any other reagents you desire including  $\text{Na}_2\text{Cr}_2\text{O}_7$  (which can oxidize a methyl group on benzene to a carboxylic acid).

In reactions where more than one product might be expected, comment on the yield and purification of the desired product.

Show reagents and isolable intermediates only - no curved arrows or transient intermediates.



**7. Corian® : Theme and Variations**

We're having our bathroom remodelled. The new sink and shower are made of Corian, which is cheap to make and expensive to buy - a big money maker for DuPont. Corian looks something like marble and has all sorts of delightful properties including stain resistance and ease of working and repair.

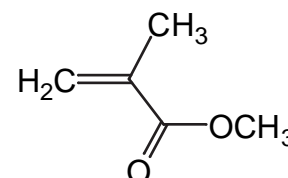
What follows is a stream-of-consciousness tour through this semester of organic chemistry prompted by thoughts about this material.

Corian is an intimate mixture of an organic polymer, mineral pigments, and hydrated alumina ( $\text{Al}_2\text{O}_3$ ), a mineral something like sand. One of the trade secrets of Corian is the *surface-active agent* that allows the minerals, which are covered with hydroxyl groups, to mix intimately with the organic polymer.

**A. (3 min) Explain briefly how soap acts as a surface-active agent.**

The organic polymer in Corian is PMMA, poly(methyl methacrylate), the free-radical polymer of the methyl ester of "methacrylic acid".

**B. (2 min) Give the systematic (IUPAC) name for the PMMA monomer methyl methacrylate:**



**C. (6 min) Suggest a synthesis of methacrylic acid from acetone and other really cheap starting materials.**

Acrylic acid gets its name from "acrolein", the simplest  $\alpha,\beta$ -unsaturated aldehyde, a compound with a very pungent odor, familiar from overheating fat.

**D.** (6 min) Suggest a multi-step **mechanism** (complete with **curved arrows**) for acid-catalyzed formation of acrolein from glycerol.

**E.** (3 min) **What is it about fat** that makes it give acrolein upon heating?

**F.** (4 min) One reason Corian is strong is because the polymer is "**cross-linked**". The identity of the cross-linking agent used during the polymerization of Corian is a secret, but it might be something like *p*-divinylbenzene. **Draw *p*-divinyl benzene and explain** how it could act to rigidify a polymer.

**G.** (4 min) Methyl methacrylate monomers polymerize to PMMA with strict regiospecificity, alternating  $\text{CH}_2$  and  $\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$  groups. Explain why the alkenes don't occasionally go in backwards.

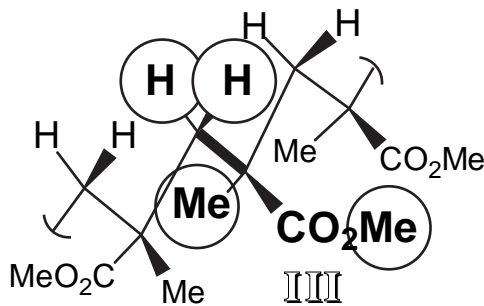
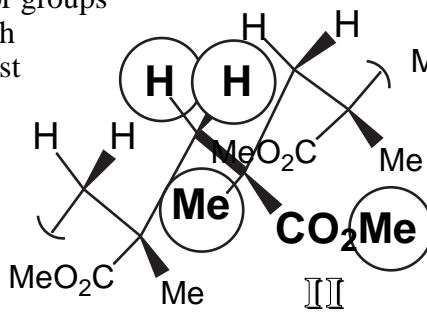
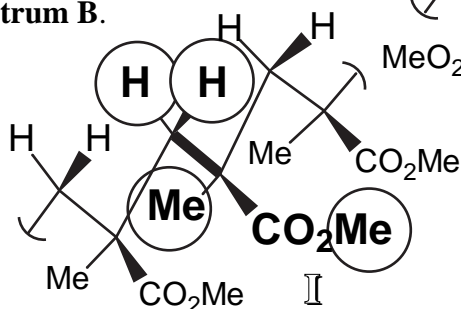
**H.** (12 min) The PMMA in Corian is stereochemically atactic. That is, along the chain a **given monomer unit** (shown in bold face) can occur in **three different environments**, numbered **I, II, III**.

Samples of PMMA that were nearly pure stereochemically were prepared independently and gave the NMR spectra shown below.

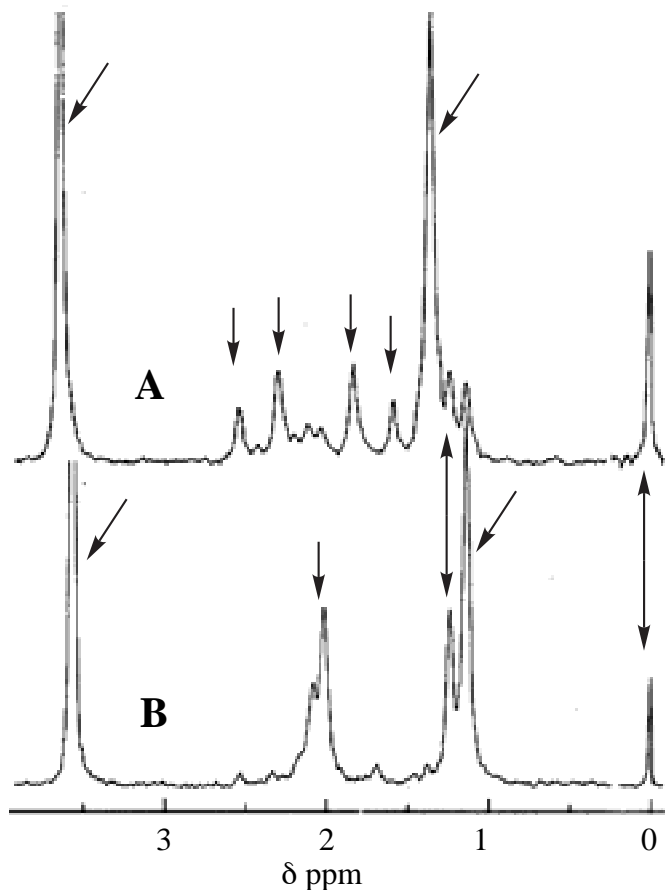
A is mostly one structure, B is mostly another, and each contains a small amount of the other structures.

a) Connect each single-headed arrow in **Spectrum A** with one (or more) circled atoms or groups in **ONE** of the structures I-III. Each circled feature in that structure must be connected to one or more single-headed arrows.

b) Do the same for **Spectrum B**.



c) Also explain the double-headed arrows.



- I. When Corian is damaged, it can be repaired by mixing two tubes to give a paste that is put in place and quickly becomes hard and indistinguishable from the original Corian. One tube contains methyl methacrylate with the minerals and cross-linking monomer. The other tube is secret, but might contain something like a "diacyl peroxide",  $\text{RCO-O-O-COR}$ , which has a bond dissociation energy of only 30 kcal/mole. The PMMA polymer molecules in Corian probably have this R group at one end.

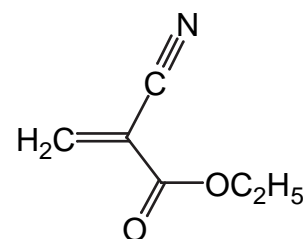
**EXPLAIN** three things:

a) (5 min) **Which bond** of the diacyl peroxide is so weak, and **why** it is **weak**.

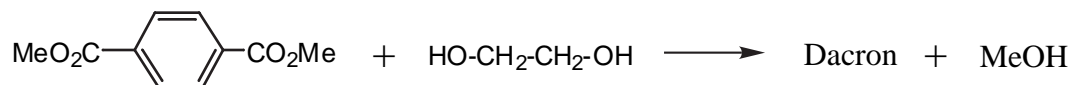
b) (2 min) **Why** there should be an **R group** at the end of the polymer.

c) (4 min) How the **mechanism of the Hunsdiecker** (or Borodin) Reaction:  $\text{R-CO}_2\text{Ag} + \text{Br}_2 \rightarrow \text{RBr}$  is related to your answer to part **b** (presence of the R group).

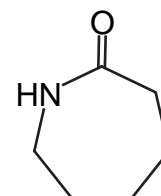
- J. (5 min) Krazy Glue is used to cement pieces of Corian together. This glue is the ethyl cyanoacrylate monomer. It polymerizes without needing any second tube (peroxide or whatever), because moisture in the air can start it polymerizing. Explain how replacing the methyl group of MMA by the cyano group of Krazy Glue allows a different sort of reaction for polymerization.



- K.** (5 min) The manufacturer claims that Corian is pretty stable to weak sodium hydroxide solution, but watch out for oven cleaner, which is very strong hydroxide. One could see how PMMA would react with hydroxide, but not in a way that would be as disastrous for the material as in the case of the Dacron, poly(ethylene terephthalate), the important fiber polymer made by reacting dimethyl terephthalate with 1,2-dihydroxyethane (below). **What is the reaction with hydroxide, and why is it so bad for Dacron?**



- L.** Nylon is another important fiber. It is a polyamide. One version (Nylon-6) is made from caprolactam, which itself is made by a "Beckmann rearrangement" of the imine from reaction of  $\text{H}_2\text{N}-\text{OH}$  with cyclohexanone. The Beckmann rearrangement is analogous in mechanism to the Baeyer-Villiger oxidation of cyclohexanone.



- a)** (5 min) Write the **mechanism** (with curved arrows) for Baeyer-Villiger reaction of cyclohexanone with a peroxyacid,  $\text{R}-\text{CO}_2\text{OH}$ .

- b)** (6 min) Write the **mechanism** (with curved arrows) for formation of caprolactam from an imine by acid-catalyzed Beckmann rearrangement.

**M.** (6 min) **Estimate** the **IR frequencies** for the carbonyl groups in dimethylterephthalate (Question K), and caprolactam (Question L), **and explain** the differences from the frequency of cyclohexanone.

Compound	Frequency (cm <sup>-1</sup> )
cyclohexanone	_____
dimethyl terephthalate	_____
caprolactam	_____

Question 8 would deserve more hints in 2003 than in 2000, when we had specifically discussed analogous reactions.

**8.** (6 min) In 1931 Barger synthesized the amino acid methionine by the following modification of the malonic ester synthesis (he also incorporates the Gabriel synthesis). **Provide a plausible structure for each of the four intermediates** (no curved arrows necessary).

