

Chemistry 125 Final Examination  
May 9, 2007

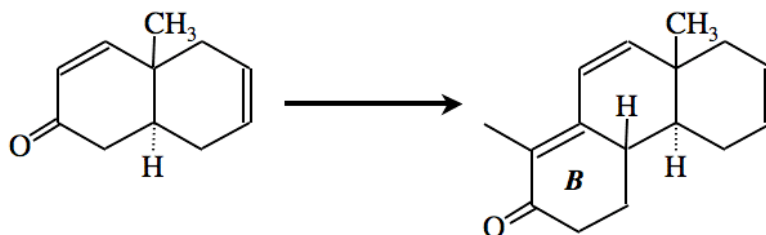
Name \_\_\_\_\_

Answer Questions 1 and 2 in a Blue Book

1. (20 min) Give a **specific** example for each of **five** (5 ONLY) of the following 8:
  - a) Markovnikov addition to an alkene
  - b) Anti-Markovnikov addition to an alkyne (an acetylene)
  - c) **Quantitative** evidence of aromatic **OR** allylic stabilization
  - d) A substituent that is deactivating and ortho,para-directing for electrophilic aromatic substitution
  - e) A protecting group used in Woodward's cortisone synthesis
  - f) NMR evidence for aromaticity.
  - g) A biological analogue of the Claisen (or acetoacetic ester) Condensation
  - h) **Two** reagents that convert bromobenzene to phenyl lithium
  
2. (36 min) How do you know? Provide **experimental** evidence to support **six** (6 ONLY) of the following 8 assertions. Be as specific as possible.
  - a) It is misleading to say that more substituted alkyl radicals are more stable.
  - b) A hydrogen is rearranging *during* the rate-determining transition state of a reaction.
  - c) S<sub>N</sub>1 substitution involves a carbon cation intermediate.
  - d) A methyl group can rearrange rapidly from one ring carbon to the next in the heptamethylcyclohexadienyl cation.
  - e) A ring system can be "aromatic" with  $4n+2$   $\pi$  electrons when  $n \neq 1$ .
  - f) It is possible to discriminate between Z and E alkene isomers spectroscopically.
  - g) S<sub>N</sub>2 substitution involves inversion of configuration at carbon.
  - h) "Electrophilic" addition to an alkene can involve an important nucleophilic component.
  
3. (9 min) Give short answers to **three** (3 ONLY) of the following 4 questions:
  - a) What is the role of NBS in allylic bromination?
  - b) Why does entropy favor twist-boat over chair cyclohexane?
  - c) What does  $J_{13C-H}$  show about a C-H bond?
  - d) Why does IR show several OH peaks for an alcohol, when NMR shows only one?

4. (8 min) Use pictures to explain **in terms of orbital energies** why the cyclization of hexatriene to cyclohexadiene is disrotatory.

5. (4 min) Draw the reagent(s) that allowed Woodward to create ring "B" of cortisone using the "Robinson Annulation" reaction.



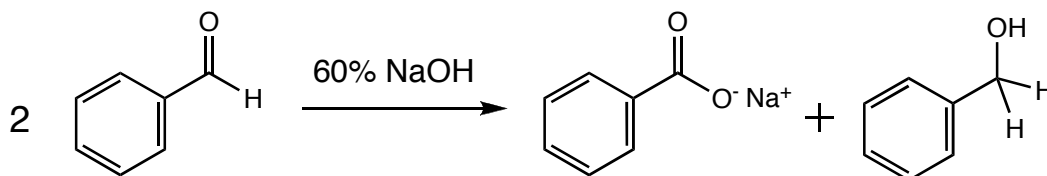
The rest of the exam relates to Benzaldehyde (Ph-CHO) and products that can be derived from it.

**YOU MAY ABBREVIATE BY USING "Ph" OR "Φ" FOR THE PHENYL GROUP**

6. (10 min) One of the first reactions discovered for benzaldehyde (Wöhler & Liebig, 1832) was its oxidation by air to benzoic acid, which is the solid in old bottles of benzaldehyde. This process is interesting because it involves two reactions, one radical and one non-radical. Identify the intermediate product and show these two mechanisms.



7. In 1853 Stanislao Cannizzaro, whom we mentioned last semester as a sponsor of Wilhelm Koerner, discovered a reaction of benzaldehyde that bears his name. In the Cannizzaro Reaction benzaldehyde acts both as an oxidizing and as a reducing agent to give benzoic acid and benzyl alcohol.



- a) (10 min) Devise a reasonable mechanism for the Cannizzaro Reaction and draw curved arrows to show its several steps.  
[Hint: decide what key atom must be transferred from one molecule to the other, and whether it makes more sense for this atom to be transferred as a cation, an anion, or a free radical.]

- b) (3 min) Say why saponification (ester + lye) has a more favorable equilibrium constant than Fischer esterification using acid catalysis, and how the Cannizzaro Reaction profits from the same advantage.

8. Benzoyl fluoride can be prepared from benzoic acid *via* benzoyl chloride, which is then treated with KF.

- a) (9 min) **Contrast the mechanisms** of the following three reactions:

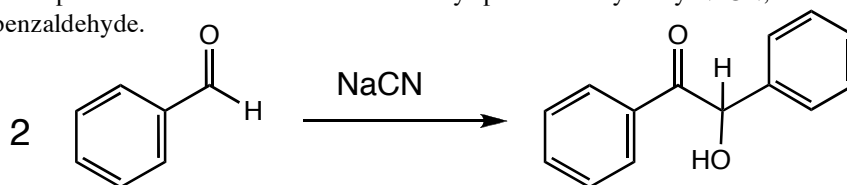
The reaction that converts benzoic acid to its acid chloride, benzoyl chloride (be sure to give the reagent)

The reaction that converts benzyl alcohol (Question 7) to benzyl chloride using the same reagent

The reaction that converts t-butanol to t-butyl chloride using HCl

- b) (2 min) Explain which of the three mechanisms above seems mechanistically analogous to the conversion of benzoyl chloride to benzoyl fluoride?

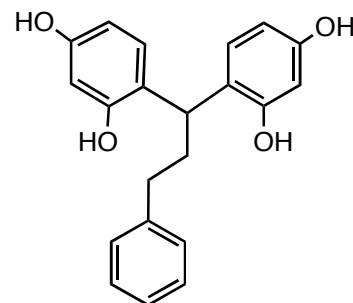
9. (15 min) In the same 1832 paper Wöhler & Liebig reported a reaction between two molecules of benzaldehyde that leads to benzoin, whose structure we now know. This “benzoin condensation” is a bit surprising because two carbonyl carbons are bonded together in the product. The reaction was due to very specific catalysis by NaCN, which happened to be present as an impurity in their benzaldehyde.



Cyanide is a fairly stable anion/leaving group, but also a nucleophile, and a base. Furthermore because the cyano group has a multiple bond, it is an analogue of the carbonyl group. *All* of these properties are important in catalysis of the benzoin condensation. **Devise and draw a plausible mechanism for this reaction.**

[Hint: the order in which the properties are important is (1) nucleophile, (2) base and carbonyl analogue, (3) leaving group.]

10. (15 min) When Martin Tanner set out to make a cage to hold cyclobutadiene he made the following compound in several steps from benzaldehyde, two molecules of resorcinol (1,3-dihydroxybenzene), and a third organic molecule. Identify the third molecule and explain how the pieces were put together (using other inorganic reagents as necessary). Be sure to mention control of regiochemistry (*i.e.* possible isomers).



11. (9 min) **Draw lines** connecting each of the benzoyl-containing molecules below to its proper IR spectrum, and comment briefly on the **relevant** spectral lines that distinguish the functional groups from one another.

