Chemistry 110B
FOURTH EXAM
April 7, 2008

Name (print) KEY

Note: Your exam should consist of 5 pages including this cover sheet. Skim the entire exam and solve the easiest problems first.

From a season-five Seinfeld episode entitled *The Lip Reader*:

In the bleachers at the tennis court. Two players are hitting the ball back and forth.

Jerry: *Are these seats unbelievable or what?*
George: *Where's the sunblock?*
Jerry: *Here.*
George: *25? You don't have anything higher?*
Jerry: *What, are you on Mercury?*
George: *I need higher. This has PABA in it, I need PABA-free.*
Jerry: *You got a problem with PABA?*
George: *Yes, I have a problem with PABA.*
Jerry: *You don't even know what PABA is.*
George: *I know enough to stay away from it.*

DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO
1. Show how you would accomplish each of the following conversions (no mechanism required, just put reagents and any important conditions over the arrows). 6 pts each row, 18 pts total.

2. Compound 1 can be made by a fairly reliable synthetic methodology. What is the name of the method? Outline your synthesis (reagents, stoichiometry, etc. over arrows) and provide a step-by-step mechanism for each of the reactions which could be used to construct this molecule. Employ the appropriate reagents in your mechanism. (synthetic plan: 5 pts; mechanism: 10 pts)
3. Linalool, a fragrant compound isolated from many plants, is 3,7-dimethyl-1,6-octadien-3-ol. It can be synthesized in the following way. Identify compounds F-J. Hint: F is the more stable isomer of the two that can form in this reaction; it would be the isomer formed under thermodynamic conditions. 10 pts

\[
\text{HBr} \quad \text{(C}_5\text{H}_9\text{Br)} \quad \text{F} \quad \xrightarrow{\text{sodioacetic ester}} \quad \text{G} \quad \text{(C}_{11}\text{H}_{18}\text{O}_3)}
\]

\[
\begin{align*}
\text{1. Dilute NaOH} \\
\text{2. H}_2\text{O}^+ \\
\text{3. heat}
\end{align*}
\]

\[
\text{H} \quad \text{(C}_8\text{H}_{14}\text{O)} \quad \xrightarrow{\text{1. LiC≡CH}} \quad \text{I} \quad \xrightarrow{\text{2. H}_2\text{O}^+} \quad \text{J} \quad \text{(Linalool)}
\]

Solomons 19.34 assigned.

4. Use a horizontally-arranged and annotated flow chart to describe how you would separate a mixture of aniline, benzoic acid, and toluene using ordinary laboratory reagents. Draw their structures and illustrate the chemistry being used. 10 pts.

Solomons 20.33 assigned.

5. Circle the stronger acid (3 pts ea)

\[
\begin{array}{c}
\text{vs.} \\
\text{vs.} \\
pKa = 20 \\
pKa = 25
\end{array}
\]

6. As we learned in class, in 1935 Domagk saved his daughter's life by administering a synthetic dye molecule named Prontosil (the molecule had shown antibiotic activity in earlier tests at his company). (a) What do you suppose is a 'key step' in the synthesis of Prontosil? Draw a few key structures to illustrate your thoughts. (b) It was later shown that this compound served as a pro-drug for the biologically active antibiotic substance. What is the structure of this compound? Why is it biologically active? (Hint: see the conversation on page 1 for a clue.) 12 pts

(a) key step in the synthesis.

(b) metabolized to

(c) brief comments on biological activity:

sulfanilamide blocks bacteria's ability to synthesize PABA, which is required for their own synthesis of DNA.
7. Provide a synthetic plan for preparing m-dibromobenzene from benzene. 8 pts

8. Using sulfur chemistry, show how you can make the transformation shown at the right to occur. Please illustrate the mechanism of this reaction. 8 pts

9. Pomona degree in hand, you happily accept a $100,000/yr job with the Oscar Mayer Corporation in the "hot dog development lab". Your first assignment is to work with another new hire and devise a better dog. Your partner hits the additives book while you review the existing ingredient list. Several days pass by. Your partner presents an idea at a group meeting: use Gesundheitamine (an anti-sneeze agent) as an additive: "this way, people who are allergic to hot dogs won't ever even know it", he says. Several minutes pass by as an uncomfortable silence descends upon the room. Out of the corner of your eye you realize the boss is nodding and smiling, somehow impressed with this outlandish proposal. You want no part of it, and can provide sound chemical reasoning as to why Gesundheitamine is not an appropriate additive. Start with the ingredient list and provide a detailed **mechanism**, incorporating other chemicals likely to be encountered in the stomach, to substantiate your reasoning. This is not an essay question. **It is a mechanism question.** (10 pts)

**Existing Ingredients:** beef, sodium erythrobate, sodium phosphate, sodium nitrite, artificial flavoring.

**Gesundheitamine**

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Na-O=N=O + H^+ → HO-N=O + H^+ → H^+ + O=N=O
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N-nitrosoamine
probable carcinogen
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