**Chemistry 222--Spring 2002--Third Problem Set  Due 5/1/02**

- You are free to discuss this problem set with anyone. As usual, you should make sure that the work that you turn in is your own, and that you thoroughly understand the answers that you put down.
- The answers to the questions on this problem set should be placed entirely on 8 1/2 x 11 inch sheets of paper, in order. Answers written on the problem set itself will not be graded.

**Part A.** For the following reactions, give the predominant product. Clearly *show* stereochemistry when appropriate (that is, draw a structure that clearly shows double bond configuration and chiral center configuration of one enantiomer).

1. \[
\begin{align*}
\text{H}_2C&-\text{CH} \quad \text{Excess LiAlH}_4 \\
\text{H} & \quad \text{Ether}
\end{align*}
\]

2. \[
\begin{align*}
\text{CH}_3\text{CH}=\text{PPh}_3 & \quad \text{THF}
\end{align*}
\]

3. \[
\begin{align*}
\text{H}_2\text{C}-\text{CH}_2 & \quad 1 \text{ equiv: } \text{HQ} \\
\text{HO} & \quad \text{TsOH} \\
\text{H}_2\text{N-NH}_2, \text{ KOH}, \Delta & \quad 2 \\
\text{H}_3\text{O}^+ & \quad 3
\end{align*}
\]

4. \[
\begin{align*}
\text{H}^+ (\text{catalyst}) & \quad \text{excess CH}_3\text{OH}
\end{align*}
\]

5. \[
\begin{align*}
\text{LDA, } -78^\circ & \quad 1 \\
\text{H}_2\text{O} & \quad 3
\end{align*}
\]
Part B. For the following pathway

1) Provide structures for compounds A, B, and C.
2) Explain how the following spectroscopic observations are consistent with your structural assignments:
   A: IR: 3300 (s, b), 1050 (s)
   NMR: There is a quartet at about 3.7 ppm in the $^1$H-NMR in acetone. When DMSO was used as the solvent (which enhances the chance of observing the coupling to OH protons), that quartet changed to a quintet.
   B: IR: 1700, 1050.
   C: IR: 1050, no 1700 or 3300.

3) Comment on the stereochemical nature of C (that is, how many isomers would be expected, and what would be the relationship between them?). Assume that you start with all possible isomers of the starting material.
4) Would the isomers of C be separable by ordinary means (for example, GC) or would they not? Explain briefly.

Part C. Reacting phenol with acetone in the presence of an acid catalyst gives a compound know as bisphenol A.$^1$

a. What other product is formed in the main reaction to produce bisphenol A?
b. Propose a mechanism for the formation of bisphenol A. You may have to combine chemistry that you know from more than one chapter in the textbook....
c. Which reactions did you use as models for the mechanism you proposed? [This is a kind of a hint: you don't need to make up the mechanism completely if you can a) for each reactant find an analogous reaction whose mechanism is described in the book; and b) make a functional substitution--for example, nucleophile for nucleophile--which involves the other functional group in the reaction.]

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$^1$Bisphenol A is used in the production of epoxy resins and polycarbonate resins. It is also one of many compounds being examined as an environmental estrogenic compound: it has weak estrogen-like properties.
Part D: Indicate how the following transformations might be carried out. *More than one step will be required.* Specify all necessary reagents, conditions, and (where appropriate) solvents. Draw structural formulas for all isolable intermediate products. Do not include mechanisms. You may use any organic or inorganic reagents necessary to accomplish these transformations.

\[
\begin{align*}
\text{Br} & \quad \rightarrow \quad \text{CH}_3 \text{CH} \quad \text{OH} \\
\text{CH} \quad \rightarrow \quad \text{H} \quad \text{O} \\
\text{O} \quad \rightarrow \quad \text{H} \quad \text{O}
\end{align*}
\]

Part E. The reaction shown below gives primarily the product shown, even though one might expect a more complicated mixture.

\[
\begin{align*}
\text{H} \quad \text{C} \quad \text{O} & \quad \rightarrow \quad \text{O} \\
\text{O} \quad \rightarrow \quad \text{Base}
\end{align*}
\]

1. Provide a reasonable mechanism for the transformation of starting material to product.
2. If you start with a single enantiomer of the starting material, will you make a single enantiomer of the product? Explain briefly.
3. Redraw the starting material, and show all of the potential sites for enolate formation (that is, all the potentially active $\alpha$-hydrogens).
4. Using your answer to number 3, how many possible aldol products are there? Explain briefly.
5. Draw the structure for one of the alternate products, and explain why it is not as likely to be formed as is the product shown above.