Hour Examination #3, Chemistry 301X - December 15, 2005, 7:30-10:00pm

"Chemiftry is the art of decompounding bodies, that is, of refolving compound bodies into their more fimple parts, and by combining thefe together, to reproduce the original compound with all its properties, and even to compound new bodies, from the different mixtures of other bodies, and that by the help of fire."

Thomas Southwell, M.D. London, 1764.

1 (20 Points). There is an error in each of the following attempted syntheses. Tell us:

First, what is the error - what would the product really be?

Next, how would you fix the problem? How would you make the desired product?

In your "fixes" you may use any inorganic reagent, TsCl, and any other organic reagent containing no more than two carbons.

2 (14 Points). In Group Problems and in the book you saw the following data:

Draw a careful "Energy vs. Reaction Progress" diagram that these data demand.

3 (18 Points). Here are three possible transformations of vinylcyclohexane into alcohols. Your jobs are top give structures for \mathbf{X} , \mathbf{Y} , and \mathbf{Z} and to find the proper reagents with which to carry out the transformations. You may pick from the following list. You must use each once, and you may use a reagent more than once. Mechanisms are not necessary. Be careful - if you intend to use a sequence of reactions

List: H₃O⁺, H₂O, B₂H₆, KOH, NaBH₄, HOOH, Hg(OAc)₂

$$??$$
 $X - \text{partial }^1\text{H NMR: 1H, m, } \delta = 3.4$

$$??$$
 $X + Y - \text{partial }^1\text{H NMR: no signal at } \delta = 3.4$

$$??$$
 $Z - \text{partial }^1\text{H NMR: 2H, t, } \delta = 3.5$

- 4 (14 Points). The famous I. B. Verständislos treated cyclopentene (cyclopentEne, please) with a mixture of Br₂ and water, and got, as he expected, a single, racemic diastereomer of a bromo alcohol as the product.
- (a) What is the product? Give a mechanism for its formation.
- I. B. then went on to separate enantiomers of this chiral material and continued with one of them. It doesn't matter which one. He treated it with HBr, expecting to get a single meso dibromide. That's not what happend. In fact he got the meso dibromide along with a diastereomeric racemic dibromide.
- (b) Show mechanistically what happened.

5 (14 Points). Ozone adds to alkenes to give an ozonide.

$$\begin{array}{c} O_3 \\ \hline \\ O_3 \\ \hline \\ Ozonide \\ \end{array}$$

Two general mechanisms can be envisioned. First (correct), ozone might add in a single step to give the ozonide directly. Second (wrong), it might add in two steps, with an intermediate intervening between starting material and product.

- (a) Draw careful, detailed arrow formalisms for both mechanisms. You will need a good Lewis "dot" structure for ozone.
- (b) Devise an experimental test that would distinguish the one-step and two-step mechanisms. Be specific exactly what alkene would you use and what would you look for?

6 (20 Points). You have a flask containing one - only one -of the three isomers of **1**. Your job is to use the following reactions that lead to **2** to tell which isomer is the structure of **1**. Please be sure to give a structure for **2** and to explain carefully how you used the data to make your choice of isomer.

- (a) Draw the three possible isomers of 1.
- (b) Here are the data explain how you can make the choice among the three possibilities. Please note: HO groups attached to benzene (cyclohexatriene) rings are slower than other OH groups to react with TsCl.

1.
$$B_2H_6$$
 $C_{10}H_{14}O_2$ $C_{10}H_{13}O_2Ts$ $C_{10}H_{13}O_2Ts$ $IR: 3500-3650 \text{ cm}^{-1}, \text{ br}$ K_2CO_3/H_2O $IR: 1670 \text{ cm}^{-1} \text{ (strong)}$ $C_{10}H_{12}O$ $C_{10}H_{12}O$

"I pledge that I have not violated the Honour Code on this examination."