“Chemiftry is the art of decompounding bodies, that is, of resolving compound bodies into their more simple parts, and by combining these 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?

(a) 
\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2 \]

1. \( \text{H}_3\text{O}^+ / \text{H}_2\text{O} \)
2. \( \text{Na}^+ - \text{N}_3 \)

(b) 
\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2 \]

1. \( \text{H}_3\text{O}^+ / \text{H}_2\text{O} \)

(c) 
\[ \text{C}_6\text{H}_{10} \]

1. \( \text{CF}_3\text{COOOH} \)
2. \( \text{KOH} / \text{H}_2\text{O} \)

(d) 
\[ \text{CH}_2=\text{CH}_2 \]

1. \( \text{HBr} \)
2. \( \text{Na}^+ - \text{OCH}_2\text{CH}_3 \)

(e) 
\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2 \]

\( \text{Br}_2 / \text{H}_2\text{O} \)

\[ \text{Br} \quad \text{Br} \quad \text{OH} \quad + \quad \text{Br} \quad \text{Br} \]
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:

![Energy vs. Reaction Progress diagram](image)

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 to give structures for X, Y, and 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: H_3O^+, H_2O, B_2H_6, KOH, NaBH_4, HOOH, Hg(OAc)_2

\[ ?? \rightarrow \quad X \quad \text{- partial } ^1\text{H NMR: 1H, } m, \delta = 3.4 \]

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

\[ ?? \rightarrow \quad Z \quad \text{- partial } ^1\text{H NMR: 2H, } t, \delta = 3.5 \]
4 (14 Points). The famous I. B. Verständislos treated cyclopentene (cyclopetEne, 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 happened. 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.

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.

1

(The OH is attached somewhere on the ring)

(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.

\[ \begin{align*}
1 \xrightarrow{1. \text{B}_2\text{H}_6} & \quad \text{C}_{10}\text{H}_{14}\text{O}_2 \quad 1 \rightarrow \quad \text{TsCl} \quad \text{C}_{10}\text{H}_{13}\text{O}_2\text{Ts} \\
2. \text{HOOC/\text{HO}^\cdot} & \quad \text{IR: 3500-3650 cm}^{-1} \text{, br} \quad \text{IR: 1670 cm}^{-1} \text{ (strong)} \quad \text{no band near 3600 cm}^{-1} \quad \text{K}_2\text{CO}_3/\text{H}_2\text{O} \quad \text{C}_{10}\text{H}_{12}\text{O} \\
\end{align*} \]

\[^{13}\text{C} \text{NMR:}\n\begin{align*}
187, 155.1, 131.7, 37.9, 35.4, 21.4 \text{ ppm}
\end{align*} \]

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