“Some students spend their lives attending scholarly sessions. Still, one finds them silent. They do not talk and do not discuss matters. More than is necessary, they are concerned with memorizing. Thus, they do not obtain much of a habit in the practice of science and scientific instruction. Some of them think that they have obtained the habit. But when they enter into a discussion or disputation, or do some teaching, their scientific habit is found to be defective. Their memorized knowledge may be more extensive than that of other scholars, because they are so much concerned with memorizing. They think that scientific habit is identical with memorized knowledge. But that is not so.”

Ibn Khaldun

1 (19 points). When the diol Z is treated with one equivalent of TsCl, A is formed. Each of the two diastereomers of A leads to a different product, C₈H₁₆O, when treated with sodium hydride, Na⁺ :H⁻.

\[
\begin{align*}
Z & \quad \xrightarrow{1 \text{ eq. TsCl}} \quad A \\
\text{HO} & \quad \text{OH} \\
\text{HC} & \quad \text{CH} \\
\end{align*}
\]

a. Draw good 3D, “sawhorse” pictures of the two diastereomers of A.

b. What are the products? Show arrow formalisms for all reactions. Explain why only one product is formed from each diastereomer.

c. When either diastereomer of Z is treated with H₃O⁺/H₂O, a new compound W, also of the formula C₈H₁₆O is formed. Hints: Compound W has a carbon-oxygen double bond in it. Compound W shows six signals in its ¹³C NMR spectrum.

Give us a structure for W and an arrow formalism for its formation.
2  (21 points). Compounds B and C give different products when treated under different conditions (of course).

Here is a very rare question in which we ask you to predict the products. No mechanisms, no arrows, just draw the products. If more than one product of the same formula is produced, tell us which will be the major product.

Please draw “Energy vs. Reaction Progress” diagrams for the reactions of B (not C). You do not have to concern yourself with the relative energies of the products in the second (bottom) reaction of B.
3 (16 points). This page shows four screen shots from the animations on your CD of the four basic reactions, $\text{SN}_1$, $\text{SN}_2$, $\text{E}_1$, and $\text{E}_2$ (no order implied).

(a) For each of the four basic reactions, draw an “Energy vs. Reaction Progress” diagram.
(b) Show the point on the diagram each of the four screenshots appears. For example, one answer might look like the picture below (none of the answers does, this picture is just to show you what we mean).

There might be more than one screen shot of the same basic reaction, and there may be no screen shot of one or more of the basic reactions.

Black = C, White = H, Red = O, Orange = Br
4 (20 points). Devise syntheses of the following molecules from bromocyclopentane. If you suggest a multiple step route, BE SURE to make clear that you are using separate steps (1. tin, 2. lead, 3. bad air) and not dumping all the reagents in at once (tin, lead, bad air).

Separate steps:   (1. tin, 2. lead, 3. bad air)
All at once: (tin, lead, bad air)

You may use the following reagents (need something else? Ask)

NaH, CH₃I, HCl, DCl, HBr, HOH, Li, Mg, ether, H₂SO₄, H₃PO₄, SOCl₂, TsCl, PBr₃, H₂, D₂, D²O, Pd, Pt, C, Ra Ni, H₂S, NaOH, NaSH, NaCl, CH₃OH, (CH₃)₃C-O⁻ +Na, (CH₃)₃COH, tin, lead, bad air.
5 (24 points). 5-Bromocycloheptene (D) reacts with HBr to give two diastereomeric products, E and F, each C\(_7\)H\(_{12}\)Br\(_2\).

\[
\begin{align*}
\text{D} & \quad \overset{\text{HBr}}{\longrightarrow} \quad \text{E} + \text{F} \\
\text{C}_7\text{H}_{12}\text{Br}_2 & 
\end{align*}
\]

E and F each reacts with K\(^+\) -SH to give a different product, C\(_7\)H\(_{13}\)BrS (G and H).

\[
\begin{align*}
\text{E} & \quad \overset{\text{KSH}}{\longrightarrow} \quad \text{G} \\
\text{F} & \quad \overset{\text{KSH}}{\longrightarrow} \quad \text{H} \\
\text{C}_7\text{H}_{13}\text{BrS} & 
\end{align*}
\]

When G and H are separately treated with Na\(^+\) -H, then neutralized with mild acid (H\(_3\)O\(^+\)) to pH = 7, G is unchanged, but H gives a new product, J, C\(_7\)H\(_{12}\)S.

\[
\begin{align*}
\text{G} & \quad \overset{1. \text{NaH}}{\longrightarrow} \quad \overset{2. \text{pH} = 7}{\longrightarrow} \quad \text{G} \\
\text{H} & \quad \overset{1. \text{NaH}}{\longrightarrow} \quad \overset{2. \text{pH} = 7}{\longrightarrow} \quad \text{J} \quad \text{C}_7\text{H}_{12}\text{S} 
\end{align*}
\]

Give structures for E, F, G, H, and J, and arrow formalisms for all reactions.

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