EXPERIMENT 3
CARBOCATION INTERMEDIATES: REARRANGEMENT, ISOMERIZATION, & REACTIVITY

Part 1: The Pinacol Rearrangement
Part 2: Acid-Catalyzed Isomerization of Maleic Acid
Part 3: Addition of Iodine to Cyclohexene and α-Pinene

Reading Assignment: Pavia, sections 7.2, 7.3, 7.6, 8.3, Smith, problem 9.83

Pre-lab Questions:
1) Write a complete and balanced equation for the rearrangement of benzopinacol into benzopinacolone, ignoring the role of the iodine reagent.
2) Using the Bond Dissociation Energies listed in Table 6.2 of Smith, estimate the ΔH° value for the pinacol rearrangement (make sure you start from a balanced equation.)

Part 1: The Pinacol Rearrangement

The pinacol rearrangement is a general reaction of 1,2-diols. It is named for the best-known example, the acid-catalyzed rearrangement of pinacol to pinacolone, shown below:

\[
\text{pinacol} \rightarrow \text{pinacolone}
\]

It is an illustration of a carbocation rearrangement that is driven by the stability of the oxygen-substituted carbocation (shown as the protonated carbonyl resonance form). It also is a demonstration of the strength of the carbon-oxygen double bond.
When a phenyl-sustituted 1,2 diol such as benzopinacol is used, there is evidence to suggest formation of a phenonium ion as an intermediate:

![Diagram of benzopinacol and benzopinacolone]

Procedure:

Into a small round bottom flask, place 400 mg of benzopinacol, 2mL glacial acetic acid, and a tiny crystal (about 5 mg) of iodine (DO NOT weigh iodine on the analytical balance – use the top loading balance only.) Attach a condenser and drying tube, and heat to reflux using a sand bath or heating mantle for about 5 minutes. Allow the solution to cool. As the solution cools, benzopinacolone will separate from the solution. Add a small amount of ethanol, mix thoroughly, and isolate your product by vacuum filtration using a Büchner or Hirsch funnel. Rinse the flask and crystals with additional ethanol to remove any remaining iodine color. Pull vacuum on the crystals for a few minutes to remove any residual ethanol. Determine the yield and m.p. of the crude product (the literature melting point can be found in the Aldrich Handbook in the lab.)

Reference:

Part 2: Acid-Catalyzed Isomerization of Maleic Acid

π-bonds cannot undergo free-rotation because rotation disrupts the parallel p-orbital overlap that constitutes a π-bond. In the presence of an acid, however, protonation of the alkene breaks the π-bond, and a carbocation is formed. Rotation about the σ-bond can now occur.
Subsequent loss of a proton can lead to either the *cis* or *trans* isomer. Under equilibrium conditions, the thermodynamically favored isomer predominates. In this experiment, maleic acid will be isomerized to fumaric acid in the presence of concentrated hydrochloric acid.

\[
\begin{align*}
\text{maleic acid} & \quad \text{H}_3\text{O}^+ \\
\text{fumaric acid} & \quad \text{HO} \quad \text{O} \quad \text{HO} \quad \text{O}
\end{align*}
\]

**Procedure:**

**CAUTION:** HCl is corrosive and toxic and can cause severe burns when in contact with the skin. If this occurs, immediately rinse affected area with cold water. Cautiously neutralize any acid spills on the lab bench with sodium bicarbonate. Notify the lab instructor immediately.

Place 200 mg of maleic acid and 0.3 mL water in a 10mL round bottom or conical shaped flask equipped with a stirbar and a reflux condenser. Add 0.25mL of concentrated HCl to the mixture. Reflux gently for 15-30 minutes using a sand bath. A precipitate will separate from the hot solution, Cool and collect the solid product using a Hirsch funnel. This material can be recrystallized from hot water. Air dry the solid and determine its weight. Determine the melting point. Pure maleic acid melts at 140-142°C. Fumaric acid has a melting point of 287°C, but sublimes at 200°C. If the solid hasn't melted by 150°C, assume it is fumaric acid. Do a mixed melting point of the solid with maleic acid.

**Reference:**

**Part 3: Addition of Iodine to Cyclohexene and α-Pinene**

In *All Creatures Great and Small*, James Herriot describes how veterinarians often disinfected wounds in large animals. The veterinarian would pack the wound with iodine, splash some turpentine on it, and stand back. The result was a violent reaction that forced gaseous iodine into the wound amid a cloud of purple vapor. This was accompanied by an equally violent reaction from the animal. The major component of turpentine is α-pinene, a bridged bicyclic compound containing both a 4-membered ring and a 6-membered ring. Although alkenes readily undergo addition reactions with chlorine and bromine, most of them are unreactive with iodine. If α-pinene is responsible for the reaction of turpentine with iodine, it must possess some structural feature that makes it more reactive than other alkenes. You will
investigate the effect of adding α-pinene to iodine, and compare it to the reaction of cyclohexene and iodine.

\[
\begin{align*}
&\text{α-pinene} \\
&\text{cyclohexene}
\end{align*}
\]

Procedure:

**CAUTION:** α-pinene is flammable and irritates the skin and eyes. The vapors are potentially harmful. Minimize contact and do not breathe vapors. The reaction with iodine may be violent; conduct under a fume hood. Wear safety goggles and adequate protective clothing.

Into two 15 cm test tubes, weigh 0.5 g iodine into each (*TOP LOADING BALANCE ONLY! Do not use the analytical balances.*) Under the hood, add 1.0 mL of cyclohexene to the first test tube in one portion. Then add 1.0 mL of α-pinene to the second test tube in one portion and step back quickly.

Write a mechanism that explains the exothermicity of the α-pinene reaction, assuming a carbocation as the initial intermediate. Write an equation showing two likely products (neither of which is a vicinal diiodide). Tell how your mechanism explains your experimental observations.

Reference:

Post-lab Questions:
1) Draw resonance structures showing all the positions at which the positive charge is delocalized on the aromatic ring in the phenonium ion. If a methoxy group (\(-\text{OCH}_3\)) or a nitro group (\(\text{–NO}_2\)) were substituted in the 4-position on the aromatic ring, how would the stability of the phenonium ion change? Compare methoxy substituted, nitro substituted and unsubstituted, and order them by increasing stability. Explain your answer.
2) Benzopinacol and benzopinacolone have nearly identical boiling points. How would you distinguish the two using only techniques that we have used in the laboratory?
3) Was the major product in the isomerization of maleic acid the *cis* or *trans* isomer? Explain why formation of one isomer is favored over the other.
4) Why is the addition of $\alpha$-pinene to iodine so exothermic? Would you expect bromination of $\alpha$-pinene to be more or less exothermic? Explain.