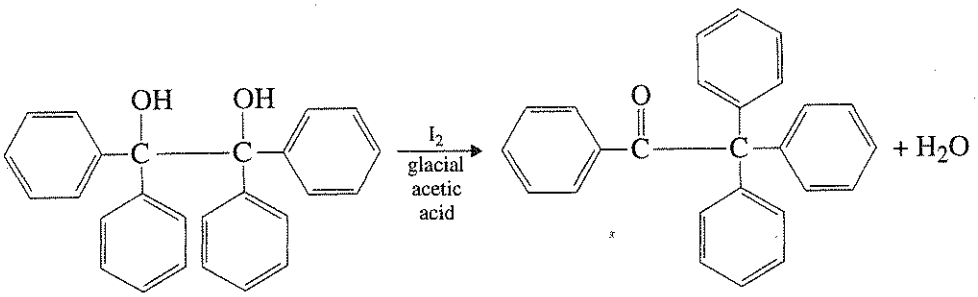
54B EXPERIMENT 54B

# *Synthesis of β-Benzopinacolone: The Acid-Catalyzed Rearrangement of Benzopinacol*

The ability of carbocations to rearrange represents an important concept in organic chemistry. In this experiment, the benzopinacol, prepared in Experiment 54A, will rearrange to **benzopinacolone (2,2,2-triphenylacetophenone)** under the influence of iodine in glacial acetic acid.




The product is isolated as a crystalline white solid. Benzopinacolone is known to crystallize in two different crystalline forms, each with a different melting point. The **alpha** form has a melting point of 206°C–207°C, whereas the **beta** form melts at 182°C. The product formed in this experiment is the β-benzopinacolone.

## REQUIRED READING

*Review:*

| | |
|---|---|
| Technique 7 | Reaction Methods, Section 7.2 |
| Technique 11 | Crystallization: Purification of Solids, Section 11.3 |
| Technique 25 | Infrared Spectroscopy, Part B |
| Technique 26 | Nuclear Magnetic Resonance Spectroscopy, Part B |

Before beginning this experiment, you should read the material dealing with carbocation rearrangements in your lecture textbook.

## SPECIAL INSTRUCTIONS

This experiment requires very little time and can be co-scheduled with another short experiment.

## SUGGESTED WASTE DISPOSAL

All organic residues must be placed in the appropriate container designated for nonhalogenated organic waste.

## PROCEDURE

In a 25-mL round-bottom flask, add 5 mL of a 0.015 *M* solution of iodine dissolved in glacial acetic acid. Add 1 g of benzopinacol and attach a water-cooled condenser. Using a small heating mantle, heat the solution under reflux for 5 minutes. Crystals may begin to appear from the solution during this heating period.

Remove the heat source, and allow the solution to cool slowly. The product will crystallize from the solution as it cools. When the solution has cooled to room temperature, collect the crystals by vacuum filtration using a small Büchner funnel. Rinse the crystals with three 2-mL portions of cold, glacial acetic acid. Allow the crystals to dry in the air overnight. Weigh the dried product, and determine its melting point. Pure β-benzopinacolone melts at 182°C. Obtain the infrared spectrum using the dry-film method (see Technique 25, Section 25.4) or as a KBr pellet (see Technique 25, Section 25.5) and the NMR spectrum in $CDCl_3$ (see Technique 26, Section 26.1).

Calculate the percentage yield. Submit the product to your instructor in a labeled vial, along with your spectra. Interpret your spectra, showing how they are consistent with the rearranged structure of the product.

## QUESTIONS

1. Can you think of a way to produce the benzophenone $n$–$\pi^*$ triplet $T_1$ *without* having benzophenone pass through its first singlet state? Explain.
2. A reaction similar to the one described here occurs when benzophenone is treated with the metal magnesium (pinacol reduction).

$$2\ Ph_2C{=}O \xrightarrow{Mg} Ph_2C(OH){-}C(OH)Ph_2$$

Compare the mechanism of this reaction with the photoreduction mechanism. What are the differences?

3. Which of the following molecules do you expect would be useful in quenching benzophenone photoreduction? Explain.

| | |
|---|---|
| Oxygen | ($S_1$ = 22 kcal/mol) |
| 9,10-Diphenylanthracene | ($T_1$ = 42 kcal/mol) |
| *trans*-1,3-Pentadiene | ($T_1$ = 59 kcal/mol) |
| Naphthalene | ($T_1$ = 61 kcal/mol) |
| Biphenyl | ($T_1$ = 66 kcal/mol) |
| Toluene | ($T_1$ = 83 kcal/mol) |
| Benzene | ($T_1$ = 84 kcal/mol) |