

## 2. Preparation of Benzopinacol via Photoreduction of Benzophenone in 2-Propanol

Topic: photochemistry, organic chemistry

Level: undergraduate general or organic chemistry

Time: 2 x 4 hours

Equipment: test tubes (13 x 100 mm), cork stoppers, parafilm or rubber septa/stopper, heavy-walled suction filtering flask, buchner funnel, filter paper, melting point apparatus, IR spectrometer (optional),  $^1\text{H}$  NMR spectrometer (optional)

Chemicals: benzophenone, benzopinacol, 2-propanol, methylene chloride, petroleum ether

### Abstract

This experiment is a study of the photoreduction of benzophenone in 2-propanol. Hydrogen abstraction by photoexcited benzophenone from 2-propanol yields benzopinacol and acetone as stable products. Benzopinacol can be easily isolated from the reaction mixture and characterized using common analytical techniques.

### Introduction

This experiment is a study of the photoreduction of benzophenone in 2-propanol which has been adapted from a procedure developed by T. Durst.<sup>1</sup> Hydrogen abstraction by photoexcited benzophenone from 2-propanol yields benzopinacol and acetone as stable products (Figure 1). Benzopinacol can be easily isolated from the reaction mixture and characterized using common analytical techniques.

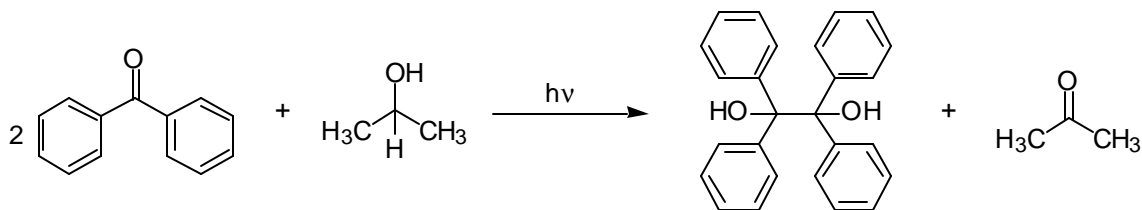


Figure 1. Hydrogen abstraction by photoexcited benzophenone from 2-propanol to give benzopinacol and acetone.

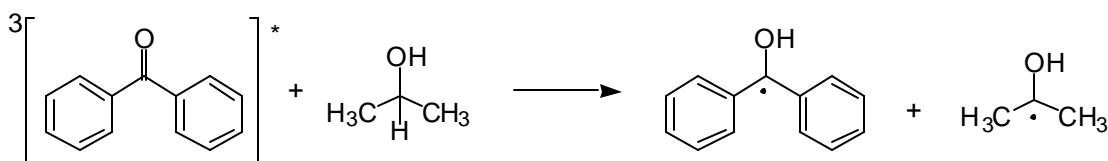
### Background and Theory

A brief discussion of benzophenone photochemistry and photophysics appears in Experiment 1. As noted there, upon photoexcitation, benzophenone efficiently forms its  $n,\pi^*$  triplet state, and it is this species that is responsible for the

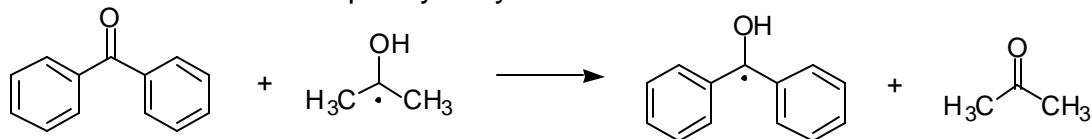
intermolecular hydrogen abstraction reaction of photoexcited benzophenone from 2-propanol. The  $n,\pi^*$  triplet state of carbonyl compounds is diradicaloid in nature with their reactivity modeled by alkoxy radicals; hence, their tendency to participate in hydrogen abstraction reactions.<sup>2</sup>

In the preparation of benzopinacol, the relevant reactions which occur after photoexcitation are:<sup>3,4</sup>

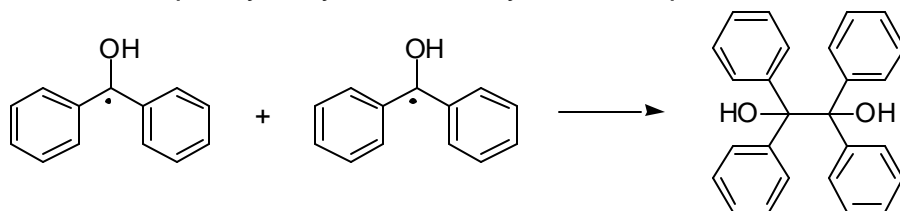
1. hydrogen abstraction from isopropanol by the  $n,\pi^*$  triplet state of benzophenone to yield the diphenyl ketyl and dimethyl ketyl radicals



2. radical transfer from the dimethyl ketyl radical to benzophenone to yield acetone and another diphenyl ketyl radical



3. dimerization of diphenyl ketyl radicals to yield benzopinacol



## Equipment and Chemicals

test tubes (13x100 mm), cork stoppers or rubber septa/stopper, parafilm, heavy-walled suction filtering flask, buchner funnel, filter paper, melting point apparatus, IR spectrometer (optional), <sup>1</sup>H NMR spectrometer (optional), benzophenone, benzopinacol, 2-propanol, methylene chloride, petroleum ether

## Procedure

1. Prepare a solution of benzophenone (0.8 g, 4.36 mmol), 2-propanol (8 mL, 104 mmol) and glacial acetic acid (1 drop) in a test tube. In order to achieve complete dissolution, gentle heating in a water bath is required.
2. Tightly stopper the test tube using either a cork which is then wrapped in parafilm, or a rubber stopper/septa. It is important that the solution not come into direct contact with the rubber as it may leach out some compounds which can quench benzophenone excited states.

3. Place the test tube in the Luzchem photoreactor using all 10 lamps and irradiate until the amount of solid which has precipitated from solution does not change (2.5 - 3 hours).
4. After the irradiation, cool the test tube in an ice-bath to precipitate more of the solid. Collect the solid by suction filtration and wash with 1 mL of cold 2-propanol. Allow the solid to air dry. Weigh the solid and determine the percent yield for the reaction.
5. Take the melting point, infrared spectrum and  $^1\text{H}$  NMR spectrum of your sample, an authentic sample of benzopinacol, and that of the starting material, benzophenone.
6. Weigh the remaining amount of solid and then recrystallize by dissolving in a minimum amount of methylene chloride and adding petroleum ether until the solution becomes cloudy. Allow the solution to cool to room temperature, then cool in an ice-bath. Collect the solid and weigh it as described in Step 4.
7. Reacquire analytical data for the recrystallized sample as described in Step 5.

## Data Analysis

Examine the analytical data obtained for your crude and recrystallized sample and compare them to those of an authentic sample of benzopinacol and benzophenone to confirm its identity as benzopinacol and to determine its purity.

## Questions

1. What photoproducts other than benzopinacol would you expect to form during the photolysis? Why are they not isolated?
2. Why must the test tube be tightly stoppered during irradiation? What would you expect to occur if the test tube were not stoppered?
3. Propose a reaction for the preparation of benzopinacol from benzophenone which does not involve photochemistry. Include the mechanism for the reaction.

## References

- (1) Durst, T. "CHM 3126: Laboratory Manual," The University of Ottawa, 2001.
- (2) Turro, N. J. *Modern Molecular Photochemistry*, Benjamin/Cummings Publishing Co.: Menlo Park, 1978.
- (3) Pitts, J. N. J.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Recktenwald, G.; Martin, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 1068-1077.
- (4) Demeter, A.; László, B.; Bérces, T. *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 1478-1485.