



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

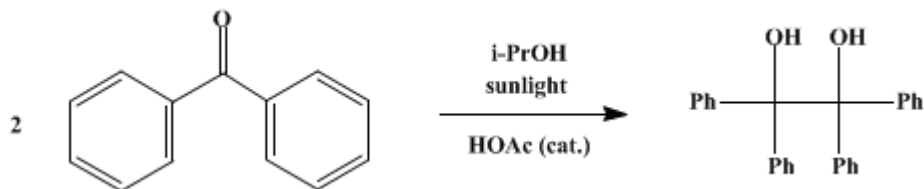
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.71 (1943); Vol. 14, p.8 (1934).

BENZOPINACOL



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1. Procedure

A mixture of 150 g. (0.82 mole) of [benzophenone](#) ([Note 1](#)), one drop of glacial [acetic acid](#) ([Note 2](#)), and 665 g. (850 cc., 11 moles) of [isopropyl alcohol](#) ([Note 3](#)) in a 1-l. round-bottomed flask is warmed to 45°. The flask is closed with a tight cork firmly wired or tied in place, and is supported in an inverted position in a tripod and exposed to direct sunlight. After three to five hours of bright sunshine crystals of [benzopinacol](#) begin to appear; after eight or ten days of exposure, depending upon the intensity of the light ([Note 4](#)), the flask is filled with crystals of [benzopinacol](#). The solution is chilled in ice and the crystalline product is filtered with suction, washed with a small quantity of [isopropyl alcohol](#), and allowed to dry in the air. The filtrate is reserved for subsequent reductions (see below). The yield of practically pure [benzopinacol](#), m.p. 188–190° ([Note 5](#)), is 141–142 g. (93–94 per cent of the theoretical amount). The product is sufficiently pure for most purposes. It may be crystallized by dissolving it in 1 l. of hot [benzene](#), filtering, and adding 400 cc. of hot ligroin (b.p. 90–100°) to the hot filtrate. After cooling in ice and filtering there is obtained 129–130 g. of purified product. The melting point is not changed by this purification.

To the [isopropyl alcohol](#) filtrate is added another 150-g. portion of [benzophenone](#), and the solution is exposed to sunlight as in the first reduction. The [benzopinacol](#) which separates is filtered and dried. The yield in the second and subsequent runs is 142–143 g. (94–95 per cent of the calculated amount). This procedure can be repeated with the same filtrate until six or seven portions (900–1050 g.) of [benzophenone](#) have been reduced.

2. Notes

1. Although a practical grade of [benzophenone](#) can be used in this preparation, it is better to have material that has been recrystallized from alcohol. Directions for preparing [benzophenone](#) are given in [Org. Syn. Coll. Vol. I, 1941, 95](#).
2. No more than one drop of [acetic acid](#) should be used. The acid is added to ensure the removal of traces of alkali, which cause decomposition of the pinacol into [benzophenone](#) and benzohydrol.
3. If [isopropyl alcohol](#) is not available, absolute [ethyl alcohol](#) can be used. With [ethyl alcohol](#) the reaction is slower and a yellow solution is obtained; nevertheless, the crystals of [benzopinacol](#) are colorless.
4. About five clear bright days are required to complete the reduction. The reaction can be interrupted at any time, the crystals filtered, and the filtrate then exposed further.
5. Since the pinacol decomposes near its melting point the latter will vary with the rate of heating. The temperatures reported here were obtained by slow heating; if the tube is placed in a bath at 150° and heated rapidly, the observed melting or decomposition point is 193–195°.

3. Discussion

[Benzopinacol](#) has been prepared by the action of [phenylmagnesium bromide](#) on [benzil](#)¹ or [methyl benzilate](#).¹ Usually it has been obtained by reduction of [benzophenone](#), the reducing agents being [zinc](#) and [sulfuric acid](#)² or [acetic acid](#),³ [aluminum](#) amalgam,⁴ and [magnesium](#) and [magnesium iodide](#).⁵ The

present method is based on a study by Cohen⁶ of the photochemical reaction discovered by Ciamician and Silber.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 73](#)

References and Notes

1. Acree, Ber. **37**, 2761 (1904).
 2. Linnemann, Ann. **133**, 26 (1865).
 3. Zagumenni, Ber. **14**, 1402 (1881).
 4. Cohen, Rec. trav. chim. **38**, 75 (1919).
 5. Gomberg and Bachmann, J. Am. Chem. Soc. **49**, 241 (1927).
 6. Cohen, Rec. trav. chim. **39**, 243 (1920).
 7. Ciamician and Silber, Ber. **33**, 2911 (1900).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Benzohydrol

ligroin

[ethyl alcohol \(64-17-5\)](#)

[sulfuric acid \(7664-93-9\)](#)

[acetic acid \(64-19-7\)](#)

[Benzene \(71-43-2\)](#)

[magnesium \(7439-95-4\)](#)

[aluminum \(7429-90-5\)](#)

[Benzil \(134-81-6\)](#)

[Benzophenone \(119-61-9\)](#)

[zinc \(7440-66-6\)](#)

[isopropyl alcohol \(67-63-0\)](#)

[Phenylmagnesium bromide \(100-58-3\)](#)

[Benzopinacol \(464-72-2\)](#)

methyl benzoate (76-89-1)

magnesium iodide

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