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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.*

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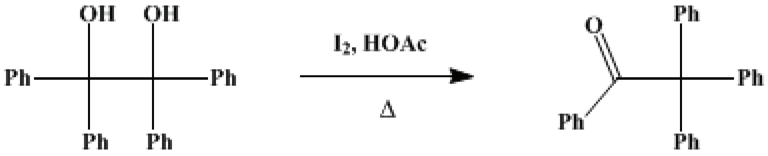
*Organic Syntheses, Coll. Vol. 2, p.73 (1943); Vol. 14, p.12 (1934).*

# β-BENZOPINACOLONE



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## 1. Procedure

In a 1-l. round-bottomed flask provided with a reflux condenser is placed a solution of 1 g. of iodine in 500 cc. of glacial acetic acid. One hundred grams (0.27 mole) of benzopinacol (Note 1) is added, and the flask is heated over a wire gauze, with shaking, until the solution boils gently. It is then refluxed for five minutes during which the solid benzopinacol disappears completely and a clear red solution is obtained (Note 2). The solution is transferred at once to a 1-l. beaker, and, upon cooling, the benzopinacolone separates in fine threads. The product is filtered with suction, washed with two or three 60-cc. portions of cold glacial acetic acid until colorless, and dried. The filtrate is reserved for subsequent preparations. The yield of practically pure benzopinacolone melting at 178–179° is 90–91 g. (95–96 per cent of the theoretical amount). If a purer product is desired the material may be dissolved in 450 cc. of hot benzene, filtered, and treated with 250 cc. of hot ligroin (b.p. 90–100°). After cooling in ice the benzopinacolone is filtered and dried. The purified product weighs 82–83 g. and melts at 179–180°.

To the acetic acid filtrate is added another 100-g. portion of benzopinacol and the reaction is carried out in the same way. The yield of benzopinacolone in the second and subsequent runs is 94–94.5 g. (98–99 per cent of the theoretical amount). This procedure can be repeated in the same filtrate until 500 g. of the pinacol has been rearranged.

## 2. Notes

1. The benzopinacol obtained by photochemical reduction of benzophenone (p. 71) may be used directly without purification.
2. Frequently the benzopinacolone begins to crystallize in the boiling solution during the last minute of heating.

## 3. Discussion

β-Benzopinacolone has been prepared by rearrangement of benzopinacol. The rearrangement has been carried out by heating benzopinacol with benzoyl chloride,[1] with acetyl chloride,[2] with acetic acid at 180–200°,[2] with dilute sulfuric acid at 180–200°,[2] and with concentrated hydrochloric acid at 200°.[2] The present procedure is based on the method described by Gomberg and Bachmann.[3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 10, 359

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## References and Notes

1. Linnemann, Ann. **133**, 28 (1865).
2. Thörner and Zincke, Ber. **10**, 1475 (1877).
3. Gomberg and Bachmann, J. Am. Chem. Soc. **49**, 246 (1927).

## Appendix
## Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ligroin

β-Benzopinacolone

| | |
|---|---|
| sulfuric acid | (7664-93-9) |
| hydrochloric acid | (7647-01-0) |
| acetic acid | (64-19-7) |
| Benzene | (71-43-2) |
| acetyl chloride | (75-36-5) |
| iodine | (7553-56-2) |
| benzoyl chloride | (98-88-4) |
| Benzophenone | (119-61-9) |
| pinacol | (76-09-5) |
| Benzopinacol | (464-72-2) |
| benzopinacolone | (466-37-5) |