



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](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.

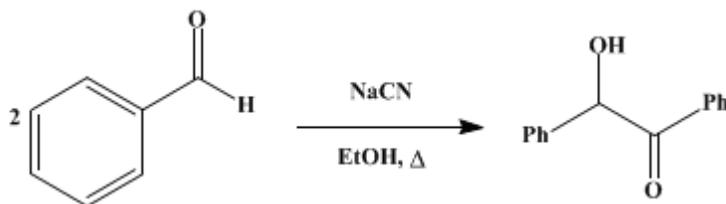
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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. 1, p.94 (1941); Vol. 1, p.33 (1921).*

## BENZOIN



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### 1. Procedure

In a 3-l. round-bottomed flask (Note 1) fitted with a reflux condenser are placed 625 cc. of 95 per cent alcohol (Note 2), 500 cc. of water, 500 g. (4.76 cc., 4.7 moles) of pure benzaldehyde (Note 3), and 50 g. of sodium cyanide (96–98 per cent). The mixture is then heated and kept boiling for one-half hour (Note 4). In the course of about twenty minutes, crystals begin to separate from the hot solution. At the end of the thirty minutes, the solution is cooled, filtered with suction, and washed with a little water. The yield of dry crude benzoin, which is white or light yellow, is 450–460 g. (90–92 per cent of the theoretical amount). In order to obtain it completely pure, the crude substance is recrystallized from 95 per cent alcohol, 90 g. of crude material being dissolved in about 700 cc. of boiling alcohol; upon cooling, a yield of 83 g. of white, pure benzoin which melts at 129° is obtained.

### 2. Notes

1. The reaction sometimes takes place with considerable violence and material may be lost through the condenser. Accordingly, a somewhat larger flask is generally desirable, or the upper end of the reflux condenser is provided with a wide tube leading to an empty flask.
2. The procedure described requires 50 per cent of the amount of dilute alcohol which is ordinarily recommended in the literature. This allows one to prepare just double the amount of material in the same sized flask. The product obtained in this way, however, is slightly yellower than that obtained when more alcohol is used, but upon recrystallization it gives just as pure a product as that obtained by recrystallization of crude material made in the presence of more solvent. The results of many experiments lead to the conclusion that, if large amounts of benzoin are to be prepared, the method described above is the better one. If, however, only a small amount is needed and a good grade of crude material is satisfactory, the larger amount of solvent is perhaps more desirable.
3. It is absolutely necessary that pure benzaldehyde be used for this reaction. The crude benzaldehyde which is obtained on the market should be washed with sodium carbonate solution, dried, distilled with minimum atmospheric exposure, and a fraction collected at 178–180°. Crude material will never give much more than a 50 per cent yield of benzoin.
4. Several times when benzoin was being prepared, the condensation took place and was complete after boiling five to ten minutes or even less, the product separating out in the hot solution with evolution of heat. The yield under these conditions was always good and the color better than when the reaction took a longer time. The cause of this occasional rapid reaction was not discovered, but it was probably due to inoculation with a little benzoin in certain of the experiments. When it takes place as just described, the flask and efficient condenser used will be sufficient to condense the sudden, rapid evolution of alcohol vapors caused by the heat of crystallization of the benzoin.

### 3. Discussion

Benzoin can be prepared by the action of an alkali cyanide on an alcoholic solution of benzaldehyde<sup>1</sup> and by the condensation of benzene with phenylglyoxal in the presence of aluminum chloride.<sup>2</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 87](#)
- [Org. Syn. Coll. Vol. 1, 89](#)
- [Org. Syn. Coll. Vol. 2, 69](#)
- [Org. Syn. Coll. Vol. 2, 159](#)
- [Org. Syn. Coll. Vol. 2, 231](#)
- [Org. Syn. Coll. Vol. 7, 95](#)

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## References and Notes

1. Wöhler and Liebig, *Ann.* **3**, 276 (1832); Zinin, *Ann.* **34**, 186 (1840); Zincke, *Ann.* **198**, 151 (footnote) (1879).
  2. Arnold and Fuson, *J. Am. Chem. Soc.* **58**, 1295 (1936).
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## Appendix

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

[alkali cyanide](#)

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

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

[sodium cyanide \(143-33-9\)](#)

[sodium carbonate \(497-19-8\)](#)

[benzaldehyde \(100-52-7\)](#)

[aluminum chloride \(3495-54-3\)](#)

[Benzoin \(119-53-9\)](#)

[Phenylglyoxal \(1074-12-0\)](#)