



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.

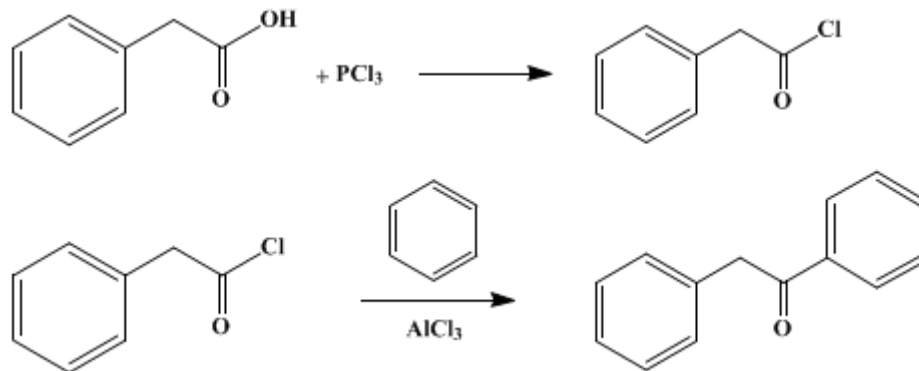
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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. 2, p.156 (1943); Vol. 12, p.16 (1932).

DESOXYBENZOIN



Submitted by C. F. H. Allen and W. E. Barker.
Checked by C. S. Marvel and Tse-Tsing Chu.

1. Procedure

To 68 g. (0.5 mole) of phenylacetic acid (Note 1) in a 1-l. flask fitted with a reflux condenser and a system for absorbing hydrogen chloride, is added 35 g. (0.25 mole) of phosphorus trichloride. The mixture is heated on a steam bath for one hour. While the contents of the flask are still warm, 400 cc. of dry benzene is added. The benzene solution of phenylacetyl chloride is decanted from the residue of phosphorous acid onto 75 g. (0.56 mole) of anhydrous aluminum chloride in a dry, 1-l. flask which can be fitted to the same condenser. The reaction is vigorous at first and cooling is necessary. The mixture is refluxed for one hour on a steam bath, then cooled and poured into a mixture of 500 g. of cracked ice and 200 g. of concentrated hydrochloric acid. The benzene layer is separated, and the aqueous layer is extracted once with a mixture of 100 cc. of benzene and 100 cc. of ether (Note 2). The ether-benzene solution is washed once with 100 cc. of water (Note 3), and then dried over 40–50 g. of calcium chloride. The solution is filtered (Note 4) with suction into a 1-l. Claisen flask, and the solvent is removed by distillation under reduced pressure (Note 5); the residue consists of a brown oil which solidifies on cooling.

The crude material (91–92 g.) is purified by distillation under reduced pressure from a 250-cc. Claisen flask (Note 6). The product distils at 160°/5 mm. (172°/15 mm.; 200°/30 mm.) as a colorless oil which solidifies on cooling. The yield is 81–82 g. (82–83 per cent of the theoretical amount based on the phenylacetic acid used) of a product which melts at 53–54°. The product is recrystallized from methyl alcohol, using 4 cc. of solvent for each gram of product (Note 7); the yield is 55–56 g. of crystals melting at 55–56°. An additional 7 g. of crystals melting at 55–56° is obtained by cooling the filtrate in an ice-salt bath. On further cooling of the mother liquors, about 5 g. of crystals melting at 54–55° is obtained. The total yield of purified product is 67–70 g. (Note 8). Further recrystallization of the product from methyl alcohol does not raise the melting point above 55–56°.

2. Notes

- Directions for preparing phenylacetic acid are given in *Org. Syn. Coll. Vol. I, 1941, 436*. A very high grade of phenylacetic acid can also be obtained from companies supplying essential oils and perfumers' supplies, and some of the acid from these commercial sources is superior to that prepared by the Organic Syntheses procedure. Since the quality of the desoxybenzoin depends upon the quality of the phenylacetic acid used, it is important to employ a superior grade of acid.
- A mixture of benzene and ether is used instead of ether alone because a more efficient separation of the two layers is obtained.
- Washing with sodium hydroxide at this point does not improve the quality of the product but does, as a result of the formation of emulsions, cause an 8–10 per cent loss in yield.

4. It is better to remove the [calcium chloride](#) by filtration than by decantation even though the solution looks clear. Small particles of [calcium chloride](#) and [aluminum chloride](#) not removed from the solution may cause bumping or even decomposition during the distillation.
5. Removal of the solvent by distillation under reduced pressure on the steam bath makes fractionation unnecessary during distillation of the product.
6. It is necessary to use a Claisen flask with a wide side-arm, since the desoxybenzoin may solidify and clog the apparatus. The distillation under reduced pressure is quiet if directions are followed carefully.
7. [Methyl alcohol](#) is the best solvent for purification. Desoxybenzoin tends to separate from [ethyl alcohol](#) as an oil.
8. Desoxybenzoin is somewhat unstable to light and consequently must be stored in dark bottles.

3. Discussion

Because of the availability of the starting materials, the most convenient methods of preparing desoxybenzoin are the Friedel-Crafts reaction,¹ described above, and the reduction of [benzoin](#).² Desoxybenzoin can also be prepared, often with very good yields, by the treatment of [bromostilbene](#) with water in a sealed tube at 180–190°;³ by the reduction of [benzil](#);⁴ by the action of [zinc](#) and [hydrochloric acid](#) on [chlorobenzil](#);⁵ from [benzene](#), [phenylacetic acid](#), and [phosphorus pentoxide](#);⁶ from [benzoyl chloride](#) and the magnesium halide derivative of [sodium phenylacetate](#);⁷ from [benzylmagnesium chloride](#) and [benzamide](#);⁸ and by alkaline hydrolysis of [desylthioglycollic acid](#).⁹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 339](#)

References and Notes

1. Graebe and Bungener, *Ber.* **12**, 1080 (1879).
2. Kohler, *Am. Chem. J.* **36**, 182 (1906); Irvine and Weir, *J. Chem. Soc.* **91**, 1388 (1907); Kohler and Nygaard, *J. Am. Chem. Soc.* **52**, 4133 (1930); Ballard and Dehn, *ibid.* **54**, 3970 (1932).
3. Limpricht and Schwanert, *Ann.* **155**, 60 (1870).
4. Japp and Klingemann, *J. Chem. Soc.* **63**, 770 (1893).
5. Thiele and Straus, *Ann.* **319**, 163 (1901).
6. Zincke, *Ber.* **9**, 1771 (1876).
7. Ivanoff and Nicoloff, *Bull. soc. chim.* (4) **51**, 1331 (1932).
8. Jenkins, *J. Am. Chem. Soc.* **55**, 704 (1933).
9. Behaghel and Schneider, *Ber.* **68**, 1588 (1935).

Appendix

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

Desoxybenzoin

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

[calcium chloride](#) (10043-52-4)

[hydrogen chloride](#),
[hydrochloric acid](#) (7647-01-0)

Benzene (71-43-2)
methyl alcohol (67-56-1)
ether (60-29-7)
sodium hydroxide (1310-73-2)
benzoyl chloride (98-88-4)
benzamide (55-21-0)
aluminum chloride (3495-54-3)
Benzil (134-81-6)
Benzoin (119-53-9)
zinc (7440-66-6)
Phenylacetic acid (103-82-2)
phosphorus trichloride (7719-12-2)
benzylmagnesium chloride (6921-34-2)
phenylacetyl chloride (103-80-0)
bromostilbene
chlorobenzil
sodium phenylacetate (114-70-5)
desylthioglycollic acid
phosphorous acid (13598-36-2)
phosphorus pentoxide (1314-56-3)