



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.

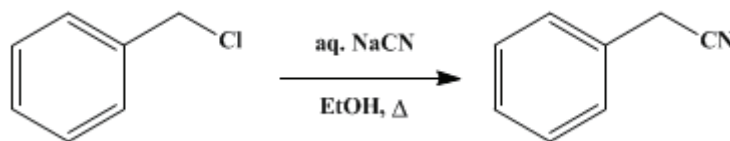
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.107 (1941); Vol. 2, p.9 (1922).

BENZYL CYANIDE

[α -Tolunitrile]



Submitted by Roger Adams and A. F. Thal.

Checked by O. Kamm and A. O. Matthews.

1. Procedure

In a 5-l. round-bottomed flask, fitted with a stopper holding a reflux condenser and separatory funnel, are placed 500 g. (10 moles) of powdered sodium cyanide (96–98 per cent pure) and 450 cc. of water. The mixture is warmed on a water bath in order to dissolve most of the sodium cyanide, and then 1 kg. (8 moles) of benzyl chloride (b.p. 170–180°) (Note 1) mixed with 1 kg. of 95 per cent alcohol is run in through the separatory funnel in the course of one-half to three-quarters of an hour. The mixture is then heated under a reflux condenser on the steam bath for four hours, cooled and filtered with suction to remove most of the sodium chloride. It is well to wash the filtered salt with a small portion of alcohol in order to remove any benzyl cyanide which may have been mechanically held.

The flask is now fitted with a condenser, and as much alcohol as possible is distilled off on the steam bath. The residual liquid is cooled, filtered if necessary, and the layer of benzyl cyanide separated. This crude benzyl cyanide is now placed in a Claisen distilling flask and distilled under reduced pressure, the water and alcohol coming over first, and finally the cyanide (Note 2). It is advantageous to use a fractionating column or, better still, a Claisen flask with a modified side arm¹ (p. 130), which gives the same effect as a fractionating column (Note 3). The material is collected at 135–140°/38 mm. (115–120°/10 mm.) (Note 4). The yield is 740–830 g. (80–90 per cent of the theoretical amount).

2. Notes

1. The quality of the benzyl chloride markedly affects the yield of pure benzyl cyanide. If a poor technical grade is used, the yields will not be more than 60–75 per cent of the theoretical, whereas consistent results of about 85 per cent or more may always be obtained when a product is used that boils over 10°. The technical benzyl chloride at hand yielded on distillation about 8 per cent of high-boiling material; a technical grade from another source was of unusual purity and boiled over a 2° range for the most part.
2. It is advisable to distil off the last portion of alcohol and water and also to distil the benzyl cyanide under reduced pressure, since under ordinary pressures a white solid invariably separates during the distillation.
3. One method of purifying the benzyl cyanide is to steam distil it after the alcohol has been first distilled from the reaction mixture. At ordinary pressures, this steam distillation is very slow and, with an ordinary condenser, requires eighteen to twenty hours in order to remove all the volatile product from a run of 500 g. of benzyl chloride. The distillate separates into two layers; the benzyl cyanide layer is removed and distilled. The product obtained in this way is very pure and contains no tarry material, and, after the excess of benzyl chloride has been removed, boils at practically constant temperature. This steam distillation is hardly advisable in the laboratory.
4. Benzyl cyanide, prepared according to the procedure just described and collected over a 5° range, is perfectly satisfactory for many purposes, such as the preparation of phenylacetic acid (p. 436) or ester (p. 270). However, the cyanide has a disagreeable odor due to the presence of benzyl isocyanide and often develops appreciable color on standing. The following treatment, suggested by John R. Johnson, removes the isocyanide and furnishes a water-white product which develops no color on standing for

several months. The once-distilled [benzyl cyanide](#) is shaken vigorously for five minutes with an equal volume of warm (60°) 50 per cent [sulfuric acid](#), prepared by adding 275 cc. of concentrated [sulfuric acid](#) to 500 cc. of water. The [benzyl cyanide](#) is separated and washed with an equal volume of saturated [sodium bicarbonate](#) solution followed by an equal volume of half-saturated [sodium chloride](#) solution. It is then dried and distilled under reduced pressure. The loss in the washings is negligible.

3. Discussion

[Benzyl cyanide](#) can be prepared from alcoholic [potassium cyanide](#) and [benzyl chloride](#).² The less expensive [sodium cyanide](#) is just as satisfactory and therefore is the better compound to use. An aqueous solution of [sodium cyanide](#) has been used.³ It has been prepared by passing [phenylacetic acid](#) and [ammonia](#) over silica gel at 500°,⁴ and by the catalytic reduction of [mandelonitrile](#).⁵

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 270](#)
- [Org. Syn. Coll. Vol. 1, 396](#)
- [Org. Syn. Coll. Vol. 1, 436](#)
- [Org. Syn. Coll. Vol. 2, 287](#)
- [Org. Syn. Coll. Vol. 2, 487](#)
- [Org. Syn. Coll. Vol. 2, 512](#)
- [Org. Syn. Coll. Vol. 3, 715](#)
- [Org. Syn. Coll. Vol. 3, 720](#)
- [Org. Syn. Coll. Vol. 4, 387](#)
- [Org. Syn. Coll. Vol. 4, 760](#)

References and Notes

1. Noyes and Skinner, *J. Am. Chem. Soc.* **39**, 2718 (1917).
 2. Cannizzaro, *Ann.* **96**, 247 (1855); Radziszewski, *Ber.* **3**, 198 (1870); Mann, *Ber.* **14**, 1645 (1881); Staedel, *Ber.* **19**, 1950 (1886).
 3. Gomberg and Buchler, *J. Am. Chem. Soc.* **42**, 2059 (1920).
 4. Mitchell and Reid, *ibid.* **53**, 328 (1931).
 5. Zelinsky, Packendorff, and Leder-Packendorff, *Ber.* **67**, 300 (1934).
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Appendix

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

[silica gel](#)

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

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

[ammonia](#) (7664-41-7)

[α-Tolunitrile](#) (100-47-0)

[sodium bicarbonate](#) (144-55-8)

sodium cyanide (143-33-9)

sodium chloride (7647-14-5)

cyanide,
isocyanide (57-12-5)

potassium cyanide (151-50-8)

benzyl chloride (100-44-7)

Benzyl cyanide (140-29-4)

Phenylacetic acid (103-82-2)

Benzyl isocyanide (10340-91-7)

mandelonitrile (532-28-5)