Organic Syntheses

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.

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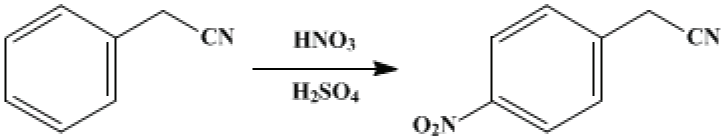
Organic Syntheses, Coll. Vol. 1, p.396 (1941); Vol. 2, p.57 (1922).

p-NITROBENZYL CYANIDE

[α-Tolunitrile, *p*-nitro-]



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1. Procedure

In a 2-l. round-bottomed flask, fitted with a stopper holding a dropping funnel and a mechanical stirrer, is placed a mixture of 275 cc. (4.3 moles) of concentrated nitric acid (sp. gr. 1.42) (Note 1) and 275 cc. (4.9 moles) of concentrated sulfuric acid (sp. gr. 1.84). This is cooled to 10° in a freezing mixture, and 100 g. (0.85 mole) of benzyl cyanide (free from alcohol and water) (Note 2) is run in slowly, at such a rate that the temperature remains at about 10° and does not exceed 20°. After all the benzyl cyanide has been added (about one hour), the ice bath is removed, and the mixture is stirred for one hour and then poured onto 1200 g. of crushed ice. A pasty mass slowly separates; more than half of this mass is *p*-nitrobenzyl cyanide, the other constituents being *o*-nitrobenzyl cyanide, and a variable amount of an oil which resists hydrolysis; apparently no dinitro compounds are formed. The mass is filtered on a porcelain funnel with suction, pressed well to remove as much oil as possible, and dissolved in 500 cc. of boiling 95 per cent alcohol. On cooling, *p*-nitrobenzyl cyanide crystallizes; the mother liquor, on distillation, gives an impure alcohol which can be used for the next run. Recrystallization from 550 cc. of 80 per cent alcohol (sp. gr. 0.86 to 0.87) yields 70–75 g. (50–54 per cent of the theoretical amount) (Note 3) of a product which melts at 115–116°.

This product is satisfactory for most purposes, and incidentally for the preparation of *p*-nitrophenylacetic acid (p. 406). Occasionally it must be free even from traces of the ortho compound; if so, it should be crystallized again from 80 per cent alcohol; it then melts at 116–117°.

2. Notes

1. Fuming nitric acid may be used, but the procedure described is less expensive.
2. The yield of 70–75 g. is obtained from benzyl cyanide, which boils over a 5° range, prepared as described on p. 107. Very pure benzyl cyanide will give a slightly higher yield, whereas commercial grades may give only 50 g. of *p*-nitrobenzyl cyanide and much oil.
3. The reaction has been also carried out with 500 g. of benzyl cyanide. Under these conditions a 5-l. flask was used, and it required two and one-half hours to add the benzyl cyanide. The yield of product was 325–370 g. (47–54 per cent of the theoretical amount).

3. Discussion

p-Nitrobenzyl cyanide has hitherto been prepared by the action of fuming nitric acid[1] on benzyl cyanide.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 406

References and Notes

1. Salkowski, Ber. **17**, 505 (1884); Pschorr, Ber. **33**, 170 (1900); Koessler and Hanke, J. Biol. Chem. **39**, 585 (1919); Robertson and Stieglitz, J. Am. Chem. Soc **43**, 180 (1921); Baker, Cooper, and Ingold, J. Chem. Soc. 426 (1928).

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

alcohol	(64-17-5)
sulfuric acid	(7664-93-9)
nitric acid	(7697-37-2)
Benzyl cyanide	(140-29-4)
p-Nitrophenylacetic acid	(104-03-0)
p-Nitrobenzyl cyanide	(555-21-5)
α-Tolunitrile, p-nitro-	(619-72-7)
o-nitrobenzyl cyanide	(610-66-2)