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.

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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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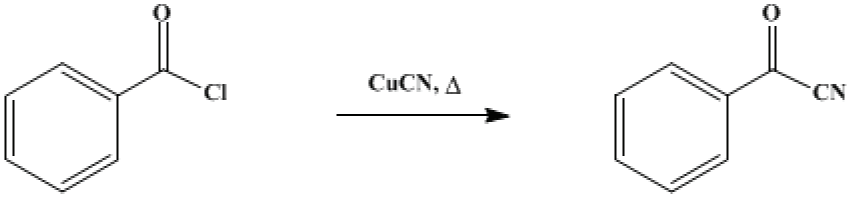
BENZOYL CYANIDE

[Glyoxylonitrile, phenyl-]



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1. Procedure

In a 500-ml. distilling flask (Note 1) fitted with a thermometer extending to within 0.5 in. of the bottom are placed 110 g. (1.2 moles) of cuprous cyanide (Note 2) and 143 g. (118 ml., 1.02 moles) of purified benzoyl chloride (Note 3). The flask is shaken to moisten almost all the cuprous cyanide and is placed in an oil bath (Note 4) which has been previously heated to 145–150°. The temperature of the bath is raised to 220–230° and maintained between these limits for 1.5 hours. During the heating the flask is frequently removed from the bath (about every 15 minutes) and the contents are thoroughly mixed by vigorous shaking (Note 5). At the end of the 1.5 hours the flask is connected with an air-cooled condenser set for downward distillation. The temperature of the bath is slowly raised to 305–310°, and distillation is continued until no more product comes over (Note 6). About 100–112 g. of crude benzoyl cyanide boiling at 207–218°/745 mm. is obtained.

The crude benzoyl cyanide is purified by fractional distillation through a column (Note 7). The low-boiling material is taken off at a reflux ratio of 25–30 to 1 until the temperature reaches 208°; about 15 g. is collected. The benzoyl cyanide is collected at a reflux ratio of 1 to 1 at a temperature of 208–209°/745 mm. (bath temperature 260–280°). The distillate solidifies to colorless crystals which melt at 32–33°; the product weighs 80–86 g. (60–65%).

2. Notes

1. It is advisable to wrap the neck of the flask with asbestos paper or asbestos tape.
2. The cuprous cyanide is dried at 110° for 3 hours before use.
3. The commercial grade of benzoyl chloride may be purified as follows: 300 ml. (363 g.) of benzoyl chloride in 200 ml. of benzene is washed with two 100-ml. portions of cold 5% sodium bicarbonate solution. The benzene layer is separated, dried over calcium chloride, and distilled. After all the benzene has distilled, pure benzoyl chloride boiling at 196.8°(cor.)/745 mm. is collected. The recovery is 225 g.
4. Hydrogenated cottonseed oil, "Coto Flakes," obtainable from the Procter and Gamble Company, Cincinnati, Ohio, is suitable for the bath. A Wood's metal bath may also be used.
5. Upon addition of the benzoyl chloride to the cuprous cyanide thorough mixing by shaking is impossible. After the mixture is heated for about 30 minutes, the solid becomes granular and mixing is easily effected.
6. The distillate should be collected in the 200-ml. round-bottomed flask which is used in the subsequent fractionation. The distillation takes about an hour. The cake of copper salts in the flask is best removed by digestion with concentrated ammonium hydroxide solution.
7. The fractionating column was of the Whitmore-Lux type[1] and had about 14 theoretical plates. The packed section was 37 by 1.1 cm. (o.d.) and was packed with 3/32-in. single-turn glass helices. The distilling flask was a 200-ml. round-bottomed flask. A metal bath or the oil bath described in (Note 4) may be used for heating.

3. Discussion

Benzoyl cyanide can be prepared by the thermal decomposition of ω-isonitrosoacetophenone,[2] from silver cyanide and benzoyl chloride,[3] from anhydrous hydrogen cyanide and benzoyl chloride in the presence of pyridine,[4] and by the thermal decomposition of phenylchloronitrocyanomethane.[5,6] It has been prepared by the vapor-phase reaction between hydrogen cyanide and benzoic anhydride in the presence of a granular catalyst (activated charcoal, alumina, or silica gel).[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 114

References and Notes

1. Whitmore and Lux, *J. Am. Chem. Soc.*, **54**, 3451 (1932).
2. Claisen and Manasse, *Ber.*, **20**, 2195 (1887).
3. Nef, *Ann.*, **287**, 307 (1895).
4. Claisen, *Ber.*, **31**, 1024 (1898).
5. Wislicenus and Shafer, *Ber.*, **41**, 4170 (1908).
6. Staudinger and Kon, *Ann.*, **384**, 115 (1911).
7. Brit. pat. 583,646 [*C. A.*, **41**, 2746 (1947)].

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

calcium chloride (10043-52-4)

Benzene (71-43-2)

sodium bicarbonate (144-55-8)

hydrogen cyanide (74-90-8)

Cuprous Cyanide (544-92-3)

benzoyl chloride (98-88-4)

Benzoic anhydride (93-97-0)

pyridine (110-86-1)

ammonium hydroxide (1336-21-6)

Benzoyl cyanide,
Glyoxylonitrile, phenyl- (613-90-1)

ω-isonitrosoacetophenone

silver cyanide (506-64-9)

phenylchloronitrocyanomethane

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