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.

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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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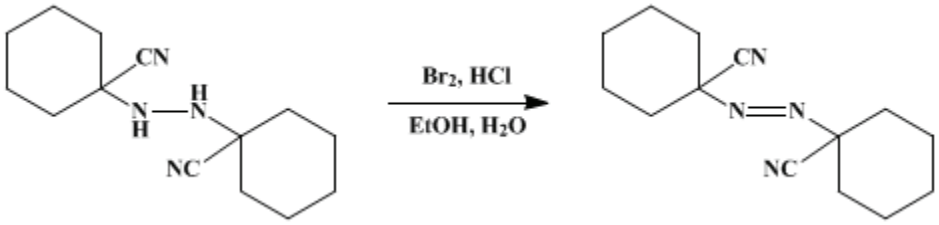
1,1'-AZO-*bis*-1-CYCLOHEXANENITRILE

[Cyclohexanecarbonitrile, 1,1'-azodi-]



Submitted by C. G. Overberger, Pao-tung Huang, and M. B. Berenbaum[1].
Checked by N. J. Leonard and E. H. Mottus.

1. Procedure

In a 600-ml. beaker equipped with a stirrer, thermometer, and dropping funnel are placed 24.6 g. (0.1 mole) of finely powdered 1,2-di-1-(1-cyano)cyclohexylhydrazine (p. **274**) and 130 ml. of 90% ethanol. To this mixture is added slowly, with cooling, 45 ml. of concentrated hydrochloric acid. The beaker is placed in an ice bath, and, after the suspension has been cooled to 10°, bromine is added at such a rate that the temperature does not rise above 15°. About 16–17 g. (about 0.1 mole) of bromine is required to reach the end point characterized by Permanent orange-yellow color. The reaction mixture is poured into 80 ml. of ice water. After 15 minutes the suspension is filtered with the aid of a Büchner funnel, washed with 250 ml. of water, and pressed dry. The solid is transferred to a 500-ml. Erlenmeyer flask, 120 ml. of boiling 95% ethanol is added, and the crude product is dissolved as rapidly as possible while being heated on a steam bath (Note 1). The solution is filtered through a fluted filter in a heated funnel, and the filtrate is placed in a refrigerator overnight. The solid is collected on a Büchner funnel and dried in a vacuum desiccator over calcium chloride. The yield of product is 20.5–22.0 g. (84–90%); m.p. 113.5–115.5° (Note 2) and (Note 3).

2. Notes

1. Prolonged heating of the solution will cause excessive decomposition of the azo compound.
2. This compound is stable indefinitely if stored at room temperature. Prolonged heating at temperatures of 80° or higher, however, will result in rapid decomposition involving possible hazards.[2]
3. 2,2'-Azo-*bis*-isobutyronitrile can be prepared in a similar manner. The product after recrystallization from 95% ethanol is obtained in a yield of 85–90%; m.p 102–103°. This compound must be regarded as an explosive.[2]

3. Discussion

1,1'-Azo-*bis*-1-cyclohexanenitrile has been prepared in a similar manner by Hartman.[3] The method has been substantiated by Overberger, O'Shaughnessy, and Shalit [4] and is a modification of that used originally by Thiele and Heuser[5] for the synthesis of 2,2'-azo-*bis*-isobutyronitrile.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 273
- Org. Syn. Coll. Vol. 4, 274

References and Notes

1. Polytechnic Institute of Brooklyn, Brooklyn, New York.
2. Carlisle, *Chem. Eng. News*, **27**, 150 (1949); **28**, 803 (1950).
3. Hartman, *Rec. trav. chim.*, **46**, 150 (1927).
4. Overberger, O'Shaughnessy, and Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949).
5. Thiele and Heuser, *Ann.*, **290**, 1 (1896).

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

1,2-Di-1-(1-cyano)cyclohexylhydrazine

ethanol (64-17-5)

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

bromine (7726-95-6)

2,2'-Azo-bis-isobutyronitrile

1,1'-AZO-bis-1-CYCLOHEXANENITRILE,
Cyclohexanecarbonitrile, 1,1'-azodi- (2094-98-6)