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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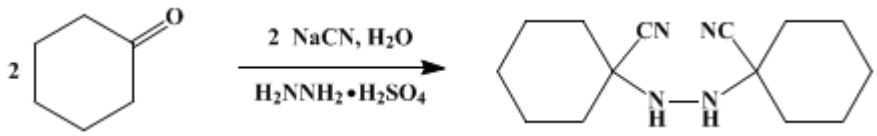
1,2-DI-1-(1-CYANO)CYCLOHEXYLHYDRAZINE

[Cyclohexanecarbonitrile, 1,1'-hydrazodi-]



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

1. Procedure

Caution! These operations should be conducted in an efficient hood.

In a 600-ml. screw-capped bottle are placed 15.4 g. (0.32 mole) of sodium cyanide, 20.5 g. (0.16 mole) of hydrazine sulfate (Note 1), and 400 ml. of ice water. The bottle is capped to prevent loss of hydrogen cyanide (Note 2) and held in an ice bath for 15 minutes. To the cooled mixture is added 29.4 g. (0.3 mole) of cyclohexanone. The bottle is recapped and cooled for an additional 15 minutes. The bottle is then shaken intermittently over a period of 6 hours and allowed to stand an additional 14 hours. The bottle is cooled again before opening. The suspension is filtered by means of suction, and the cake is washed thoroughly with 250 ml. of ice water. After the crude product has been pressed dry on the filter (Note 3), it is transferred to a 500-ml. Erlenmeyer flask and 150 ml. of boiling 95% ethanol is added. The suspension is brought into solution as rapidly as possible by warming on a hot plate (Note 4) and is filtered quickly through a prewarmed 7.5-cm. Büchner funnel. An additional 10 ml. of hot 95% ethanol is used to dissolve any organic residue on the filter, and the combined filtrates are warmed to redissolve any precipitate. The solution is allowed to stand undisturbed for 6 hours in an icebox. The product is collected on a Büchner funnel, washed with 15 ml. of cold 95% ethanol, and then dried over solid calcium chloride in a vacuum desiccator. The yield of product is 24.5–26 g. (66–70%); m.p. 147–149° (Note 5).

2. Notes

1. Technical hydrazine sulfate of known purity is suitable.
2. Both hydrazine and hydrogen cyanide are toxic, and appropriate precautions should be taken.
3. The checkers have used the dry, crude product directly in the conversion to 1,1'-azo-*bis*-1-cyclohexanenitrile (see p. 66) with an over-all yield of 72% based upon cyclohexanone.
4. Excessive or prolonged heating will result in a decreased yield owing to decomposition of the product.
5. 1,2-Di-2-(2-cyano)propylhydrazine (2,2'-hydrazo-*bis*-isobutyronitrile) may be prepared in a similar manner from acetone. The crude product (m.p. 89–91°; yield 88–93%) can be oxidized directly to 2,2'-azo-*bis*-isobutyronitrile. The dried impure material can be recrystallized from ether; m.p. 91.5–92.5°; (72–77%).

3. Discussion

1,2-Di-1-(1-cyano)cyclohexylhydrazine has been prepared by a procedure similar to that used by Hartman.[2] The procedure has been substantiated by Overberger, O'Shaughnessy, and Shalit.[3]

References and Notes

1. Polytechnic Institute of Brooklyn, Brooklyn, New York.
2. Hartman, *Rec. trav. chim.*, **46**, 150 (1927).
3. Overberger, O'Shaughnessy, and Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949).

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

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

1,2-Di-2-(2-cyano)propylhydrazine (2,2'-hydrazo-bis-isobutyronitrile)

ethanol (64-17-5)

calcium chloride (10043-52-4)

ether (60-29-7)

Cyclohexanone (108-94-1)

sodium cyanide (143-33-9)

hydrogen cyanide (74-90-8)

acetone (67-64-1)

Hydrazine sulfate (10034-93-2)

hydrazine (302-01-2)

2,2'-Azo-bis-isobutyronitrile

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

Cyclohexanecarbonitrile, 1,1'-hydrazodi- (17643-01-5)