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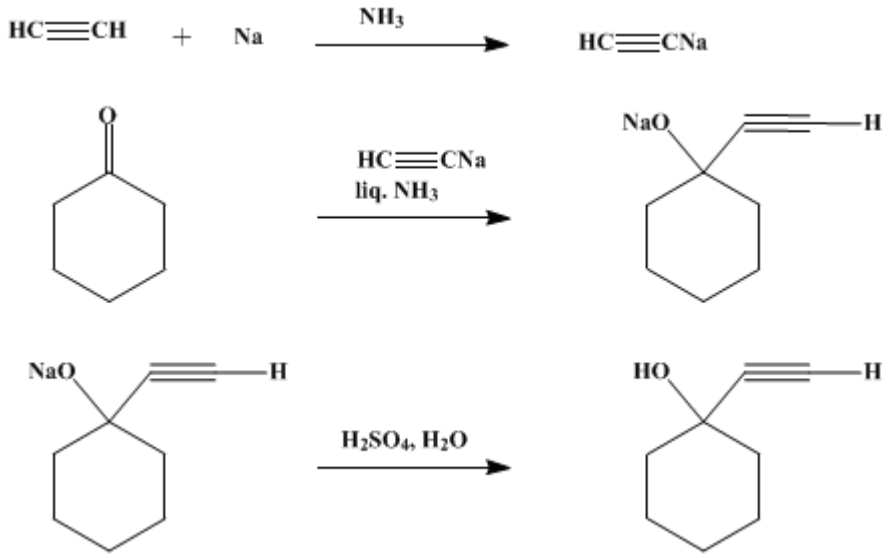
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.029.0047

Organic Syntheses, Coll. Vol. 3, p.416 (1955); Vol. 29, p.47 (1949).

1-ETHYNYLCYCLOHEXANOL

[Cyclohexanol, 1-ethynyl-]



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1. Procedure

A rapid stream of dry acetylene is passed into approximately 1 l. of liquid ammonia in a 2-l. three-necked flask equipped with a gas inlet tube and a mechanical stirrer while 23 g. (1 gram atom) of sodium is added over a period of 30 minutes (Note 1) and (Note 2). The flow of acetylene is then reduced (Note 3), and 98 g. (1 mole) of cyclohexanone is added dropwise. When this addition, which requires about an hour, is completed, the reaction mixture is allowed to stand for about 20 hours to permit the evaporation of nearly all the ammonia (Note 4).

The solid residue is decomposed by adding approximately 400 ml. of ice and water, and the resulting mixture is carefully acidified with 50% sulfuric acid (Note 5). The organic layer is dissolved in 100 ml. of ether and washed with 50 ml. of brine. The original aqueous phase and the brine wash are then extracted with two 50-ml. portions of ether. The combined ethereal solutions are dried over anhydrous magnesium sulfate and filtered, and the ether is distilled. The product is then distilled under reduced pressure through a good column (Note 6). The yield of 1-ethynylcyclohexanol is 81–93 g. (65–75%), b.p. 74°/14 mm.; n_D^{20} 1.4822 (Note 7).

2. Notes

1. The preparation of sodium acetylide is based on the procedure of Vaughn, Hennion, Vogt, and Nieuwland.[2]
2. The blue color of dissolved sodium is discharged so rapidly by the acetylene that it seldom spreads through the entire mixture.
3. The flow of acetylene may be terminated before the cyclohexanone is added. This operation, however, is alleged to increase the formation of glycol.[3]
4. If all the ammonia is allowed to evaporate and the residual solid is exposed to the air the yields may be decreased.
5. Upwards of 70 ml. is required. The amount depends upon the quantity of ammonia remaining.
6. The submitters and the checkers used a 15-cm. Vigreux column.
7. The product may solidify to a colorless solid, m.p. 30°.

3. Discussion

An attractive alternative procedure for the preparation of 1-ethynylcyclohexanol which gives yields of 80–90% employs the potassium salt of *tert*-amyl alcohol to effect the addition of acetylene to cyclohexanone.[4,5,6] This condensation has been brought about by a suspension of sodium amide in ether[7,8,9,10,11] and by potassium hydroxide in ether.[12] 1-Ethynylcyclohexanol has also been prepared by the action of acetylene on the sodium enolate of cyclohexanone[13] and by the action of sodium acetylide on cyclohexanone in liquid ammonia.[14] The procedure described here is essentially that of Campbell, Campbell, and Eby.[3]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 22
- Org. Syn. Coll. Vol. 4, 13

References and Notes

1. This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.
2. Vaughn, Hennion, Vogt, and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).
3. Campbell, Campbell, and Eby, *J. Am. Chem. Soc.*, **60**, 2882 (1938).
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10. Levina and Vinogradova, *J. Applied Chem. U.S.S.R.*, **9**, 1299 (1936) [*C. A.*, **31**, 2587 (1937)].
11. *Org. Syntheses*, **20**, 41 (1940), Note 11.
12. Azerbaev, *J. Gen. Chem. U.S.S.R.*, **15**, 415 (1945) [*C. A.*, **40**, 4683 (1946)].
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14. Milas, MacDonald, and Black, *J. Am. Chem. Soc.*, **70**, 1831 (1948).

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

brine

sodium enolate of cyclohexanone

sulfuric acid (7664-93-9)

acetylene (74-86-2)

ammonia (7664-41-7)

ether (60-29-7)

Cyclohexanone (108-94-1)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

magnesium sulfate (7487-88-9)

sodium amide (7782-92-5)

1-Ethynylcyclohexanol,
Cyclohexanol, 1-ethynyl- (78-27-3)

sodium acetylide

potassium salt of tert-amyl alcohol (41233-93-6)