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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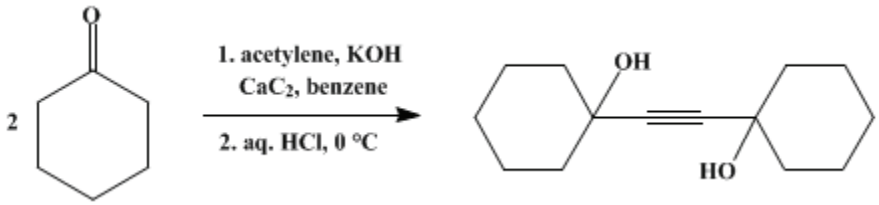
1,1'-ETHYNYLENE-*bis*-CYCLOHEXANOL

[Cyclohexanol, 1,1'-ethynylenedi-]



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1. Procedure

In a 2-l. three-necked flask (Note 1), fitted with a dropping funnel, condenser (equipped with a Drierite tube), and efficient stirrer driven by a powerful motor, is placed a mixture of 600 ml. of benzene, 56 g. (0.85 mole) of 85% potassium hydroxide (Note 2), and 76.4 g. of powdered calcium carbide (Note 3). While this mixture is being stirred vigorously, 85 g. (0.87 mole) of cyclohexanone is added over a period of 0.5–1 hour. The mixture is dark gray and will become warm, but no external cooling is necessary. Stirring is continued, and within 24 hours the contents congeal (Note 4). This semisolid is allowed to stand for an additional 4 days (Note 5).

The flask is immersed in an ice bath, and a solution containing 200 ml. of concentrated hydrochloric acid and 200 ml. of water is added cautiously (Note 6) over a period of 4–6 hours. The dark solid is separated by filtration with the aid of a large Büchner funnel. This impure product is air-dried and digested with 900 ml. of boiling carbon tetrachloride, and the insoluble portion is collected on a Büchner funnel and subsequently extracted with 100 ml. of hot acetone and again filtered. When the filtrates are kept overnight in a refrigerator, 47.3–50.3 g. (49–52%) of a colorless crystalline product separates; m.p. 106.5–109°. Partial evaporation of the combined filtrates, followed by effective cooling, gives an additional 7.8–12.9 g. (8–13%) of 1,1'-ethynylene-*bis*-cyclohexanol; m.p. 100–109° (Note 7).

2. Notes

1. The submitters employed a 12-l. resin flask equipped with Lightning Stirrer whose shaft and blades were of stainless steel when using 10 times the quantity of starting materials reported here.
Any evolution of acetylene is best accommodated by a rubber tube which leads outside or to a good hood.
2. Either pellets or flakes of potassium hydroxide are powdered in a ball mill.
3. Technical calcium carbide of approximately 100 mesh was obtained from the Union Carbide and Carbon Corporation, New York, New York. The amount of calcium carbide used is in excess and based on an activity of 75%.
4. Stirring is continued until the mass has set solidly; it is desirable for a channel to exist around the stirrer shaft to facilitate the subsequent decomposition.
5. Decreased yields result from shorter periods of standing.
6. It is advisable to bore several holes into the solid mass by means of a stirring rod in order to permit better contact with the acid. Initial addition of the acid should be slow, and a total of 4–6 hours should be allowed for this operation, since considerable heat and acetylene are evolved.
7. The product can be recrystallized from carbon tetrachloride or acetone, or sublimed at reduced pressure, to yield a product melting at 109–111°.

3. Discussion

This method is based on the procedure of Kazarin.[2] The same substance has been prepared by the

reaction of the dimagnesium halide[3] or dilithium derivative[4] of acetylene with cyclohexanone, and also by the reaction of cyclohexanone with acetylene in the presence of potassium *tert*-butoxide followed by the preparation of the Grignard reagent of this compound and reaction again with cyclohexanone.[5]

It has been claimed that the yield of the present reaction is improved when it is carried out in the presence of an acetal or ethylene glycol dialkyl ether.[6] Petrov et al.[7] have reported that they obtained almost a 100% yield of the glycol when cyclohexanone was treated with acetylene and double the amount of potassium hydroxide.

References and Notes

1. University of Maryland, College Park, Maryland.
2. Kazarin, *J. Gen. Chem. U.S.S.R.*, **4**, 1347 (1934).
3. Dupont, *Ann. chim.*, [8] **30**, 485 (1913).
4. Viehe, Franchimont, and Valange, *Chem. Ber.*, **92**, 3064 (1959).
5. Pinkney, Nesty, Wiley, and Marvel, *J. Am. Chem. Soc.*, **58**, 972 (1936).
6. Bergmann, Sulzbacher, and Herman, *J. Appl. Chem. (London)*, **3**, 39, (1953).
7. Petrov, Mitrofanova, and Lesyuchevskaya, *Doklady Akad. Nauk S.S.S.R.*, **68**, 83 (1949) [*C. A.*, **44**, 1903 (1950)].

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

calcium carbide

acetylene (74-86-2)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

Cyclohexanone (108-94-1)

carbon tetrachloride (56-23-5)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

potassium tert-butoxide (865-47-4)

1,1'-ETHYNYLENE-bis-CYCLOHEXANOL,
Cyclohexanol, 1,1'-ethynylenedi- (78-54-6)