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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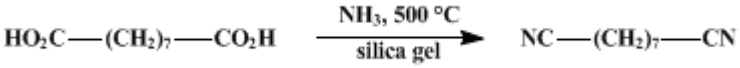
Organic Syntheses, Coll. Vol. 4, p.62 (1963); Vol. 34, p.4 (1954).

AZELANITRILE



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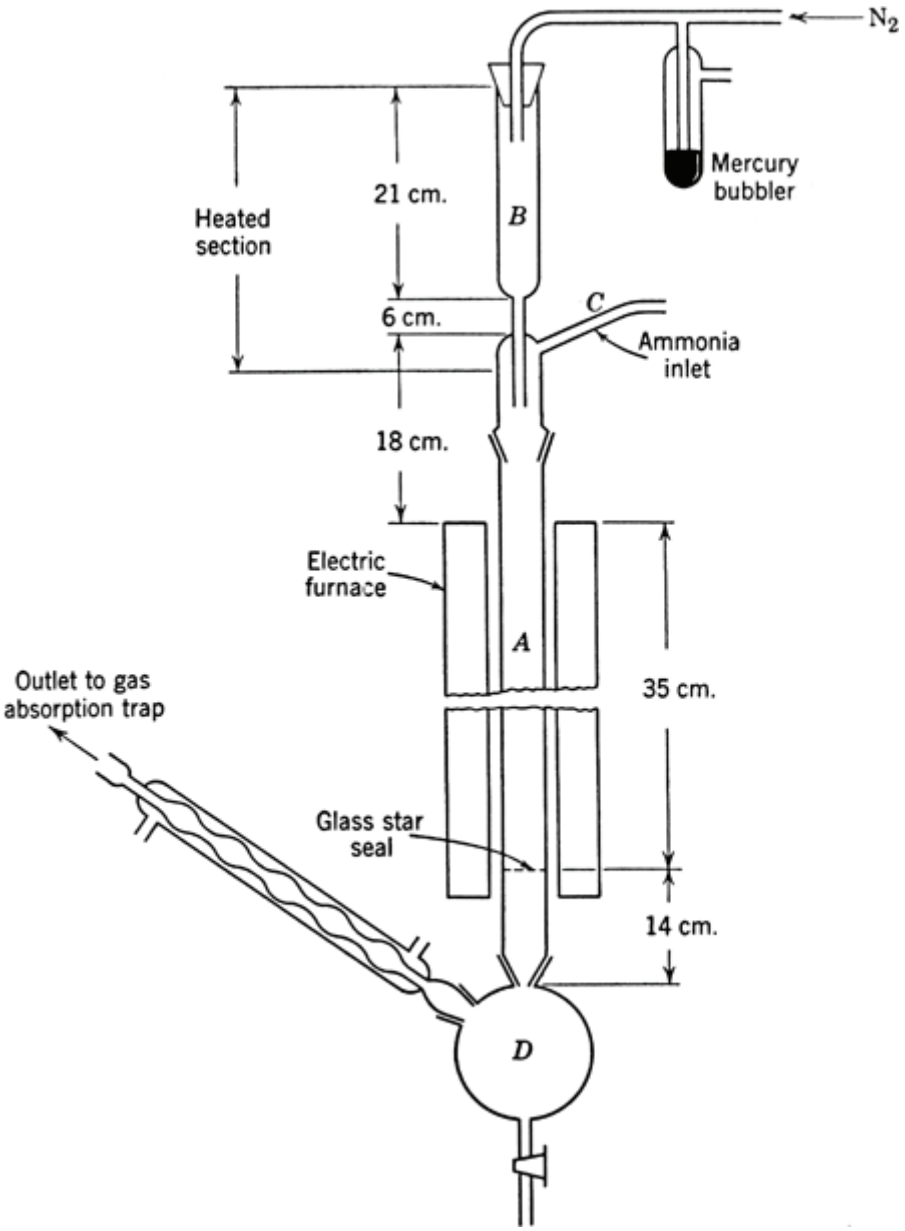
Checked by N. J. Leonard and R. W. Fulmer.

1. Procedure

Caution! This preparation should be conducted in a hood to avoid exposure to ammonia.

The reaction is carried out in the apparatus shown in Fig. 3. *A* is a Pyrex combustion tube, 54 cm. long and 3.5 cm. in diameter, having a glass star seal or indentations 14 cm. from the lower end to support the catalyst, and fitted with ground-glass joints. *B* is a Pyrex tube, 21 cm. long and 3.5 cm. in diameter, which has a 6-cm. length of 6-mm. capillary tubing attached at the lower end. The capillary tube is attached to a ground-glass joint and an inlet tube, *C*, is inserted above the end of the capillary tube. The top section of the apparatus (above the first ground-glass joint) is covered with asbestos and wound with 14 ft. of No. 22 Chromel A resistance wire. *D* is a 500-ml. round-bottomed two-necked flask with ground-glass joints and a 4-mm. stopcock sealed to the bottom. An efficient condenser is attached to the flask and connected to a gas absorption trap.[2] The hot junction of a pyrometer is placed in contact with the glass combustion tube *A* at its center, and the tube is wrapped with a thin layer of asbestos paper. An electric furnace with a 33-cm. heated section which is rated at 6.8 amp. (110 v.) is used to heat the combustion tube.

Fig. 3.



A piece of glass wool is placed on the star seal, and the combustion tube is filled with 74 g. (110 ml.) of 14- to 20-mesh silica gel (Note 1). The tube is heated to 500°, and nitrogen is passed through the column for 30 minutes to activate the catalyst. Anhydrous ammonia is then passed through the column at a rate of 3.9 moles per hour (Note 2). Molten azelaic acid, 100 g. (0.53 mole) (Note 3), is poured into the reservoir *B*, which is maintained at 108–112° by means of the electrically heated jacket, and allowed to drop onto the hot silica gel over a 4-hour period (Note 4). After the azelaic acid has been added, ammonia is passed through the tube for an additional period of 30 minutes, with the temperature maintained at 500°, to complete the removal of product from the combustion tube.

Water (100 ml.) and ether (350 ml.) are added to the condensate in the receiver *D*, and the mixture is shaken. The aqueous layer is removed, and the ethereal solution is washed with 75 ml. of 6*N* sodium hydroxide solution. The ethereal solution is washed with water until the washings are neutral and is dried over anhydrous magnesium sulfate. The ether is removed under reduced pressure by warming with a water bath, and the residue is distilled through a Vigreux or packed column. The azelanitrile is collected at 120–121°/0.2 mm., 175–176°/6 mm., in a yield of 50–54 g. (63–68%), n_D^{25} 1.4443–1.4448 (Note 5) and (Note 6).

2. Notes

1. Refrigeration grade silica gel, 14- to 20-mesh, obtained from the Davison Chemical Corporation, Baltimore, Maryland, was used.
2. A manometer-type flow meter[3] was calibrated by passing ammonia through the meter into a standard solution of 4*N* hydrochloric acid containing a few drops of phenolphthalein solution. The time required for exact neutralization of a measured volume of acid was recorded, together with the pressure differential, in millimeters, between the manometer arms. The logarithm of the rate of flow in moles per hour plotted against the logarithm of the pressure, for various rates of flow, gave a straight-line plot which was used to determine flow rates for other pressure differentials.
3. Azelaic acid obtained from Emery Industries, Inc., Cincinnati, Ohio, was recrystallized from water to a melting point of 101–102°.
4. Comparable results have been obtained when the acid was added over a 2-hour period. It is desirable to maintain a nitrogen atmosphere over the acid at a pressure slightly above that of the ammonia flow to prevent reduction of the acid flow by salt formation in the capillary.
5. Cooling the receiver *D* may help prevent loss of product by mechanical carry-over in the gas flow.
6. This preparation illustrates a general method for producing nitriles from monocarboxylic[4] and dicarboxylic acids.[5]

3. Discussion

Azelanitrile has been prepared in 80% yield by treating 1,7-dibromoheptane with potassium cyanide;[6] by treating 1,7-diiodoheptane with potassium cyanide;[7] from azelaic acid through the intermediate acid chloride and diamide;[8] in 60–70% yield by the dehydration of the diamide of azelaic acid;[9] and by the action of sodium amide and acetonitrile on the 1,5-dihalopentanes.[10]

References and Notes

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

diamide of azelaic acid

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

acetonitrile (75-05-8)

sodium hydroxide (1310-73-2)

nitrogen (7727-37-9)

potassium cyanide (151-50-8)

phenolphthalein (77-09-8)

Azelaic acid (123-99-9)

magnesium sulfate (7487-88-9)

Azelanitrile (1675-69-0)

sodium amide (7782-92-5)

1,7-dibromoheptane (4549-31-9)

1,7-diiodoheptane (51526-03-5)