



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.

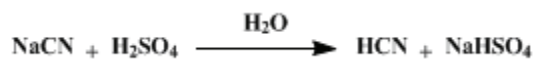
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.314 (1941); Vol. 7, p.50 (1927).

HYDROGEN CYANIDE (ANHYDROUS)

[Hydrocyanic acid]



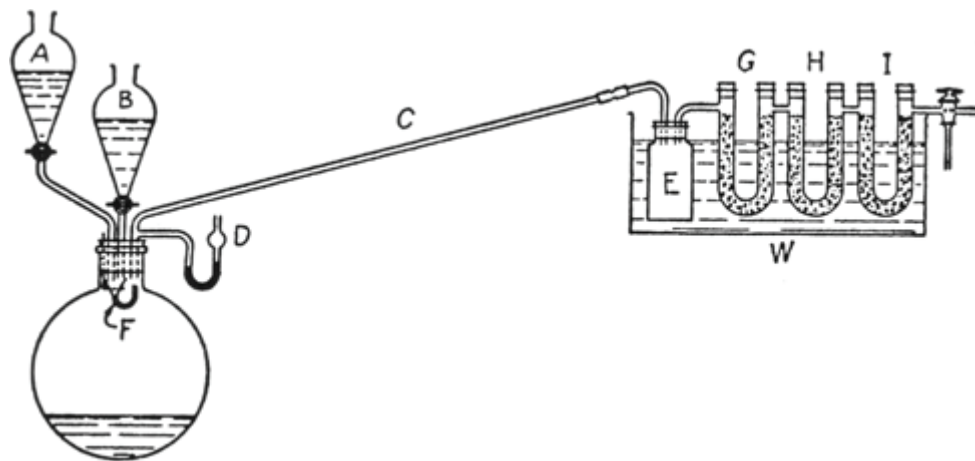
Submitted by K. Ziegler

Checked by Henry Gilman and L. C. Heckert.

1. Procedure

A 5-l. round-bottomed flask, set up in a good hood (Note 1), is fitted with a three-holed rubber stopper that holds two 250-cc. separatory funnels, A and B (Fig. 18). A small funnel F (about 3–4 cm. in diameter) is suspended directly under the outlets of the two separatory funnels and is attached to the rubber stopper by a loop of stiff copper wire. The discharge tube of the funnel is bent in the shape of a U so that its end is about 1 cm. below the top of the funnel. In the third hole of the rubber stopper is inserted an inclined glass tube, C, of about 10-mm. internal bore and approximately 50 cm. long. A mercury safety vent, D, is sealed in the side of this tube. C acts as an air condenser and leads to an empty gas bottle, E, of about 250-cc. capacity and then to three large U-tubes, G, H, and I, filled with anhydrous calcium chloride. The gas bottle and the U-tubes are contained in a water bath, W, warmed to 30–40°. The last calcium chloride tube is fitted with a three-way glass stopcock so that the gaseous anhydrous hydrogen cyanide may be used directly or diverted to an efficient condenser for liquefaction. The condenser is a glass coil of 4–5 mm. bore and about 50 cm. long that is surrounded by ice (Note 2) contained in a percolator arrangement like that described on p. 117.

Fig. 18.



One of the separatory funnels is filled with dilute sulfuric acid prepared by the careful addition of 392 g. (213 cc., 4 moles) of concentrated sulfuric acid to 830 cc. of water. The other separatory funnel is filled with a solution of 203 g. (4 moles) of commercial sodium cyanide (about 96 per cent) dissolved in sufficient water to make 500 cc. of solution. Evolution of hydrogen cyanide takes place on the simultaneous addition of the two solutions. Practically all the reaction occurs in the funnel, F, and the sodium bisulfate solution continuously drains into the flask so that fresh solutions are always present. The solution in the funnel remains clear as long as sufficient sulfuric acid is present. An excess of sodium cyanide colors the solution yellow and leads to the formation of a muddy brown precipitate (Note 3). By adjusting the flow of solutions the rate of evolution is easily controlled, and the preparation requires no attention beyond that involved in the occasional replenishment of the solutions in the separatory funnels. The last part of the hydrogen cyanide can be driven from the apparatus by boiling the bisulfate solution for a few minutes. The yield of acid melting at -15° to -14.5° is 100–105 g. (93–

97 per cent of the theoretical amount) (Note 4) and (Note 5).

2. Notes

1. Gattermann¹ recommends that the operator smoke during the preparation, for he found that a trace of hydrogen cyanide is sufficient to give the tobacco smoke a highly characteristic flavor. This preliminary warning is useful in case of leaky apparatus or a faulty hood.
2. It is essential that the coil be cooled with ice only. A freezing mixture causes solidification of the hydrogen cyanide with consequent clogging of the apparatus.
3. If the reaction is slowed up considerably or interrupted so that the solution becomes cool, sodium bisulfate crystallizes both in the funnel and in the generating flask.
4. The hydrogen cyanide is best kept over anhydrous calcium chloride. In this way it remains clear and water-white for months; otherwise, it soon becomes yellow, owing to the formation of azulmic acid. Concentrated hydrochloric acid (two drops per 500 g. of hydrogen cyanide) has also been recommended as a stabilizer.²
5. If larger quantities of hydrogen cyanide are desired, the apparatus may be modified as suggested by Lindemann³ by using a four-holed rubber stopper in the generating flask and fitting it with a siphon tube by means of which the sodium bisulfate solution can be removed from time to time. With this modification the generating flask need be of only 2- to 3-l. capacity. Hydrogen cyanide may be prepared conveniently, probably in lower yields than in the procedure described, by adding the saturated sodium cyanide solution one-half inch below the surface of 50 per cent sulfuric acid contained in a flask. The residual amount is expelled by warming the flask on a steam bath. The apparatus is the same as that used for generating hydrogen chloride (p. 293) by passing aqueous hydrochloric acid into sulfuric acid (W. W. Hartman, private communication).

3. Discussion

Hydrogen cyanide can be prepared by the action of sulfuric acid on potassium ferrocyanide,¹ potassium cyanide⁴ or sodium cyanide.⁵ The procedure described is based on the methods of Ziegler⁵ and Lindemann.⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 14
- Org. Syn. Coll. Vol. 6, 334

References and Notes

1. Gattermann, Ann. **357**, 318 (1907).
2. Slotta, Ber. **67**, 1030 (1934).
3. Lindemann, Ann. **431**, 291 (1923).
4. Villars, J. Am. Chem. Soc. **52**, 64 (1930).
5. Ziegler, Ber. **54**, 110 (1921); Lindemann, Ann. **431**, 290 (1923). Pauer, Monatsh. **58**, 1 (1931).

Appendix

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

azulmic acid

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

sodium cyanide (143-33-9)

hydrogen cyanide,
hydrocyanic acid (74-90-8)

potassium cyanide (151-50-8)

sodium bisulfate (7681-38-1)

potassium ferrocyanide