



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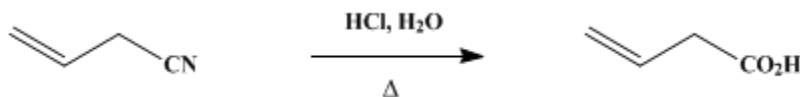
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.851 (1955); Vol. 24, p.96 (1944).

VINYLACETIC ACID

[3-Butenoic acid]



Submitted by Edward Rietz

Checked by C. F. H. Allen and James VanAllan.

1. Procedure

In a 500-ml. flask attached to a reflux condenser is placed a mixture of 67 g. (80 ml., 1 mole) of allyl cyanide¹ (Note 1) and 100 ml. (1.2 moles) of concentrated hydrochloric acid (sp. gr. 1.19). The mixture is heated by a small flame and is shaken frequently. After 7–8 minutes, the reaction begins, a voluminous precipitate of ammonium chloride appears, the temperature rises rapidly, and the mixture refluxes. After 15 minutes the flame is removed, 100 ml. of water is added, and the upper layer of the acid is separated (Note 2). The aqueous layer is extracted with two 100-ml. portions of ether. The extracts and the acid are combined and distilled. Most of the ether is removed at atmospheric pressure (Note 3), (Note 4), and (Note 5), and the remainder is removed as the pressure is diminished. The acid is collected at 70–72°/9 mm. after a fore-run of approximately 40 g. The yield of crude acid is 50–53 g. (52–62%) (Note 5).

Although this product is pure enough for most purposes, it contains small amounts of by-products which cannot be removed by distillation. Further purification is accomplished by the following procedure: In a 250-ml. three-necked round-bottomed flask fitted with a stirrer, a small dropping funnel, and a thermometer for reading low temperatures, 24 g. of sodium hydroxide is dissolved in 80 ml. of water. While the temperature of *of the solution* is maintained at 8–15° by external cooling, 45 g. (40.5 ml.) of the impure vinylacetic acid is added; this operation requires 25 minutes. This solution is transferred to a 600-ml. conical separatory funnel and extracted with 50 ml. of chloroform (Note 6) and (Note 7). The alkaline solution is *immediately* transferred to a 1-l. beaker, and 300 ml. of dilute sulfuric acid (Note 8) and (Note 9) is added with stirring. This acid solution is *at once* extracted with three 100-ml. portions of chloroform (Note 7) and (Note 10). The solvent is then removed by distillation, first at atmospheric pressure and then at reduced pressure, from a 200-ml. modified Claisen flask. The residue is distilled under reduced pressure. Almost all the material boils at 69–70°/12 mm. (163°/760 mm.). The recovery is 30–33 g. (75–82%) (Note 11).

2. Notes

1. An improved procedure for preparation of allyl cyanide (3-butenenitrile) is as follows: In a dry (washed with absolute ethanol and absolute ether) 500-ml. three-necked flask, equipped with a sealed mechanical stirrer and a 90-cm. bulb condenser set vertically and protected by a calcium chloride tube, are placed 85 g. of dry cuprous cyanide (commercial, or prepared as previously described;¹ dried for 72 hours in an oven at 110° just before use), 0.25 g. of potassium iodide, and 72.5 g. of allyl chloride (dried over calcium chloride and freshly distilled; b.p. 45–47°). The stirrer is started, and the mixture is heated on a water bath. After about 6 hours the reaction is substantially complete, as indicated by cessation of the refluxing; heating is continued for 1 hour beyond this point. With larger runs it may be necessary to moderate the reaction by removing the water bath when vigorous refluxing sets in. This usually occurs about 3–5 hours after heating is started. Runs of the size described do not require any special attention. The water bath is replaced by an oil bath, the condenser is set downward for distillation, and stirring is continued while the allyl cyanide is distilled into a 100-ml. distilling flask. Near the end of the distillation it may be necessary to discontinue stirring, and it is advisable to reduce the pressure somewhat to aid in the removal of the last portion of the product. The distillate is redistilled, and 50–53 g. (79–84%) of allyl cyanide boiling at 116–122° is collected. (Private communication from Curtis W.

- Smith and H. R. Snyder; checked by W. E. Bachmann and G. Dana Johnson.)
2. This amounts to 90–95 g. A separatory funnel of about 600-ml. capacity is the most convenient size.
 3. The first ether extract contains 10 g. of nitrile; the second extract contains 4.5 g.
 4. This procedure is shorter and less tedious than the more common method of drying and fractionating the ethereal solution.
 5. A Dry Ice trap, inserted between the oil pump and the apparatus, condenses 5–10 g. of unchanged allyl cyanide. The yield of crude acid, after allowing for the recovered nitrile, is 62–72%.
 6. This extraction removes about 1 g. of non-acidic impurity.
 7. Ether can be substituted for chloroform without materially decreasing the yield.
 8. This is prepared by diluting 16.5 ml. of concentrated sulfuric acid to 300 ml.
 9. Contact with alkali results in the isomerization of vinylacetic acid to crotonic acid.
 10. The first two extractions remove 27–28 g.; the last one, 3–4 g.
 11. When cooled in a Dry Ice-acetone bath the acid should remain clear until it crystallizes at -36° to -35° . This indicates freedom from crotonic acid.²

3. Discussion

The only practical methods for the preparation of vinylacetic acid involve hydrolysis of allyl cyanide;^{3,4} carbonation of allylmagnesium bromide^{5,6} or an alkali salt of propylene.⁷ The malonic acid synthesis is less satisfactory than the hydrolysis of allyl cyanide.⁴

References and Notes

1. *Org. Syntheses Coll. Vol. 1*, 46 (1941).
 2. Fichter, *Ber.*, **35**, 938 (1902).
 3. Falaise and Frogner, *Bull. soc. chim. Belg.*, **42**, 433 (1933) [*C. A.*, **28**, 2329 (1934)].
 4. Linstead, Noble, and Boorman, *J. Chem. Soc.*, **1933**, 560.
 5. Houben, *Ber.*, **36**, 2897 (1903).
 6. Gilman and McGlumphy, *Bull. soc. chim. France*, (4) **43**, 1327 (1928).
 7. Morton, Brown, Holden, Letsinger, and Magat, *J. Am. Chem. Soc.*, **67**, 2224 (1945).
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Appendix

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

allyl cyanide (3-butenenitrile)

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

potassium iodide (7681-11-0)

Allyl cyanide (109-75-1)

Cuprous Cyanide (544-92-3)

allyl chloride (107-05-1)

Malonic acid (141-82-2)

crotonic acid (3724-65-0)

Vinylacetic acid,
3-Butenoic acid (625-38-7)

Allylmagnesium bromide (1730-25-2)