



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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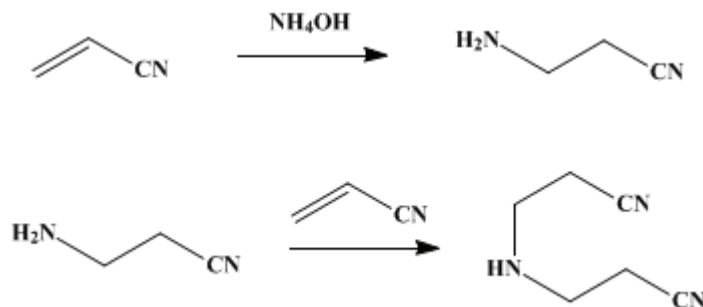
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.93 (1955); Vol. 27, p.3 (1947).

β -AMINOPROPIONITRILE and bis-(β -CYANOETHYL)-AMINE

[Propionitrile, β -amino-, and propionitrile, β,β' -iminodi-]



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Checked by Homer Adkins and James M. Caffrey.

1. Procedure

Acrylonitrile is a poisonous compound. All steps in the procedure up to the distillation of the products should be carried out in a hood.

The reactions are carried out in 1-l. heavy-walled bottles provided with rubber stoppers which must be wired securely in place (Note 1). In each of four bottles are placed 400 ml. of concentrated ammonium hydroxide (28–30% ammonia) and 100 ml. (80 g., 1.5 moles) of cold acrylonitrile (Note 2). The rubber stoppers are immediately wired in place (Note 3). Each bottle is then shaken intermittently until after about 5 minutes the reaction mixture becomes homogeneous. Thereupon, the bottle, wrapped in a towel, is immediately set away under a hood (Note 4).

The reaction mixtures are allowed to stand a few hours or overnight and then are transferred to a 3-l. flask. The water and ammonia are distilled under reduced pressure as rapidly as possible until the boiling point is about 50°/20 mm. (Note 5). The higher-boiling products (395 g.) are then transferred to a 1-l. Claisen flask and fractionated under reduced pressure.

The crude primary amine (138–149 g.) is distilled over the range 75–110°/21 mm. (Note 6), and the crude secondary amine (213–226 g.) in the range 130–150°/1 mm. The primary amine, b.p. 79–81°/16 mm. or 87–89°/20 mm. (n_D^{20} 1.3496), after refractionation, is obtained in a yield of 130–140 g. (31–33%) (Note 7). The secondary amine, b.p. 134–135°/1 mm. (n_D^{20} 1.4640), is obtained in a yield of about 210 g. (57%) (Note 8).

2. Notes

1. The 1-l. centrifuge bottles (Corning No. 1280) carrying No. 6 rubber stoppers, as used for catalytic hydrogenation, are suitable for carrying out reactions under pressures up to at least 3 atm. The submitter used a heavy, selected 2-l. round-bottomed flask instead of the four bottles specified in the procedure above.
2. The acrylonitrile should be free of polymer. If there is uncertainty as to its quality, the acrylonitrile should be redistilled.
3. The temperature of the mixture does not rise during the period of solution of the acrylonitrile in the ammonium hydroxide. However, almost immediately thereafter the temperature of the solution begins to rise slowly, reaching a value of about 65° after an interval of perhaps 10 minutes. There is no significant rise in pressure within the bottle until the temperature of the reaction mixture begins to rise. The maximum pressure reached is apparently less than 2 atm.
4. The checkers placed the wrapped bottles within a 10-gal crock located under a hood. There is no

danger that the bottles will be broken by the pressure developed. However, if a stopper is not firmly held, it may be pushed out, in which event a portion of the reaction mixture will foam out of the bottle.

5. The submitter used a special apparatus suitable for the rapid evaporation of water under reduced pressure. The checkers used standard flasks. Better yields result from the rapid removal of water.

6. It is not necessary to purify the crude primary amine by redistillation if it is to be used immediately for the preparation of β -alanine. However, the moist nitrile is not stable in storage, pressure being developed in a container stored at room temperature.

7. Yields of 60–80% of the primary amine¹ have been obtained by introducing the acrylonitrile below the surface of the aqueous ammonia preheated at 110° in a steel reactor suitable for pressure reactions.

8. Yields of 88.5% of the secondary amine, as well as 6% *tris*-(β -cyanoethyl) amine, have been obtained by adding the acrylonitrile dropwise to aqueous ammonia whose amount was to the amount of acrylonitrile as 0.53 mole:1 mole.²

3. Discussion

β -Aminopropionitrile and *bis*-(β -cyanoethyl) amine have been made by the addition of anhydrous³ or aqueous ammonia⁴ to acrylonitrile. β -Aminopropionitrile has been made from β -chloropropionitrile and liquid ammonia (90% yield).⁵ *bis*-(β -Cyanoethyl) amine may be converted to β -aminopropionitrile by distillation at atmospheric pressure.

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 3*, 34

References and Notes

1. Ford, Buc, and Greiner, *J. Am. Chem. Soc.*, **69**, 844 (1947).
2. Wiedeman and Montgomery, *J. Am. Chem. Soc.*, **67**, 1994 (1945).
3. Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Am. Chem. Soc.*, **66**, 725 (1944).
4. Buc, Ford, and Wise, *J. Am. Chem. Soc.*, **67**, 92 (1945).
5. U. S. pat. 2,443,292 [*C. A.*, **42**, 7322 (1948)].

Appendix

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

ammonia (7664-41-7)

ammonium hydroxide (1336-21-6)

β -Alanine (107-95-9)

β -Aminopropionitrile,
Propionitrile, β -amino- (151-18-8)

acrylonitrile (107-13-1)

bis-(β -cyanoethyl) amine,
bis-(β -CYANOETHYL)-AMINE,
propionitrile, β,β' -iminodi- (111-94-4)

β -chloropropionitrile (542-76-7)

tris-(β -cyanoethyl) amine

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