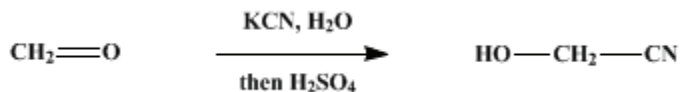


Glycolonitrile



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1. Procedure

This preparation should be carried out under a good hood since poisonous hydrogen cyanide may be evolved.

In a 1-l. three-necked flask, fitted with a stirrer, thermometer for reading low temperatures, and a dropping funnel, and surrounded by an ice-salt bath, is placed a solution of 130 g. (2.0 moles) of potassium cyanide in 250 ml. of water. With stirring, a solution of 170 ml. (2.0 moles) of commercial 37% formaldehyde solution¹ and 130 ml. of water is admitted slowly from the dropping funnel at such a rate that the temperature never rises above 10° (about 40 minutes is required). After 10 minutes' standing, 230 ml. of dilute sulfuric acid (57 ml. of concentrated sulfuric acid, sp. gr. 1.84, in 173 ml. of water) is added with stirring, the same low temperature being maintained. A copious precipitate of potassium sulfate is formed. The pH of the solution is then about 1.9. A 5% potassium hydroxide solution is then added, dropwise, and with cooling, until the pH is about 3.0 (determined either by means of a pH meter or tropaeolin 00 paper); about 4 ml. of the solution is required. The flask is then removed from the cooling bath, 30 ml. of ether is added, and the mixture is well shaken. The salt is removed by filtration, using a 14-cm. Büchner funnel, and washed with 30 ml. of ether. The filtrate is poured into a 1-l. continuous ether extractor² and extracted for 48 hours with 300 ml. of ether (Note 1). The ether extract is dried for 3–4 hours over 15 g. of anhydrous calcium sulfate (Drierite) (Note 2) and filtered. Ten milliliters of absolute ethanol is added to the filtrate, and the ether is removed on a steam bath (Note 3). The residue is distilled under reduced pressure using a flask having a Vigreux side arm. After a small (2–3 ml.) fore-run, the glycolonitrile distils smoothly at 86–88°/8 mm. (102–104°/16 mm.). The yield of pure glycolonitrile (Note 4) amounts to 86.5–91 g. (76–80%).

2. Notes

1. It is impractical to extract more than 40–45% of the nitrile without using a continuous ether extractor. A slightly lower yield is obtained if the extraction is continued for only 24 hours. The reaction mixture may be extracted in portions if the available flask is smaller than that specified.
2. Anhydrous sodium sulfate can be used equally well, but its drying action is slower, at least 24 hours being advisable.
3. If the ethanol is omitted, the nitrile shows a strong tendency to polymerize during the removal of the ether, especially when most of the ether has distilled.
4. The ethanol serves as a preservative before and after the distillation. Glycolonitrile obtained without the use of ethanol usually cannot be kept more than a few days; it sometimes turns brown within 24 hours. Some samples of ethanol-stabilized glycolonitrile have been preserved in sealed bottles for 2 years, whereas other samples polymerized in a few months.

3. Discussion

Glycolonitrile has usually been prepared by the interaction of formaldehyde and an alkali cyanide in aqueous solution³ of which the procedure outlined is a modification. A more recent development is the cyanohydrin interchange method.^{4,5} Glycolonitrile has also been prepared by a catalytic oxidation of methanol and ammonia in the vapor phase.⁶

References and Notes

1. *Org. Syntheses* Coll. Vol **1**, 378, Note 1 (1941).
 2. *Org. Syntheses* Coll. Vol. **2**, 378 (1943).
 3. Polstorff and Meyer, *Ber.*, **45**, 1911 (1912).
 4. Kung, U. S. pat. 2,259,167 [*C. A.*, **36**, 494 (1942)].
 5. Mowry, *J. Am. Chem. Soc.*, **66**, 372 (1944).
 6. U. S. pat. 2,405,963 [*C. A.*, **40**, 7231 (1946)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethanol (64-17-5)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)

methanol (67-56-1)

ether (60-29-7)

formaldehyde (630-08-0)

potassium sulfate (37222-66-5)

hydrogen cyanide (74-90-8)

sodium sulfate (7757-82-6)

potassium cyanide (151-50-8)

calcium sulfate (7778-18-9)

potassium hydroxide (1310-58-3)

Glycolonitrile (107-16-4)