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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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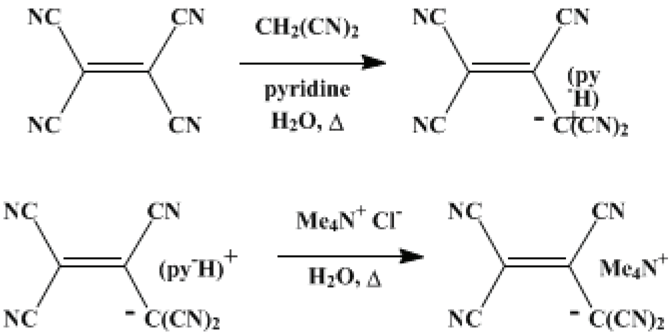
Organic Syntheses, Coll. Vol. 5, p.1013 (1973); Vol. 41, p.99 (1961).

TETRAMETHYLAMMONIUM 1,1,2,3,3-PENTACYANOPROPENIDE

[1-Propene-1,1,2,3,3-pentacarbonitrile, tetramethylammonium salt]



Submitted by W. J. Middleton and D. W. Wiley[1].
Checked by James Cason and William T. Miller.

1. Procedure

Caution! This reaction must be carried out in an efficient hood because large amounts of hydrogen cyanide are evolved. It is also recommended that tetracyanoethylene not be allowed to come into contact with the skin.

A solution of 6.6 g. (0.10 mole) of malononitrile (Note 1) in 8.7 g. (0.11 mole) of pyridine and 25 ml. of water is prepared in a 125-ml. Erlenmeyer flask and stirred mechanically (no stirrer seal required) as there is added rapidly in small portions a total of 12.8 g. (0.10 mole) of powdered recrystallized tetracyanoethylene (Note 2). The resulting mixture is warmed on a hot plate as stirring is continued until complete solution occurs (5–10 minutes, (Note 3)). The hot dark solution is poured into a swirled solution of 12.1 g. (0.11 mole) of tetramethylammonium chloride (Note 4) in 500 ml. of water. The resultant mixture is heated almost to boiling to give a dark-red solution, which is then allowed to cool spontaneously to room temperature. After final cooling in an ice bath, the orange needles of tetramethylammonium 1,1,2,3,3-pentacyanopropenide are collected by suction filtration and washed with two 100-ml. portions of cold water. This product is dissolved in 500 ml. of hot water, decolorized with about 5 g. of activated carbon, and allowed to crystallize as described above. The yield of bright yellow-orange needles, m.p. 314–315° (Note 5), is 19.5–20.5 g. (81–85%).

2. Notes

1. Malononitrile, m.p. 30–31°, obtained from Winthrop-Stearns Corp., New York, N. Y., is satisfactory.
2. Tetracyanoethylene is available from the Aldrich Chemical Company, Inc., or may be prepared by a simplified version of the procedure of Carboni.[2] In the simplified version, 99 g. of molten malononitrile is added to 450 ml. of cold water in the apparatus of Part A. This is followed by about 250 g. of ice and 158 ml. of bromine. The bromine is added during 5–10 minutes, and during the addition enough ice (about 200 g.) is added to maintain the temperature at 10–15°. The mixture is stirred at 20° for one hour. A heavy layer of dibromomalononitrile is separated, and the aqueous layer is extracted with two 50-ml. portions of 1,2-dichloroethane. The dibromomalononitrile and the extracts are combined, dried over magnesium sulfate, and added to 750 ml. of dry 1,2-dichloroethane in the flask of Part B. Twenty grams of copper power is added, and the mixture is heated to gentle reflux with stirring. An exothermic reaction generally occurs; when it subsides, or after about 10 minutes, a second 20-g. portion is added, and this process is continued until 120 g. has been added. The mixture is refluxed a total of 4-6 hours. The solids are separated from the hot mixture on a fluted filter, which is washed with a little hot 1,2-

dichloroethane. The filtrate is stored overnight at 0–5°. Nearly colorless tetracyanoethylene crystallizes out. It is separated on a Büchner funnel, washed with a little 1,2-dichloroethane, and dried in a vacuum desiccator; weight 29–38 g. (30–40%). It is over 98% pure as judged by its ε_{max} (pure tetracyanoethylene has $\lambda_{max}^{CH_2Cl_2}$ 277 mμ (ε 12,050), 267 mμ (ε 13,600)). It is pure enough for most purposes, but can be sublimed at 1 mm. (bath 130–140°) if very pure material is needed (private communication from E. L. Martin and H. D. Carlson via B. C. McKusick).

3. The rate of solution depends upon the fineness of the tetracyanoethylene powder; however, solution should occur soon after the temperature reaches 60–70°.

4. A technical grade of tetramethylammonium chloride is satisfactory, provided old samples that have absorbed considerable water are not used.

5. In a heated block, the checkers observed melting points in the range 318–321°.

3. Discussion

Tetramethylammonium 1,1,2,3,3-pentacyanopropenide has been prepared by the base-catalyzed hydrolysis of tetracyanoethylene,[3] and by the present method, which is more economical of tetracyanoethylene.

4. Merits of Preparation

Tetramethylammonium 1,1,2,3,3-pentacyanopropenide is useful for preparation of pentacyanopropenide salts of other metal and quaternary ammonium cations by metathesis.[3] The free acid, which may be obtained by use of an ion-exchange resin,[3] has an ionization constant comparable to that of a strong mineral acid ($pK_a < -8.5$; the anion is not detectably protonated in 12*M* sulfuric acid).[4]

References and Notes

1. Contribution No. 482 from Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Delaware.
2. R. A. Carboni, *Org. Syntheses*, Coll. Vol. **4**, 877 (1963).
3. W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).
4. R. H. Boyd, unpublished experiments.

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

1-Propene-1,1,2,3,3-pentacarbonitrile, tetramethylammonium salt

copper power

sulfuric acid (7664-93-9)

hydrogen cyanide (74-90-8)

bromine (7726-95-6)

1,2-dichloroethane (107-06-2)

activated carbon (7782-42-5)

pyridine (110-86-1)

magnesium sulfate (7487-88-9)

Malononitrile (109-77-3)

Tetracyanoethylene (670-54-2)

dibromomalononitrile

Tetramethylammonium 1,1,2,3,3-pentacyanopropenide (53663-17-5)

tetramethylammonium chloride (75-57-0)