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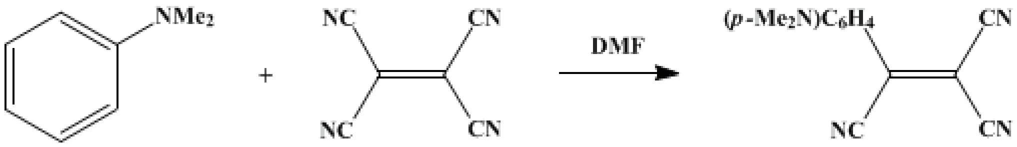
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.039.0068

Organic Syntheses, Coll. Vol. 4, p.953 (1963); Vol. 39, p.68 (1959).

p-TRICYANOVINYL-N,N-DIMETHYLANILINE

[Ethenetricarbonitrile, *p*-dimethylaminophenyl-]



Submitted by B. C. McKusick and L. R. Melby[1].
Checked by James Cason and Ralph J. Fessenden.

1. Procedure

> *Caution! Because hydrogen cyanide is formed in this reaction, all operations up to the recrystallization of the product should be carried out in a good hood. Contact of tetracyanoethylene with the skin should be avoided.*

A solution of 26.6 g. (28 ml., 0.22 mole) of N,N-dimethylaniline in 65 ml. of dimethylformamide is placed in a 250-ml. beaker clamped about 30 cm. above the base of a ring stand. The beaker is provided with a mechanical stirrer and thermometer. An iron ring is attached to the ring stand below the beaker so that the temperature of the reaction mixture can be controlled by raising or lowering an ice bath or hot water bath. Recrystallized tetracyanoethylene (p. 877) (25.6 g., 0.20 mole) is added in small portions over a period of about 5 minutes with good stirring. The rate of addition is such as to maintain the temperature at 45–50°, and occasional cooling with an ice bath may be necessary to keep the temperature within this range.

When all the tetracyanoethylene has been added, the reaction mixture is stirred at 45–50° for 10 minutes, and heat is supplied as needed by a water bath. *p*-Tricyanovinyl-N,N-dimethylaniline generally crystallizes out as a dark-blue solid during this period. At the end of the heating period, the mixture is chilled in an ice bath for 30 minutes. The tricyanovinyl compound is collected on a Büchner funnel, pressed dry with the help of a filter dam, and washed successively with 20 ml. of methanol and 40 ml. of ether. It weighs 25–30 g. after being dried in air.

The crude product is purified by recrystallization from 160–180 ml. of acetic acid. The solution (Note 1) is allowed to cool slowly to room temperature, and *p*-tricyanovinyl-N,N-dimethylaniline is collected on a Büchner funnel and washed successively with 20 ml. of methanol and 40 ml. of ether. The product, 23–26 g. (52–58%), is obtained as dark-blue needles, m.p. 173–175° (Note 2).

2. Notes

1. The acetic acid solution is so deep a red color that it is necessary to hold the flask over a bright light in order to determine when all the solid has dissolved. The solution will dye the skin with a fast red color.
2. Although the crystals have a very dark blue appearance, the solutions are deep red; in acetone, λ_{max} 517 mμ (ε 41,500).

3. Discussion

p-Tricyanovinyl-N,N-dimethylaniline has been prepared by adding hydrogen cyanide to *p*-dimethylaminobenzalmalononitrile and oxidizing the adduct.[2] The present procedure, an adaptation of one that has been published,[2] is the more convenient preparative method. It can be applied to a wide variety of secondary and tertiary aromatic amines to give *p*-tricyanovinylarylamines that, like the present one, are dyes.[2] Other types of aromatic compounds also condense with tetracyanoethylene in this manner. Thus one can obtain 4-tricyanovinyl-2,6-dimethylphenol from 2,6-dimethylphenol, 2-tricyanovinylpyrrole from pyrrole, and 9-tricyanovinylphenanthrene from phenanthrene.[3]

References and Notes

1. Contribution No. 484 from Central Research Department, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Delaware.
2. McKusick, Heckert, Cairns, Coffman, and Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958); Heckert (to E. I. du Pont de Nemours & Co.), U. S. pat. 2,889,335 [*C. A.*, **54**, 1877 (1960)].
3. Sausen, Engelhardt, and Middleton, *J. Am. Chem. Soc.*, **80**, 2815 (1958).

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

acetic acid (64-19-7)

methanol (67-56-1)

ether (60-29-7)

hydrogen cyanide (74-90-8)

acetone (67-64-1)

N,N-dimethylaniline (121-69-7)

Pyrrole (109-97-7)

phenanthrene (85-01-8)

dimethylformamide (68-12-2)

Tetracyanoethylene (670-54-2)

4-tricyanovinyl-2,6-dimethylphenol

2,6-dimethylphenol (576-26-1)

2-tricyanovinylpyrrole

9-tricyanovinylphenanthrene

p-Tricyanovinyl-N,N-dimethylaniline,
Ethenetricarbonitrile, p-dimethylaminophenyl- (6673-15-0)

p-dimethylaminobenzalmalononitrile (2826-28-0)