



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.

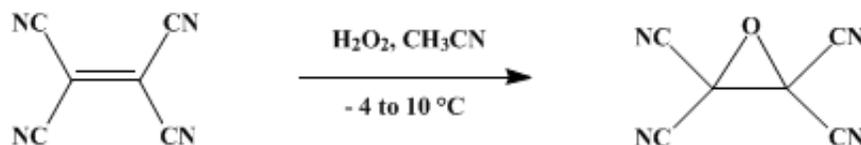
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.

TETRACYANOETHYLENE OXIDE

[Ethanetetracarbonitrile, 1,2-epoxy-]



Submitted by W. J. Linn¹

Checked by A. Eschenmoser, W. Lusuardi, and R. Scheffold.

1. Procedure

*Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. Peroxy compounds should be added to the organic material, never the reverse. For relatively fast reactions, the rate of addition of the peroxy compound should be slow enough so that it reacts rapidly and no significant unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peroxy compound is being added, and cooling should generally be provided since many reactions of peroxy compounds are exothermic. New or unfamiliar reactions, particularly those run at elevated temperatures, should be run first on a small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds (including unreacted peroxy compounds) have been destroyed. Decomposition of active oxygen compounds may be accomplished by the procedure described in Korach, M.; Nielsen, D. R.; Rideout, W. H. *Org. Synth.* 1962, 42, 50 (*Org. Synth.* 1973, Coll. Vol. 5, 414). [Note added January 2011].*

Caution! Both tetracyanoethylene and tetracyanoethylene oxide slowly evolve hydrogen cyanide when exposed to water. Therefore all operations should be conducted in an efficient hood and contact with the skin should be avoided.

In a 500-ml. Erlenmeyer flask fitted with an efficient stirrer and thermometer are placed 25.6 g. (0.2 mole) of tetracyanoethylene (Note 1) and 150 ml. of acetonitrile (Note 2). The flask is surrounded by an ice-salt bath and the stirrer is started. When the temperature is about -4° , 21 ml. of 30% hydrogen peroxide is added from a buret at the rate of 3–5 ml. of per minute. The rate is adjusted to keep the temperature at 10 – 12° (Note 3). Near the end of the addition, the color of the reaction mixture changes from dark amber to pale yellow. When all the peroxide has been added, the reaction mixture is stirred with efficient cooling for 3–4 minutes. Without delay the solution is then poured slowly, with very rapid stirring, into a mixture of 500 ml. of water and approximately 250 g. of crushed ice contained in 2-l. beaker (Note 4). The solid is filtered rapidly by suction through a coarse, sintered-glass funnel and washed with 200 ml. of ice water. For best results the product is dried on the funnel with continuous suction for 3–4 hours and recrystallized from 1,2-dichloroethane (10 ml. per g.) (Note 5). The yield of nearly colorless needles melting at 177 – 178° (sealed capillary) is 17.1–19.6 g. (59–68%) (Note 6). The infrared spectrum of the oxide (Nujol mull) is simple and useful in product identification. In addition to the strong $\text{-C}\equiv\text{N}$ absorption at 4.38μ , there are bands at 7.68, 8.47, 8.66, 10.54, and 11.23μ .

2. Notes

1. Tetracyanoethylene may be purchased from the Columbia Organic Chemicals Co., the Eastman Kodak Co., or prepared by the method of Carboni.² This procedure has been simplified in this laboratory as

follows.³

To 450 ml. of cold water in the apparatus of Part A² there is added 99 g. (1.5 moles) of molten malononitrile followed by 250 g. of ice and 158 ml. (3.05 moles at 25°) 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 1 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 powder 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 allowed to reflux a total of 4–6 hours. The solids are separated from the hot mixture using a fluted filter paper, 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 Buchner funnel, washed with a little 1,2-dichloroethane, and dried in a vacuum desiccator; weight 29–38 g. (30–40%). The purity of the product is over 98% as judged by the ϵ_{\max} [pure tetracyanoethylene has $\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$ 277 m μ (ϵ 12,050) 267 m μ (ϵ 13,600)]. It is pure enough for most purposes including synthesis of the epoxide. If very pure material is needed, tetracyanoethylene can be recrystallized from 1,2-dichloroethane (15 ml. per g.) or sublimed at 130–140° at 1 mm.

2. Eastman Kodak Co. practical grade is sufficiently pure for the reaction.

3. The rate of addition of hydrogen peroxide is fairly fast initially but is slowed to maintain the indicated temperature. It is important to get the reaction over in a short time (5–7 minutes) for the best yield.

4. It is wise to use a mechanical or magnetic stirrer in order to induce rapid crystallization of the product. Prolonged contact of the product with water at this stage diminished the yield markedly. The presence of anions, *e.g.*, chloride, can lead to more rapid decomposition of the product, and it is best to use distilled water and ice prepared from distilled water at this point. If the oil cannot be induced to crystallize rapidly, more ice water should be added.

5. If it is necessary to interrupt the preparation before recrystallization, the product should be stored in a desiccator with continuous evacuation until it is absolutely dry.

6. This preparation has been carried out on a 4.2-mole scale using essentially the same procedure with only a slight diminution in yield. In larger runs the crude product may be more efficiently washed by rapidly resuspending the filter cake in fresh ice water, filtering, and drying. The only problem is that of drying the product rapidly. The drying can be hastened on a large scale by heating the mass on the funnel slightly with an infrared lamp.

3. Discussion

The usual method for epoxidation of an olefin with a peracid fails when the double bond is substituted with an electron-withdrawing group.⁴ This difficulty has been circumvented in certain cases by the use of a very strong peracid; *i.e.*, peroxytrifluoroacetic acid, in the presence of a buffer⁵ or by the use of alkaline hydrogen peroxide.⁶ In the latter case, the attack is by the hydroperoxide anion.⁷ This method is normally not applicable to the synthesis of epoxynitriles because of the simultaneous conversion of the nitrile to an amide group.⁸ However, the four nitrile groups of tetracyanoethylene so diminish the electron density at the double bond that it is attacked by hydrogen peroxide in the absence of any added base. There is no significant attack on the nitrile groups when the reaction is carried out rapidly in a mutual solvent for the olefin and peroxide.⁹ Olefins that are somewhat less electrophilic, *e.g.*, phenyltricyanoethylene and diethyl 1,2-dicyanoethylene-1,2-dicarboxylate, can be epoxidized by essentially the same procedure using a catalytic amount of a mild base such as pyridine.¹⁰

Slight variations in the procedure described above have been used to prepare tetracyanoethylene oxide. Hydrogen peroxide in ether or *t*-butyl hydroperoxide in benzene¹¹ gives the epoxide in higher yield than the present method but requires large amounts of organic solvents and is not readily adaptable to large-scale preparations. An apparent contradiction of the opening statement above is the observation that tetracyanoethylene *can* be epoxidized with a peracid.¹² This is undoubtedly due to *nucleophilic*

attack by the peracid or its anion on the electron-deficient double bond, a mechanism which cannot operate with olefins containing only one or two electronegative substituents. An example of this type of epoxidation is the preparation of [1,1-dicyano-2,2-bis\(trifluoromethyl\)ethylene oxide](#).¹³

[Tetracyanoethylene oxide](#) does not undergo reactions typical of epoxides of simple hydrocarbon olefins. Entirely new types of reactions are observed; *e.g.*, cleavage by nucleophilic reagents into the elements of [dicyanomethylene](#) and [carbonyl cyanide](#)¹⁰ and cleavage of the carbon-carbon bond, followed by addition to a wide variety of olefins, acetylenes, and aromatic compounds.¹⁴ For example, [tetracyanoethylene oxide](#) adds thermally to adjacent positions on the [benzene](#) ring to give [1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran](#).

References and Notes

1. Contribution No. 1277 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.
2. [R. A. Carboni](#), *Org. Syntheses Coll. Vol. 4*, 877 (1963).
3. Based on the work of Dr. E. L. Martin and Mr. H. D. Carlson.
4. [D. Swern](#), *Org. Reactions*, **7**, 378 (1953).
5. [W. D. Emmons](#) and [A. S. Pagano](#), *J. Am. Chem. Soc.*, **77**, 89 (1955).
6. [E. Weitz](#) and [A. Scheffer](#), *Ber.*, **54**, 2327 (1921).
7. [C. A. Bunton](#) and [G. J. Minkoff](#), *J. Chem. Soc.*, 665 (1949).
8. [J. V. Murray](#) and [J. B. Cloke](#), *J. Am. Chem. Soc.*, **56**, 2749 (1934).
9. [W. J. Linn](#) (to E. I. du Pont de Nemours and Co.), U.S. Patent 3,238,228 (1966).
10. [W. J. Linn](#), [O. W. Webster](#), and [R. E. Benson](#), *J. Am. Chem. Soc.*, **87**, 3651 (1965).
11. [A. Rieche](#) and [P. Dietrich](#), *Ber.*, **96**, 3044 (1963).
12. Unpublished observations from this laboratory.
13. [W. J. Middleton](#), *J. Org. Chem.*, **31**, 3731 (1966).
14. [W. J. Linn](#) and [R. E. Benson](#), *J. Am. Chem. Soc.*, **87**, 3657 (1965).

Appendix

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

[Benzene](#) (71-43-2)

[acetonitrile](#) (75-05-8)

[hydrogen cyanide](#) (74-90-8)

[bromine](#) (7726-95-6)

[1,2-dichloroethane](#) (107-06-2)

[copper powder](#) (7440-50-8)

[pyridine](#) (110-86-1)

[hydrogen peroxide](#) (7722-84-1)

[magnesium sulfate](#) (7487-88-9)

[Malononitrile](#) (109-77-3)

[Tetracyanoethylene](#) (670-54-2)

Tetracyanoethylene oxide,
Ethanetetracarbonitrile, 1,2-epoxy- (3189-43-3)

phenyltricyanoethylene

diethyl 1,2-dicyanoethylene-1,2-dicarboxylate

1,1-dicyano-2,2-bis(trifluoromethyl)ethylene oxide

dicyanomethylene

carbonyl cyanide (1115-12-4)

1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran

peroxytrifluoroacetic acid

dibromomalononitrile

hydroperoxide anion

t-butyl hydroperoxide (75-91-2)