Organic Syntheses

A Publication
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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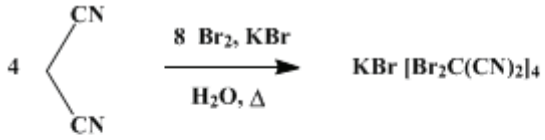
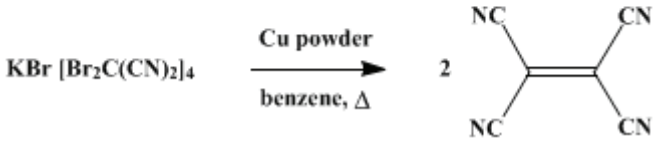
TETRACYANOETHYLENE

[Ethenetetracarbonitrile]





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1. Procedure

Caution! Tetracyanoethylene slowly evolves hydrogen cyanide when exposed to moist air at room temperature. This material should be handled under a hood, and contact with the skin should be avoided. The first step in the preparation should also be carried out under a hood, since bromine is used.

A. *Dibromomalononitrile-potassium bromide complex.* In a 2-l. three-necked flask equipped with an efficient stirrer, a dropping funnel, and a thermometer are placed 900 ml. of cold water, 99 g. (1.5 moles) of malononitrile (Note 1), and 75 g. (0.63 mole) of potassium bromide. The flask is then placed in an ice-water bath, the stirrer is started, and the thermometer is adjusted to extend into the liquid but not into the path of the stirrer. When the temperature of the mixture has dropped to 5–10° (much solid crystallizes), 488 g. (158 ml. at 25°, 3.05 moles) of bromine is added over a period of 2.5 hours. The stirring is continued for an additional 2 hours, while the temperature is held at 5–10°. The precipitated solid complex is collected on a Büchner funnel, washed with 150 ml. of ice-cold water and sucked as dry as possible for about 1 hour (Note 2) and (Note 3). The grainy product is then dried to constant weight in a vacuum desiccator over phosphorus pentoxide, at the pressure obtained with an aspirator (Note 4) and (Note 5). The yield of light-yellow product is 324–340 g. (85–89%) (Note 3).

B. *Tetracyanoethylene*. A mixture of 254 g. (0.25 mole) of the dibromomalononitrile-potassium bromide salt and 1 l. of dry benzene is placed in a 2-l. three-necked flask fitted with a sealed mechanical stirrer and a reflux condenser. The stirrer is started (Note 6), and 100 g. (1.57 g. atoms) of precipitated copper powder (Note 7) is added. The mixture is heated at reflux with constant stirring for 10–16 hours. The benzene layer becomes progressively deeper yellow as the reaction proceeds. At the end of the reaction period, the hot mixture is filtered by gravity, using a fluted paper. Most of the heavy solid is easily retained in the flask and is heated under reflux with 300 ml. of dry benzene, with stirring, for 30 minutes. Filtration of the hot mixture is carried out as before. Two 25-ml. portions of hot benzene are used to wash the precipitate and are decanted through the filter.

The combined filtrates are concentrated to approximately 350 ml. and cooled overnight at about 5°. The crystals are filtered by suction, washed with two 25-ml. portions of cold benzene, and dried in a vacuum desiccator (Note 8). The product weighs 35–40 g. (55–62%) and melts at 197–199° in a sealed capillary tube (Note 9) and (Note 10). This material is suitable for subsequent reactions if it is used within a day or two, although it gives somewhat lower yields than obtained with recrystallized material. This product may be purified, to yield material stable to storage, by recrystallization from nine times its weight of dry chlorobenzene (Note 11). There is recovered 85–90% of light beige crystals (Note 12) and

(Note 13) melting at 199–200° (sealed capillary tube.).

2. Notes

1. The malononitrile was obtained from the Winthrop-Stearns Corp., New York, N. Y., and melted at 30–31°.
2. The vapors of dibromomalononitrile-potassium bromide complex are irritating to the eyes and nose. The solid causes discoloration of the skin on contact. Manipulations should be carried out with gloves in a hood.
3. An additional few grams of product separates from the filtrate during this period, and a little more separates during 1–2 days' standing. This material amounts to 10–20 g. (2.5–5%) additional yield satisfactory for the next step.
4. The product may also be dried in a vacuum oven at 50°; however, the deposition of some free dibromomalononitrile on the walls of the oven renders this method of drying less advantageous. If an oil pump is used to evacuate the desiccator, it should be protected by an adequate trap containing solid sodium hydroxide.
5. It is essential that the complex be thoroughly dried; otherwise the yield of tetracyanoethylene in the subsequent step is materially decreased.
6. Dryness of the complex may be assured, and checked, by attaching a distillation head to the third neck of the flask and distilling benzene until the distillate has run clear for a few milliliters. If the apparatus and reagents were properly dried, only 10–20 ml. of slightly cloudy distillate should be observed.
7. The precipitated copper powder, Grade MD 98, was obtained from Metals Disintegrating Co., Elizabeth, New Jersey.
8. The crude product retains the odor characteristic of dibromomalononitrile and will stain the skin. Pure tetracyanoethylene is practically odorless.
9. The capillary is sealed in order to prevent sublimation; it should not be evacuated unless totally immersed in the heating bath, otherwise sublimation into the cooler part of the sealed capillary will occur.
10. A small additional quantity of less pure product may be obtained by heating the mother liquor with 20 g. of fresh copper powder for 1 hour with stirring, then filtering and concentrating the filtrate to about 100 ml. An equal volume of cyclohexane is added to the hot concentrate, and the mixture is cooled at about 5° for about 30 minutes. Following this procedure in one run, the checkers obtained a yield of 2.9 g. which was recrystallized from 26 g. of chlorobenzene to give 2.1 g. of unattractive material with a poor melting point.
11. The solubility of tetracyanoethylene in chlorobenzene apparently increases sharply as the boiling point of the solvent is approached. Thus the crystals should be extracted in boiling chlorobenzene. Chlorobenzene may be conveniently dried by distilling until the distillate no longer runs cloudy (azeotrope, b.p. 90°, 28.4% water).
12. The crystals, which are yellow when wet with chlorobenzene, become light-colored as the solvent is removed during drying.
13. If an especially good product is desired, the recrystallized material is sublimed at 130–140° /1 mm. A still better product with no trace of color may be obtained by subliming the recrystallized tetracyanoethylene through activated carbon. For example, 35 g. of tetracyanoethylene is placed in a glass thimble and covered with 20–25 g. of activated wood charcoal chips (4–8 mesh). The mouth of the thimble is covered with a coarse grade of filter paper which is held in place by wiring. The thimble is placed in a sublimer, and the sublimation is carried out at 1–2 mm. (bath temperature 175–190°). The tetracyanoethylene is recovered in 80–90% yield as a colorless, hard crystalline mass that melts at 201–202° (sealed tube).

3. Discussion

The procedure given above for the dibromomalononitrile-potassium bromide complex is essentially that of Ramberg and Wideqvist.[2] Tetracyanoethylene has also been prepared by passing malononitrile and chlorine through a hot tube at 400°.[3] The present procedure, based on that described by Cairns et al.,[3] appears to be the best preparative method. Metals, other than copper, have been used to effect the reaction.[4] Tetracyanoethylene, the first example of a percyanoölefin, has shown exceptional reactivity in

a number of addition reactions. For example, it is a very active dienophile, reacting rapidly at room temperature with many 1,3-dienes to give the corresponding Diels-Alder products.[5] With aromatic hydrocarbons, it forms π-complexes of characteristic colors ranging from yellow to green,[6] and it has been used as a color-forming reagent in paper chromatography of aromatic compounds.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 243
- Org. Syn. Coll. Vol. 4, 276
- Org. Syn. Coll. Vol. 4, 953
- Org. Syn. Coll. Vol. 5, 1007
- Org. Syn. Coll. Vol. 5, 1013

References and Notes

1. Contribution No. 480 from Central Research Department, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Delaware.
2. Ramberg and Wideqvist, *Arkiv Kemi, Mineral. Geol.*, **12A**, No. 22 (1937).
3. Cairns, Carboni, Coffman, Engelhardt, Heckert, Little, McGeer, McKusick, Middleton, Scribner, Theobald, and Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958); Heckert (to E. I. du Pont de Nemours & Co., U. S. pat. 2,794,823 [*C. A.*, **51**, 16514 (1957)].
4. Heckert and Little (to E. I. du Pont de Nemours & Co., U. S. pat. 2,794,824 [*C. A.*, **51**, 16515 (1957)].
5. Middleton, Heckert, Little, and Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).
6. Merrifield and Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).
7. Tarbell and Huang, *J. Org. Chem.*, **24**, 887 (1959).

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

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

hydrogen cyanide (74-90-8)

bromine (7726-95-6)

copper (7440-50-8)

cyclohexane (110-82-7)

carbon (7782-42-5)

chlorobenzene (108-90-7)

chlorine (7782-50-5)

potassium bromide (7758-02-3)

Malononitrile (109-77-3)

Tetracyanoethylene,
Ethenetetracarbonitrile (670-54-2)

Dibromomalononitrile-potassium bromide

dibromomalononitrile

phosphorus pentoxide (1314-56-3)