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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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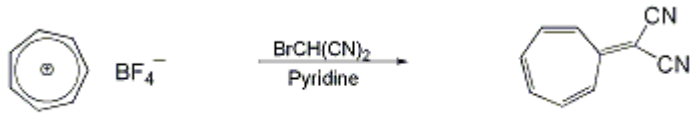
SYNTHESIS OF 8,8-DICYANOHEPTAFULVENE FROM CYCLOHEPTATRIENYLIUM TETRAFLUOROBORATE AND BROMOMALONONITRILE

[Propanedinitrile, 2,4,6-cycloheptatrien-1-ylidene-]



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Checked by Yuping Qiu and Amos B. Smith, III.

1. Procedure

Caution! All operations should be conducted in a well-ventilated hood with breathing protection.

An oven-dried, 1-L, three-necked, round-bottomed flask, equipped with a nitrogen gas inlet, magnetic stirring bar, dropping funnel, thermometer, and condenser, under an inert nitrogen atmosphere, is placed in an ice bath and charged, while stirring, with 500 mL of pyridine and 17.79 g of cycloheptatrienylium tetrafluoroborate **1** [2] (0.1 mol) at 0°C (Note 1). Bromomalononitrile (14.49 g, 0.1 mol) (Note 2) is added drop by drop within a 10-min period, and the mixture is vigorously stirred at that temperature for 1 hr. The ice bath is replaced by a water bath, the temperature is gradually raised to 40° C, and the stirring mixture is kept at that temperature for 5 hr. The solvent is distilled off under reduced pressure below 40°C. To the resultant residue, 1 L of chloroform ($CHCl_3$) is added and the solution is filtered to remove insoluble pyridinium tetrafluoroborate . The chloroform solution is evaporated to remove a trace amount of pyridine (Note 3), and the residue is chromatographed with Wakogel C-300 (400 g) and chloroform (Note 4). The red solution that is eluted is evaporated and the mass obtained recrystallized from ethanol to yield 12.34 g (80.0% of 8,8-dicyanoheptafulvene , **2**, red needles, mp 199-200°C (lit.[3] 198-199°C, lit.[4] 201-202°C) (Note 5).

2. Notes

1. Pyridine, purified by distillation immediately before use must be anhydrous. Cycloheptatrienylium (tropylium) tetrafluoroborate, **1**, was prepared by the method of Conrow[2] and its purity was at least 99%. Aldrich Chemical Company, Inc. , also provides **1**.
2. Bromomalononitrile was prepared by bromination of malononitrile by the method of Ferris, et al.[5] To this end, bromine (48.5 g, 0.30 mol) was added over a period of 5 hr to malononitrile (20 g, 0.30 mol) dissolved in water (300 mL) in an ice bath, and kept overnight under those conditions. A slight brown-white precipitate separated from the solution. It was washed with water and taken up in $CHCl_3$ (100 mL). After drying (Na_2SO_4) and concentrating under reduced pressure to about one half the original volume, the solution was cooled in a refrigerator to deposit colorless crystals, which were then purified by recrystallization from $CHCl_3$ to give 21 g (48%) of the desired bromomalononitrile , mp 63-64°C (Ferris, et al.,[5] reported 20% yield).
3. Prior to chromatography, pyridine must be thoroughly eliminated by distillation. Use of dilute acid fractionation gave an inferior result.
4. From the less polar yellowish fractions, β,β-dicyanostyrene (0.23 g, 1.5%) was obtained before elution of the desired compound.
5. 8,8-Dicyanoheptafulvene **2** had the following spectroscopic properties: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.88-7.00 (m, 4 H) and 7.34 (dm, 2 H, J = 12.1) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 70.1, 114.6 (2C), 135.4 (2C), 137.4 (2C), 138.9 (2C), and 163.7 ; IR (KBr) cm^{-1}: 2196, 1634, 1584, 1520, 1488, 1404,

1372, 1267, 886, 829, 763, 603, and 538 .

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Previously, 8,8-dicyanoheptafulvene, **2**, was prepared by (a) thermolysis of 2,2-bis (cycloheptatrienyl)malononitrile [3] and (b) acetic anhydride-mediated condensation of tropone with malononitrile.[4] Since 8,8-dicyanoheptafulvene, **2**, is a representative stable heptafulvene, its synthetic utility and potential for functional materials warrant an efficient synthesis. As method (a) involves disproportionation of two cycloheptatriene units, and method (b) uses tropone derivatives as the starting material, it was desirable to develop a practical method of synthesizing 8,8-dicyanoheptafulvene, **2**, from the cycloheptatrienylium salt. The late Kitahara and co-workers attempted the preparation of 8,8-dicyanoheptafulvene, **2**, based on this concept. Although they were partially successful, no experimental information is available; the literature[6] simply states that (an unspecified) base-treatment of cycloheptatrienylium salt with bromomalononitrile, according to Kitahara, formed β,β-dicyanostyrene.

The present procedure emphasizes pyridine as the solvent with mild heating. When pyridine is partially replaced with acetonitrile, the yield of 8,8-dicyanoheptafulvene, **2**, drops to less than 40%.

The present procedure is applicable only to bromomalononitrile; various α-halogen active methylene derivatives, (e.g., diethyl chloromalonate, methyl bromoacetoacetate) led predominantly to the formation of ring-contracted styrene derivatives. On the other hand, substituted cycloheptatrienylium salts with bromomalononitrile gave the desired dicyanoheptafulvene derivatives in excellent yields. One notable example is the synthesis of 5- and 7-(dicyanomethylene)-2,3-dihydrocyclohepta-1,4-dithiins.[7]

References and Notes

1. Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka, 816, Japan. Professor Takeshita's present address: Tohwa Institute for Science, Tohwa University, Chikushi-ga-oka, Minami-ku, Fukuoka, 815 Japan.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

8,8-Dicyanoheptafulvene:
2,4,6-Cycloheptatriene-$\Delta^{1,\alpha}$-malononitrile (8);
Propanedinitrile, 2,4,6-cycloheptatrien-1-ylidene- (9); (2860-54-0)

Cycloheptatrienylium tetrafluoroborate: Aldrich:

Tropylium tetrafluoroborate:
Cycloheptatrienylium, tetrafluoroborate (1−) (8,9); (27081-10-3)

Bromomalononitrile, Malononitrile, bromo- (8);
Propanedinitrile, bromo- (8); (1885-22-9)

Pyridinium tetrafluoroborate:
Pyridine, tetrafluoroborate (1−) (8,9); (505-07-7)

Malononitrile: HIGHLY TOXIC (8);
Propanedinitrile (9); (109-77-3)

Bromine (8,9); (7726-95-6)