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New Approaches to Tetracyanoquinodimethane

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Synopsis. New synthetic methods of tetracyanoquinodimethane from terephthaloyl dichloride were presented. Conversion of terephthaloyl dichloride to 1,4-bis(dicyanobenzoyloxymethyl)benzene, followed by debenzoyloxylation and succeessive oxidation afforded TCNQ.

Tetracyanoquinodimethane (TCNQ) is an excellent electron acceptor and readily forms conducting charge-transfer complexes with various donors. Owing to the electrical properties of TCNQ charge-transfer complexes, several approaches to TCNQ have been developed1) We wish to report the synthetic method of TCNQ from terephthaloyl dichloride in a few steps. Terephthaloyl dichloride was converted to terephthaloyl dicyanide (**3**) with copper(I) cyanide. The reaction of terephthaloyl dicyanide with potassium cyanide and benzoyl chloride under ultrasonic irradiation2) yielded 1,4-bis(dicyanobenzoyloxymethyl)benzene (**4**). Compound **4** was also prepared by the treatment of terephthaloyl dichloride with potassium cyanide, benzoyl chloride, and 18-crown-63) in dichloromethane and water. These reactions were carried out under heterogeneous conditions. Conversion of compound **4** to TCNQ was achieved by four methods. i) Benzoyloxy group of compound **4** was removed electrochemically4) to give 1,4-bis(dicyanomethyl)-benzene ($TCNQH_2$), and $TCNQH_2$ was oxidized with *N*-iodosuccinimide (NIS) to afford TCNQ. ii) Reduction of compound **4** with zinc dust in acetic acid, followed by the oxidation with *N*-iodosuccinimide gave TCNQ. iii) Conversion of compound **4** to TCNQ was effected with triphenylphosphine–bromine complex in chlorobenzene. iv) Flash pyrrolysis of compound **4** under reduced pressure also afforded TCNQ.

In these approaches, it may be noted that the starting material is terephthaloyl dichloride, all reagents are inexpensive, and the cyanation reagents are easy to handle.

Experimental

Melting points were uncorrected. IR spectra were obtained on Hitachi 260—10 spectrophotometer. ^{1}H NMR spectra were measured on a Bruker AM360 instrument and the chemical shifts are given in δ-values with respect to TMS used as internal standard. Mass spectra were taken on a JMS-DX300 mass spectrometer.

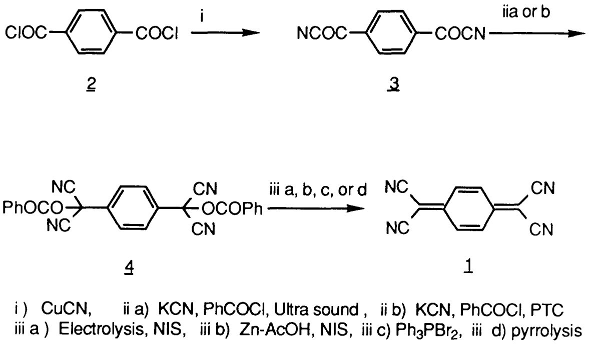
Terephthaloyl Dicyanide (3). The mixture of terephthaloyl dichloride (50.0 g, 0.25 mol) and CuCN (46.3 g, 0.52 mol) in dry acetonitrile (500 ml) was refluxed overnight. After removal of volatiles, the resulting residue was extracted with hot benzene (100 ml×3). The combined organic layer was evaporated and the resulting residue was sublimed under reduced pressure (1 Torr; 1 Torr=133.322 Pa, 100 °C) to give 42.1 g of a colorless powder. Yield 87%. Mp 142—145 °C (lit,5) 140—142 °C).

1,4-Bis(dicyanobenzoyloxymethyl)benzene (4). The mixture of terephthaloyl dicyanide (1.0 g, 5.6 mmol), KCN (1.8 g, 27.6 mmol), and benzolyl chloride (4.0 g, 28.5 mmol) in dry acetonitrile (6.5 ml) was placed in a test tube fitted with a screw cap. Ultrasound irradiation of the mixture was performed at 50 °C for 3.5 h, immersed in an ultrasonic cleaner. The insoluble materials were filtered off and the filtrate was condensed under reduced pressure. The resulting residue was purified by silica-gel chromatography and recrystallized from acetonitrile to give 1.5 g, of colorless prisms. Yield 60%. Mp 232—235 °C, IR (KBr disk) 2245, 1740 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ=8.13 (3 4H), 8.08—7.55 (m 10H). MS (*m/z*) M$^+$ 446. Calcd for $C_{26}H_{14}O_4N_4$: C, 69.95; H, 3.16; N, 12.55%. Found: C, 69.81; H, 3.23; N, 12.65%.

A mixture of terephthaloyl dicyanide (5.0 g, 27.8 mmol), KCN (9.0 g, 0.14 mmol), benzolyl chloride (20 g, 0.14 mmol), and 18-crown-6 (360 mg, 1.38 mmol) in dry acetonitrile (50 ml) and water (0.08 ml) was stirred for 5 h at room temperature. The insoluble materials were filtered off. After the same procedure mentioned above, 5.6 g of colorless prisms were obtained. Yield 45%. Mp 232—235 °C.

Tetracyanoquinodimethane (1). i) A 100 ml H-type divided electrolysis cell was fitted with a Pb anode and a carbon cathode. A solution of compound **4** (89 mg, 0.2 mmol) and tetraethylammonium tosylate (3.01 g, 10.6 mmol) in concd H_2SO_4 (0.2 ml) and CH_2Cl_2 (20 ml) was placed in the cathodic compartment and in the anodic compartment was placed the solution of tetraethylammonium tosylate (3.01 g, 10.6 mmol) in CH_2Cl_2 (20 ml). The stirred catholyte was electrochemically reduced at 20 mA (current density 6.7 mA cm^{-2}) with N_2 bubbling. After 4.2 mol^{-1} of electricity was passed through the reaction system, the catholyte was taken into a 50 ml round-bottomed flask, to which was added *N*-iodosuccinimide (90 mg, 4.0 mmol). The reaction mixture was stirred for 30 min, washed with H_2O (10 ml×2), dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residue was purified by silica-gel chromatography to give 29 mg of orange microcrystals. Yield 71%. Mp 293—294 °C (lit;1) 291—293 °C). ^{1}H NMR ($CDCl_3$) δ=7.38 (s, 4H). IR (Nujol) 2230 cm^{-1}.

ii) To a solution of compound **3** (100 mg, 0.22 mmol) in acetic acid (10 ml) and THF (10 ml) was added Zn dust (2.0 g). After stirring for 10 min at room temperature, the insoluble materials were filtered off and the filtrate was concentrated. The resulting residue was dissolved in acetonitrile



i) CuCN, ii a) KCN, PhCOCl, Ultra sound, ii b) KCN, PhCOCl, PTC
iii a) Electrolysis, NIS, iii b) Zn-AcOH, NIS, iii c) Ph_3PBr_2, iii d) pyrrolysis

Scheme 1. Approaches to TCNQ from terephthaloyl dichlonide.

(10 ml). To the solution was added NIS (120 mg, 0.53 mmol). The reaction mixture was stirred for 30 min at room temperature and then the solvent was evaporated. The residue was purified by silica-gel chromatography to afford 21 mg of orange microcrystals. Yield 46%. Mp 293—294 °C.

iii) To a solution of Ph_3P (131 mg, 0.50 mmol) in chlorobenzene (10 ml) was added bromine (88 mg, 0.55 mmol) and pale yellow crystals were formed. After the addition of compound **3** (100 mg, 0.55 mmol), the mixture was heated for 5 h. Removal of volatiles and purification of the residue by silica-gel chromatography gave 22 mg of orange microcrystals. Yiled 49%. Mp 293—294 °C.

iv) Compound **3** (100 mg, 0.22 mmol) was placed in a Pyrex tube of 0.8 mm diameter. The tube was heated at 750 °C under reduced pressure (0.3 Torr). The sublimated products were dissolved in dichloromethane and purified by chromatography to yield 9 mg of orange microcrystals. Yiled 19%. Mp 293—294 °C.

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