The Bromination of 1, 1, 3, 3-Tetracyanopropane*

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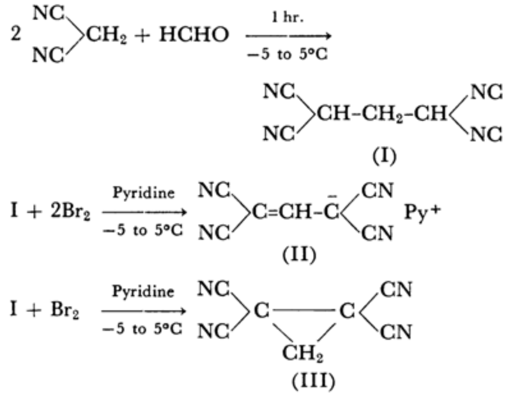
Two compounds were obtained by the bromination of 1,1,3,3-tetracyanopropane[1] (I) in the presence of pyridine.



(I)

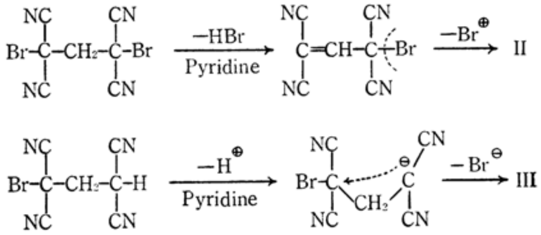
(II)

(III)

When I was brought into reaction with two moles of bromine, a white crystalline solid (II) melting at 157—159°C was obtained. II was pyridinium-1, 1, 3, 3-tetracyanopropenide. The sodium salt of the same compound has been reported by Urushibara.[2]

When I was brought into reaction with one mole of bromine, a white crystalline solid (III) was obtained, it melted at 224°C and sublimed at 150—180°C under diminished pressure. Its properties and melting point agree with those for 1, 1, 2, 2-tetracyanocyclopropane reported by Scribner et al.[3]

Thus, the reaction gave quite different products when the mole numbers of bromine were changed. The mechanism of the reaction may be supposed to be as follows:



It is known that the active methylene is readily brominated by bromine in the presence of pyridine. In the case of the reaction using two moles of bromine, both active hydrogens are replaced by bromine and bromotetracyanopropene is formed by the elimination of hydrogen bromide. A cation of bromine is liberated from the propane to give tetracyanopropenide anion (II). It was recoginized by Trofimenko et al.[4] that the bromocation was produced from bromotricyanomethane.

On the other hand, when one mole of bromine is used, the first step is the replacement o one of the active hydrogens of I by bromine, and then the another active hydrogen is eliminated by pyridine. The cyclopropane ring is formed by an intramolecular condensation.

This reaction provides an excellent route for the preparation of III.

Experimental

Pyridinium-1, 1, 3, 3-tetracyanopropenide (II).—Four grams (0.028 mol.) of 1, 1, 3, 3-tetracyanopropane, 10 g. (0.0625 mol.) of bromine and 38 ml. of acetonitrile

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[1] O. Diels, H. Gartner and R. Kaack, *Ber.*, **45**, 3445 (1912).

[2] Y. Urushibara, This Bulletin, **2**, 2798 (1927).

[3] R. M. Scribner, G. N. Sausen and W. W. Princhard, *J. Org. Chem.*, **25**, 1440 (1960).

[4] S. Trofimenko, E. L. Little and H. F. Mower, ibid., **27**, 433 (1962).

were mixed at −5°C and then 9.0 g. (0.114 mol.) of pyridine was added over a period of 10 min. The mixture was stirred at 0°C for two hours until the red-orange solution became colorless; then the solution was poured into a mixture of 20 ml. of concentrated hydrochloric acid and 40 g. of crushed ice. The solution was concentrated at low temperature in vacuo and the white solid which was precipitated out from the solution was collected and washed with a mixture of cold water, alcohol and petroleum ether, and dried in a vacuum desiccator. It was then recrystallized from tetrahydrofurane to give 1.2 g. (34.3%) of white crystalls, m. p. 157—159°C.

Found: C, 64.98; H, 3.76; N, 31.76. Calcd. for $C_{11}H_7N_5$: C, 65.1; H, 5.78; N, 31.70%.

IR: 4.55 (CN), 6.14, 6.24, 6.38, 6.55, 6.75, 7.45, 8.10, 9.55, 10.6, 11.2, 12.3, 13.5 μ.

1,1,2,2-Tetracyanocyclopropane (III).—Ten grams (0.07 mol.) of 1, 1, 2, 2-tetracyanopropane, 12.5 g. (0.78 mol.) of bromine and 100 ml. of acetonitrile were mixed at 0.°C and then 11.3 g. (0.143 mol.) of pyridine was added over a period of 15 min. When the mixture was stirred at 0°C for an hour, it lost its red-orange color. The solution was then poured into a mixture of 30 ml. of concentrated hydrochloric acid and 60 g. of crushed ice. After an hour, a white solid separated from the solution. The product was collected and washed with a mixture of cold water, alcohol and petroleum ether, and dried in a vacuum desiccator. It was crystallized from ethyl acetate to give 7.5 g. (76.0%) of white crystals, m. p. 220—224°C. It sublimed at about 150°C (1 mmHg).

Found: C, 59.16; H, 1.42; N, 39.42. Calcd. for $C_7H_2N_4$: C, 58.62; H, 1.78; N, 39.42%.

IR: 3.23, 3.32, 4.43(CN), 6.90, 7.01, 8.25, 9.07, 9.88, 13.8 μ.

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