

On the Reaction of 2,5-Dihalothiophenes with Tetracyanoethylene Oxide

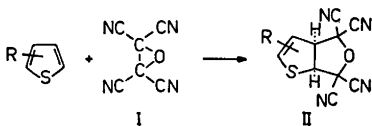
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The reaction between 2,5-dihalothiophenes or 2,5-dihaloselenophenes and tetracyanoethylene oxide leads to 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (IIIa) and 2,5-bis(dicyanomethylene)-2,5-dihydroselenophenes (III d), respectively. Possible reaction paths are discussed.

The reaction of 2,5-bis(dicyanomethylene)-3-bromo-2,5-dihydrothiophene (III b), obtained from 2,3,5-tribromothiophene and tetracyanoethylene oxide, with thiophenol gave 2,5-bis(dicyanomethylene)-3-phenylthio-2,5-dihydrothiophene (VII).

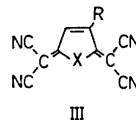
Linn and coworkers^{1,2} have shown that tetracyanoethylene oxide (I) adds to olefins and also to aromatic systems like benzene and thiophene in a stereospecific manner to give derivatives of tetracyanotetrahydrofurans. In connection with our general study of this cycloaddition reaction in the thiophene series, we made attempts to rearomatize the 1,1,3,3-tetracyano-1,3,3a,6a-tetrahydrothieno [2,3-c]-furans (II) formed and in this way open a new route to 2,3-disubstituted thiophenes.



Our rearomatization attempts have hitherto failed. One of our hopes was that this could be achieved by adding I to 2,4- or 2,5-dibromothiophene followed by elimination of hydrogen bromide. 2,4-Dibromothiophene did not react.

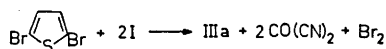
* Taken in part from the Ph.D. thesis of Bengt Uppström, University of Lund, 1973.

When 2,5-dibromothiophene was heated with I in ethylene bromide solution a red liquid started to reflux after a few hours. This liquid was distilled off and boiled at 60–65 °C and was identified as carbonyl cyanide by its reaction with *N,N*-dimethylaniline, yielding bis(*p*-dimethylaminophenyl)dicyanomethane.³ From the reaction mixture, which contained 2,3,5-tribromothiophene and tetrabromothiophene (identified by combined VPC-MS analyses), an intense yellow compound could be isolated which by elemental analysis and mass spectrometry was shown to have the composition C₁₀H₂N₄S. The IR spectrum of this compound was unusually simple, showing only a few peaks, but indicated the presence of *sp*²-hybridized C–H bonds and of nitrile groups. The ¹H NMR spectrum showed only one sharp peak at δ 7.33. The structure of this product was determined by X-ray crystallography and shown to be 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (IIIa).⁴



- a X = S, R = H
 b X = S, R = Br
 c X = S, R = Cl
 d X = Se, R = H
 e X = Se, R = Br

From the products formed in this reaction, the following stoichiometry seems reasonable:



The molecular bromine which is formed reacts immediately with the excess of 2,5-dibromothiophene to give 2,3,5-tribromothiophene and tetrabromothiophene. We checked of course that these compounds were not formed upon refluxing 2,5-dibromothiophene in ethylene bromide. Nor could we detect any appreciable amounts of carbonyl cyanide upon refluxing only I in ethylene dibromide. Based upon the above mentioned stoichiometry, the yield of IIIa calculated on I was as high as 70 %.

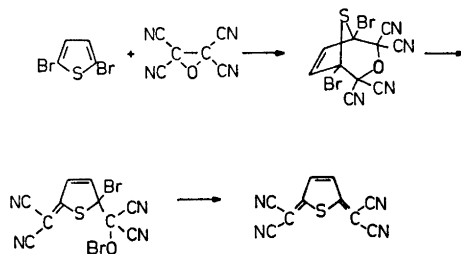
As we could find no precedent for this reaction in the literature, we were interested in studying its scope. We found that 2,3,5-tribromothiophene reacted similarly, yielding a compound $C_{10}HBrN_2S$ (IIIb), which was hydrogenolysed to IIIa over Pd on carbon. Also 2,3,5-trichlorothiophene, 2,5-dibromo- and 2,3,5-tribromoselenophene reacted similarly to give 3-chloro-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (IIIc), 2,5-bis(dicyanomethylene)-2,5-dihydro-selenophene (IIIId), and 3-bromo-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (IIIe). The yields, however, were in these cases much lower: 16, 26 and 38 %, respectively. Removal of carbonyl cyanide during the reaction by distillation, which in the reaction between 2,5-dibromothiophene and I doubled the yield, had no effect in these cases.

The reaction most probably also occurred with 2,3,5-triiodothiophene, but due to separation difficulties the product was not obtained pure. In the reaction of 2,5-dibromo-3-methyl thiophene with I only traces of the expected product were obtained.

In spite of several changes in the experimental conditions the yields could unfortunately not be increased. The long initiation period before carbonyl cyanide appeared in the reaction mixture led us to believe that the reaction was perhaps radical in nature. However, the addition of benzoyl peroxide had no effect on the reaction rate.

The mechanism of the reaction must be rather complex. The formation of carbonyl cyanide obviously makes the simple mechanism indicated in Scheme 1 less likely, if it is assumed that IIIa and carbonyl cyanide are formed in the same reactions.

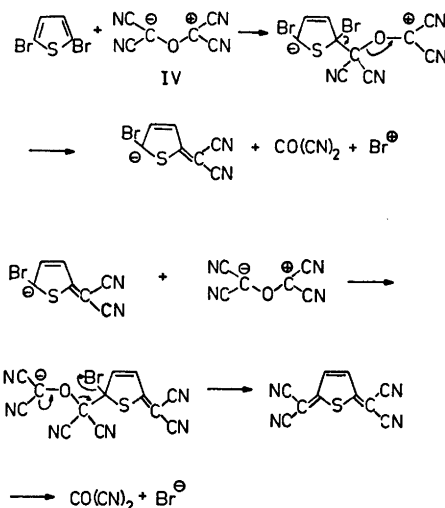
In this mechanism, it is assumed that I adds over the 2,5-position instead of the normal cycloaddition over the 2,3-bond. The bicyclic



Scheme 1.

adducts open and after complex elimination of Br_2O , IIIa is obtained. However, this path does not explain the formation of carbonyl cyanide.

In the normal cycloadditions of I to olefins and aromatics a 1,3-dipolar form of I (IV) has been assumed to be the reactive intermediate.⁵ The following complex mechanism, shown in Scheme 2, can therefore be envisaged.

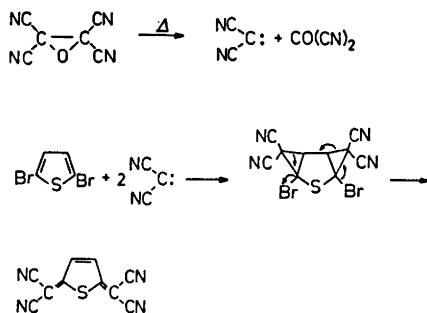


Scheme 2.

It is assumed that the 1,3-dipolar form of I first reacts as a nucleophile and the second molecule as an electrophile.

The opposite orders of attack are of course also possible, but appear even less likely than the reaction path indicated in Scheme 2. An important objection to this mechanism is the sluggishness with which non-activated halothiophenes undergo nucleophilic aromatic substitution.

Linn and coworkers^{6,7} found that I was very susceptible to nucleophilic attack, which formally led to cleavage into the elements of carbonyl cyanide and dicyanomethylene. It is therefore not unlikely that by thermal dissociation or induced by nucleophilic species small amounts of dicyanomethylene are in equilibrium with I and that IIIa is formed as indicated in Scheme 3.



Scheme 3.

Schemes 2 and 3 are both in accordance with the products obtained.

We tried to obtain support for the mechanism in Scheme 3 by reacting 2,5-dibromothiophene with dicyanomethylene in the absence of carbonyl cyanide. Streith and Cassel,⁸ through photolysis of pyridinium dicyanomethylide,⁷ generated dicyanomethylene which added to benzene.

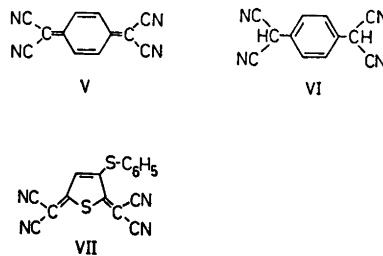
However, both photolytic and thermal attempts to obtain IIIa from 2,5-dibromothiophene and pyridinium dicyanomethylide failed. Dicyanomethylene has also been obtained from dicyanodiazomethane,⁹ but due to the explosive nature of this precursor no experiments were undertaken with it.

A weak support for the mechanism indicated in Scheme 3 stems from the fact that in a few experiments tetracyanoethylene was observed as a minor by-product. This could possibly have been formed through dimerization of dicyanomethylene. The mechanism indicated in Scheme 1 could be disproven (or proven) by the use of ¹³C labelled I.

The mass spectra of III show very little fragmentation. The total intensity of all other ions is 15% of that of the molecular ion, indicating the stability of these compounds. The

two unsubstituted derivatives primarily lose HCN from the molecular ion, and this is also true for the 3-methyl derivative. The halogen-substituted compounds first lose the halogen atom and the HCN.

Compounds III are analogues of the interesting tetracyanoquinodimethane (V). This compound can easily be reduced to *p*-phenylenedimalononitrile (VI) by reagents such as thiophenol, mercaptoacetic acid or hydroiodic acid.¹⁰ Compound IIIa was, however, decomposed by hydroiodic acid and with thiophenol the starting material was recovered. IIIb on the other hand yielded with thiophenol in acetic acid a beautifully red, difficultly soluble compound, m.p. 215–216°C, which according to mass spectrum and elemental analyses had the composition C₁₆H₆N₄S₂. Its NMR spectrum, which due to its difficult solubility had to be recorded in trifluoroacetic acid, shows two peaks at δ 7.08 and δ 6.64 with the relative intensities 5:1. These facts indicate that the compound is 3-phenylthio-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (VII) and that nucleophilic substitution of the olefinic bromine had occurred.



EXPERIMENTAL

2,5-Bis(dicyanomethylene)-2,5-dihydrothiophene (IIIa). A solution of 24.0 g (0.10 mol) of 2,5-dibromothiophene and 5.0 g (0.035 mol) of tetracyanoethylene oxide¹¹ in 50 ml of 1,2-dibromoethane was heated with stirring in an oil-bath at 160°C, in an apparatus arranged for distillation. After 3 h carbonyl cyanide started to distill off, b.p. 60–65°C. After heating for an additional 2 h, 1.8 g (65%) of carbonyl cyanide was obtained, characterized through reaction with *N,N*-dimethylaniline, yielding bis(*p*-dimethylaminophenyl)dicyanomethane, m.p. 193–194°C; literature value,⁸ m.p. 192–193°C. The reaction mixture was cooled, carbon tetrachloride added, the precipitate filtered off and recrystallized, yielding 2.5 g (70%) of the

title compound, m.p. 182–183°C. The first filtrate was distilled and the high-boiling distillation residue (1.8 g) consisted according to VPC (column OV-17 (3 %) on gaschrom Q, 3 m × 3 mm) of 70 % 2,3,5-tribromothiophene and 30 % of tetrabromothiophene. NMR (CD_3COCD_3): δ 7.33. IR (KBr): 3120, 3100, 3050, 2220, 1550, 810, and 700 cm^{-1} . Mass spectrum (m/e , %): 212, 7; 211, 14; 210, 100; 185, 5; 183, 6; 121, 8; 118, 6; 108, 13; 94, 15; 83, 5; 82, 10; 76, 8; 75, 15; 70, 11; 69, 13; 64, 6; 63, 6; 62, 6; 57, 8; 55, 7; 45, 15; 43, 12; 41, 6; 40, 5; 38, 8; 37, 5; 32, 5; 28, 5; 27, 5. [Found: C 58.02; H 1.11; N 25.72; S 15.41. Calc. for $\text{C}_{10}\text{H}_2\text{N}_4\text{S}$: C 57.14; H 0.96; N 26.65; S 15.25.]

3-Bromo-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (IIIb). A solution of 10.0 g (0.070 mol) of tetracyanoethylene oxide and 64.0 g (0.20 mol) of 2,3,5-tribromothiophene in 100 ml of 1,2-dibromoethane was refluxed for 24 h and filtered hot. After 2 d a black tarry product was isolated which was extracted with benzene in a Soxhlet apparatus. Evaporation yielded 2.8 g (28 %) of the title compound, m.p. 173–175°C after recrystallization from benzene or chloroform. NMR (CD_3COCD_3): δ 8.22. IR (KBr): 3090, 2220, 1545, 1520, and 810 cm^{-1} . Mass spectrum (m/e , %): 292, 7; 291, 15; 290, 100; 289, 14; 288, 99; 265, 5; 263, 5; 210, 17; 209, 17; 199, 6; 165, 8; 157, 6; 145, 10; 144, 6; 138, 5; 124, 10; 121, 5; 120, 10; 119, 5; 118, 15; 113, 6; 108, 15; 106, 10; 101, 13; 100, 15; 98, 5; 94, 15; 93, 5; 92, 5; 89, 10; 88, 5; 87, 7; 86, 12; 82, 15; 81, 5; 80, 5; 79, 8; 76, 10; 75, 15; 74, 5; 70, 15; 69, 15; 68, 5; 64, 12; 63, 18; 62, 15; 61, 5; 60, 5; 49, 10; 45, 13; 44, 12; 38, 13; 37, 12; 32, 10. [Found: C 41.6; H 0.52; Br 27.7; N 19.1; S 10.9. Calc. for $\text{C}_{10}\text{HBrN}_4\text{S}$: C 41.5; H 0.35; Br 27.6; N 19.4; S 11.1.]

Hydrogenolysis of 3-bromo-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene. In a Parr hydrogenation apparatus, 200 ml of peroxide-free dioxane, and 1.16 g of 3-bromo-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene were placed. The mixture was hydrogenated at 5 atm. for 24 h, the catalyst filtered off and the dioxane removed *in vacuo*. The tarry residue was extracted with benzene, the benzene solution evaporated to a small volume, and then chromatographed on a silica gel column using benzene as eluent. 0.3 g (36 %) of 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene, having the spectral properties as the sample described above was obtained.

3-Chloro-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (IIIc). A solution of 18.7 g (0.10 mol) of 2,3,5-trichlorothiophene, 7.0 g (0.049 mol) of tetracyanoethylene oxide in 50 ml of 1,2-dibromoethane was refluxed for 48 h. The solution was filtered hot and evaporated to a volume of about 10 ml. The tarry product was filtered off and recrystallized from benzene (charcoal) to give 0.90 g (16 %) of the title compound, m.p. 180–181°C. NMR (CD_3COCD_3) δ 8.15. IR (KBr): 3090, 2220, 1550, 920, and

865 cm^{-1} . Mass spectrum (m/e , %): 247, 5; 246, 40; 245, 15; 244, 100; 209, 8; 118, 8; 94, 10. [Found: C 49.1; H 0.55; Cl 14.35; N 22.95; S 13.00. Calc. for $\text{C}_{10}\text{HClN}_4\text{S}$ (244.7): C 49.09; H 0.41; Cl 14.49; N 22.90; S 13.11.]

2,5-Bis(dicyanomethylene)-2,5-dihydro-selenophene (III d). A solution of 28.9 g (0.10 mol) of 2,5-dibromoselenophene,¹² 5.0 g (0.035 mol) of tetracyanoethylene oxide in 50 ml of 1,2-dibromoethane was refluxed for 48 h. After filtration, evaporation and recrystallization from benzene, 1.2 g (26 %) of the title compound, m.p. 199–201°C, was obtained. NMR (CD_3COCD_3): δ 7.93. IR (KBr): 3120, 3050, 2220, 1545, and 810 cm^{-1} . Mass spectrum (m/e , %): 259, 12; 258, 100; 257, 8; 256, 50; 255, 16; 231, 6; 178, 5; 142, 11; 140, 5; 125, 6; 124, 5; 118, 5; 101, 5; 100, 5; 93, 5; 80, 16; 78, 8; 76, 6; 75, 12; 63, 5; 62, 5. [Found: C 47.56; H 1.20; N 21.48. Calc. for $\text{C}_{10}\text{H}_2\text{SeN}_4$ (257.1): C 46.71; H 0.79; N 21.79.]

3-Bromo-2,5-bis(dicyanomethylene)-2,5-dihydro-selenophene (III e). A solution of 36.8 g (0.10 mol) of 2,3,5-tribromoselenophene¹² and 5.0 g (0.035 mol) of tetracyanoethylene oxide in 50 ml of 1,2-dibromoethane was refluxed for 48 h. After filtration and evaporation, the residue was chromatographed on silica gel using benzene as eluent, yielding 2.2 g (38 %) of the title compound, m.p. 165–166°C. NMR (CD_3COCD_3): δ 8.28. IR (KBr): 3080, 2215, 1535, and 750 cm^{-1} . Mass spectrum (m/e , %): 340, 12; 339, 10; 338, 78; 337, 12; 336, 100; 335, 16; 334, 45; 333, 12; 332, 14; 330, 11; 258, 5; 257, 16; 255, 6; 168, 11; 166, 10; 161, 12; 157, 6; 150, 8; 141, 12; 140, 5; 130, 5; 124, 16; 101, 16; 100, 12; 98, 5; 86, 7; 80, 21; 78, 6; 75, 18; 62, 7. [Found: C 35.64; H 0.56; Br 23.73; N 16.64; Se 23.40. Calc. for $\text{C}_{10}\text{HBrN}_4\text{Se}$ (336.0): C 35.75; H 0.30; Br 23.78; N 16.67; Se 23.50.]

3-Phenylthio-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (VII). To a solution of 1.0 g (0.0035 mol) of 3-bromo-2,5-bis(dicyanomethylene)-2,5-dihydrothiophene in 100 ml of acetic acid, 0.55 g (0.0050 mol) of thiophenol was added and the acetic acid evaporated over night. The solid residue was washed with a little ether and chromatographed on silica gel using chloroform-ether (4:1) as eluent, yielding 0.60 g (54 %) of the title compound, m.p. 215–216°C. NMR (CF_3COOH): $\delta_{\text{C}_6\text{H}_5}$ 7.08, δ_4 6.64. IR (KBr): 3070, 2230, 2210, 1538, 1490, 830, and 740 cm^{-1} . Mass spectrum (m/e , %): 320, 5; 318, 100; 293, 5; 292, 5; 291, 77; 261, 5; 260, 5; 259, 5; 254, 5; 253, 5; 233, 5; 210, 5; 110, 5; 109, 5; 108, 5; 94, 5; 89, 5; 84, 5; 83, 5; 77, 43; 75, 5; 69, 5; 66, 5; 65, 5; 51, 52; 50, 5; 45, 5; 39, 5. [Found: C 59.58; H 2.09; N 16.79; S 20.53. Calc. for $\text{C}_{18}\text{H}_8\text{N}_4\text{S}_2$ (318.4): C 60.30; H 1.90; N 17.60; S 20.14.]

IR spectra were recorded on a Perkin-Elmer 257 Grating Infrared Spectrophotometer, NMR spectra on a Varian A-60 spectrometer and mass spectra on an LKB 9000 mass spectrometer. The gas chromatographic analyses were

performed with a Perkin-Elmer 900 gas chromatograph.

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