REACTION OF CYCLOOCTATETRAENYLDIPOTASSIUM WITH DISULFIDES AND THIOCYANATO DERIVATIVES OF THE THIOPHENE SERIES

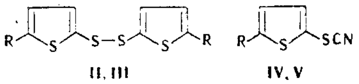
Z. V. Todres, F. M. Stoyanovich,
Ya. L. Gol'dfarb, and D. N. Kursanov

UDC 547.734

In contrast to organometallic compounds of the phenyllithium type, cyclooctatetraenyldipotassium on reaction with disulfides and thiocyanato derivatives of the thiophene series in tetrahydrofuran does not give thio ethers but enters into an electron-transfer reaction and is converted to cyclooctatetraene. Thiophene derivatives form the potassium salts of the corresponding thiols. When insufficient amounts of cyclooctatetraenyldipotassium are present, thiocyanatothiophenes are converted to disulfides. It is shown that the latter can be obtained as a result of the reaction of thienyl mercaptides with thiocyanatothiophenes.

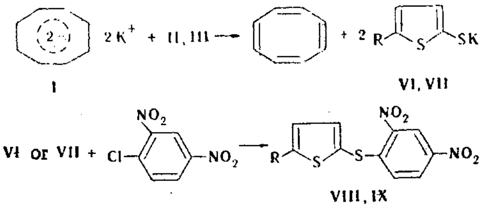
Organolithium compounds react with disulfides and thiocyanato derivatives of the aromatic series to give thio ethers [1, 2]. For example, 3-thiocyanatothiophene reacts with butyllithium to give butyl 3-thienyl sulfide [2]. The products of this type of substitution can also be obtained by using cyclooctatetraenyldipotassium (I): it is capable of giving diacetylcyclooctatrienes on reaction with acetyl chloride [3].

We have studied the reaction of I in tetrahydrofuran (THF) with disulfides and thiocyanato derivatives (II-V) of the thiophene series and, on the basis of the results, have arrived at the conclusion that thio ethers are not formed in this case and that the reaction reduces to transfer of electrons from I to II-V.



II R=H; III R=SC_4H_9-*t*; IV R=H; V R=SCN

In all cases, we established the quantitative conversion of I into cyclooctatetraene. Moreover, disulfides II and III give the potassium salts of the corresponding thiophenethiols (VI, VII), which were isolated as the 2,4-dinitrophenyl derivatives (VIII, IX) in yields up to 70%.



III,VIII R=H; VII, IX R=SC_4H_9-*t*

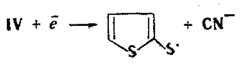
Thiocyanatothiophene IV reacts with an equimolecular amount of I by undergoing cleavage to mercaptide VI, which was isolated as the sulfide (VIII) (in 70 % yield), and to potassium cyanide. Consequently,

---

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 632-636, May, 1973. Original article submitted May 22, 1972.

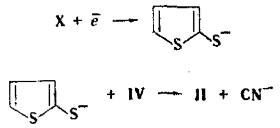
the thiocyanato group, like the S—S group, enters into reaction with I as a two-electron acceptor.

As previously shown in [4], the transfer of electrons from I is stepwise, such that a cyclooctatetraene anion radical is formed in an intermediate step. It can be assumed that the transfer of one electron to the 2-thiocyanatothiophene (IV) molecule will lead to the formation of a thienylthiyl radical.



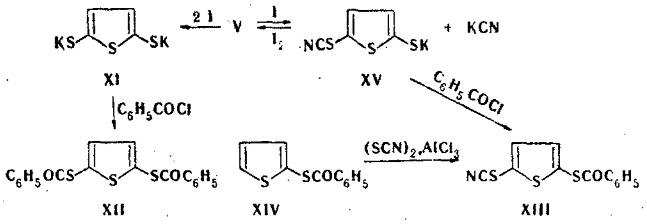
X

On coupling, thienylthiyl radicals X should have given dithienyl disulfide II. We detected disulfide II in a mixture with the starting thiocyanato derivative (IV) and the theoretical amount of cyclooctatetraene in the products of the reaction of 2 moles of 2-thiocyanatothiophene (IV) with one mole of I. Disulfide II may also be formed without emergence of the thienylthiyl radicals (X) from the solvent cage due to their conversion to the more stable thienyl mercaptide anions on reaction with the cyclooctatetraene anion radical. On reaction with the unchanged 2-thiocyanatothiophene, the mercaptide anions could give the disulfide.



We have shown that under the conditions of the investigated reactions, i.e., in THF and at low temperatures, thiocyanatothiophene IV reacts with potassium thiophenoxide to give a mixture of dithienyl and diphenyl disulfides.

In addition to thiocyanato derivative IV, we also studied 2,5-dithiocyanatothiophene (V). This compound on polarographic reduction in THF gives one wave with $E_{1/2} = -1.28$ V (relative to an aqueous saturated calomel electrode), which corresponds to the irreversible transfer of four electrons. On reaction with 2 moles of I in THF, 2,5-dithiocyanatothiophene (V) (1 mole) is converted to dimercaptide XI, which we identified through the dibenzoyl derivative (XII), which was isolated in 70% yield. The transfer of electrons from I to 2,5-dithiocyanatothiophene (V) can also be carried out in a stepwise fashion (in contrast to the reduction on a dropping mercury electrode in the same solvent). If equimolecular amounts of I and V are used, 2-thiocyanato-5-(benzoylmercapto)thiophene (XIII), which is identical to a sample of genuine structure obtained from 2-(benzoylmercapto)thiophene (XIV), can be isolated after treatment of the reaction mass with benzoyl chloride. The isolation of XIII in pure form is difficult, and the yield did not exceed 45%. However, the starting dithiocyanatothiophene (V) was not present in the reaction products. Our reverse reaction of XV with the potassium cyanide present in the solution, which occurs during the action of a solution of iodine in THF on the reaction mixture, serves as a distinct proof of the conversion of V to XV. As a result of this treatment, we reversibly isolated 2,5-dithiocyanatothiophene (V) in almost quantitative yield. *

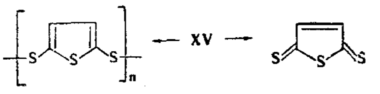


Thus potassium 2-thiocyanato-5-thienyl mercaptide (XV) is stable in absolute THF. The addition of 25% acetic acid to this solution causes destabilization, and this leads to the precipitation of a crystalline substance that does not contain nitrogen. Potassium cyanide is also formed in amounts that approximately correspond to the starting amount of dithiocyanato derivative V. Consequently, the cyanide ion also splits

---

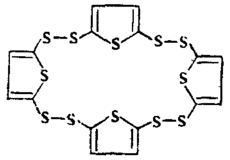
* The conversion of thiophenols to thiocyanato derivatives under the influence of cyanogen bromide is well known [5]. We have shown that it is also possible under the conditions of our experiments if 2,2'-dithienyl disulfide (II) is initially converted to thienyl mercaptide VI by the action of I in THF and then into 2-thiocyanatothiophene (IV) on treatment of the product of this reaction with iodine and potassium cyanide.

out from thiocyanato mercaptide XV. This cleavage process can be conceived of as proceeding due to both intermolecular reaction of the thiocyanato and mercaptide groups and due to an electron shift from the mercaptide group to the thiocyanato group within a single molecule. In the first case, a polymer with disulfide bonds (XVI) could be formed, while in the second case, trithiomaleic anhydride (XVII) could be formed.



XVI XVII

The substance obtained crystallizes from toluene and melts on heating to 150° to give a transparent resin. The reaction product does not react with dienes of the furan and hexachlorocyclopentadiene types. Its PMR spectrum contains only one signal – a singlet at δ 7.07 ppm – while its mass spectrum displays $[(C_4H_2S)_5S_5]^+$, $[(C_4H_2S)_4S_6]^+$, $[(C_4H_2S)_3S_8]^+$, $[(C_4H_2S)_2S_7)^+$, and $[(C_4H_2S)S_4]^+$ ion peaks (the m/e values are, respectively, 570, 520, 502, 388, and 210). In addition, ions with a lower disulfide sulfur content up to fragments of the $[(C_4H_2S)_n]^+$ type are observed. It should be noted that 2,2'-dithienyl disulfide (II) disintegrates similarly, successively losing two sulfur atoms to give $[(C_4H_3S)_2S]^+$ and $[(C_4H_3S)_2]^+$ fragments, respectively. On the basis of the spectral data, it can be concluded that the reaction product obtained from XV is a polysulfide of the $(C_4H_2S)_nS_m$ type. However, the mass spectra do not make it possible to decide whether an individual compound or a mixture of polysulfides containing a different number of links is formed. Construction of molecular models from the "Eugon-atom" set shows that structures with three or more links ($n \geq 3$) are sterically possible. According to ebulliographic data, the molecular weight of the polysulfide corresponds to tetramer XVIII. Thus either a principal portion of the substance is characterized by structure XVII, or a polysulfide with n = 3 is found in such a ratio with polysulfides with $n > 3$ that the average molecular weight corresponds to tetramer XVIII.



XVIII

EXPERIMENTAL

All of the experiments were carried out under a stream of argon. The THF was purified to remove traces of oxygen, peroxides, and moisture and was distilled in a stream of argon over benzophenone potassium salt prior to use. The melting points were determined with a Boetius microscope stage. The yield of cyclooctatetraene was found by gas-liquid chromatography (GLC) with a KhROM-2 chromatograph. The column (225 cm long with an inner diameter of 0.4 cm) was filled with 10% Tween-85 on Chromosorb W (60-80 mesh). The column temperature was 72°, and the carrier gas was nitrogen (at a pressure of 0.3 kg/cm^2). The method used for the calculations was presented in [6].

Action of I on 2,2'-Dithienyl Disulfide (II). A solution of 0.208 g (0.9 mmole) of II in THF was mixed at −40° with a solution of 0.9 mmole of I [6] in THF, and 0.5 ml of 25% acetic acid was added at −10° after 20 min. During the addition, the yellow color weakened, and the precipitate that formed after mixing dissolved. The yield of cyclooctatetraene was 100%. The THF was distilled from the reaction mass in a stream of argon at 15 mm, and the oily residue was dissolved in absolute ether. The solution was filtered, and the filtrate was mixed with a solution of 0.366 g (1.8 mmole) of 2,4-dinitrochlorobenzene in absolute alcohol. The mixture was heated on a boiling-water bath for 15 min and filtered hot; the precipitated potassium chloride was washed on the filter with hot alcohol. The combined filtrate on standing yielded 0.36 g (70%) of 2-thienyl-2',4'-dinitrophenyl sulfide (VIII) with mp 118-119.5°. The sample was identified from a mixed-melting-point determination with a genuine sample [7]. In another experiment, 0.0625 g (1 mmole) of potassium cyanide was added at −10° to a solution obtained by mixing solutions in THF of I (1 mmole) and 0.221 g (1 mmole) of II, after which a solution of 0.488 g (1 mmole) of iodine in THF was added. The mixture was stirred for 3 h, and the formation of 2-thiocyanatothiophene (IV) was established by GLC with a column filled with a mixture of Chromosorb G and polyethylene glycol adipate (5%) at 175°.

Action of I on 2,2-Di(5-tert-butylmercaptothienyl) Disulfide (III). The reaction of 0.450 g (1.1 mmole) of III and 1.1 mmole of I in THF by the method described above gave 0.45 g (55%) of 5-tert-butylmercapto-2-thienyl-2',4'-dinitrophenyl sulfide (IX) with mp 124-125° (from alcohol). Found: C 45.8; H 3.9; S 25.8%. $C_{14}H_{14}N_2O_4S_3$. Calculated: C 45.4; H 3.8; S 26.0%. A sample of sulfide IX obtained from 5-tert-butylmercapto-2-thiophene thiol [8] had mp 124.5-125.5° and did not depress the melting point of the sample described above.

Action of I on 2-Thiocyanatothiophene (IV). Sulfide VIII, with mp 116.5-119°, was obtained in 79% yield from 0.173 g (1.23 mmole) of IV and 1.23 mmole of I in THF; the product did not depress the melting point of the sulfide with a known structure. In a parallel experiment, the formation of the cyanide ion was established (by conversion to Prussian blue).

Reaction of 2,5-Dithiocyanatothiophene (V) with I. A. A solution obtained by mixing 0.125 g (0.63 mmole) of V and 1.25 mmole of I in THF was treated at −10° with 0.43 ml (3.8 mmole) of freshly distilled benzoyl chloride to give cyclooctatetraene in 98% yield. Removal of the solvent gave 0.16 g (70%) of 2,5-di(benzoylmercapto)thiophene (XII) with mp 70-78°; after recrystallization from petroleum ether the product had mp 79-81°; a mixture with an authentic [9] sample* had mp 80-81°.

B. 5-Thiocyanato-2-benzoylmercaptothiophene (XIII) [0.12 g (40%)], with mp 76-78° (from heptane), was obtained from 0.231 g (1.16 mmole) of V and 1.16 mmole of I with the subsequent addition of 0.487 g (3.48 mmole) of benzoyl chloride. No melting-point depression was noted for a mixture of this product with a genuing sample (see below). Comparable samples gave identical spots during chromatography on a thin layer of Al_2O_3 [with benzene−hexane (5:1) as the eluent].

In special experiments, solutions of 0.573 g (2.9 mmole) of dithiocyanatothiophene V and 2.9 mmole of I in THF were mixed at −40°, after which 2 ml of 25% acetic acid was added at −10°. The resulting precipitate was removed by filtration and crystallized from toluene to give 0.8 g of the polysulfide; the yield was 50% based on tetra[(2,5-thienylene) disulfide] (XVII). The product began to melt at 150° and at 160° was irreversibly converted to a transparent resin. It was insoluble in most organic solvents, except for carbon disulfide and hot toluene. Found: C 33.2; H 1.4; S 65.7%, Mol.wt. (ebulliographically†) 575. $C_{16}H_8S_{12}$. Calculated: C 32.8; H 1.4; S 65.8%; Mol.wt. 585. Cyclooctatetraene (99%) and cyanide ion (75% by iodimetry) were found in the filtrate from the precipitate. The cyanide ion was also identified qualitatively from the formation of Prussian blue.

Reaction of 2-Thiocyanatothiophene (IV) with Potassium Phenylmercaptide. A solution of 0.535 g (2.45 mmole) of diphenyl disulfide was mixed with 2.45 mmole of I in THF at −60°, and a white precipitate appeared. At −5°, 0.72 ml (6.4 mmole) of benzoyl chloride was introduced into the mixture. The yield of cyclooctatetraene was 100%. The solvent was evaporated, and the residue was successively crystallized from alcohol and hexane to give 0.5 g (40%) of S-benzoylthiophenol with mp 55-56°. A sample of known structure had the same melting point and gave an identical spot on a thin layer of aluminum oxide in a hexane−ether (9:1) system. The starting disulfide was not found in this case.

A 0.202-g (1.43 mmole) sample of 2-thiocyanatothiophene (IV) was added at −5° to a suspension of potassium phenylmercaptide, obtained during repetition of the experiment from 0.156 g (0.715 mmole) of diphenyl disulfide and 0.715 mmole of I in THF. The precipitated thiophenoxide was dissolved, and the resulting solution on chromatography on a thin layer of aluminum oxide in a hexane − ether (4:1) system gave one spot coinciding with the spot from a specially prepared mixture of diphenyl disulfide and dithienyl disulfide II; thiocyanatothiophene IV was not present. It is known that unsymmetrical disulfides disproportionate to give a mixture of symmetrical disulfides [10].

5-Thiocyanato-2-(benzoylmercapto)thiophene (XIII) from 2-(Benzoylmercapto)thiophene (XIV). A solution of 10.57 g (48 mmole) of 2-(benzoylmercapto)thiophene (XIV)‡ in 200 ml of absolute ether was added at −5° to a solution of 48 mmole of dithiocyanogen in 100 ml of absolute ether, after which 0.5 g of anhydrous aluminum chloride was added, and the mixture was stirred at 0° for 15 min and at 10° for 2.5 h. The reaction mass was then poured into 800 ml of ice water, and benzene was added to dissolve the precipitate. After separation, the organic layer was washed with water until it gave a negative reaction for

---

*We thank M. A. Kalik for providing us with this sample.

† The determinations were carried out with an ÉP-2 ebulliograph from the Special Design Office of the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

‡ Obtained by Schotten−Baumann benzoylation of 2-mercaptothiophene (the product had mp 58-59°).

thiocyanate ion, and it was then dried and evaporated. The residue was crystallized from heptane to give 8.4 g (63%) of thiocyanatothiophene XIII with mp 79-80°. Found: C 51.7; H 2.5; S 34.7%. $C_{12}H_7OS_3$. Calculated: C 51.9; H 2.6; S 34.7%.

LITERATURE CITED

1. H. Gilman and F. Webb, J. Am. Chem. Soc., 71, 4062 (1949).
2. S. Gronowitz and R. Hakansson, Arkiv Kemi, 17, 73 (1961).
3. T. Cantrell and H. Shechter, J. Am. Chem. Soc., 85, 3300 (1963).
4. Z. V. Todres, V. Sh. Tsveniashvili, S. I. Zhdanov, and D. N. Kursanov, Dokl. Akad. Nauk SSSR, 181, 906 (1968).
5. K. Kottke, F. Friedrich, and R. Poloudek-Fabini, Arch. Pharm., 300, 583 (1967); Ref. Zh. Khim., 9Zh386 (1968).
6. Z. V. Todres, Izv. Akad. Nauk SSSR, Ser. Khim., 1749 (1970).
7. H. Hartough, Thiophene and Its Derivatives, New York, (1952), p. 434.
8. B. P. Fedorov and F. M. Stoyanovich, Zh. Organ. Khim., 1, 194 (1965).
9. Ya. L. Gol'dfarb and M. A. Kalik, Khim. Geterotsikl. Soedin., 788 (1968).
10. E. Reid, Organic Chemistry of Bivalent Sulphur, Vol. 3, New York (1955), p. 356.