SYNTHESIS AND SOME REACTIONS OF SULFIDES OF THE THIOPHENE SERIES

XV. Synthesis of Dimercaptothiophenes*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, pp. 788–792, 1968

UDC 547.732'425'279.07:541.49

By the action of four equivalents of sodium in liquid ammonia on the bis(alkylmercapto)thiophenes I, II, and IX we have obtained the corresponding dimercaptothiophenes VII, IX, and VIII, which were characterizied in the form of their dibenzoyl derivatives XI–XIII. The dimercaptothiophenes VII and VIII and the o-alkylthiothiophenethiols III and IV form the internally complex compounds XIV–XVII with metal acetates.

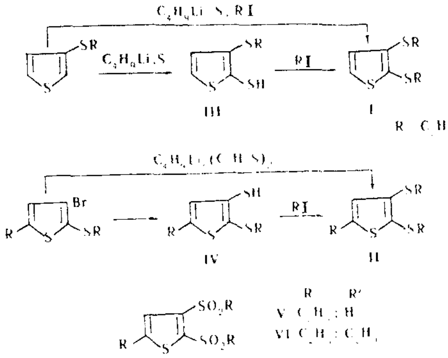
In recent years, ligands containing sulfur, selenium, and tellurium, but especially sulfur, have been studied intensively [1]. The investigation of the electronic structure and reactions of sulfur-containing complexes is of interest, in particular, for comparing their properties with the properties of the analogous oxygen compounds. Among the numerous sulfur-containing ligands and chelates it is possible to isolate a new interesting type—complexes of α-dithiones and α-dithiols, which possess unusual physical and chemical properties because of their peculiar electronic structure due to the presence of two sulfur atoms in the molecule [2–5].

In the development of our investigations on the synthesis of complex-forming compounds of the thiophene series [6], it appeared of interest to study the possibility of obtaining derivatives containing two mercapto groups or one mercapto and one alkylthio group in adjacent positions of the thiophene ring. It must, in addition, be mentioned that thiophenedithiols, besides being used as complex-forming agents, may serve, like the corresponding benzene derivatives, as the starting materials for further synthesis [7].

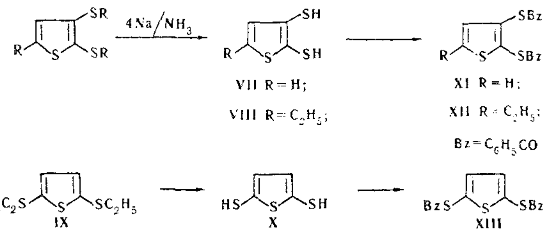
Of the four possible isomeric dimercaptothiophenes, 3,4-thiophenedithiol, synthesized by the action of butyllithium and sulfur on 4-bromo-3-thiophenethiol, was described by Gronowitz in 1962. Attempts to obtain the 2,4- and 2,3-isomers from the corresponding bromothiophenethiols and also 2,5-thiophenedithiol from 2,5-dilithiothiophene or the bromomagnesium derivatives and sulfur proved unsuccessful [8, 9]. It is probable that this can be explained by the ease of oxidation of the bisthienylmercaptides under the conditions of the synthesis through the corresponding lithium-substituted derivative and also by the low stability of the initial bromothiophenethiols.

Consequently, it appeared desirable to us to use another route—the action of sodium in liquid ammonia on bis(alkylthio)thiophenes, which has previously been used successfully in the synthesis of mono- and polymercapto derivatives of benzene [10] and also of thiophenethiols [11].

We synthesized the required 2,3-bis(ethylthio)thiophene (I) by the action of butyllithium, sulfur, and ethyl iodide on ethyl 3-thienyl sulfide. 5-Ethyl-2,3-bis(ethylthio)thiophene (II) was obtained with a yield of 43% by the action of butyllithium and diethyl disulfide on 3-bromo-5-ethyl-2-ethyl-thiothiophene, but purer products were obtained in better yields by the alkylation of the corresponding thiophenethiols III and IV. On oxidation with 30% H_2O_2 in glacial acetic acid, the bis-sulfides I and II formed the corresponding bis-sulfones V and VI.



As in the case of the mono(alkylthio)thiophenes, the reaction of sulfur in liquid ammonia with the bis(alkylthio)thiophenes I and II took place smoothly, and the action of four equivalents of sodium on one mole of the bis-sulfides gave a 60–80% yield of the corresponding bismercaptans VII and VIII. 2,5-Bis(mercapto)-thiophene (X) was obtained similarly from 2,5-bis(ethylthio)thiophene IX (the IX was obtained in our laboratory by M. L. Kirmalova) by a previously published method [12].



The bis(mercapto)thiophenes—reddish viscous liquids distilling in a vacuum with decomposition—were characterized in the form of the bisbenzoylthio derivatives XI–XIII.

On reaction with copper or nickel acetates, 2,3-dimercaptothiophene (VII) formed black infusible powders insoluble in the usual organic solvents. They are probably polymeric complexes of 2,3-dimercaptothiophene analogous to the polymeric complexes of bis(dithioglyoxal)nickel [2]. When copper acetate was used,

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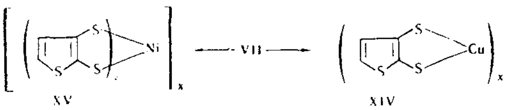
*For part XIV, see [15].

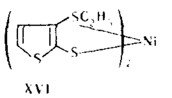
Dimercapto-and Bis(benzoylthio)thiophenes

Compound	Name	Bp, °C (mm)	n_D^{20}	Mp, °C	Empricial formula	Found, %			Calculated, %			Yield of unpurified product, %
						C	H	S	C	H	S	
VII	2,3-Dimercaptothiophene	75—80 (4)	1.6765	—	—	—	—	—	—	—	—	73.5
XI	2,3-Bis(benzoylthio)thiophene	—	—	86—87	$C_{18}H_{12}O_2S_3$	60.66	3.50	27.08	60.65	3.39	26.99	55.5
X	2,5-Dimercaptothiophene	85 (5)	1.6571	—	—	—	—	—	—	—	—	85
XIII	2,5-Bis(benzoylthio)thiophene	—	—	83.5—85	$C_{18}H_{12}O_2S_3$	60.87	3.46	26.94	60.65	3.39	26.99	55
VIII	5-Ethyl-2,3-dimercaptothiophene	105—107 (5)	1.6092	—	—	—	—	—	—	—	—	70
XII	2,3-Bis(benzoylthio)-5-ethylthiophene	—	—	110 (decomp.)	$C_{20}H_{16}O_2S_3$	62.12	4.16	24.10	62.46	4.19	24.97	55

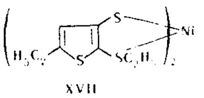
the product, judging from the data of elementary analysis, corresponded to the composition XIV, and when nickel acetate was used to composition XV.

With nickel acetate, 3-ethylthio-2-mercaptothiophene (III) and 5-ethyl-2-ethylthio-3-mercaptothiophene (IV) give the complex compounds XVI and XVII in which the ratio of metal to ligand is 1: 2. In contrast to the complex XIV and XV, they have definite melting points and are readily soluble in the usual organic solvents (benzene, chloroform, acetone):





XVI



XVII

EXPERIMENTAL

2,3-Bis(ethylthio)thiophene (I). In a current of nitrogen at 20°-25° C, 4.5 g of butyllithium in 40 ml of ether was added to 10 g (0.07 mole) of ethyl 3-thienyl sulfide [13] in 5 ml of dry ether. The solution was boiled for 30 min and then, at −10° C, 2.3 g of dry finely-ground sulfur was added and, after 20 minutes (when the sulfur had dissolved completely), at 20° C, 12 g of ethyl iodide. The mixture was boiled for 6 hr and was treated as has been described [14]. This gave 8.9 g (62.4% yield) of 2,3-bis(ethylthio)thiophene, bp 110°-111° C (3 mm), d_4^{20} 1.1506; n_D^{20} 1.6040. Found, %: C 46.71; H 5.96; S 47.65; MR_D 61.09. Calculated for $C_8H_{12}S_3$, %: C 47.01; H 5.92; S 47.07; MR_D 61.22.

2,3-Bis(ethylsulfonyl)thiophene (V). A mixture of 3 g (14.5 mmole) of 2,3-bis(ethylthio)thiophene in 30 ml of glacial acetic acid and 6 ml of 30% H_2O_2 was heated in the boiling water bath for 3 hr. The solution was poured onto ice and neutralized with 30% NaOH solution. The white precipitate that deposited on standing was filtered off and was reprecipitated twice from ethyl acetate with n-nonane. This gave 2.1 g (53.5% yield) of V, mp 104.5°—105.5° C (white needles). Found, %: C 35.93; H 4.48; S 35.75. Calculated for $C_8H_{12}O_4S_3$, %: C 35.80; H 4.50; S 35.84.

3-Ethylthio-2-mercaptothiophene (III). An ethereal solution of lithium 3-ethylthio-2-thienylmercaptide obtained from 20 g (0.14 mole) of ethyl 3-thienyl sulfide, 8.9 g (0.14 mole) of butyllithium and 4.5 g of sulfur as described above was hydrolyzed with 50 ml of dilute hydrochloric acid (1 : 1) with cooling. After the usual working up, 18.5 g (70% yield) of distilled 3-ethylthio-2-mercaptothiophene was obtained with bp 89°-91° C (3 mm), n_D^{20} 1.6370. Found, %: C 40.66; H 4.60; S 54.24. Calculated for $C_6H_8S_3$, %: C 40.87; H 4.57; S 54.36.

2,4-Dinitrophenyl 3-ethylmercapto-2-thienyl sulfide, mp 90°-91° C (from ethanol). Found, %: C 42.53; H 3.00; S 28.44. Calculated for $C_{12}H_{10}N_2O_4S_3$, %: C 42.09; H 2.94; S 28.10.

5-Ethyl-2-ethylthio-3-mercaptothiophene (IV). At 0° C, an ethereal solution of 20 g (0.31 mole) of butyllithium was added to 75 g (0.3 mole) of 3-bromo-5-ethyl-2-ethylthiothiophene [14] in 200 ml of dry ether and, after 40 minutes' stirring at −10° C, 9.6 g of sulfur was added. The white suspension was hydrolyzed with dilute hydrochloric acid (1 :1) and worked up by the usual method. Distillation afforded 38.5 g (yield 64%) of 5-ethyl-2-ethylthio-3-mercaptothiophene, bp 110°-111° C (3 mm); n_D^{20} 1.5960. Found, %: C 47.34; H 5.93; S 46.30. Calculated for $C_8H_{12}S_3$, %: C 47.01; H 5.92; S 47.07.

5-Ethyl-2,3-bis(ethylthio)thiophene (II). A mixture of 10 g (0.05 mole) of 5-ethyl-2-ethylthio-3-mercaptothiophene (IV) in 30 ml of a 10% methanolic solution of KOH and 10 g (10% excess) of ethyl bromide was boiled for 6 hr, and then the methanol was distilled off and the residue was diluted with an equal volume of water and extracted with ether. The extract was washed with 10% NaOH solution and with water and was dried with $CaCl_2$, after which the ether was driven off and the residue was distilled in vacuum. This gave 9.1 g of the bis-sulphide II yield 80%, bp 142°-144° C (4 mm), d_4^{20} 1.0966, n_D^{20} 1.5820. Found, %: C 52.29; H 7.13; S 40.71; MR_D 70.54. Calculated for $C_{10}H_{16}S_3$, %: C 51.67; H 6.94; S 41.39; MR_D 70.46.

5-Ethyl-2,3-bis(ethylsulfonyl)thiophene (VI). This was obtained with a yield of 65% as described above for 2,3-bis(ethylsulfonyl)thiophene (V). After recrystallization from heptane and from a mixture of hexane and ethyl acetate, mp 98°-98.5° C. Found, %: C 40.49; H 5.32; S 32.46. Calculated for $C_{10}H_{16}O_4S_3$, %: C 40.52; H 5.44; S 32.45.

Action of sodium in liquid ammonia on the bis(alkylthio)thiophenes I, II, and IX. In a current of argon, 0.1 g-atom of sodium was added in small portions to a mixture of 0.025 mole of the bis(alkylthio)thiophene in an equal volume of ether and a tenfold volume of liquid ammonia until a stable blue color had appeared. After 30 min, the excess of sodium was decomposed with ammonium chloride, the ammonia was evaporated off, and the residue was treated with 30 ml of benzene and 30 ml of water. The aqueous layer was separated off, extracted with benzene, and acidified with HCl (1 :1). The oil that separated out was extracted with benzene, washed with water, and dried with $CaCl_2$. The resulting benzene solution of the mercaptan was used for further reactions. The bismercaptans VII, VIII, and X distilled in vacuum with decomposition (~50%), and therefore the boiling points and values of n_D^{20} given in the table have only an indicative value.

The bis(benzoylthio)thiophenes XI-XIII. An aliquot part of a benzene solution of a dimercaptothiophene (see above) was extracted with 10% NaOH solution, and to the alkaline extract was gradually added an equivalent amount of benzoyl chloride with shaking. The bis(benzoylmercapto)thiophenes separated in the form of viscous oils which solidified on trituration with ethanol and ethyl acetate and were recrystallized from ethyl acetate (see table).

Complex compound of 2,3-dimercaptothiophene with copper (XIV). A solution of 0.5 g of copper acetate in ethanol was added to 0.3 g (~2 mmole) of redistilled 2,3-dimercaptothiophene (VII), obtained by the evaporation of its benzene solution (see above), in 3 ml of chloroform. The black powder that deposited (0.5 g) was twice reprecipitated from dimethylformamide with methanol. The complex did not melt below 360° C and did not dissolve in the usual organic solvents. Found, %: C 22.83; H 1.10. Calculated for $C_4H_2S_3Cu$, %: C 22.89; H 0.96.

Complex compound of 2,3-dimercaptothiophene with nickel (XV). A solution of 0.15 g of nickel acetate in methanol was added to 0.8 g (~5 mmole) of the dimercaptan VII in 15 ml of methanol. The black precipitated that deposited was washed with ethanol and was twice reprecipitated from dimethylformamide with methanol. This gave 0.75 g of a complex which did not melt below 360° C and was insoluble in the usual organic solvents. Found, %: C 28.06; H 1.86. Calculated for $C_8H_4S_6Ni$, %: C 27.52; H 1.15.

Bis(3-ethylthio-2-mercaptothiophene)nickel (XVI). A solution of 0.15 g of nickel acetate in methanol was added to 0.3 g (~1.7 mmole) of 3-ethylthio-2-mercaptothiophene (III) in 5 ml of methanol. A dark oily precipitate deposited which partially crystallized on standing. The crystals were filtered off, washed with ethanol, and dried. After two reprecipitations from chloroform with methanol, 0.1 g (a 28.6% yield) of bis(3-ethylthio-2-mercaptothiophene)nickel was obtained with mp 128°-130° C in the form of dark red crystals soluble in benzene, chloroform, and acetone. Found, %: C 34.92; H 3.34. Calculated for $C_{12}H_{14}S_6Ni$, %: C 35.21; H 3.45.

Bis(5-ethyl-2-ethylthio-3-mercaptothiophene)nickel (XVII). This was obtained as described above for the complex XV from 0.5 g of the thiol IV and 0.22 g of nickel acetate in methanol. This gave 0.2 g of a brown powder with mp 130°-133° C (after two reprecipitations from chloroform with methanol). Found, %: C 41.16; H 4.85. Calculated for $C_{16}H_{22}S_6Ni$, %: C 41.29; H 4.76.

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20 June 1966

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