NEW ELECTRON DONOR – BIS(3-OXY-1,5-DITHIAPENTANO)TETRATHIAFULVALENE

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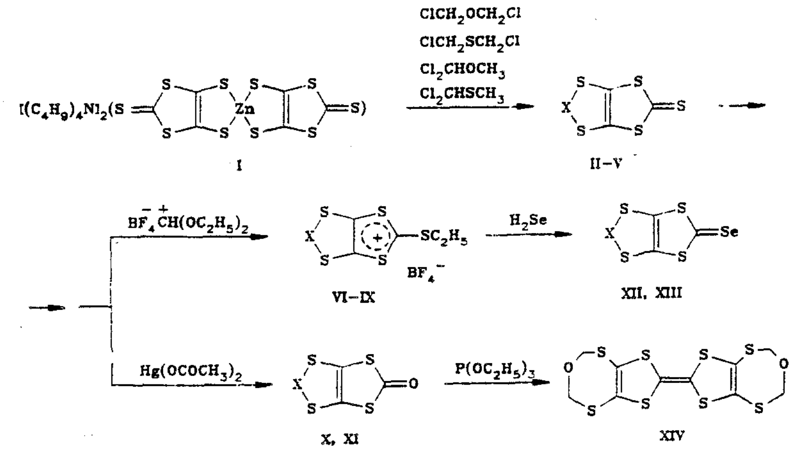
The reactions of bis(tetrabutylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate with dichlorinated ethers and thioethers gave derivatives of the 1,3-dithiole-2-thione that were used for the synthesis of the corresponding 1,3-dithiole-2-ones and 1,3-dithiole-2-selenones. A new electron donor, bis-(3-oxy-1,5-dithiapentano)tetrathiafulvalene, was obtained from 4,5-(3'-oxa-1',5'-dithiapentane)-1,3-dithiole-2-one.

"Organic metals" based on bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF) with inorganic anions have a number of interesting electrophysical properties, superconductivity among them [1-6]. Conductors based on BEDT-TTF are characterized as having attained the highest critical temperature for superconductivity among known organic compounds [4, 6]. Consequently, there is great interest in the synthesis of new donor molecules with similar structures.

We have studied the reactions of bis(tetrabutylammonium)bis-(1,3-dithiole-2-thione-4,5-dithiolato)zincate I, with dichlorinated ethers and thioethers. As a result, we have obtained 1,3-dithiole-2-thione derivatives II-V. These have then been used to synthesize the corresponding analogs of BEDT-TTF (see scheme below).

The starting zincate, I, was obtained by the reduction of carbon disulfide according to [7]. Unlike the previously described reaction of I with dibromoethane [8], which requires heating for 5 h, the reaction of chlorinated ethers and thioethers with zincate I gives the corresponding thiones II-V, in high yield after only 5 min at 50°C. We converted compounds II and III into selenones XII and XIII via the fluoroborates VI and VII, by the action of hydrogen selenide on the latter. Fluoroborates VIII and IX also were synthesized from thiones IV and V, but their conversion to selenones by reaction with hydrogen selenide was not successful. All of the fluoroborates were obtained by us by alkylation of the thiones with diethoxycarbonium fluoroborate [9].

Not one of the thiones and selenones obtained gave the expected coupling products, analogs of BEDT-TTF, when heated with triethyl phosphite. Thus thiones II and III on being heated with mercuric acetate were converted into ketones X and XI. Thiones IV and V, con-



II, VI, X, XII X=CH_2OCH_2; III, VII, XI, XIII X=CH_2SCH_2; IV, VIII, X=$CH(OCH_3)$; V, IX X=$CH(SCH_3)$

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TABLE 1. Physical Chemical and Spectral Characteristics of the Compounds Synthesized

Compound	T_{mp} (T_{decomp}), °C	IR spectrum, cm^{-1}	PMR spectrum, chemical shift, ppm*	S Found, %	Empirical fromula	S Calc., %	Yield, %
II	175—176	1070, 1050 (C=S)	5,03 (4H, c, CH_2); $CDCl_3$; 4,75 (4H, c, CH_2)	66,9	$C_5H_4OS_5$	66,7	98
III	188—190	1065, 1040 (C=S)	4,2 (4H, c, CH_2)	76,1	$C_5H_4S_6$	75,0	98
IV	111—112	1055, 1050 (C=S)	3,2 (3H, c, CH_3); 7,2 (1H, c, CH)	66,7	$C_5H_4OS_5$	66,7	85
V	102—103	1060, 1045 (C=S)	2,25 (3H, c, CH_3); 6,45 (1H, c, CH)	75,1	$C_5H_4S_6$	75,0	79
VI	(165—170)	1470, 1385, 1380, 1070, 918, 790, 670, 520, 470, 445	1,2 (3H, т, CH_3); 3,0 (2H, к, CH_2); 4,7 (4H, д, CH_2)	44,9	$C_7H_9BF_4OS_5$	45,0	100
VII	(155—160)	1450, 1380, 1080, 905, 875, 678, 540, 483	1,17 (3H, т, CH_3); 3,0 (2H, к, CH_2); 4,23 (4H, c, CH_2)	51,6	$C_7H_9BF_4S_6$	51,7	100
VIII	(85—90)	1450, 1380, 1070, 945, 794, 778, 500, 463		44,8	$C_7H_9BF_4OS_5$	45,0	100
IX	(95—98)	1455, 1385, 1060		51,5	$C_7H_9BF_4S_6$	51,7	100
X	132—134	1660 (C=O)	4,75 (4H, c, CH_2)	57,0	$C_5H_4O_2S_4$	57,2	82
XI	195—196	1590 (C=O)	4,2 (4H, c, CH_2)	66,6	$C_5H_4OS_5$	66,7	80
XII	175—176	1455, 1370, 1050, 950 (C=Se), 905, 678, 504	5,05 (4H, c, CH_2)	44,4	$C_5H_4OS_4Se$	44,7	85
XIII	188—190	1470, 1390, 955 (C=Se), 858, 721, 510, 423	4,25 (4H, c, CH_2)	52,7	$C_5H_4S_5Se$	52,8	78
XIV	260—262	1470, 1375, 1334, 1292, 1230, 1044, 998, 915, 698, 674, 505		61,4	$C_{10}H_8O_2S_8$	61,6	5

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*Compounds II, III, VI, VII, XI-XIII in d_6-DMSO; IV, V, and X in $CDCl_3$.

taining five-membered rings, form stable complexes with mercuric acetate that are not destroyed on boiling at 180°C and do not permit the corresponding ketone to form.

Heating ketone X with triethylphosphite at 130-140°C gives a new electron donor, bis-(3-oxy-1,5-dithiapentano)tetrathiafulvalene (XIV), the heating of which with tetracyanoquinodimethane gives a complex in the form of a fine powder, black in color.

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-487C spectrometer (80 MHz) at 20°C with HMDS as an internal standard. The IR spectra were obtained from thin layers of a petroleum jelly mull, on an IKS-29 spectrophotometer.

4,5-(3'-Oxa-1',5'-dithiapentano)-1,3-dithiole-2-thione (II). Freshly distilled 1,2-dichlorodimethyl ether, 4.6 g (0.04 mole) in 20 ml of acetone, as poured into a solution of 18.9 g (0.02 mole) of compound I in 200 ml of acetone. The reaction mixture was heated to 50°C, held for 5 min, cooled to 0°. After 2 h, the yellow-orange crystals were filtered off and recrystallized from alcohol.

4,5-(1',3',5'-Trithiapentano)-1,3-dithiole-2-thione (III), 4,5-(2'-methoxy-1',3'-dithiapropano)-1,3-dithiole-2-one (IV), and 4,5-(2'-methylthio-1',3'-dithiapropano)-1,3-dithiole-2-thione (V) were prepared by the analogous procedures.

2-S-Ethyl-4,5-(3'-Oxa-1',5'-dithiapentano)-1,3-dithiolium Fluoroborate (VI). To a solution of 4.8 g (0.02 mole) of thione II in 70 ml of chloroform are added simultaneously 4.9 g (0.03 mole) of the ortho ester and 4.3 g (0.03 mole) of boron trifluoride etherate. The reaction mixture is boiled for 5 min, cooled, and 200 ml of dry ether are added. The orange, finely crystalline precipitate that forms, is filtered off and washed with dry ether.

2-S-Ethyl-4,5-(1',3',5'-trithiapentano)-1,3-dithiolium fluoroborate (VII), 2-S-ethyl-4,5-(2'methoxy-1',3'-dithiapropano)-1,3-thiolium fluoroborate (VIII) and 2-S-ethyl-4,5-(2'-

methylthio-1',3'-dithiapropano)-1,3'dithiolium fluoroborate were obtained in an analogous manner.

4,5-(3'-Oxa-1',5'-dithiapentano)-1,3-dithiole-2-thione (X). A hot solution of 4 g (0.013 mole) of mercuric acetate in 50 ml of acetic acid was added to a solution of 2.4 g (0.01 mole) of thione II in 100 ml of chloroform and a yellow precipitate of the complex of thione II with mercuric acetate formed. The reaction mixture was boiled for 3 h and the color of the precipitate gradually changed to brown because of the formation of mercuric sulfide. The precipitate was filtered off and washed with chloroform. The organic layer was washed with water, sodium carbonate solution, and again with water, then dried over anhydrous sodium sulfate. The solvent was evaporated off and the 1.8 g of light yellow crystalline substance obtained in the residue was purified by recrystallization from alcohol.

4,5-(1',3',5'-Trithiapentano)-1,3-dithiole-2-one (XI) was obtained in an analogous manner.

4,5-(3'-Oxa-1',5'-dithiapentano)-1,3-dithiole-2-selenone (XII). A stream of H_2Se was passed through a suspension of 3.6 g (0.01 mole) of IV boron trifluoride in 20 ml of methanol at 20°C until no more precipitate formed. The precipitate was filtered off and recrystallized from benzene to obtain 2.4 g of selenone XII in the form of a red-brown, finely crystalline powder.

4,5-(1',3',5'-Trithiapentano)-1,3-dithiole-2-selenone (XIII) was obtained in an analogous manner.

Bis(3-oxa-1,5-dithiapentano)tetrathiafulvalene (XIV). Ketone X, 2.24 g (0.01 mole), was heated with 5 ml of triethylphosphite in a stream of argon for an hour at 130°C. A finely crystalline, yellow powder precipitated when the mixture was cooled to 20°C. The product was filtered off and washed with ether.

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