

NEW METHOD FOR THE SYNTHESIS  
OF TETRATHIOFULVALENE

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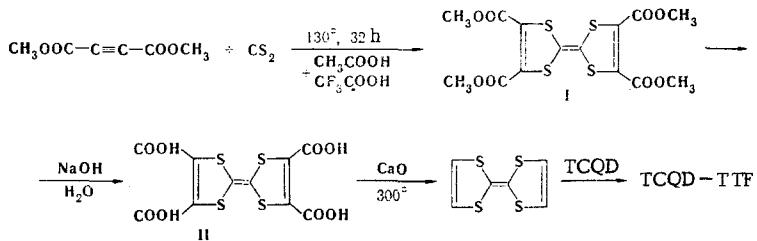
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A new method for the synthesis of tetrathiofulvalene is presented, and conditions for the synthesis of its complex with 7,7,8,8-tetracyanoquinonedimethane are described.

The complex of tetrathiofulvalene (TTF) with 7,7,8,8-tetracyanoquinonedimethane (TCQD) has unique electrophysical properties (a "metal" trend of the dependence of the conductivity on the temperature [1-4] and a sharp increase in conductivity at 60°K by a factor from 10 to 500 [1, 4, 5] as compared with the conductivity at room temperature).

The known synthesis of TTF is realized by condensation of the disodium salt of cis-1,2-dimercapto-1,2-dicyanoethylene with thiophosgene, subsequent hydrolysis of the 4,5-dicyano-1,3-dithiol-2-thione, decarboxylation of the resulting acid, and oxidation of the resulting 1,3-dithiol-2-thione to a dithiolium cation, which couples in the presence of triethylamine. There are ten steps in this synthesis and the TTF is obtained in 10% yield based on the starting carbon disulfide [6, 7].

We propose a rather simple two-step synthesis of TTF on the basis of the readily accessible 3,3',4,4'-tetracarboxy-2,2',5,5'-tetrathiofulvalene tetramethyl ester (I), obtained in 9.7% yield by condensation of carbon disulfide with dimethyl acetylenedicarboxylate [8]. We increased the yield of I to 36% by changing the conditions somewhat [8]. Tetracarboxylate I undergoes saponification to give acid II in 77% yield; the decarboxylation of acid II gives TTF in 15% yield. Thus the overall yield of TTF is 4%.



EXPERIMENTAL

3,3',4,4'-Tetracarbomethoxy-2,2',5,5'-tetrathiofulvalene (I). A mixture of 6 g of dimethyl acetylenedicarboxylic acid, 10 g of carbon disulfide, and 10 ml of acetic acid containing one to two drops of trifluoroacetic acid was heated in a sealed ampul at 130° for 36 h, after which it was cooled and diluted with benzene-hexane (1:1). The resulting precipitate was removed by filtration and recrystallized from benzene-hexane (1:1) to give 3.3 g (36%) of dark-red needles of I with mp 169-170° (in agreement with the melting point in [8]).

3,3',4,4'-Tetracarboxy-2,2',5,5'-tetrathiofulvalene (II). A mixture of 0.66 g of ester I, 100 ml of 5% KOH, and 2 ml of ethanol was stirred at 50° for 3 h, after which the solution was filtered, the solid material was suspended in 100 ml of 5% KOH, and the treatment was repeated. The filtrates obtained after three treatments with alkali were combined and acidified to pH 2. The resulting precipitate of acid II was removed by filtration to give 0.44 g (77%) of a product with mp 300° (dec., from acetone). Found: C 31.5; H 1.0%.  $\text{C}_{10}\text{H}_4\text{O}_8\text{S}_4$ . Calculated: C 31.6; H 1.1%.

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2,2,5,5-Tetrathiofulvalene (TTF). A 1-g sample of CaO and 0.3 g of acid II were ground in a mortar, and the mixture was heated in *vacuo* (1 mm) at 300°. The sublimed tetrathiofulvalene was collected to give the product in 15% yield. Yellow crystals with mp 100–102° (mp 98–102° [7]) were obtained after chromatography on silica gel (elution with benzene) and slow evaporation of the solvent in an inert atmosphere.

7,7,8,8-Tetracyanoquinonedimethane–2,2,5,5-Tetrathiofulvalene (TCQD–TTF) Complex. The TTF was vacuum sublimed twice prior to the synthesis of this complex. The TCQD was crystallized twice from acetonitrile and vacuum sublimed twice to give a product with mp 298–299.5°. Solutions of 1 g of TTF in 60 ml of hot benzene and 1 g of TCQD in 100 ml of hot acetonitrile were poured together, and the resulting mixture was allowed to cool for 4 h in a nitrogen atmosphere. The resulting precipitate was removed by filtration to give 1.6 g (80%) of the complex. A 1:1 complex was formed at all reagent ratios. Found: C 52.8; H 2.0%.  $C_{12}H_4N_4 \cdot C_6H_4S_4$ . Calculated: C 52.9; H 2.0%. Single crystals of the complex were grown by slow cooling of a solution of the complex in acetonitrile in an inert atmosphere.

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#### SYNTHESIS AND STRUCTURES OF 1-METHYL-2,1,3-BENZOTHIA(SELENA)DIAZOLIUM SALTS

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Mixtures of quaternary salts with isomeric structures, the ratio between which depends on the nature of the substituent, are obtained by dimethyl sulfate alkylation of derivatives of 2,1,3-benzothia(selena)diazoles containing a substituent in the benzene ring. Individual 1-methyl-2,1,3-benzothia(selena)diazolium salts are obtained in good yields by treatment of 4(5)-substituted N-methyl-o-phenylenediamine dihydrochlorides with thionyl chloride or selenious acid.

It is known [1] that benzothia(selena)diazolium salts are formed when 2,1,3-benzothia(selena)diazole is heated with dimethyl sulfate. The alkylation of 5(6)-substituted benzothia(selena)diazole has not yet been investigated. The introduction of a substituent in the condensed benzene ring of these heterocycles renders the nitrogen atom in them nonequivalent, and one might therefore have assumed that the alkylation of such substituted compounds could proceed in two directions to give isomers II and III.

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