Chemistry of Heterocyclic Compounds, Vol. 42, No. 4, 2006

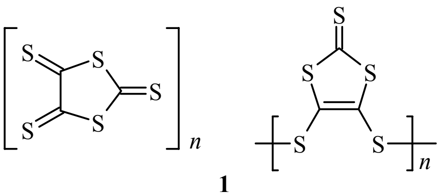
SYNTHESIS OF 1,3-DITHIOLE-2-THIONES AND TETRATHIAFULVALENES USING OLIGO-(1,3-DITHIOLE-2,4,5-TRITHIONE). (REVIEW)*

G. G. Abashev[1] and E. V. Shklyaeva[2]

Methods for the synthesis of 1,3-dithiole-2-thiones, based on [4+2] cycloaddition of the 1,3-dithiole-2,4,5-trithione oligomer to various unsaturated acyclic, carbocyclic, and heterocyclic compounds, are reviewed. Methods for the production of substituted tetrathiafulvalenes, which can be regarded as derivatives of bis(ethylenedithio)tetrathiafulvalene, from 1,3-dithiole-2-thiones synthesized by this method are described.

Keywords: 1,3-dithiole-2-thione, 1,3-dithiol-2-one, 1,3-dithiole-2,4,5-trithiol(ane), substituted donors, tetrathiafulvalenes, [4+2] cycloaddition.

The synthesis of a new heterocyclic compound in the form of the 1,2-dithiolane-2,4,5-trithione oligomer (1,3-dithiole-2,4,5-trithione) (**1**) was first mentioned in 1988 [1]. This compound is particularly interesting for chemists seeking starting compounds for the production of organic conducting and superconducting materials based on substituted tetrathiafulvalenes. Of special interest among the latter are the radical-ion salts and charge-transfer complexes created based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) (**2**), which forms a wide range of conducting organic compounds. Chemical modification of the molecule of compound **2** is one of the important directions in the search for new donating molecules.



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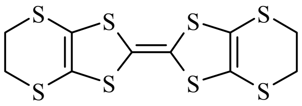

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The 1,3-dithiole-2,4,5-trithione oligomer (**1**) (two ways of representing this compound are shown in the scheme) is, first, a representative of the class of 1,3-dithiole-2-thiones – some of the main intermediate products in the synthesis of tetrathiafulvalenes. Second, the compound contains the ready-made skeleton of half the molecule of compound **2**. Third, it offers the potential possibility of modifying this half of the molecule by the addition of various unsaturated compounds. The method for its synthesis developed by the group led by

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* Dedicated to the memory of Professor O. Neilands.

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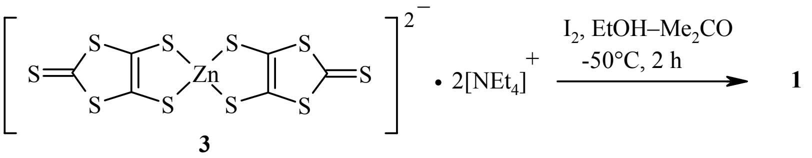
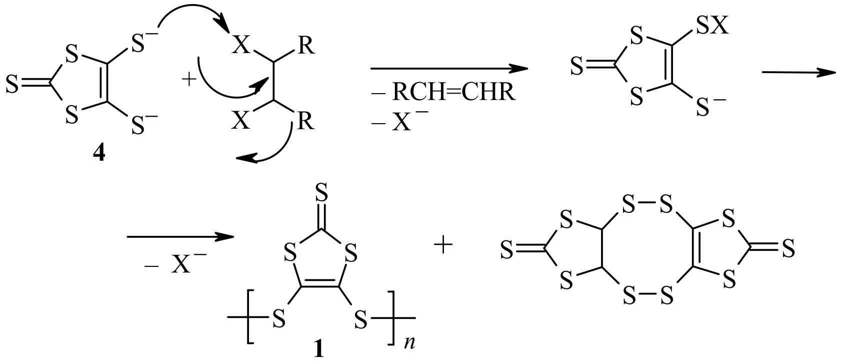
[1] Institute of Technical Chemistry, Urals Branch of the Russian Academy of Sciences, Perm 614990, Russia; e-mail: gabashev@psu.ru. [2] Natural-Sciences Institute, Perm 614990, Russia; e-mail: gabashev@psu.ru.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 483-502, April, 2006. Original article submitted November 17, 2005.

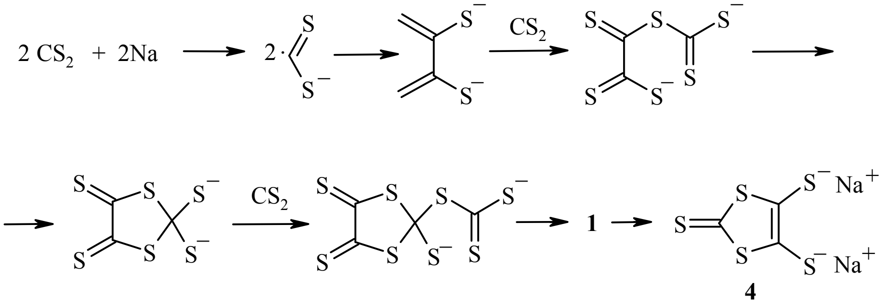
O. Neilands [1, 2] made it possible at once to produce a sufficient quantity of the compound suitable for use without further purification. The method involves the oxidation of bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolate) zincate (**3**) with iodine at low temperature (-55°C) [1]. It is also possible to use SO_2Cl_2 and $(COCl)_2$ as oxidizing agents, where the reactions take place at room temperature [3].



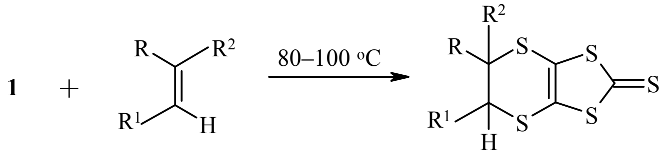
Somewhat later papers reporting the formation of this compound in other reactions of the zincate **3** were published. It was found that certain 1,2-dihaloalkanes at room temperature lead to instantaneous and practically quantitative transformation of the zincate **3** into the trithione **1**. Such reactions were observed for 4,5-dichloro-1,3-dioxolan-2-one, 3,4-dibromofuran-2,5-dione, and 3,4-dibromo-1-phenylpyrrole-2,5-dione. The mechanism of this transformation probably includes initial nucleophilic attack by the thiolate anion on the halogen atom [3].



A stage with the formation of the trithione **1** was also proposed during discussion of the mechanism of formation of the zincate **3** from carbon disulfide [4].



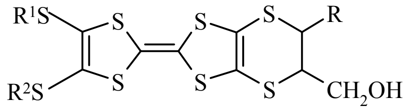
It was found that the oligomer **1** undergoes depolymerization at a temperature around 80-100°C and at this moment represents an effective 4π component in pericyclic reactions of the Diels–Alder type ([4+2] cycloaddition). Both electron-saturated and electron-depleted dienophiles react with it well. The reaction is usually conducted by boiling the respective dienophile with an excess of the trione in such solvents as benzene, toluene, thiophene, and dioxane and even in water. O. Neilands and coworkers synthesized a series of substituted thiolethiones by the reaction of 1,3-dithiole-2,4,5-trione with various alkenes [1, 2, 5], and the *cis* or *trans* isomers were formed depending on the structure of the alkene.



5a–m

5	R	R^1	R^2
a	$C_{10}H_{21}$	H	H
b	$C_{16}H_{33}$	H	H
c	CO_2H	H	H
d	CO_2Me	H	H
e	$CONH_2$	H	H
f	$(CH_2)_3CO_2H$	H	H
g	CH_2OH	H	CH_2OH
h	H	CH_2OH	CH_2OH
i	CO_2Me	H	CO_2Me
j	C_8H_{17}	H	$(CH_2)_7CO_2H$
k	H	$(CH_2)_3$	$(CH_2)_3$
l	H	$(CH_2)_4$	$(CH_2)_4$
m	H	CH_2OH	H

Compound **5m** was synthesized later (2001) [6, 7] and was used for the production of the unsymmetrical tetrathiafulvalene **6**, from which stable Langmuir–Blodgett films in particular were obtained [6] ($R^1 = R^2 = C_{17}H_{35}$). By using compounds **5m** and **5i** it was possible to synthesize radical-ion salts having semiconductor-type conductivity [7].

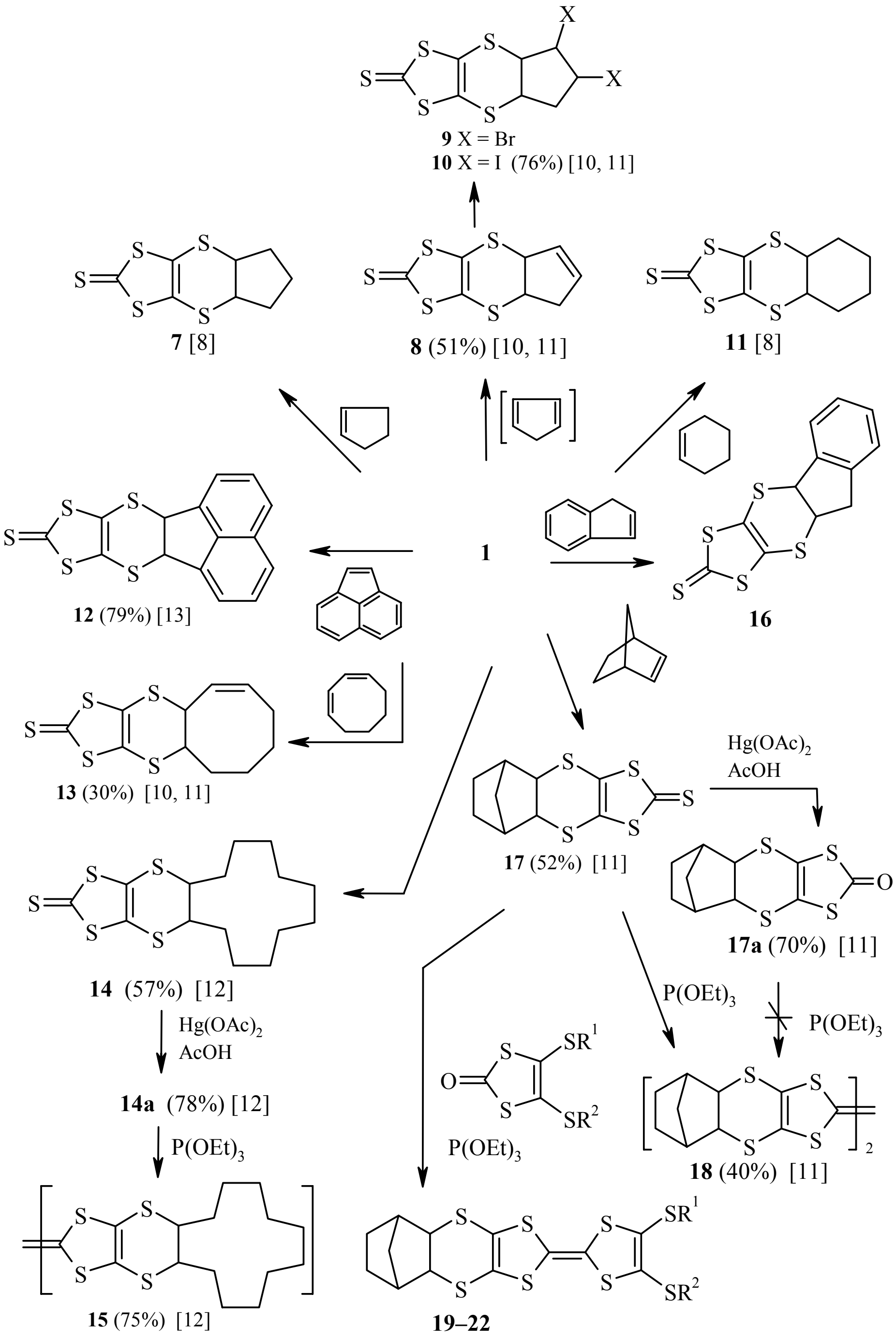


6

[TTF **6**]$_2ClO_4$ R = H,
$R^1 + R^2 = CH_2–CH_2$, $\sigma = 0.68$ $S·m^{-1}$;
[TTF **6**]$_2$Cl R = CH_2OH,
$R^1 + R^2 = CH_2–CH_2$, $\sigma = 0.10$ $S·m^{-1}$
(*S* = siemens, the unit of electrical conductivity)

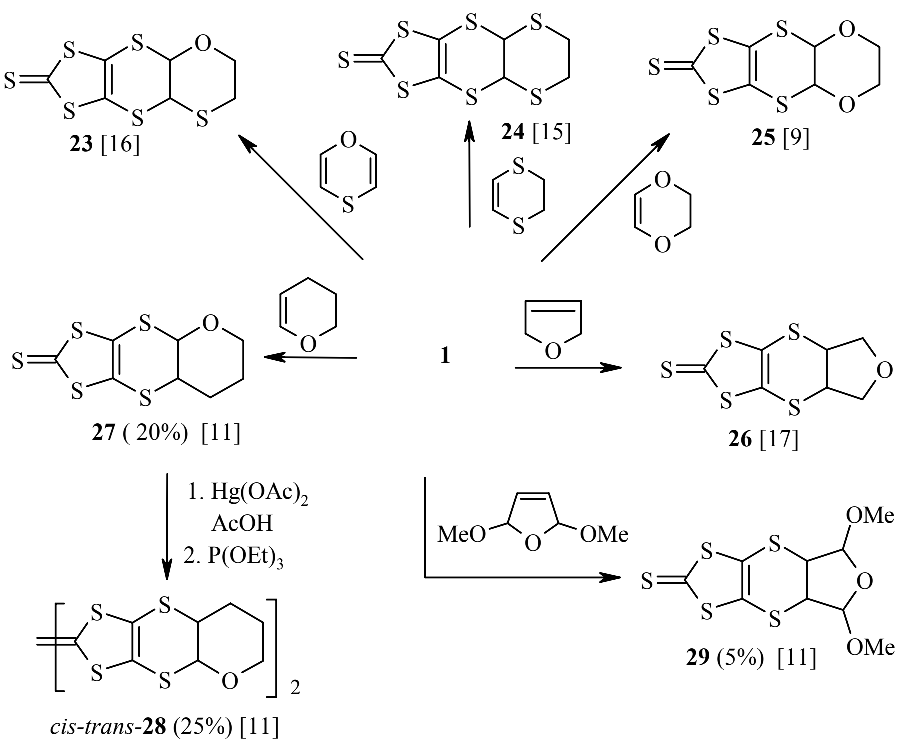
A fairly large number of papers have been published on the reaction of the trithione with various cyclic unsaturated compounds, such as cyclohexene and cyclopentene [8], 1,4-dioxene [9], cyclopentadiene, indene, 1,3-cyclooctadiene, and norbornene [10, 11], cyclododecene [12], and acenaphthene [13]. It is difficult to produce the 1,3-dithiole-2-thiones synthesized by this method in other ways.

The 1,3-dithiole-2-thiones shown in the scheme were used for further transformations. Thus, the thione **8** was subjected to direct halogenation, leading to good yields of the diiodo derivatives **9** and **10**. Some of the obtained 1,3-dithiole-2-thiones were used in the synthesis of symmetrical and unsymmetrical tetrathiafulvalenes. For example, the symmetrical tetrathiafulvalenes **15** and **18** were obtained from compounds **14** and **17**. It is interesting that 1,3-dithiole-2-thione **17** and not its oxygen analog 1,3-dithiol-2-one **17a** was used for the production of compound **18**, although cross-linking by the action of triethyl phosphite is usually more successful with 1,3-dithiol-2-ones than with the 2-thiones. This compound **17** was also used for the synthesis of the unsymmetrical tetrathiafulvalenes **19-22** [14]. Some of them **20-22** contain a β-cyanoethylthio group, the properties of which (S-protecting group) can then be used to modify the obtained tetrathiafulvalenes.



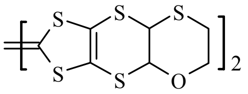
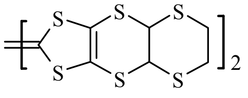
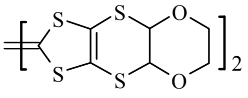
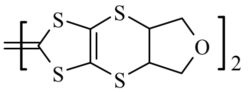
19 $R^1 + R^2 = CH_2CH_2$[11]; **20** $R^1 = Me$, $R^2 = CH_2CH_2CN$ [14]; **21** $R^1 = R^2 = CH_2CH_2CN$ [14];
22 $R^1 = CH_2CH_2CN$, $R^2 = CH_2CO_2Me$ [14]

The trithione **1** has been used fairly widely in [4+2] cycloaddition reactions with unsaturated heterocycles containing one or two double bonds and identical or different heteroatoms [9, 11, 15-17].



Oxidation of the 1,3-dithiole-2-thiones **23-27** with Hg(OAc)$_2$ in acetic acid to the corresponding 1,3-dithiol-2-ones and their subsequent cross-linking in trialkyl phosphites gave the symmetrical tetrathiafulvalenes **28** and **23a-26a**; the voltammetric characteristics were investigated for the latter (Table 1). It was found that they were fairly close to bis(ethylenedithio)tetrathiafulvalene in their donating characteristics (E_1 = 0.57; E_2 = 0.733 V) [18].

TABLE 1. The One-Electron Oxidation–Reduction Potentials

Compound	Formula of TTF	Solvent for CV*	E_1, V	E_2, V
23a		PhCN	0.56	0.90
24a		PhCN	0.68	0.94
25a		MeCN	0.58	0.82
26a		MeCN	0.60	0.91

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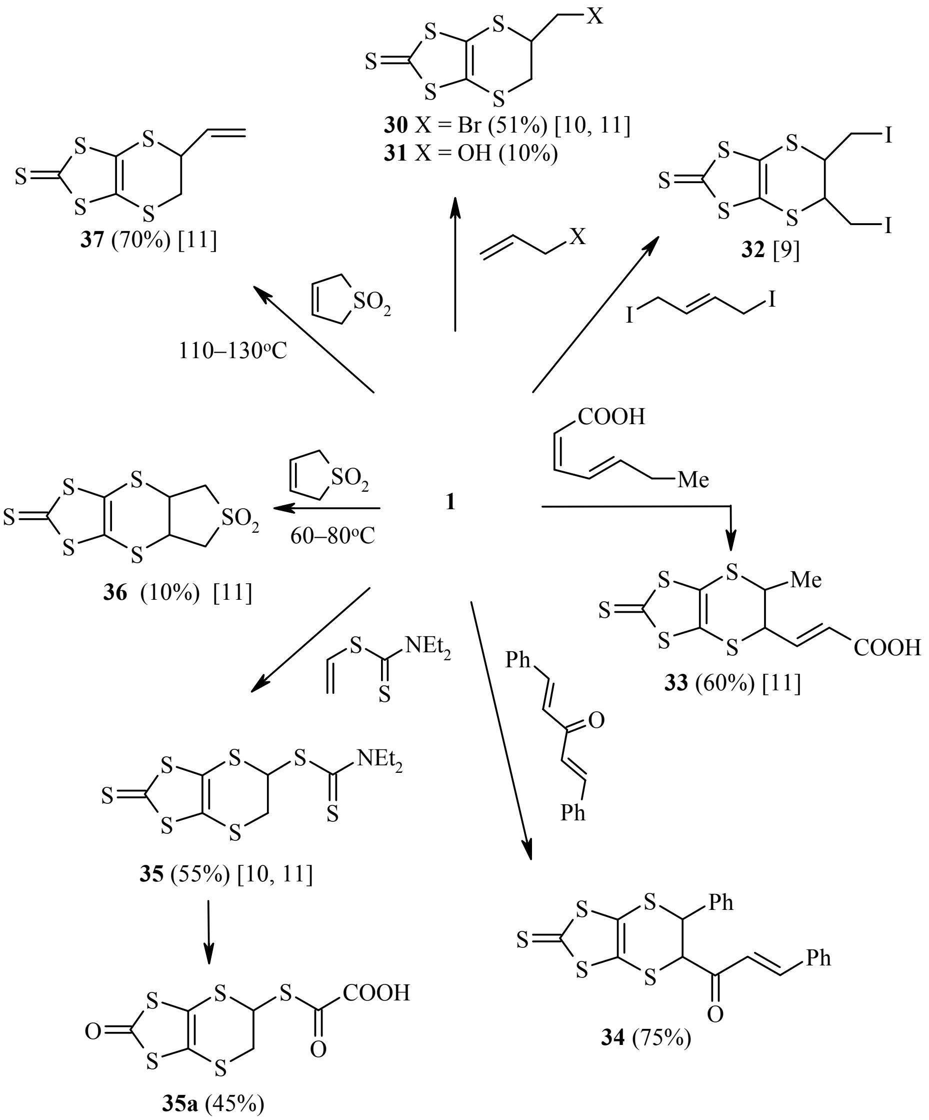
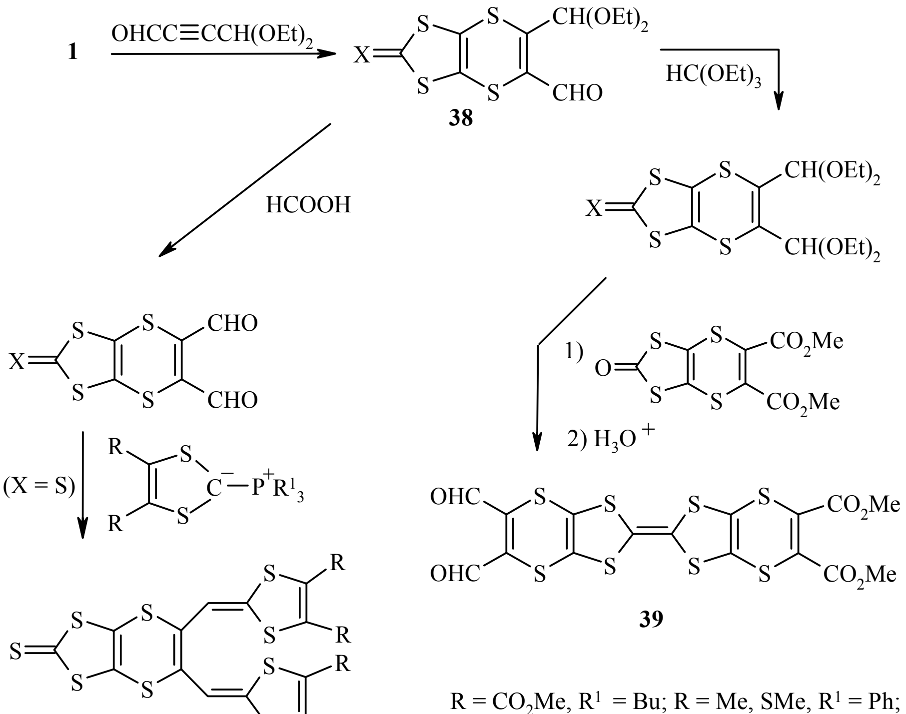
* CV = cyclic voltammetry.

It is undoubtedly of interest to investigate the reaction of the diene **1** with dienophilic components having such a structure. After their addition in the obtained adduct there remains the possibility of further chemical modification (active double bonds, active halogen atoms, functional groups), as was done, for example, in [1, 2]. The authors in [11] studied the reaction of allyl bromide, 1,4-diiodobutene, allyl alcohol, vinyl diethyldithiocarbamate, sorbic acid and its ethyl ester, dibenzylideneacetone, and sulfolene with the trithione **1**. It was shown that the reaction with allyl alcohol gives a small yield of the adduct **31**. Replacement of the benzene by other solvents (toluene, dioxane, water) did not substantially affect the yield. It is known that sulfolene behaves as a source of butadiene in many syntheses, and its reaction with the oligomer **1** at various temperatures was therefore studied. Thus, in the range of 60-80°C (benzene) sulfolene reacted as a cyclic compound and gave a small yield of the thiolethione **36**, containing an oxidized sulfur atom. At 100-130°C (toluene, xylene) it behaved as a source of 1,4-butadiene and gave a good yield of the adduct **37**, which contained an exocyclic double bond.



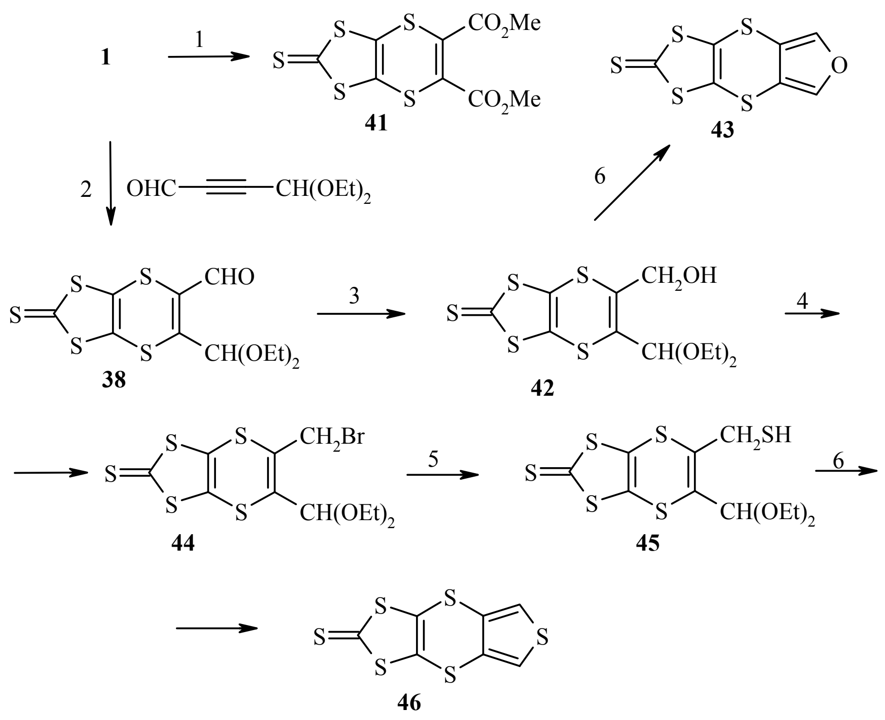
The reaction of the trithione **1** with vinyl diethyldithiocarbamate was conducted under different conditions in the absence of a solvent [10], i.e., in a melt of the second reaction component (the thiocarbamate). The yield of the reaction product **35** was fairly high (~55%). When compound **35** was heated with mercury acetate in acetic acid, the thioamide group was hydrolyzed to carboxyl at the same time as the C=S group was replaced by C=O; the product of this reaction was the thiol-2-one **35a**. Cyclization of the trithione **1** with 1,4-diiodo-2-butene led to the corresponding di(iodomethyl)-substituted 4,5-bis(ethylenedithio)-1,3-dithiole-2-thione **32**, suitable for further transformation. The reaction of the oligomer **1** with sorbic acid and its ethyl ester was investigated. In the second case a poorly separable mixture of compounds was formed. In the case of the acid itself practically the only isolated product was compound **33** containing a free carboxyl group. With this compound it was proposed to synthesize the esters of aliphatic acids used for the production of Langmuir–Blodgett films. Compound **34** was obtained as the only product from reaction of the trithione and dibenzylideneacetone in ratios of 1:1 and 2:1. The result was not affected by change in the temperature regime (benzene → toluene → xylene).

The authors of [19, 20] reported the use of the trithione **1** for the synthesis of S-enriched analogs of tetrathiafulvalene. They investigated the reaction of the trithione with aldehydes of the acetylene series. One of the obtained compounds (the thione **38**) proved to be a suitable synthon for the production of substituted 1,3-dithiole-2-thiones. By varying the order of removal and introduction of the protection for the C=O group in compound **38** it was possible to use the compound in condensation reactions. Here tetrathiafulvalenes of both normal structure (e.g., **39**) and "split" structure, i.e., structures in which the two 1,3-dithiole rings of the tetrathiafulvalene are as it were separated by a conjugated bridge (e.g., compound **40**), can be formed.



R = CO_2Me, R^1 = Bu; R = Me, SMe, R^1 = Ph;
X = O, S

By using the reaction of the oligomer **1** with carbonyl derivatives of the acetylene series [19, 20], the authors of [21] synthesized the interesting 1,3-dithiole-2-thiones **43** and **46**, in which the 1,3-dithiole ring is condensed with a 1,4-dithiin ring, and the latter in turn was condensed with thiophene or furan rings.



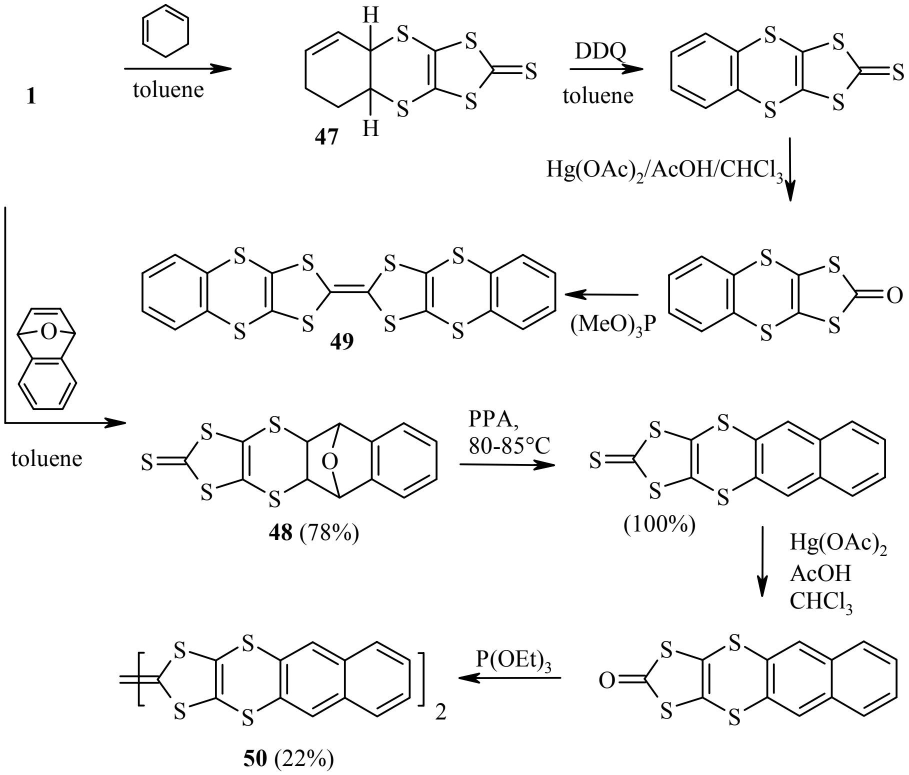
1. Dimethyl butynediolate, 2,6-lutidine, 80°C, 10 min; 2. Toluene, 2,6-lutidine, 70°C, 45 min; 3. $NaBH_4$, THF, ~20°C, 2 min; 4. $PPh_3 + CBr_4$, THF; 5. NaSH, MeOH, THF, -20°C, 2.5 min, HCl, 50°C; 6. HCO_2H, CH_2Cl_2, AcOH, ~20°C, 1 h

Symmetrical tetrathiafulvalenes were synthesized from the obtained compounds **41**, **43**, and **47**, and the crystal structure of the furan derivative and the electrochemical behavior of all the new tetrathiafulvalenes were studied. By analyzing the reaction of the diacetals and monoacetals of acetylenedicarbaldehyde shown above, of acetylenedicarbaldehyde itself, and of other analogous acetylene compounds from the standpoint of their activity as dienophiles in these reactions the authors of [19, 20] were able to reach certain preliminary conclusions concerning the activity of such dienophiles in cycloaddition reactions [22]. It was found that di-E-substituted alkynes are more active than the monosubstituted compounds (E – substituent at the acetylene bond, i.e., CN, CHO, $CH(OR)_2$, COR, CO_2R, $CONR_2$). Monosubstituted alkynes with one unsubstituted position containing functional groups are more active than the R-substituted alkynes, while the latter are more active than the di-R-substituted alkynes (R represents groups with donating character), which are practically inert in these reactions.

$$E{\equiv}E > H{\equiv}E \gg E{\equiv}R \ggg R{\equiv}R$$

First it can be stated that the higher the electrophilicity of the substituent E, the higher the reactivity of the alkyne containing this substituent: CN ~ CHO > CO_2R > COR.

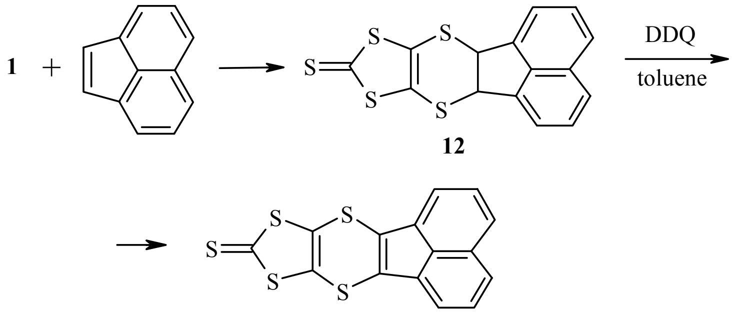
The reaction of the oligo(1,3-dithiole-2,4,5-trithione) **1** with rings containing several double bonds gave the linear 1,3-dithiole-2-thiones **47** and **48** [23]. The authors assumed that replacement of the peripheral 1,2-ethanediyl group in the bis(ethylenedithio)tetrathiafulvalene molecule by condensed aromatic rings would lead to an increase in the size of the unit cell and also to parallel π–π interaction of the aromatic rings, leading to the appearance of possible new types of packing. It was these motives that led the authors to strive to obtain two bis(ethylenedithio)tetrathiafulvalene derivatives, i.e., the dibenzo derivative **49** and the dinaphtho derivative **50**.



DDQ – dichlorodicyanoquinone

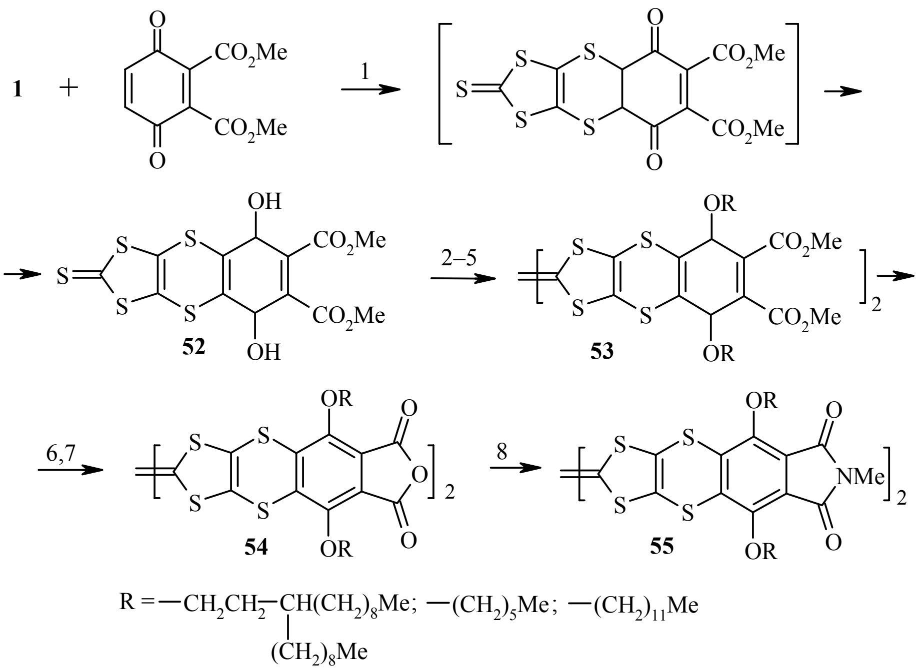
It should be noted that the dibenzo derivative **49** had been obtained earlier from 1,2-dimercaptobenzene by a five-stage synthesis, where the total yield of the product was only 4% [21]. Williams and coworkers used [4+2] cycloaddition of oligo(1,3-dithiole-2,4,5-trithione) to the corresponding olefins as the key stage in the synthesis of annelated derivatives of bis(ethylenedithio)tetrathiafulvalene, where the yield of compound **49** amounted to 37% [24].

The reaction of 1,3-dithiole-2,4,5-trithione with acenaphthene gave the previously mentioned cyclic adduct **12**, the dehydrogenation of which with dichlorodicyanoquinone gave the 1,3-dithiole-2-thione **51** [13]; the obtained thiones were used for the synthesis of tetrathiafulvalenes and their salts with tetracyanoquinodimethanes [25].



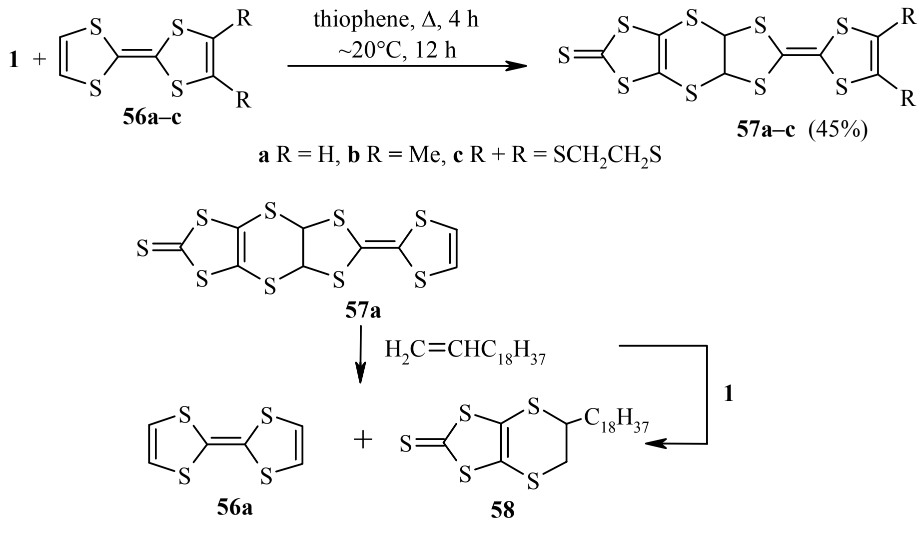
51

Tetrathiafulvalenes **53-55**, which exhibit liquid-crystalline characteristics, were synthesized from 1,3-dithiole-2-thione **52**, obtained by the [4+2] cycloaddition of substituted quinone to the trithione **1** in THF [26].



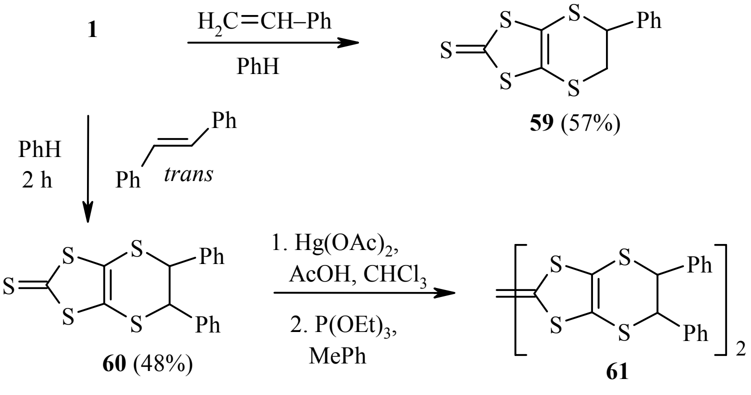
1. THF, Δ, 8 h; 2. Ac_2O, 4-N,N-dimethylaminopyridine (DMAP), CH_2Cl_2, 2 h, 94%; 3. $Hg(OAc)_2$, AcOH, 4 h, 94%;
4. $P(OMe)_3$, PhH, Δ, 5 h, 60%; 5. RX, K_2CO_3, DMF, Δ, 74-94%; 6. KOH, THF, MeOH, Δ, 5 h, 78%;
7. 90°C, vacuum, 5 h, 88%; 8. $MeNH_2·HCl$, K_2CO_3, DMAP, DMF, $CHCl_3$, 3 Å molecular sieves, 80°C, 3 days, 60%

Such [4+2] cycloaddition found an interesting application in [27, 28]. The tetrathiafulvalenes **56a-c** (tetrathiafulvalene, 6,7-dimethyltetrathiafulvalene, and 6,7-ethylenedithiotetrathiafulvalene), the double bonds of which are known to be very inactive, were used as unsaturated component. The reactions were conducted in boiling thiophene, and as a result the corresponding cyclic adducts **57a-c** were obtained with fairly high yields particularly in the case of 6,7-ethylenedithiotetrathiafulvalene **57c**. It was found that the reaction of compound **1** with tetrathiafulvalene **56a** is reversible. Thus, 60-68% of the initial compound **56a** was isolated when the cyclic adduct was heated in boiling toluene. A decrease and not an increase in the yield with increase in the heating time was also observed in the reaction of the trithione **1** with dicyclopentadiene [11]. It is interesting



that the corresponding 1,3-dithiole-2-thione **58** is formed with a yield of 70-75% in addition to the tetrathiafulvalene **56a** when compound **57a** is heated in toluene in the presence of eicosene. The product could be obtained directly by the reaction of compound **1** with eicosene under the conditions of [4+2] cycloaddition.

trans-Stilbene and styrene were also used as dienophile in reactions with compound **1** [29].

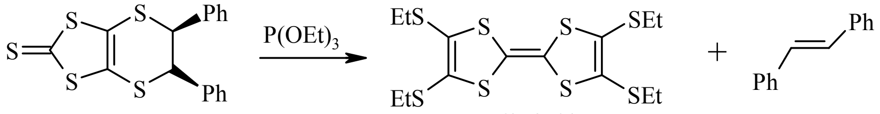


59 (57%)

60 (48%)

61

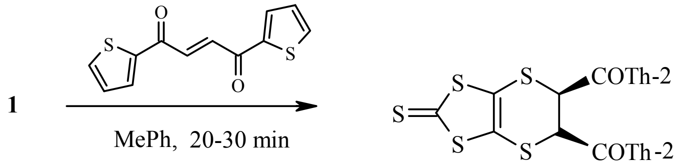
Later on [30] the same authors found that *trans*-stilbene is eliminated when the obtained 4,5-(α,α'-diphenylethylenedithio)-1,3-dithiole-2-thione (**60**) is boiled in pure triethyl phosphite (without a solvent), as demonstrated by ^{1}H NMR, Fourier, UV, and mass spectroscopy, and tetra(ethylthio)tetrathiafulvalene (**62**) is formed instead of the expected tetrathiafulvalene **61**. This fact provides indirect evidence for the reversibility of the reactions of the trithione oligomer **1** with unsaturated compounds. The phosphorus probably attacks at the sp^3-carbon atom, and this is followed by an Arbuzov rearrangement [30].



60

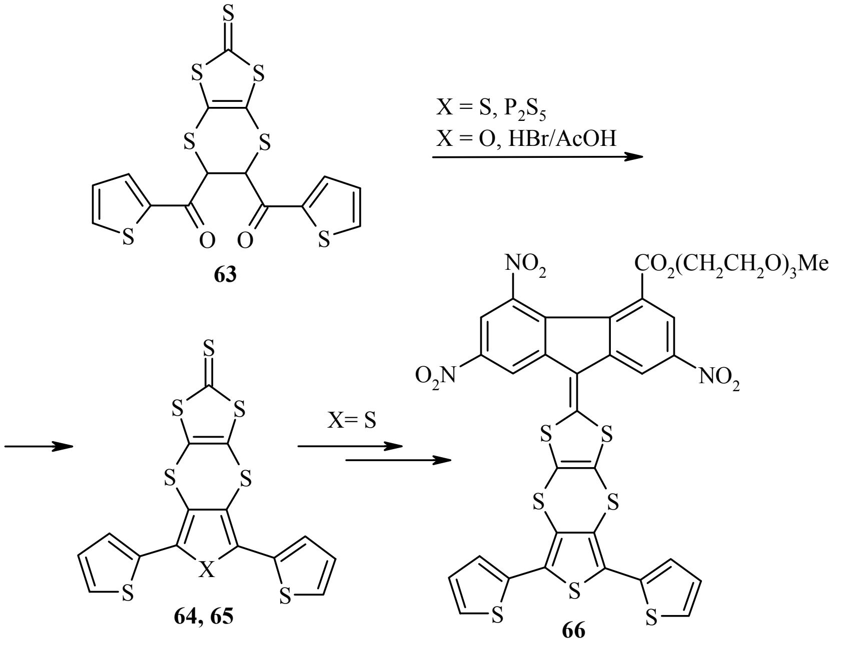
62 35%

The reaction of the trithione **1** with 1,2-di(α-thenoyl)ethylene gives a good yield of the stable *trans*-diketone **63**, containing a thiophene fragment (73% on the chromatographically purified substance) [31].



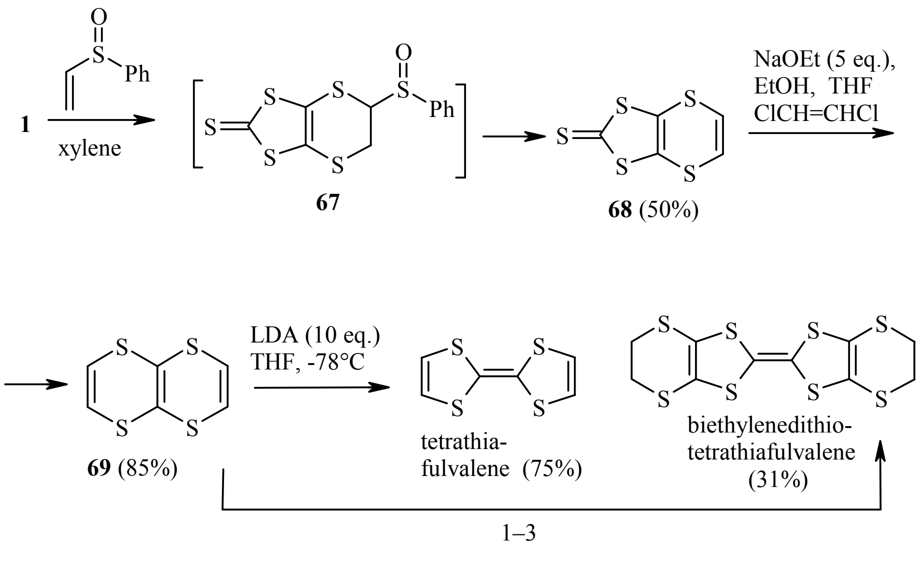
63

A high yield of the final product was achieved by using an excess of the oligomer **1**, while in the reverse case the yield was greatly reduced. This probably results from reaction of the obtained adduct with the oligomer **1**. 1,3-Dithiole-2-thione **63** was used for the production of the corresponding furan **64** and thiophene **65** derivatives. The 1,3-dithiole-2-thione (**65**), annelated with a substituted thiophene ring, was used for the synthesis of compound **66**, the molecule of which contains both electron-donating and electron-withdrawing fragments [31].



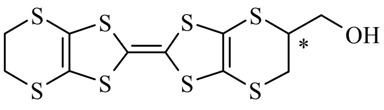
Compounds **63**-**66** are of interest as monomers for the production of thiophene-containing polymers, since the α positions of their thiophene rings are free and are suitable for participation in polymerization.

4,5-Vinylidenedithio-1,3-dithiole-2-thione (**68**) was obtained by boiling compound **1** in xylene [32] with phenyl vinyl sulfoxide, the synthetic equivalent of acetylene in the Diels–Alder reaction, through the intermediate adduct **67**. It was then used for the production of 1,4,5,8-tetrathianaphthalene (**69**), which by isomerizing in an alkaline medium (an excess of lithium diisopropylamide, -78°C) forms unsubstituted tetrathiafulvalene, while in the presence of 1,2-dibromoethane and sulfur it forms biethylenedithio-tetrathiafulvalene (e.g., see [33]).

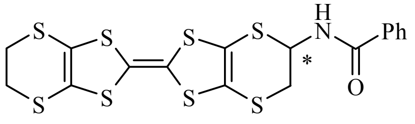


1. Lithium diisopropylamide (LDA), 10 eq., THF, -78°C;
2. S_8, 4.1 eq., -78°C; 3. $Br(CH_2)_2Br$, 24°C, 30%

In reaction with unsymmetrically substituted alkenes the trithione oligomer **1** forms adducts containing asymmetric centers in the 1,4-dithiin ring. According to the authors of [34, 35], this can be used for the production of chiral conducting systems. Some of the tetrathiafulvalenes investigated in this work are presented below.

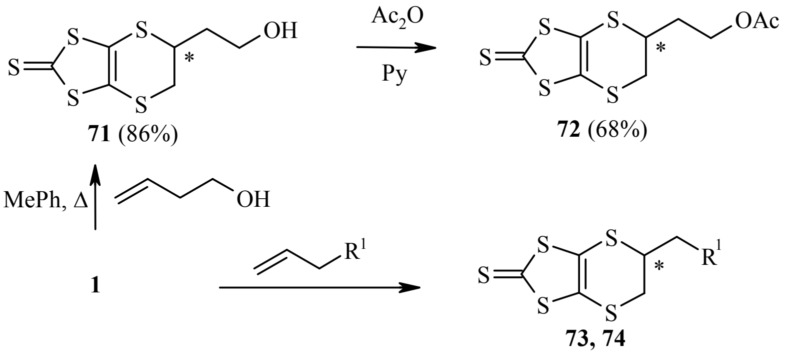


70a



70b

In [35], in particular, the production and transformations of substituted 1,3-dithiole-2-thiones **71-74**, containing an asymmetric carbon atom, were described.



71 (86%)

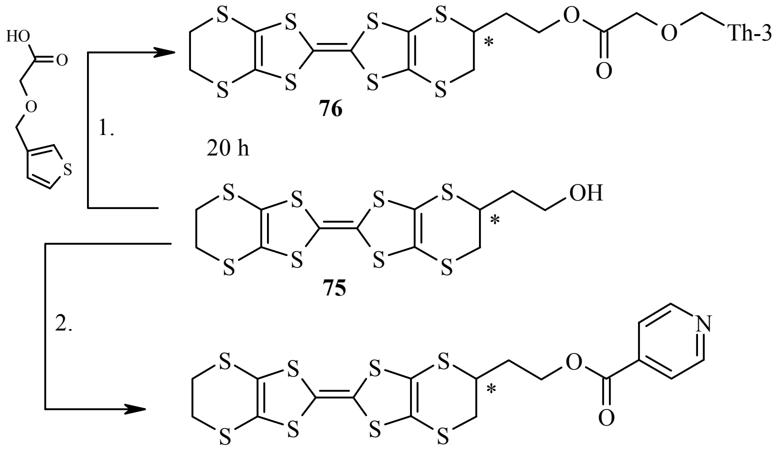
72 (68%)

1

73, 74

73 R^1 = OAc (67%);
74 R^1 = NHBoc (67%)

The 1,3-dithiole-2-thione **71** obtained by this method and hardly obtainable by other methods became the key compound in the synthesis of a group of tetrathiafulvalenes **75-77**, which can be regarded as monosubstituted biethylenedithiotetrathiafulvalenes. Thus, the unsymmetrical tetrathiafulvalene **75** was synthesized after replacing the C=S group in the acyl derivative **72** by C=O by the action of $Hg(OAc)_2$ in acetic acid and chloroform, cross-linking the obtained 1,3-dithiol-2-one with 1,3-dithiole-4,5-ethylenedithio-2-thione, and removing the protecting group with THF/HCl. It was converted into the functionally substituted tetrathiafulvalenes **76** and **77**:



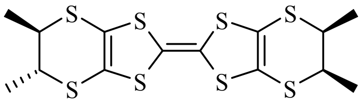
76

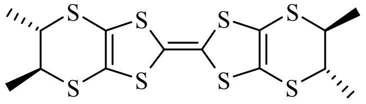
75

77

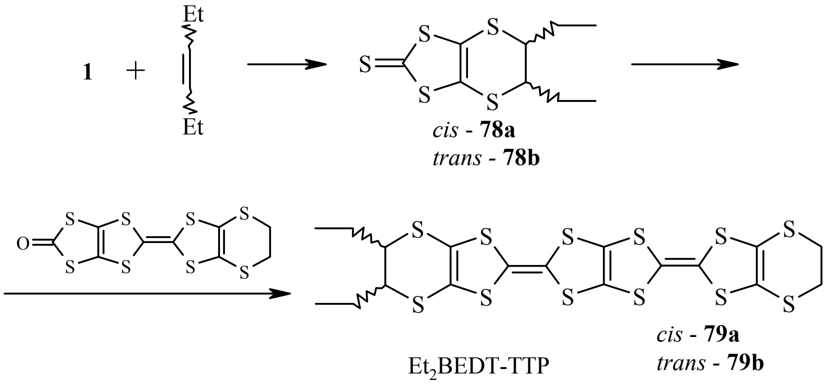
1. DCC = dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, CH_2Cl_2, 20 h.
2. Isonicotinoyl chloride, pyridine

In many papers on the reactions of the trithione trimer **1** it was shown that its reaction with unsaturated compounds takes place stereospecifically, particularly in the case of the *trans* form of the unsaturated compound (e.g., see [2, 5, 36]). After the reaction of the trithione with the alkenes the substituents in the obtained adduct can be either in the *cis* form or in the *trans* form. If different 1,3-dithiole-2-thiones (-2-ones) (e.g., half *trans*, half *cis*) are used during further cross-linking with trialkyl phosphites or other reagents, the production of several different tetrathiafulvalenes can be expected [35], for example:





This feature was used in the production of an organic conductor containing stereochemically constructed donor–salt stacks with the composition $(Et_2BEDT\text{-}TTP)_2HgI_3$. The production scheme and the composition of the donor **79** in this salt are shown below.

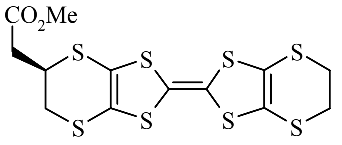

cis - **78a**
trans - **78b**

Et_2BEDT-TTP

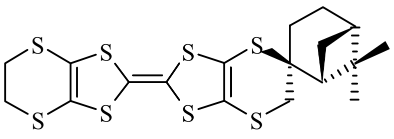
cis - **79a**
trans - **79b**

Et_2BEDT-TTP = diethyl(bisethylenedithiotetrathiafulvalene)tetrathiapentalene

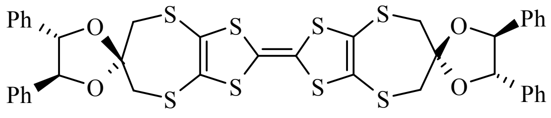
When 100% *trans*-3-hexene was used at the first stage, the stereochemically pure *trans*-1,3-dithiole-2-thione **78b** was isolated as a result of the reaction. If *cis*-hexene containing 4% of the *trans* form was used, a mixture of isomers was obtained (yield 23%, **78a**:**78b** = 85:15, based on the ^{1}H NMR spectra). If the *trans* isomer **78b** was cross-linked with 5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalen-2-one by the action of trimethyl phosphite, only the *trans* isomer **79b** was obtained (yield 25%). The diastereomers **78a**,**b** and **79a**,**b** differ quite distinctly from each other in the chemical shifts of the methine protons: 3.51 and 3.10 (*cis* and *trans*) for the 1,3-dithiolethiones **78a**,**b**, 3.39 and 2.99 ppm for the tetrathiafulvalenes **79a**,**b**. It was not possible to separate the mixture of *cis* and *trans* isomers by chromatography on account of the proximity of the R_f values. Enantiomerically pure tetrathiafulvalenes **80-82** were obtained in [38] using this same characteristic.



80

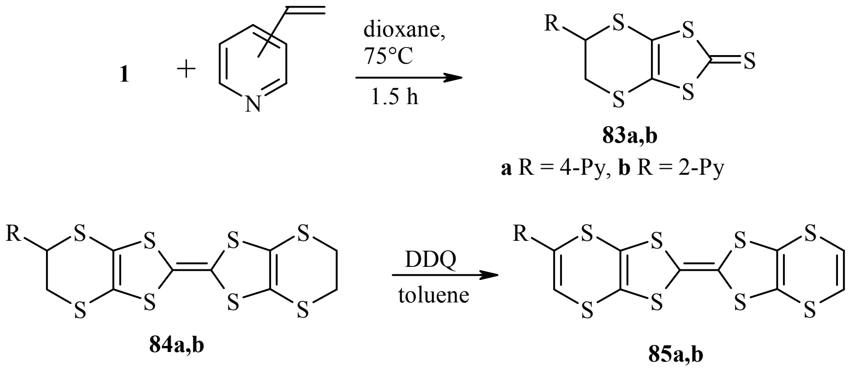


81

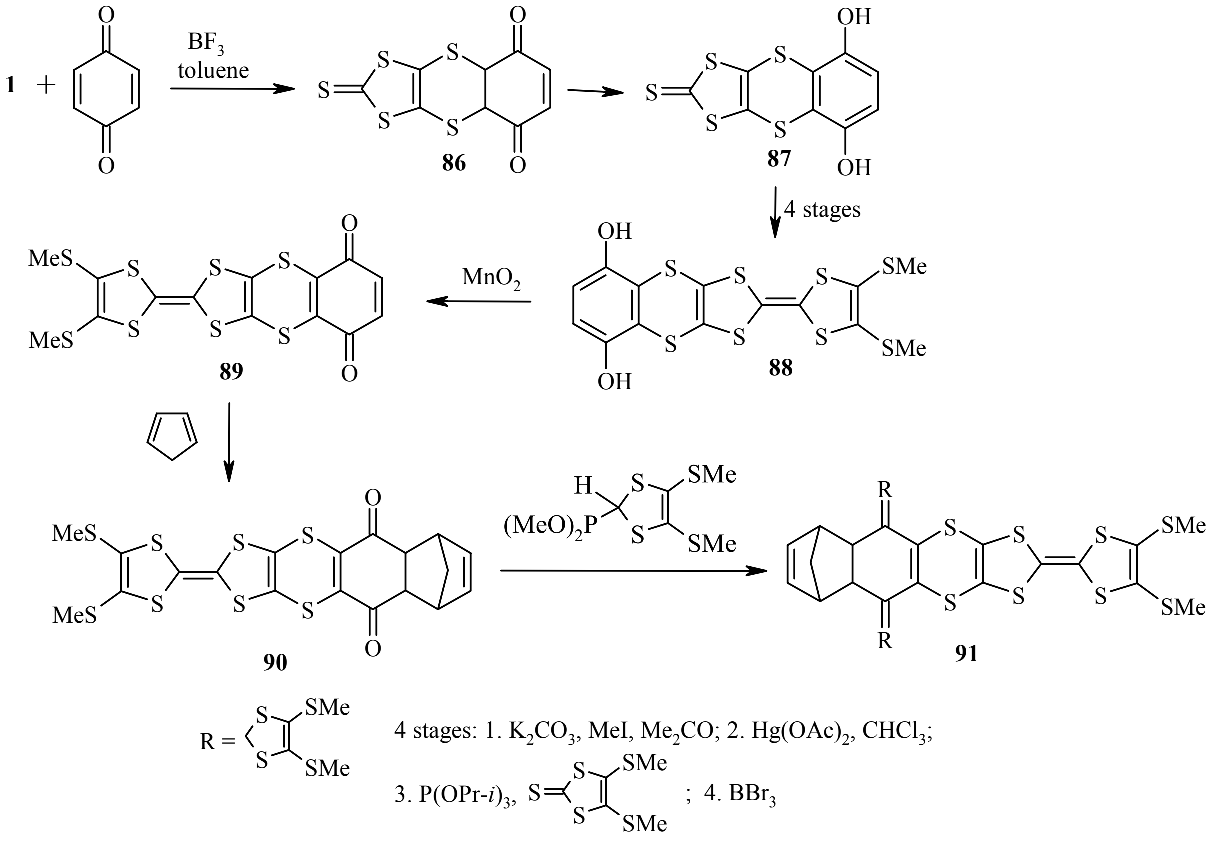


82

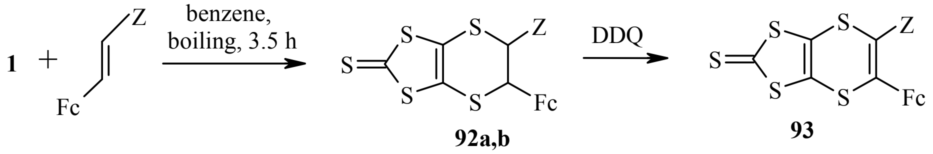
Reaction of the trithione and 2(4)-vinylpyridine led to the adducts **83a**,**b** [39], which were oxidized to 1,3-dithiol-2-ones, and the unsymmetrical tetrathiafulvalenes **84a**,**b** (monosubstituted bis(ethylenedithio)-tetrathiafulvalenes) were obtained by cross-coupling. By boiling in toluene in the presence of dichlorodicyanoquinone a double bond was introduced into compounds **84a**,**b** with yields of 20 and 44% (after chromatographic purification).



The same authors investigated the reaction of the trithione oligomer **1** with *p*-benzoquinone [40]. It was shown that in the reaction under standard conditions for this reaction the yield of the required product **86** amounted to only 1%. The yield was increased a little (to 10%) if BF$_3$ was added. The tetrathiafulvalenes **88-90** were synthesized successively from the obtained 1,3-dithiole-2-thiones **86** and **87** by cross-coupling, and the tetrathiafulvalene **91** containing crossed fragments was finally obtained.



The 1,3-dithiole-2,4,5-trithione oligomer **1** was used to prepare the 1,3-dithiole-2-thiones **92** and **93**, containing ferrocene fragments [41]. It is known that ferrocene has attracted considerable attention on account of its interesting and varied properties. It is, for example, an electron donor, has reversible oxidation–reduction characteristics, and also has catalytic properties. The scheme of these transformations is presented below.



a Z = H (94%); **b** Z = Fc (70%)

Thus, it is seen that the reaction of the 1,3-dithiole-2,4,5-trithione oligomer with unsaturated compounds described in the review is an extremely productive method and very often the only method for the synthesis of 1,3-dithiole-2-thiones containing a substituted 1,4-dithiin ring.

The work was carried out with financial support from the Russian Fundamental Research Fund (Grants Nos. 04-03096035-Ural and 05-03-32849a).

REFERENCES

1. Ya. Ya. Katsens and Ya. N. Kreitsberga, USSR Inventor's Certificate 1428753; *Byull. Izobr.*, **37** (1988).
2. O. Ya. Neiland, Ya. Ya. Katsens, and Ya. N. Kreitsberga, *Zh. Org. Khim.*, **25**, 658 (1989).
3. N. Svenstrup and J. Becher, *Synthesis*, 215 (1995).
4. J. C. Lodmell, W. C. Anderson, M. F. Hurley, and J. Q. Chambers, *Anal. Chim. Acta*, **129**, 49 (1981).
5. V. Yu. Khodorkovskii, G. G. Pukitis, A. Ya. Puplovskii, A. S. Edzhinya, and O. Ya. Neiland, *Khim. Geterotsikl. Soedin.*, 131 (1990).
6. H. Li, D. Zhang, Yu Xu, W. Xu, G. Yu, X. Li, and D. Zhu, *Synth. Met.*, **123**, 385 (2001).
7. H. Li, D. Zhang, B. Zhang, Y. Yao, W. Xu, D. Zhu, and Zh. Wang, *J. Mater. Chem.*, **10**, 2063 (2000).
8. R. Medne, J. Kacens,I. L. Kraupsha, and O. Neilands, *Khim. Geterotsikl. Soedin.*, 1317 (1991).
9. A. I. Kotov, C. Faulmann, P. Cassoux, and E. V. Yagubskii, *J. Org. Chem.*, **59**, 2626 (1994).
10. G. G. Abashev, V. S. Russkikh, and E. V. Shklyaeva, *Zh. Org. Khim.*, **31**, 1705 (1995).
11. G. G. Abashev, E. V. Shklyaeva, and A. G. Tenishev, in: *Prospects for Natural Sciences in the Western Urals, Collections of Papers of International Conference* [in Russian], Perm (2001), Vol. 1, p. 8.
12. G. G. Abashev, E. V. Shklyaeva, V. S. Russkikh, and S. Krol, *Mendeleev Commun.*, 157 (1997).
13. M. R. Bryce, A. K. Lay, A. S. Batsanov, and J. A. K. Howard, *Tetrahedron Lett.*, **40**, 801 (1999).
14. G. G. Abashev, E. V. Shklyaeva, K. Yu. Lebedev, A. N. Nedugov, S. N. Popov, and I. V. Osorgina, in: *International Conference on the Chemistry of Heterocyclic Compounds, Dedicated to the Ninetieth Birthday of Prof. Aleksei Nikolaevich Kost* [in Russian], Moscow State University, Moscow (2005), p. 99.
15. R. V. Pisarev, V. V. Kalashnikov, A. I. Kotov, and E. G. Yagubskii, *Izv. Akad. Nauk. Ser. Khim.*, 775 (1996).
16. I. Hellberg, K. Balodis, M. Moge, P. Korall, and I.-U. Von-Schultz, *J. Mater. Chem.*, **7**, 31 (1997).
17. Ya. Yoshiro, T. Masaaki, and I. Kenichi, *Mol. Cryst. Liq. Cryst.*, **380**, 203 (2002).
18. H. Nishikawa, *Database of Organic Conductors, http://www.ossc.kuchem.kyoto-u.ac.jp/database/1 synt/TTFderivl.pdf.*

19. P. Leriche, A. Gorgues, M. Jubault, J. Becher, S. Uriel, J. Orduna, and J. Garin, *Synth. Met.*, **70**, 1143 (1995).
20. Ph. Leriche, A. Gorgues, M. Jubault, J. Becher, J. Orduna, and J. Garin, *Tetrahedron Lett.*, **36**, 1275 (1995).
21. R. Berridge, I. M. Serebryakov, P. J. Skabara, E. Orti, R. Viruels, R. Pou-Amerigo, S. J. Coles, and M. B. Hursthouse, *J. Mater. Chem.*, **14**, 2822 (2004).
22. A. Gorgues, P. Hudhomme, and M. Salle, *Chem. Rev.*, **104**, 5551 (2004).
23. J. P. Parakka, A. M. Kini, and J. M. Williams, *Tetrahedron Lett.*, **37**, 8085 (1996).
24. J. P. Parakka, A. M. Kini, and J. M. Williams, *Synth. Met.*, **86**, 805 (1997).
25. M. R. Bryce, A. K. Lay, A. Chesney, A. S. Batsanov, J. A. K. Howard, U. Buser, F. Gerson, and P. Merstetter, *J. Chem. Soc. Perkin Trans. 2*, 755 (1999).
26. R. A. Bissell, N. Boden, R. I. Bushby, C. W. G. Fishwick, E. Holland, B. Movaghar, and G. Ungar, *Chem. Commun.*, **113** (1998).
27. V. Y. Khodorkovsky, J. Y. Becker, and J. Bernstein, *Synth. Met.*, **56**, 1931 (1993).
28. V. Y. Khodorkovsky, J. Y. Becker, and J. Bernstein, *Synthesis*, 1071 (1992).
29. D.-Y. Noh, H.-J. Lee, J. Hong, and A. E. Underhill, *Tetrahedron Lett.*, **37**, 7603 (1996).
30. H.-J. Lee and D.-Y. Noh, *Bull. Korean Chem. Soc.*, **19**, 340 (1998).
31. P. J. Skabara, I. M. Serebryakov, D. M. Roberts, I. F. Perepichka, S. J. Coles, and M. B. Hurthouse, *J. Org. Chem.*, **64**, 6418 (1999).
32. R. Andreu, J. Garin, J. Orduna, and J. M. Royo, *Tetrahedron Lett.*, **41**, 5207 (2000).
33. R. L. Meline and R. L. Elsenbaumer, *Synthesis*, 617 (1997).
34. J. D. Wallis and J.-P. Griffiths, *J. Mater. Chem.*, **15**, 347 (2005).
35. J.-P. Griffiths, R. J. Browan, A. Arola Arnal, G. Appleby, and J. D. Wallis, *J. Phys. IV Fr.*, **114**, 487 (2004).
36. A. M. Kini, J. P. Parakka, Urs Geiser, H.-H. Wang, F. Rivas, E. DiNino, S. Thomas, J. D. Dudek, and J. M. Williams, *J. Mater. Chem.*, **9**, 883 (1999).
37. Sh. Kimura, Sh. Hanazato, H. Kurai, T. Mori, Y. Misaki, and K. Tanaka, *Tetrahedron Lett.*, **42**, 5729 (2001).
38. J.-P. Griffiths, H. Nie, R. J. Brown, P. Day, and J. D. Wallis, *Org. Biomol. Chem.*, **3**, 2155 (2005).
39. Wei Xu, D. Zhang, H. Li, and D. Zhu, *J. Mater. Chem.*, **9**, 1245 (1999).
40. D. Zhang, W. Xu, Ch. Jia, H. Li, and D. Zhu, *ARKIVOC, ii*, 165 (2003).
41. H.-J. Lee and D.-Y. Noh, *J. Mater. Chem.*, **10**, 2167 (2000).
42. G. G. Abashev, E. V. Shklyaeva, V. S. Russkikh, and S. Krol, *Mendeleev Commun.*, 155 (1997).