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PYRIMIDOTETRATHIAFULVALENES.
2. TRIMETHYLSILYLATION OF 5,7-DIOXO(4H, 6H)-1,3-DITHIOLO-[4,5-d]PYRIMIDINE-2-SELONE AND THE USE OF THE SILYLATED PRODUCT FOR THE SYNTHESIS OF 2,4-DIOXOPYRIMIDOTETRATHIAFULVALENES

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The trimethylsilylation of 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-selone with bis(trimethylsilyl) acetamide enables pyrimido-tetrathiafulvalene derivatives to be prepared in benzene solution and increases the yield of the target compounds compared with the reaction of the unsilylated selone in DMF solution. The intermediate 2,4-bis(trimethyl-silyloxy)pyrimidotetrathiafulvalenes were sensitive to hydrolysis. The previously undescribed [2,4-dioxo(1H,3H)pyrimido]di-(methylthio)tetrathiafulvalene has been obtained. The redox properties of the compounds obtained have been investigated by cyclic current–potential measurements.

In a previous study [1] we showed that tetrathiafulvalenes of a new type, viz., 2,4-dioxopyrimido-tetrathiafulvalenes, are obtained in extremely moderate yield (20-30%) from 5,7-dioxo(4H, 6H)-1,3-dithiolo[4,5-d]pyrimidine-2-selone (I) and substituted 1,3-dithiole-2-selones in the presence of triphenylphosphine in DMF solution. The aim of the present study was to improve the method of synthesis to achieve higher yields. We were influenced by the idea that the reaction would proceed better in a nonpolar solvent, so the initial selone needs to be present in a more soluble state. This is presumably possible by silylation of the uracil portion of selone (I).

Hexamethyldisilazane or a mixture of hexamethyl-disilazane and chlorotrimethylsilane is usually used for the trimethylsilylation of uracil derivatives [2, 3]. On boiling with hexamethyldisilazane the selone (I) dissolves, and on cooling the solution red needles of the supposed 5,7-bis-(trimethylsilyloxy)-1,3-dithiolo[4,5-d]pyrimidine-2-selone (II) are isolated. However partial decomposition occurs under these conditions (150°C) with the elimination of selenium. Consequently it is more favorable to use bis(trimethylsilyl)acetamide to obtain (II) since the former is a more reactive silylating agent [4] and reacts with (I) in benzene or toluene at 60-70°C and in acetonitrile even at room temperature. The selone (I), which is insoluble in benzene, forms an orange–red solution on heating in the presence of bis(trimethylsilyl)acetamide, from which it is possible to isolate crystalline selone (II). The substance is sensitive to atmospheric moisture and is hydrolyzed in the air in a few minutes, consequently the absorption of the carbonyl groups of selone (I) are always observed in the IR spectrum of (II).

We used the benzene solution of selone (II) without isolating it in the crystalline state for the synthesis of 2,4-dioxopyrimidotetrathiafulvalenes assuming that the small excess of silylating agent will not interfere with the dimerization of the selones.

The dimerization of the silylated selone (II) occurs in benzene solution in the presence of triphenylphosphine with the formation of bis[2,4-di(trimethylsilyloxy)-pyrimido]tetrathiafulvalene (III) which is readily hydrolyzed on adding alcohol. The insoluble bis[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene (IV) is precipitated in 56% yield. Purification was carried out conveniently through its tetrabutylammonium salt. The yield calculated on selone (I) was about 40%, which is double that by the variant proposed previously in [1].

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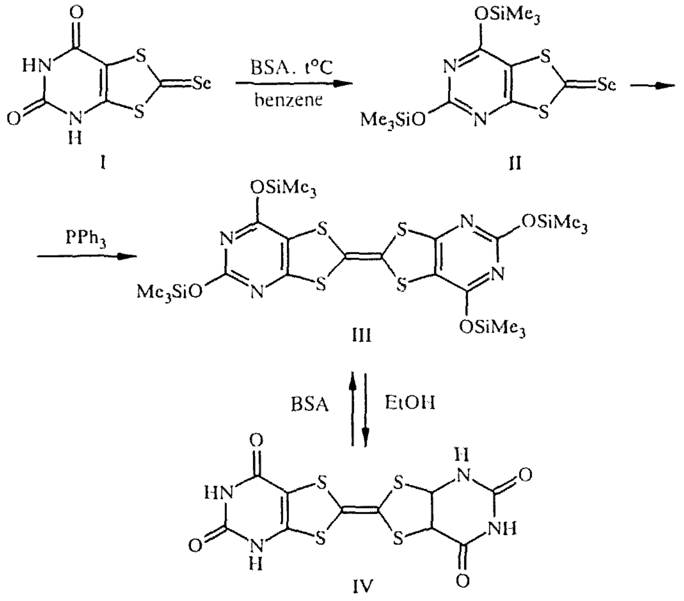
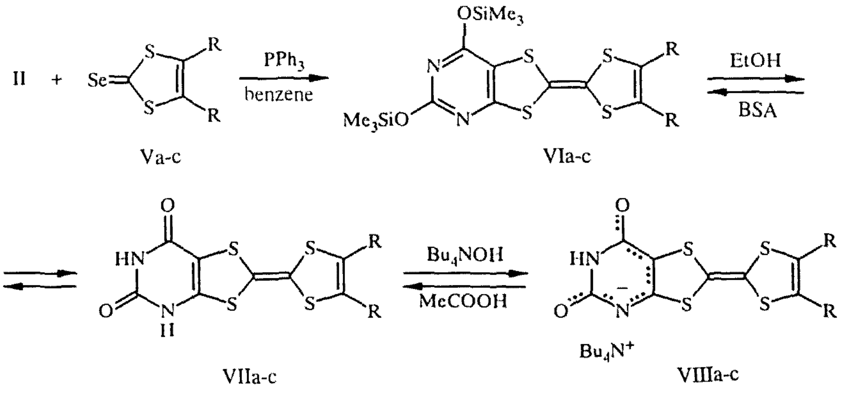
TABLE 1. Results of the Cyclic Current–Potential Measurements of 2,4-Dioxo-(1H,3H)pyrimidotetrathiafulvalene Derivatives in Acetonitrile Solution

Compound	First cycle		Second cycle	
	E_{ox}^1/E_{red}	E_{ox}^2/E_{red}	E_{ox}^1/E_{red}	E_{ox}^2/E_{red}
VIIb	0,7 / 0,63	0,98 / 0,83	0,7 / 0,63	0,98 / 0,83
1-Methyl [1]	0,7 / 0,61	0,99 / 0,87	0,7 / 0,61	0,99 / 0,87
VIa	0,58; 0,77 / 0,55	0,94 / 0,84	0,74 / 0,55	0,94 / 0,84
With anhydrous base electrolyte $Bu_4N^+ClO_4^-$	0,6; 0,8 / 0,52	0,98 / 0,82	0,8 / 0,52	0,98 / 0,82
III	0,8 / 0,55	1,05 / 0,81	0,77 / 0,55	1,03-/ 0,81
With anhydrous base electrolyte $Bu_4N^+ClO_4^-$	0,6; 0,75 / 0,57	0,98 / 0,85	0,75 / 0,57	0,98 / 0,85



The advantage of the silylation method is seen clearly in this example.

The silylated selone (II) was also reacted with triply substituted 1,3-dithiole-2-selones with the aim of obtaining unsymmetrical tetrathiafulvalenes. The reaction was carried out particularly successfully with 4,5-dimethyl-1,3-dithiole-2-elone (Va).



V—VIII a R = Me, b R = SMe, c RR = SCH_2CH_2S

The yield of unpurified [2,4-dioxo(1H,3H)pyrimido]-dimethyltetrathiafulvalene (VIIa) was 65-70%. After purification through the tetrabutylammonium salt the yield was 50% (yield was 30% by the method of [1]).

Reaction with 4,5-di(methylthio)-1,3-dithiole-2-selone (Vb) gave a new compound, viz. [2,4-dioxo(1H,3H)pyrimido]-di(methylthio)tetrathiafulvalene (VIIb), the yield of which was 24% calculated on the selone (I). It is necessary to note that compound (VIIb) was not obtained in pure form on carrying out the reaction by the method in [1]. Reaction with ethylenedithio-1,3-dithiole-2-selone in benzene solution gave [2,4-dioxo(1H,3H)pyrimido]ethylenedithio-tetrathiafulvalene (VIIc) which was isolated from solution in about 30% yield. After purification through the tetrabutylammonium salt the yield of compound (VII) was about 20%. In this case it was not possible to increase the yield compared with that by the former method [1].

The trimethylsilylated tetrathiafulvalenes (III) and (VI) are formed as intermediates in the reactions described above. It is possible to obtain them in a pure state using the trimethylsilylation of the tetrathiafulvalenes (IV) and (VII) with bis-(trimethylsilyl)acetamide or hexamethyldisilazane. Compounds (III) and (VIa) formed orange needle crystals, they were more stable than the silylated selone (II), and may be recrystallized from hexane. They were characterized by their IR spectra in which the carbonyl group absorption of the uracil portion was not observed. On contact with atmospheric moisture, gradual hydrolysis still took place and after 15-20 h in the air the silylated tetrathiafulvalenes were converted completely to the initial tetrathiafulvalenes. In solution the hydrolysis goes rapidly if the solvent contains traces of moisture. It was not possible to obtain clearly interpretable cyclic current–potential measurements of the silylated tetrathiafulvalenes, probably as a result of this.

Cyclic current–potential measurements were taken in acetonitrile solution to characterize the redox properties of the new tetrathiafulvalenes (Table 1). The new tetrathiafulvalene (VIIb) is characterized by the same oxidation potential as (VIIa), i.e., the methylthio groups exert the same effect as the methyl groups. It is difficult to interpret the results obtained for the trimethylsilylated tetrathiafulvalenes. The cyclic current–potential measurements changed on going from the first cycle to the second and depended on the presence of moisture in the electrolyte. This may be explained by the partial or complete hydrolysis of the compound in solution or on the electrode. It may be concluded that the completely silylated tetrathiafulvalenes are oxidized more readily than the tetrathiafulvalenes themselves (~0.6 V), but the rapid hydrolysis and fission of the trimethylsilyl groups increase the oxidation potential. Since the hydrolysis is stepwise then a monosilyl derivative might be expected to appear at the electrode. Consequently it is necessary to use a special procedure, excluding completely the possibility of hydrolysis, for the precise characterization of the redox properties of the silylated tetrathiafulvalenes.

Trimethylsilylation of 2,4-dioxopyrimidotetrathiafulvalenes may serve as a good method of converting these poorly soluble compounds into a form soluble even in low-polarity solvents. The facile hydrolysis of the silyl group makes it possible to prepare coatings and composites containing 2,4-dioxopyrimidotetrathiafulvalenes.

EXPERIMENTAL

The IR spectra were taken on a Specord M-80 instrument in Nujol mulls. The PMR spectra were obtained on a Bruker WH-90 instrument with TMS as internal standard. The cyclic current–potential measurements were taken on a PI-60-1 potentiostat in the three-electrode mode. The operating electrode was glass–graphite (0.27 cm^2), the reference electrode Ag/AgCl, and the rate of potential scanning was 200 mV/sec.

Bis[2,4-di(trimethylsilyloxy)pyrimido]tetrathiafulvalene (III) $C_{18}H_{36}N_4O_4S_4Si_4$. Bis(trimethylsilyl)-acetamide (0.45 ml, 2 mmole) and heptane (3 ml) were added to tetrathiafulvalene (IV) (0.16 g, 0.43 mmole) and the mixture boiled for 5 min. After cooling the solution, the precipitated solid was filtered off and washed with hexane. Compound (III) was obtained as orange needles (0.21 g, 80%). IR spectrum, ν, cm^{-1}: 850, 956, 1004, 1048, 1144, 1246, 1308, 1524, 1540.

Bis[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene (IV) $C_{10}H_4N_4O_4S_4$. The selone (I) (1.06 g, 4 mmole) was suspended in benzene (5 ml), bis(trimethylsilyl)acetamide (1.85 ml: 8 mmole) was added, and the mixture boiled until selone (I) had dissolved (1-2 min). The solution was cooled to 20°C and a solution of triphenylphosphine (2.0 g, 8 mmole) in benzene (10 ml) added. The mixture was heated to 60°C, left at 20°C for 12 h, and filtered. Ethanol (20 ml) was added to the filtrate. The precipitated solid was filtered off (0.93 g), washed with benzene, and then suspended in ethanol (10 ml). A 10% aqueous solution (10 ml: 4 mmole) of tetrabutylammonium hydroxide was added, the mixture heated to 60°C, and filtered. The filtrate was diluted with water. The tetrabutylammonium salt of tetrathiafulvalene (IV) obtained (0.9 g, 54%) was crystallized from acetonitrile, dissolved in ethanol, and acetic acid (2 ml) added. The precipitated solid was filtered off, giving compound (IV) (0.3 g, 41%) [1].

[2,4-Bis(trimethylsilyloxy)pyrimido]dimethyltetrathiafulvalene (VIa) $C_{16}H_{24}N_2O_2S_4Si_2$. Compound (VIIa) (0.32 g) was boiled in hexamethyldisilizane for 40 min and the solution filtered hot. After cooling, the solid obtained was crystalized from hexane. Compound (VIa) (0.4 g, 87%) was obtained as fine orange needles IR spectrum, ν, cm^{-1}: 850, 958, 1004, 1050, 1146, 1244, 1310, 1540.

[2,4-Dioxo(1H,3H)pyrimido]dimethyltetrathiafulvalene (VIIa) $C_{10}H_8N_2O_2S_4$. Bis(trimethylsilyl)acetamide (2.7 ml, 1.2 mmole) was added, to a suspension of selone (I) (2.65 g, 1 mmole) in benzene 15 ml, the mixture was heated at 60°C for 5 min, and then cooled to 20°C. A solution of compound (Va) (3.5 g, 2 mmole) in benzene (30 ml) was added followed by a solution of triphenylphosphine (15.7 g, 6 mmole) in benzene (35 ml). The mixture was left at 20°C for 24 h, filtered, and ethanol (20 ml) added to the filtrate. The precipitated solid was filtered off and washed with benzene. The residue (4.0 g) was suspended in DMF (20 ml), a 10% aqueous solution (26 ml) of tetrabutylammonium hydroxide was added, the mixture heated to 60°C, and filtered. The filtrate was diluted with water. The tetrabutylammonium salt (VIIIa) (3.5 g, 63%) which was obtained was crystallized from acetonitrile (3.3 g obtained), dissolved in ethanol (40 ml), and acetic acid (5 ml) added. The solution was filtered off. Compound (VIIa) (1.6 g, 50%) was obtained [1].

[2,4-Dioxo(1H,3H)pyrimido]di(methylthio-tetrathiafulvalene (VIIb) $C_{10}H_8N_2O_2S_6$. The selone (I) (0.35 g, 1.3 mmole) was suspended in benzene (5 ml), bis(trimethylsilyl)-acetamide (0.67 ml, 3 mmole) was added, and the mixture boiled until selone (I) had dissolved (~2 min). The solution was cooled to 20°C, a solution of selone (Vb) (0.63 g, 2.3 mmole) in benzene (5 ml) was added followed by a solution of triphenylphosphine (1.9 g, 7.2 mmole) in benzene (5 ml). The mixture was heated to 50°C, left at 20°C for 24 h, filtered, and ethanol (5 ml) added to the filtrate. The precipitated solid was filtered off and washed with benzene. The solid was suspended in acetonitrile (5 ml), a 10% aqueous solution (1.3 ml) of tetrabutylammonium hydroxide was added, the mixture heated to 60°C, and filtered. The filtrate was diluted with water and the solid crystallized from acetonitrile. Compound (VIIIb) (0.2 g, 25%) was obtained as orange crystals of mp 141-142°C. IR spectrum, ν, cm^{-1}: 1618, 2875, 2960, 3100, 3400. PMR spectrum, δ ($CDCl_3$): 1.00 (12H, t, $-CCH_3$), 1.3-1.8 (16H, m, $C-CH_2-C$), 2.41 (6H, s, $-SCH_3$), 3.20 (8H, m, NCH_2-), 8.4 (1H, s, $-NH$). Compound (VIIIb) was dissolved in acetonitrile and acetic acid (1 ml) added. Compound (VIIb) [0.12 g, 24% calculated on (I)] was obtained as yellow–orange crystals of mp >260°C. IR spectrum, ν, cm^{-1}: 1576, 1644, 1720, 2800-3120. PMR spectrum, δ ($DMSO-D_6$): 2.44 (6H, s, $-CH_3$), 11.42 (1H, s, $-N^1H$), 11.90 (1H, s, $-N^3H$). Redox measurements, V: $E_{ox}{}^1 = 0.7$, $E_{ox}{}^2 = 0.98$, $E_{red}{}^1 = 0.83$, $E_{red}{}^2 = 0.63$.

[2,4-Dioxo(1H,3H)pyrimido]ethylenedithiotetrathiafulvalene (VIIc) $C_{10}H_6N_2O_2S_6$. Selone (I) (1.72 g, 6.5 mmole) was suspended in benzene (30 ml), bis(trimethylsilyl)-acetamide (1.46 ml, 6.5 mmole) was added, and the mixture boiled until selone (I) had dissolved (~5 min). The ethylenedithioselone (Vc) (3.1 g, 11.4 mmole) in benzene (150 ml) was added to the cooled solution, followed by a solution of triphenylphosphine (9.4 g, 36 mmole) in benzene (40 ml). The mixture was stirred for 1 h at 20°C, then heated to 50°C, and left at 20°C for 12 h. The mixture was filtered, and ethanol (50 ml) and acetic acid (10 ml) added to the filtrate. The precipitated solid was filtered off and washed with ethanol. Tetrathiafulvalene (VIIc) (0.7 g, 28.5%) was obtained as orange crystals. For purification the compound was suspended in ethanol (10 ml), a 10% aqueous solution (5 ml) of tetrabutylammonium hydroxide was added, and the mixture filtered. Acetic acid (2 ml) was added to the filtrate, the precipitated solid was filtered off, and washed with ethanol. Tetrathiafulvalene (VIIc) (0.4 g, 16%) was obtained [1].

REFERENCES

1. O. Ya. Neiland, V. Zh. Tilika, and A. S. Édzhinya, Khim. Geterotsikl. Soedin., No. 8, 1122 (1992).
2. K. Ochi, K. Miyamoto, Y. Miura, H. Mitsui, and I. Matsunaga, Chem. Pharm. Bull., **33,** No. 4, 1703 (1985).
3. G. A. Tolstikov, F. V. Sharipova, L. A. Baltina, and L. V. Spirikhin, Khim. Geterotsikl. Soedin., No. 9, 1235 (1990).
4. J. F. Klebe, H. Finkbeiner, and D. H. White, J. Am. Chem. Soc., **88,** 3390 (1966).