SYNTHESIS OF DERIVATIVES OF NEW HETEROCYCLIC SYSTEM 5,7-DIOXO(4*H*,6*H*)-1,3-DITHIOLO[4,5-*d*]PYRIMIDINE ON THE BASIS OF BARBITURIC ACID

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The 5-phenyliodonium betaine of barbituric acid reacts with sodium diethyldithiocarbamate to form 5-(diethylaminothiocarbonylthio)barbituric acid, which is cyclized in concentrated H_2SO_4 solution to form the cation of 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine, isolated in the form of the perchlorate and the chloride. These salts are split by sodium sulfide or selenide, forming 5-[diethylaminothio(seleno)carbonylthio]-4-thiobarbituric acids, which are cyclized by the action of concentrated HCl in an organic solvent to form 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidinethione(selenone)-2. The thione and the selenone, as NH acids, form salts; alkylation of the tetrabutylammonium salt affords $N_{(4)}$-alkyl and N,N'-dialkyl derivatives. The compounds that were obtained have been characterized by IR and PMR spectra.

S-(2-Oxoalkyl)-*N*,*N*-dialkyldithiocarbamates serve as the starting compounds for the synthesis of 2-dialkylamino-1,3-dithiolium salts [1, 2]. These starting materials can be synthesized readily from α-haloketones and salts of *N*,*N*-dialkyldithiocarbamic acids. Halogen-substituted β-diketones are less suitable for this purpose, because of possible side reactions (oxidation of the dithiocarbamate ion, and splitting of the ion as a consequence of the high acidity of the cyclic 2-halo-1,3-diketones). One of the present authors had shown previously [3] that phenyliodonium betaines of the cyclic β-diketone dimedone react readily, and in the desired direction, with dithiocarbamates. We set ourselves the task of obtaining analogous derivatives of barbituric acid (I) in order to pass on to nitrogen-containing derivatives of the 1,3-dithiol, specifically, to a condensed heterocyclic system containing uracil and 1,3-dithiol rings: 5,7-dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidine.

The 5-phenyliodonium betaine of barbituric acid (II) was described previously by one of the present authors [4]. We have now been successful in improving the method of synthesizing the betaine II, using DMF as the solvent, with a consequent shortening of the reaction time. The low solubility of the betaine II in organic solvents is a problem in carrying out the reaction of the betaine with sodium diethyldithiocarbamate. We have been able to perform the desired reaction by prolonged mixing (6 days, room temperature) of a suspension of the betaine II in a solution of the dithiocarbamate in dimethylformamide. Treatment of the mixture with ultrasound at the start of the experiment has a favorable effect on the reaction. As a result, the sodium salt of 5-diethylaminothiocarbonylthiobarbituric acid (III) is obtained, and unreacted betaine II remains (15—20%). We did not obtain the sodium salt in the pure form, but rather converted it to 5-(diethylaminothiocarbonylthio)barbituric acid (IV). The yield of compound IV is 45—50% on the betaine charged, or 60-70% on the betaine reacted. Compound IV is obtained in the form of yellowish crystals that dissolve in water when heated, giving a strong acidic reaction (pH ~ 2). The substance is evidently very acidic, similar to halobarbituric acids [5]. Its IR spectrum (Table 1) indicates that the substance exists in the crystalline state in the enol form (intense absorption at 1585 cm^{-1} [5]. In the PMR spectrum, two nonequivalent ethyl groups are manifested; this indicates retarded rotation around the $S_2C—NR_2$ bond.

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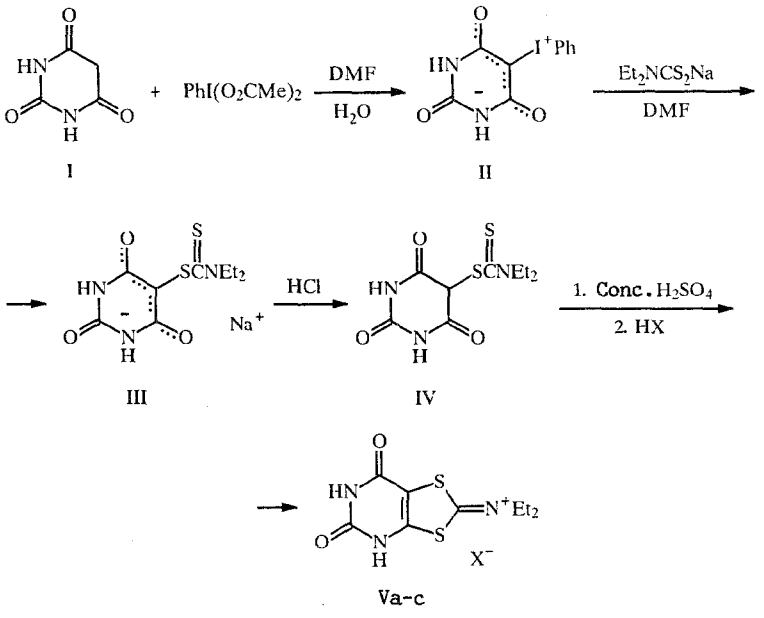
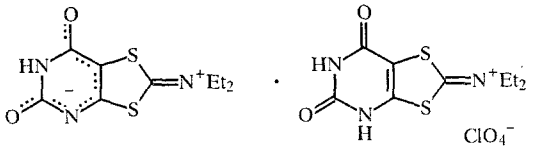


a X = HSO_4; b X = ClO_4; c X = Cl

In concentrated H_2SO_4 at 50—55°C, the compound IV undergoes cyclization to form the bisulfate of 5,7-dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidine (Va), which is difficult to obtain in analytically pure form. The perchlorate Vb and the chloride Vc crystallize readily from acidified aqueous solutions, the chloride being considerably more soluble in water than the perchlorate. In the IR spectrum, carbonyl absorption that is characteristic for the uracil system [6] is observed. In the PMR spectrum, signals are observed from equivalent ethyl groups and also from NH groups, the intensity of which is less than expected, in view of dissociation at the N—H bond.

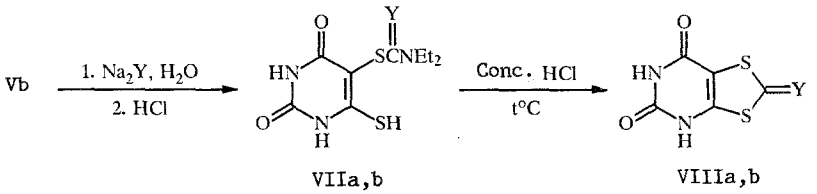
The salts of V are NH acids (pK 3.3 in aqueous solution [7]) that form an inner salt upon ionization. When the perchlorate Vb is crystallized from water (pH ~ 5—6), the "double salt" VI is obtained, crystallizing with one mole of the perchlorate Vb per mole of inner salt.



VI

When the perchlorate is crystallized in the interval pH 3—4, crystals can be obtained with chlorine contents intermediate between Vb and VI. Upon crystallization from strongly acidic solutions of perchloric acid, the crystals that are obtained have a higher content of chlorine and better solubilities in acetone and water in comparison with Vb. In basic solutions (pH > 9), the salts of V undergo rapid hydrolytic splitting.

When the salts of V are treated with aqueous solutions of sodium sulfide or selenide, the products of splitting are 5-substituted 4-thiobarbituric acids: 5-diethylaminothiocarbonylthio-4-thiobarbituric acid VIIa and 5-diethylaminoselenocarbonylthio-4-thiobarbituric acid VIIb [8]. Judging from the IR spectra, these substances exist in the crystalline state in the enthiol form, i.e., they are derivatives of 6-mercaptouracil.



VII, VIIIa Y = S; b Y = Se

TABLE 1. Characteristics of Compounds IV—X

Compound	Empirical formula	IR spectrum, cm^{-1}		PMR spectrum, δ, ppm			Yield, % (and method)
		1500...1800	3000...3600	CH_3	CH_2	NH	
IV	$C_9H_{13}N_3O_3S_2 \cdot H_2O$	1585, 1665, 1700	3140, 3430	1,16; 1,31 (6H, 2t)	3,80; 3,90 (4H,2q)	11,03 (2H, br.s)	46 (A), 51 (B)
Va	$C_9H_{13}N_3O_6S_3 \cdot H_2O$	1559, 1603, 1685, 1710(sh)	3470	1,35 (6H,t)	3,89 (4H, q)	9,67 (1H, br.s)	80 (A), 79 (B)
Vb	$C_9H_{12}ClN_3O_6S_2$	1556, 1608, 1662, 1705	3145	1,34 (6H,t)	3,9 (4H, q)	12,04 (1H, br.s)	83
Vc	$C_9H_{12}ClN_3O_2S_2$	1559, 1605, 1685, 1710	3075	1,35 (6H,t)	3,92 (4H, q)	11,9 (1H, br.s)	89
VI	$C_{18}H_{23}ClN_6O_8S_4$	1565, 1596, 1670, 1720	3135, 3485	1,29 (12H, t)	3,94 (8H, q)	11,2 (2H, br.s)	58
VIIa	$C_9H_{13}N_3O_2S_3$	1537, 1632, 1735	3175	1,20; 1,41 (6H, 2t)	3,86 (4H, m)	10,93; 11,08 (2H, 2 br.s)	86
VIIb	$C_9H_{13}N_3O_2S_2Se$	1544, 1632, 1742	3120, 3188, 3420	1,27; 1,42 (6H,2t)	3,38 (4H, m)	10,80; 11,0(2H, 2br.s)	70
VIIIa	$C_5H_2N_2O_2S_3$	1560, 1650 1668, 1695	3100			11,70 (br.s)	80
VIIIb	$C_5H_2N_2O_2S_2Se$	1535, 1640, 1700	3100			11,64 (br.s) 11,4; 12,1(2 (br.s)*	66 (A), 86 (B)
IXa	$C_5HN_2NaO_2S_3 \cdot H_2O$	1616, 1650, 1670	3065, 3570				80
IXb	$C_{21}H_{37}N_3O_2S_3$	1610, 1635	3070	1,05 (12H,t)	3,26 (8H, m, CH2– N) 1,64 (16H,m , C– CH_2– C)		82
IXc	$C_5HN_2NaO_2S_2Se \cdot H_2O$	1610, 1642	3080, 3580				80
IXd	$C_{21}H_{37}N_3O_2S_2Se$	1608, 1642	3050	1,00 (12H, t)	3,25 (8H, m, CH_2–N) 1,60 (16H, m, C–CH_2–C)		70
Xa	$C_6H_4N_2O_2S_2Se$	1552, 1642, 1688, 1716, 1730(sh)	3240	3,30 (3H,s)		11,20 (1H, br.s)	62
Xb	$C_7H_6N_2O_2S_2Se$	1570, 1656, 1708		3,36; 3,47 (s)*			62 (A), 58 (B)

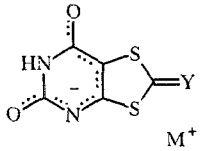
*Spectrum of compound VIIIb obtained in $CDCl_3$ + DMSO–d_6, compound Xb in $CDCl_3$, others in DMSO–d_6.

The PMR spectra show that for compounds VII, the same as for IV, the ethyl groups are nonequivalent.

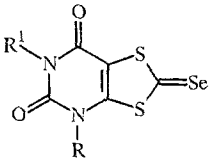
The compounds VII, upon heating in an organic solvent in the presence of concentrated HCl, are cyclized, splitting out diethylammonium chloride and forming new condensed heterocyclic systems: the yellow 5,7-dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidinethione-2 (VIIIa) and the red 5,7-dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidineselenone-2 (VIIIb). In the IR spectra of the latter, in the carbonyl absorption region, we observe maxima that are characteristic for the uracil system; for the thione VIIIa we observe absorption of the $S_2C{=}S$ grouping at 1065 cm^{-1}; and for the selenone VIIIb we observe absorption of the $S_2C{=}Se$ grouping at 960 cm^{-1}. Compound VIIb is cyclized far more readily than VIIa.

The selenone VIIIb is formed in the presence of either hydrochloric or acetic acid; it is also formed (although more slowly) when heated in ethanol.

The compounds VIII are dibasic NH acids; in aqueous solution, for the VIIIa, $pK_1 = 5.09$ and $pK_2 = 11.6$; for the VIIIb, $pK_1 = 4.84$ and $pK_2 = 12.19$ [7]. They form stable salts with either inorganic or organic cations. We have obtained the sodium and tetrabutylammonium salts (IX). The thione and selenone are stable in alkaline media (pH ~ 14).



IXa-d



Xa,b

1) IXa) Y = S, M = Na; IXb) Y = S, M = Bu_4N; IXc) Y = Se, M = Na; IXd) Y = Se, M = Bu_4N; Xa) R = Me, R^1 = H; Xb) R = R^1 = Me.

The sodium salts IXa,c are moderately soluble in water, poorly soluble in organic solvents; the tetrabutylammonium salts, in contrast, are poorly soluble in water but readily soluble in chloroform, ethanol, or acetonitrile.

The salts IXb,d can be used to obtain *N*-alkyl derivatives. This has been shown in the case of the selenone VIIIb. When an acetonitrile solution of IXd is treated with dimethyl sulfate, the methyl derivative Xa is obtained. We can assume that the alkylation takes place mainly at the $N_{(4)}$ atom, since ionization of the selenone is effected at this atom [7]. In the subsequent alkylation of Xa by dimethyl sulfate in the presence of 1.2 moles of tetrabutylammonium hydroxide, or the alkylation of IXd in the presence of 2.5 moles of tetrabutylammonium hydroxide, the dimethyl derivative Xb is formed. The selenones VIIIb and X have been used to obtain tetrathiafulvalenes of a new type; this will be covered in a subsequent communication.

EXPERIMENTAL

The IR spectra were taken in a Specord M-80 instrument, on suspensions in white mineral oil or hexachlorobutadiene; the PMR spectra were obtained in a Bruker WH-90 instrument, internal standard TMS, in DMSO-d_6 solution. Data on the IR and PMR spectra are presented in Table 1.

For all of the new compounds, we obtained elemental analyses for C, H, N, S, and Cl, which matched the calculated values.

5-Phenyliodonium Betaine of Barbituric Acid (II). A 45-g quantity (0.352 mole) of anhydrous barbituric acid was dissolved in 1 liter of 50% aqueous DMF at 40°C. Also, a 112-g quantity (0.348 mole) of phenyliodosyl diacetate was dissolved in 1 liter of 50% aqueous DMF. The two solutions were filtered and mixed together; a colorless, fine precipitate was formed immediately. The reaction mixture was chilled to 5-10°C; after a few hours, the precipitate was separated by vacuum filtration, washed on the filter with water and acetone, and air-dried, obtaining the betaine II in the form of a colorless, finely crystalline substance, yield 112 g (97%).

5-Diethylaminothiocarbonylthiobarbituric Acid, Monohydrate (IV·H_2O). A. To a suspension of 19.4 g (0.059 mole) of the betaine II in 290 ml of DMF, 13.3 g (0.059 mole) of sodium diethyldithiocarbamate trihydrate was added, and the mixture was stirred for 48 h at 20°C with overnight interruptions. The color of the reaction mixture, originally dark

yellow, gradually became paler. At the end of the reaction, the suspension was diluted with 1100 ml of diethyl ether; the colorless powder was separated by vacuum filtration, washed with ether, and air-dried. Next, the powder was suspended in 200 ml of water and stirred for 20 min at 40°C, after which the unreacted II was filtered off (~15% of the original amount taken). The filtrate was acidified with acetic acid, upon which the solution became turbid. After 1 h, activated carbon was mixed with the solution and then filtered out. Then 20 ml of concentrated HCl was added to the filtrate, and the mixture was then left 1 day in a refrigerator for crystallization. The yellowish product crystals were filtered off, washed with water, and air-dried. Obtained 7.9 g (46% on II charged) of the monohydrate of IV. For additional purification, a solution of 1 g of this monohydrate in 30—40 ml of water was refluxed with activated carbon and filtered, after which 4 ml of concentrated HCl was added to the hot filtrate. After the cooled mixture had been held in a refrigerator, 0.8 g of the monohydrate of IV was obtained in the form of shiny leaflets.

B. In 80 ml of DMF, 6.6 g (0.02 mole) of II and 6.75 g (0.03 mole) of sodium diethyldithiocarbamate trihydrate were suspended; the mixture was treated ultrasonically for 2 h at 10—15°C and then left overnight, after which the mixture was further treated as described above for method **A**. Yield of IV·H_2O 3.0 g.

Bisulfate of 5,7-Dioxo-2-diethylimmonio(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidine, Monohydrate (Va·H_2O). A. A mixture of 5.86 g (0.02 mole) of the monohydrate of IV and 25 ml of concentrated H_2SO_4 was held for 1 h at 50—55°C. The cooled reaction mixture was diluted with 250 ml of dry acetone and filtered; the filtrate was further diluted with 350 ml of dry acetone and left for 1 day in a refrigerator. Obtained the bisulfate Va in the form of a colorless, finely crystalline powder that darkened in storage. Yield 5.7 g.

B. The mixture of the monohydrate of IV and sulfuric acid that was indicated above in method **A** was diluted with 350 ml of ethyl acetate and 350 ml of diethyl ether. The colorless oil that separated out was stored in a refrigerator until it crystallized. Yield of yellowish bisulfate monohydrate Va·H_2O 5.9 g.

Perchlorate of 5,7-Dioxo-2-diethylimmonio(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidine (Vb). A solution of 28.4 g (0.08 mole) of the bisulfate Va in 300 ml of water was neutralized with sodium carbonate to pH 2—3 and then filtered; the filtrate was heated to 35—40°C, and a solution of 10.9 g (0.089 mole) of sodium perchlorate in a minimum quantity of water was added. The colorless crystals of the product Vb that precipitated during storage in a refrigerator were filtered off and washed with a small quantity of water. Yield 23.7 g.

Chloride of 5,7-Dioxo-2-diethylimmonio(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidine (Vc). To a solution of 1 g of the bisulfate Va·H_2O in 5 ml of water, activated carbon was added, and the mixture and stirred and filtered; then 1 ml of concentrated HCl and 10 ml of acetone were added to the filtrate, after which it was allowed to stand for 1 day in a refrigerator. The chloride Vc was recovered in the form of shiny leaflets, yield 0.7 g (90%). For additional purification, 1 g of the chloride was dissolved in 10 ml of water at 70—80°C and shaken with activated carbon, after which the solution was filtered, diluted with 1 ml of concentrated HCl and 20 ml of acetone, and held in a refrigerator. Yield 0.9 g.

Double Salt of Betaine of 5,7-Dioxo-2-diethylimmonio(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidine and Perchlorate of 5,7-Dioxo-2-diethylimmonio(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidine (VI). A 2-g quantity (5.6 mmoles) of the perchlorate Vb was dissolved in 20 ml of water at 60—70°C, 0.23 g (2.7 mmoles) of $NaHCO_3$ was added, and the mixture was heated to 90—95°C. The yellowish solution that was obtained (pH 5—6) was filtered, and the filtrate was stored in a refrigerator. The product VI was recovered in the form of shiny yellowish flakes. Yield 1 g.

5-Diethylaminothiocarbonylthio-4-thiobarbituric Acid (VIIa). A 3.7-g quantity (0.01 mole) of the bisulfate Va was dissolved in 30 ml of water and poured into a solution of 4.8 g (0.02 mole) of sodium sulfide nonahydrate in 30 ml of water. After 30 min, activated carbon was added and then filtered out; the filtrate was acidified with 3 ml of concentrated HCl. A colorless, finely crystalline precipitate of VIIa separated out; this was filtered off, washed with water on the filter, and air-dried. Yield 2.5 g.

5-Diethylaminoselenocarbonylthio-4-thiobarbituric Acid (VIIb). A 7.8-g quantity (0.022 mole) of the bisulfate Va was dissolved in 50 ml of water; this solution was poured into an aqueous solution of sodium selenide prepared from 2 g (0.025 mole) of selenium and 2 g of sodium borohydride in 200 ml of water in an argon atmosphere. The mixture was stirred for 20 min, after which it was acidified with concentrated HCl to a strongly acidic reaction. A finely crystalline product VIIb precipitated; this was filtered off and washed with water. Yield 5.2 h. The acid VIIb turns red rapidly in storage.

5,7-Dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidinethione-2 (VIIIa). A 1.8-g quantity of compound VIIa was dissolved in 18 ml of DMF at 60°C. To this solution, 9 ml of concentrated HCl was added in portions over the course of 10 min at ~80°C, after which the mixture was filtered. The dark-yellow filtrate was held in a refrigerator for 1 day, recovering 1 g of a yellow product. The filtrate was diluted with water, obtaining another 0.1 g of the thione VIIIa. Total yield 1.1 g.

5,7-Dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidineselenone-2 (VIIIb). A. A 9.71-g quantity (0.033 mole) of the monohydrate of IV was stirred with 38 ml of concentrated H_2SO_4 for 1 h at 50—55°C. The transparent solution that was obtained was poured onto 200 g of ice, neutralized with potassium carbonate to pH ~ 2, and poured into a solution of sodium selenide, prepared from 3.15 g (0.04 mole) of selenium and 3.02 g (0.08 mole) of sodium borohydride in 150 ml of water. The mixture was stirred for 1 h at 20°C and then acidified with dilute hydrochloric acid to pH < 2. The colorless precipitate that resulted from this operation was filtered off, washed with water, and suspended in 50 ml of ethanol; then 10 ml of concentrated HCl was added to the suspension and stirred for 1 h at 60—70°C. The next day, the precipitate was filtered off, washed with water, and air-dried. Obtained 5.8 g of the product VIIIb in the form of a red powder, mp 250°C (decomp.).

B. An aqueous solution of 7.9 g (0.022 mole) of the perchlorate Vb was added to an ethanol solution of sodium hydroselenide, prepared from 1.97 g (0.025 mole) of selenium and 0.95 g (0.025 mole) of sodium borohydride in 150 ml of absolute ethanol. The mixture was stirred for 30 min and then acidified with hydrochloric acid to pH < 2; the resulting precipitate was suspended in 50 ml of acetic acid and stirred for 15 min at ~60°C. The next day, the mixture was diluted with 50 ml of water, and the precipitate was filtered off and washed with water. Obtained 5.0 g of the product VIIIb, mp 250°C (decomp.).

Sodium Salt of 5,7-Dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidinethione-2, Monohydrate (IXa·H_2O). A 0.4-g quantity (1.83 moles) of the thione VIIIa, finely ground, was suspended in 20 ml of methanol; the suspension was heated to boiling, and 20 ml of an aqueous solution of 0.04 g (2 mmoles) of NaOH was added gradually. The thione dissolved slowly, and the sodium salt IXa began to separate in the form of a finely crystalline yellow powder. Yield 0.37 g.

The salt can be recrystallized from 50% aqueous methanol (20 ml of solvent per 0.1 g of substance).

Tetrabutylammonium salt of 5,7-Dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidinethione-2 (IXb). A 0.35-g quantity (1.6 mmoles) of the thione VIIIa was dissolved with heating in 50 ml of water containing 0.04 g (2 mmoles) of NaOH, after which 0.8 g (2.5 mmoles) of tetrabutylammonium bromide was added to the solution. The salt IVb was recovered as a yellow precipitate. Yield 0.6 g, mp 209—212°C (from methanol).

Sodium Salt of 5,7-Dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidineselenone-2, Monohydrate (IXc·H_2O). To 0.4 g (0.0015 mole) of the selenone VIIIb in 20 ml of methanol, while boiling, 16 ml of a 0.1 N aqueous NaOH solution was added in portions, and the mixture was rapidly filtered. The filtrate was held for 1 day in a refrigerator; a finely crystalline orange-brown product was recovered, IXc·H_2O, yield 0.37 g.

Tetrabutylammonium Salt of 5,7-Dioxo(4*H*,6*H*)-1,3-dithiolo[4,5-*d*]pyrimidineselenone-2 (IXd). A 4.0-g quantity (0.015 mole) of VIIIb was suspended in 160 ml of ethanol, 47 ml (0.018 mole) of a 10% aqueous solution of tetrabutylammonium hydroxide was added, and the mixture was held for about 5 min at 35—40°C until the VIIIb was completely dissolved. The mixture was filtered, and the filtrate was diluted with 500 ml of water. This resulted in the precipitation of 5.3 g of IXd. After crystallization of this product from acetonitrile, obtained 4.5 g of IXd in the form of orange crystals, mp 211—212°C.

4-Methyl-5,7-dioxo-1,3-dithiolo[4,5-*d*]pyrimidineselenone-2 (Xa). A 0.5-g quantity (0.001 mole) of IXd was dissolved in 50 ml of acetonitrile, while heating to ~40°C; 0.2 ml (0.002 mole) of dimethyl sulfate was added; after 10 min the solution was filtered, and the filtrate was left at 20°C. The next day, the precipitate (0.22 g) was separated by filtration and then crystallized from acetonitrile. Obtained 0.17 g of Xa in the form of red crystals, mp > 230°C (decomp.).

4,6-Dimethyl-5,7-dioxo-1,3-dithiolo[4,5-*d*]pyrimidineselenone-2 (Xb). A. A 0.53-g quantity (0.002 mole) of VIIIb was suspended in 50 ml of acetonitrile. Then, 15 ml of a methanol solution containing 0.0054 mole of tetrabutylammonium hydroxide and 1.6 ml (0.016 mole) of dimethyl sulfate was added. The mixture was held for 15 min at 50°C, then left at 20°C for 24 h. The resulting precipitate (0.25 g) was separated by filtration and crystallized from ethanol. Obtained 0.36 g of Xb in the form of fine red needles, mp > 150°C (decomp.).

B. A 0.28-g quantity (0.001 mole) of Xa was suspended in 15 ml of acetonitrile. Then, 4 ml of methanol containing 0.0012 mole of tetrabutylammonium hydroxide and 0.12 ml (0.0016 mole) of dimethyl sulfate was added. The mixture was heated to ~60°C and then left for 12 h at 20°C. The precipitate was filtered off and crystallized from ethanol. Obtained 0.17 g of Xb in the form of red crystals, mp > 150°C (decomp.).

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