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# SYNTHESIS OF 4- AND 6-METHYL DERIVATIVES OF 5,7-DIOXO(4H,6H)-1,3-DITHIOLO[4,5-d]PYRIMIDINE BASED ON METHYLBARBITURIC ACIDS, SPECTROSCOPIC CHARACTERISTICS AND ACIDITY CONSTANTS

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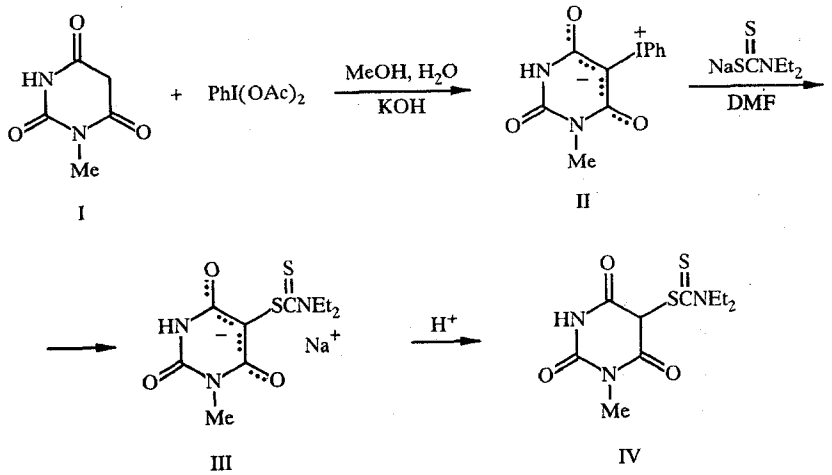
*We have obtained previously unknown 1-methyl- and 1,3-dimethyl-5-diethylaminothiocarbonylthiobarbituric acids by reaction of sodium diethyldithiocarbamate with 5-phenyliodonium betaines of 1-methyl- and 1,3-dimethylbarbituric acids. Cyclization of these compounds upon heating in conc. $H_2SO_4$ gives methyl-substituted 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium hydrosulfates; the derivative of 1-methylbarbituric acid forms a mixture of 4-methyl- and 6-methyl-substituted compounds (2:1). We isolated perchlorates of 4-methyl- and 4,6-dimethyl-substituted derivatives in pure form. By treatment of the immonium salt with sodium sulfide or selenide, we obtained 4-methyl- and 4,6-dimethyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-thiones and 4-methyl-, 6-methyl-, and 4,6-dimethyl-2-selenones. We characterized the isomeric 4- and 6-methyl-substituted selenones by electronic absorption spectra and ionization constants (7.65 and 4.0). The differences in the pK values and in the electronic absorption spectra makes it possible to distinguish the substitution site in N-mono-substituted derivatives of 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine.*

Recently it was shown [1] that 5-phenyliodonium betaine of barbituric acid upon reaction with sodium diethyldithiocarbamate forms 5-diethylaminothiocarbonylthiobarbituric acid, which serves as the starting reagent for obtaining derivatives of the novel heterocyclic system 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine.

In order to obtain and characterize 4- and 6-methyl- and 4,6-dimethyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidines, in this paper we have investigated the reactions of 5-phenyliodonium betaines of 1-methyl- and 1,3-dimethylbarbituric acids.

The betaine of 1-methyl-5-phenyliodoniobarbituric acid (II) is studied here for the first time.

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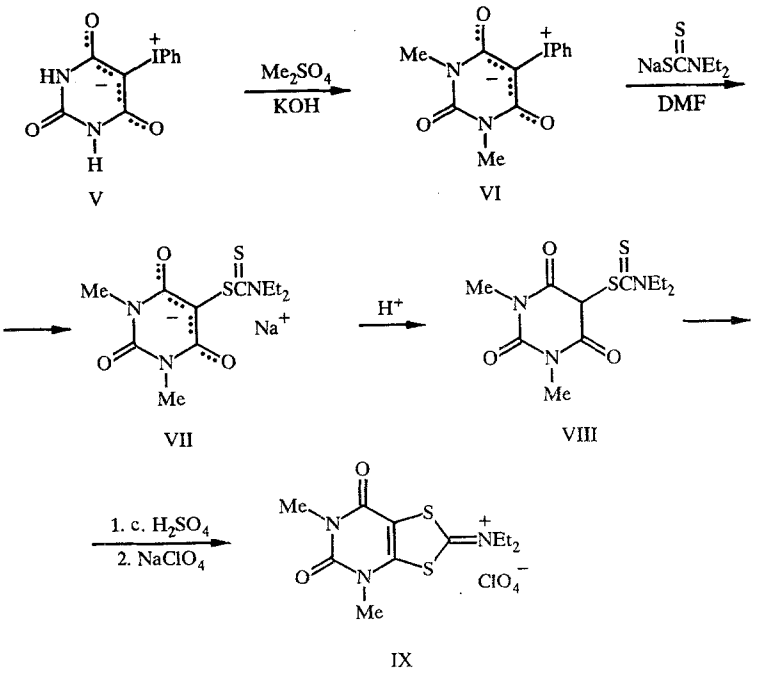
The betaine of 1,3-dimethyl-5-phenyliodoniobarbituric acid (VI) was obtained by alkylation of the betaine of 5-phenyliodoniobarbituric acid (V) by dimethylsulfate as in [3]. The betaine V was synthesized according to the technique in [1].




V VI VII VIII IX

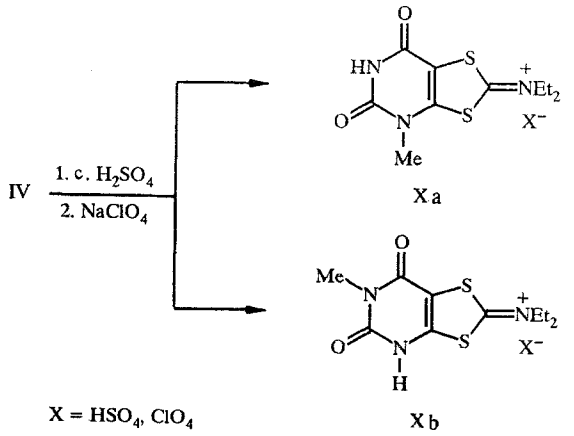
Upon reaction of the betaines II and VI with sodium diethyldithiocarbamate in DMF solution, we obtained 1-methyl- and 1,3-dimethyl-5-diethylaminothiocarbonyl thiobarbituric acid (IV, VIII). Betaines II and VI, in contrast to the unsubstituted betaine V [1], relatively rapidly dissolve in the reaction mixture; therefore a significantly shorter time is required for the reaction to go to completion (~72 h).

Upon dilution with ether, at first the sodium salts of III and VII were isolated from the reaction mixture, which however immediately were converted to the corresponding acids IV and VIII (by acidification of aqueous solutions of the indicated salts): colorless crystalline materials. The acid IV is isolated in the form of the monohydrate, which does not lose water after recrystallization from ethanol or 2-propanol. The yields of derivatives IV and VIII were ~80%.

Upon heating in conc. $H_2SO_4$, compound VIII undergoes cyclization with formation of the 4,6-dimethyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium cation, isolated in the form of the perchlorate IX, which is not very soluble in water.

In the case of the analogous reaction of cyclization of the monomethyl derivative IV, we should expect that the reaction proceeds in two directions with formation of a mixture of two isomeric salts: 4-methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium (Xa) and 6-methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium (Xb).

Cyclization was carried out upon heating acid IV in conc. $H_2SO_4$ at 70-80°C for 4 h. Upon completion of the reaction, the reaction was poured into a mixture of ethylacetate with diethyl ether. Upon treatment of the aqueous solution of the oily hydrosulfate of sodium perchlorate isolated in ~40% yield, we obtained a mixture supposedly of perchlorates Xa and Xb.




Xa

Xb

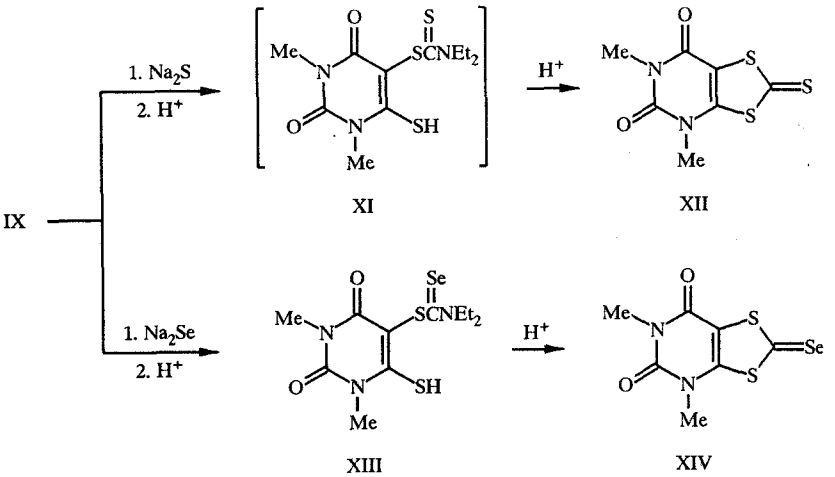
X = $HSO_4$, $ClO_4$

TABLE 1. Spectral Characteristics of Derivatives of Barbituric Acid and 5,7-Dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine

| Compound | IR spectrum, $cm^{-1}$ (characteristic adsorption maxima) | | PMR spectrum, δ, (DMSO-$D_6$ or $CDCl_3$) DMSO |
|---|---|---|---|
| II | 3172, 3044 | 1680, 1592 | 3,08 (3H, s, $CH_3$); 7,40 and 7,50 (3H, m, $C_6H_5$); 7,77 (2H,m, $C_6H_5$); 10,45 (1H, s, NH) |
| IV·$H_2O$ | 3364, 3108, 2976, 2810 | 1706, 1596, 1272, 1206 | 1,24and1,37 (6H, two t $CH_3$—C); 3,32 (3H, s $CH_3$—N); 3,70 и 3,90 (4H, two t, $CH_2$—N); 8,48 (1H, NH) |
| VIII | 2980, 2840 | 1680, 1674, 1088 | 1,23 and.37 (6H, two t, $CH_3$—C); 3,35 (6H, s, $CH_3$—N); 3,75 and 3,91 (4H, two q., $CH_2$—N) |
| IX | 2988, 2944, 2896 | 1720, 1652, 1544 | 1,51 (6H, two m, $CH_3$—C); 3,35 and 3,64 (6H, two q $CH_3$—C); 3,90 4,03 (4H, m $CH_2$—N) |
| Xa | 3160, 3108, 2988, 2824 | 1714, 1664, 1602, 1552, 1092, 864 | 1,50 (6H, t, $CH_3$—C); 3,55 (3H, s, $CH_3$—N); 3,90 (4H, m, $CH_2$—N); 12,5 (1H, br.s NH) |
| XII | 2920 | 1697, 1569, 1065 | 3,40 (3H, s $CH_3$—$N_{(6)}$); 3,48 (3H, s, $CH_3$—$N_{(4)}$) |
| XIV | 2975, 2898 | 1698, 1655, 1566, 958 | 3,36 (3H, s, $CH_3$—$N_{(6)}$); 3,47 (3H, s, $CH_3$—$N_{(4)}$) |
| XVI | 2964, 2856 | 1716, 1690, 1641, 1552, 950 | 3,31 (3H, s, $CH_3$—N); 11,20 (1H, s, NH) |
| XVIII | 3152, 3028 | 1692, 1562, 1080, 1052, 846 | 3,37 (3H, s, $CH_3$—N); 12,08 (1H, s, NH) |
| XIX | 3130, 2980, 2930 | 1734, 1718, 1632, 1578, 1582, 1515, 1016, 954 | 3,11 (3H, s, $CH_3$—N); 12,01 (1H, s, NH) ($CDCl_3$); 3,14 (DMSO-$D_6$) |

However, we found that the reaction product is not a mixture of perchlorates but rather is a pure substance, since in this PMR spectrum of even an unrecrystallized sample we observed only one signal from the N-methyl group at δ 3.57 ppm.

The perchlorates IX and X were used to obtain the corresponding dithiolthiones and dithiolselenones. Upon dissolving the perchlorate IX in an aqueous solution of sodium sulfide and acidifying the reaction mixture with HCl, we obtained the yellow crystalline 4,6-dimethyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-thione (XII) in ~60% yield.



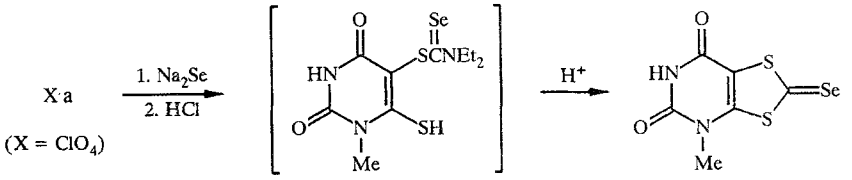

In order to obtain the corresponding 2-selenone (XIV), the perchlorate IX was treated with an aqueous solution of sodium selenide; after acidification of the reaction mixture by HCl, we isolated the red crystalline 4,6-dimethyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-selenone (XIV) in 65% yield. In contrast to the unsubstituted 2-thione and 2-selenone [1], in this case we could not isolate the intermediate products (the 5-substituted derivatives of 4-thiobarbituric acid IX and XIII), since their further cyclization occurs even in the reaction mixture. We isolated the thione XII here for the first time, but the selenone XIV obtained upon alkylation of the corresponding unsubstituted pyrimidine selenone by dimethylsulfate is described in [1].

TABLE 2. Electronic Absorption Spectra and Acidity Constants of Some Derivatives of 5,7-Dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine in Aqueous Solutions

| Compound | pH of solution | $\lambda_{max}$, nm and $\varepsilon$ in region 240-500 nm | | | $pK_a$ |
|---|---|---|---|---|---|
| XVI | 2,4 | 286 (5300) | 340 (2000) | 426 (20900) | 7,6 ± 0,1 |
| | 10,0 | 293 (4900) | | 436 (21700) | |
| XIX | 1,1 | 278 (6800) | | 422 (17600) | 4,0 ± 0,1 |
| | 9,4 | 306 (10400) | | 435 (17200) | |
| 5,7-Dioxo-(4H, 6H)-(1,3-dithiolo[4,5-d]pyrimidine-2-selenone [4] | 2,0 | 280 (5000) | | 425 (17300) | 4,84 ± 0,04 |
| | 8,0 | 308 (8100) | | 438 (16300) | |
| | 2,4 | 267 (7300) | 336 (3800) | 388 (18100) | 7,65 ± 0,05 |
| | 10,0 | 276 (6900) | 310...320 (2600) | 399 (18100) | |
| 5,7-Dioxo-(4H, 6H)-1,3-dithiolo[4,5-d]pyrimidine-2-thione [4] | 2,0 | 264 (7300) | 330 (3650) | 384 (18500) | 5,09 ± 0,04 |
| | 8,0 | 290 (12000) | 323 (4400) | 402 (14000) | |

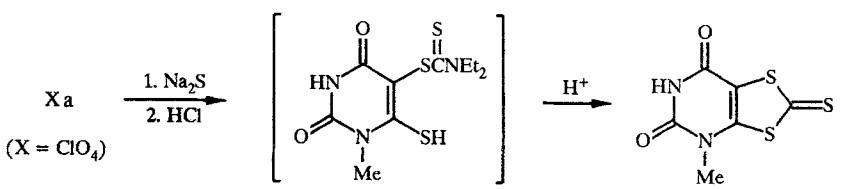
Analogous conversions were also accomplished with the perchlorate of X. Upon treatment of the perchlorate X with an aqueous solution of sodium selenide followed by acidification of the reaction mixture with HCl, we isolated a dark red crystalline selenone which, judging from the PMR spectrum, contains the intermediate cleavage product as an impurity: 5-diethylaminoselenocarbonylthio-3(1)-methyl-4-thiobarbituric acid (XV) (in the spectrum, we observe low-intensity signals from the N-ethyl groups). With the goal of obtaining this intermediate, the reaction mixture was first acidified with acetic acid; but even in this case the product contained a significant amount of selenone and compound XV could not be isolated in pure form.

After recrystallization of the unpurified selenone from ethanol with addition of conc. HCl, we isolated the pure selenone (XVI), whose PMR spectrum is identical to the spectrum of 4-methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-selenone (XVI) obtained by alkylation of the unsubstituted selenone [1]. From this we concluded that the isolated perchlorate is probably the Xa isomer.




XV XVI

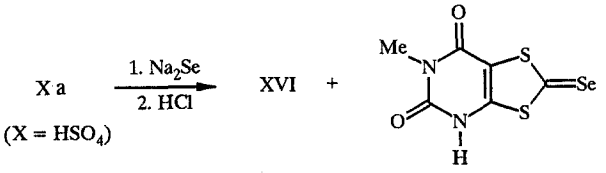
In order to obtain the 4-methyl-5-7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-thione (XVIII) (which is not described in the literature), the perchlorate Xa was treated with an aqueous solution of sodium sulfide. The solution obtained, after acidification with HCl, gives the thione XVIII with i (judging from the PMR spectrum) 3-methyl-5-diethylaminothiocarbonyl-thio-4-thiobarbituric acid (XVII) as an impurity. After recrystallization from ethanol with addition of HCl, we isolated the pure thione XVIII: a yellow crystalline material. Yield, 50%.




XVII XVIII

In the PMR spectrum of the thione XVIII, we also observe only one signal from the N-methyl group at 3.37 ppm, which confirms the presence of a single isomer.

Since it seemed unlikely that cyclization of 1-methyl-5-diethylaminothiocarbonylthiobarbituric acid unambiguously occurs in only one direction with formation of the salt Xa, we hypothesized that the second isomer Xb cannot be isolated due to its good solubility. Therefore in order to obtain the N-methyl-substituted selenones, we used another method, eliminating the stage of isolation of the perchlorate X in the crystalline state. For this, after the reaction of cyclization of compound IV, the solution was diluted with water, neutralized by sodium carbonate, and introduced into reaction with sodium selenide. After acidification of the reaction mixture with HCl, we obtained a dark red reaction product, which after repeated treatment with HCl (so the cyclization went to completion) was converted to a mixture of isomeric selenones XVI and XIX. Evidence for this came from the appearance in the PMR spectrum of two signals from the N-methyl groups (at 3.30 and 3.10 ppm); the ratio of the isomers is XVI:XIV ~ 2:1 (judging from the integrated intensity of the signals).




XIX

By crystallization of this mixture from ethanol or 50% DMF, we obtained the pure 4-methyl isomer XVI.

For isolation of the 6-methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-]pyrimidine-2-selenone (XIX), after separation of the isomer XVI the ethanol filtrate was evaporated to dryness, the dry residue (containing ~70% compound XIX) was separated on a chromatographic column (silica gel, chloroform–ethylacetate, 3:1), and recrystallized from 30% ethanol. Thus we obtained and characterized the isomer XIX: a reddish brown crystalline material which dissolves well in ethanol, acetone, and hot water.

The isomers XVI and XIX are rather well separated on a Silufol chromatographic plate ($R_f$ respectively 0.64 and 0.78; chloroform–ethylacetate, 3:1). We could obtain two isomeric N-methyl-substituted XVI and XIX, which we considered necessary to characterize by the electronic absorption spectra and the ionization constants. The electronic absorption spectra and the ionization constants were measured earlier for the N-unsubstituted derivatives of dithiolopyrimidine [4]. In the electronic absorption spectra of compounds XVI and XIX, we observe significant differences upon going from the unionized form to the anion (a change in pH from 1-2 to 9-10). For the 6-methyl-substituted XIX, we observe a bathochromic shift of the maximum in the region 270-350 nm with an increase in intensity, as is characteristic for ionization of uracil derivatives at the $N_{(1)}$–H bond [4]. In contrast, for the 4-methyl-substituted XVI in the indicated region, we observe only a slight shift in the maximum and decrease in the absorption intensity (Table 2). We see the same for the 4-methyl-substituted thione XVIII. Thus the electronic absorption spectra confirm the structure assigned to XVI and XIX and at the same time serve as a tool for determining the position of the methyl group.

The differences between isomers XVI and XIX are manifested even more clearly in the acidity constants measured spectrophotometrically in aqueous solutions [4]. We showed that the 6-methyl derivative XIX is an NH-acid which is 3.5 orders of magnitude stronger than the 4-methyl derivative XVI ($pK_a$ respectively 4.0 and 7.6). The 4-methyl-substituted thione XVIII is a very weak NH-acid (see Table 2). The N-unsubstituted selenone has a $pK_a$ = 4.84 [4]. We can say that the value of the NH-acidity is a sensitive tool for establishing the position of the substituent at the nitrogen atoms for 4- or 6-derivatives of dithiolopyrimidine.

## EXPERIMENTAL

The IR spectra of the compounds were taken on the Specord M-80; the $^1H$ NMR spectra were taken on the Bruker WH-90, internal standard TMS. The electronic absorption spectra were taken on the Specord UV-VIS. The ionization constants were measured using the technique described in [4].

The elemental analysis data for C, H, Cl, I, N, and S for the new compounds correspond to the calculated values.

**Betaine of 1-methyl-5-phenyliodoniobarbituric acid (II, $C_{11}H_9IN_2O_3$).** A solution of 3.22 g (10 millimoles) phenyliodosyldiacetate in 40 ml methanol was added with stirring and water-cooling to a solution of 1.42 g (10 millimoles)

1-methylbarbituric acid (I) in 20 ml 1 N aqueous solution of sodium hydroxide. The colorless betaine (II) began to precipitate immediately. The reaction mixture was allowed to stand at room temperature for 1 h, then the betaine II was filtered off, washed on the filter with dilute (1:1) methanol and then with a small amount of acetone. Product yield, 2.8 g (81%). $T_{mp}$ 253-257°C (decomp.). The betaine was obtained as practically pure. As needed, it can be recrystallized from 50% DMF, but this results in significant losses. $T_{mp}$ 255-260°C (decomp.).

**1-Methyl-5-diethylaminothiocarbonylthiobarbituric Acid (IV, $C_{10}H_{15}N_3O_3S_2 \cdot H_2O$).** 2.26 g (10 millimoles) sodium diethyldithiocarbamate trihydrate was added to a suspension of 3.44 g (10 millimoles) betaine II in 15 ml DMF. The reaction mixture was stirred at room temperature with a magnetic stirrer until dissolution (20-30 min). The solution formed was held at ~20°C for 48 h. The reaction mixture was diluted with 100 ml absolute ether; in this case, an oily residue of the sodium salt of 1-methyl-5-diethylaminothiocarbonylthiobarbituric acid (III) was isolated. The solvents were poured off, the residue was dissolved in 30 ml hot water, and the solution was acidified with HCl to pH 2. The colorless crystalline precipitate of the acid IV was gradually isolated. The product was filtered and washed with water on the filter. Yield, 2.2 g (71%). $T_{mp}$ 97-102°C (from ethanol).

**1,3-Dimethyl-5-diethylaminothiocarbonylthiobarbituric acid (VIII, $C_{11}H_{17}N_3O_3S_2$).** Obtained analogously to compound IV from 3.58 g (10 millimoles) betaine VI. Product yield, 2.42 g (80%). Compound VIII was a colorless crystalline material. $T_{mp}$ 125-130°C (from ethanol or 2-propanol).

**4,6-Dimethyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium Perchlorate IX, $C_{11}H_{16}ClN_3O_6S_2$).** 5 ml conc. $H_2SO_4$ was added to 1.3 g (4 millimoles) compound VIII. The reaction mixture was heated for 4 h at a temperature of 70-80°C. After cooling, first 75 ml ethylacetate and then 100 ml diethyl ether were added to the reaction mixture, which was allowed to stand for 24 hrs at ~5°C. The solvent was decanted from the oily product formed, the residue was dissolved in 10 ml water, the solution was neutralized with sodium carbonate to pH 3-4 and filtered as needed. 1.3 g sodium perchlorate was added to the filtrate. The colorless precipitate of compound IX was filtered off and washed with a small amount of water. Product yield, 0.9 g (55%). $T_{mp}$ 165-166°C. After recrystallization from water with addition of perchloric acid, $T_{mp}$ 174-175°C.

**4,6-Dimethyl-5,7-dioxo-(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-thione (XII, $C_7H_6N_2O_2S_2$).** 0.8 g (0.2 millimoles) perchlorate IX was added to a solution of 1 g (4.2 millimoles) $Na_2S \cdot 9H_2O$ in 100 ml water. The reaction mixture was held for 1 h, the solution obtained was filtered as needed and acidified with hydrochloric acid. The yellow precipitate of thione XII was filtered and recrystallized from ethanol. Product yield, 0.3 g (59%). $T_{mp}$ 173-174°C.

**4,6-Dimethyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-selenone (XIV, $C_7H_6N_2O_2S_2Se$).** The reaction was carried out under an argon atmosphere at room temperature. An aqueous solution of sodium selenide was prepared from 0.3 g (3.8 millimoles) Se and 0.3 g (7.2 millimoles) sodium borohydride in 75 ml water. 1.2 g (3 millimoles) perchlorate IX was added to the solution with stirring. The mixture was stirred for 30 min; the solution obtained was acidified with HCl. The red precipitate of selenone XIV was filtered and washed with water on the filter. Product yield, 0.6 g (66%). $T_{mp}$ > 160°C (gradual decomposition). After recrystallization from ethanol, $T_{mp}$ > 170°C (gradual decomposition).

**4-Methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium Perchlorate (Xα, $C_{10}H_{14}ClN_3O_6S_2$).** 3 ml conc. $H_2SO_4$ was added to 0.58 g (2 millimoles) compound IV. The reaction mixture was heated from 4 h at a temperature of 70-80°C. A cloudy solution was formed. After cooling, the reaction mixture was diluted with 50 ml ethylacetate, then 70 ml diethyl ether was added and it was allowed to stand for 24 h at ~5°C. The solvent was decanted from the oily layer formed, the residue was dissolved in ~10 ml water, the solution was treated with sodium carbonate up to pH 3-4 and filtered. 0.5 g (4 millimoles) sodium perchlorate was added to the filtrate. The colorless precipitate of perchlorate Xa was filtered and washed with water on the filter. Product yield, 0.32 g (43%). $T_{mp}$ 240-245°C. After recrystallization from water containing $HClO_4$, $T_{mp}$ was 243-245°C.

**4-Methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-thione (XVIII, $C_6H_4N_2O_2S_3$).** 0.74 g (2 millimoles) perchlorate Xa was added to a solution of 1 g (4.2 millimoles) $Na_2S \cdot 9H_2O$ in 100 ml water. The reaction mixture was allowed to stand for 1 h and the solution obtained was filtered. The filtrate was acidified with HCl. The yellow precipitate was filtered and washed with water. Yield of thione XVIII, 0.22 g (50%). $T_{mp}$ 240-255°C. The compound was recrystallized from ethanol with addition of conc. HCl, $T_{mp}$ 255-260°C.

**4-Methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-selenone (XVI, $C_6H_4N_2O_2S_2Se$).** The reaction was carried out under an argon atmosphere at room temperature. 0.74 g (2 millimoles) perchlorate Xa was added gradually with mixing by a magnetic stirrer to a solution of sodium selenide prepared from 0.2 g (2.5 millimoles) selenium and 0.2 g (5.3 millimoles) sodium borohydride in 50 ml water. The reaction mixture was stirred for 30 min. The argon supply was shut off

and the solution obtained was acidified with HCl to pH ~2. After 12 h, the red precipitate of selenone XVI was filtered and washed with water on the filter. Obtained: 0.5 g (89%) unpurified selenone. $T_{mp}$ 300°C. This was crystallized from ethanol with addition of conc. HCl. The compound is identical to that described earlier in [1].

**6-Methyl-5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-selenone (XIX, $C_6H_4N_2O_2S_2Se$).** 10 ml conc. $H_2SO_4$was added to 1.84 g (6 millimoles) compound IV. The mixture was heated for 4 h at a temperature of 70-80°C. After cooling, the cloudy solution formed was poured into 150 ml water and neutralized with sodium carbonate to pH ~7. The filtered solution was poured gradually with stirring into a freshly prepared aqueous solution of sodium selenide, prepared from 0.68 g (8.6 millimoles) Se and 0.68 g (18 millimoles) $NaBH_4$ in 150 ml water under an argon atmosphere. The reaction mixture was stirred for 30 min under an argon atmosphere; then the argon supply was shut off, the solution was acidified with HCl to a pH of 1-2 and allowed to stand for 12 h. The red precipitate was filtered and washed with water on the filter. The product was suspended in 25 ml conc. HCl and after 8 h was filtered and washed with water. Obtained: 1.45 g (86%) of a mixture of isomeric selenones XVI and XIX. Thin-layer chromatography data (Silufol UV plates, eluent chloroform–ethylacetate, 3:1): for compound XIX, $R_f$ 0.78; for compound XVI, $R_f$ 0.64.

In order to obtain pure 4-isomer XVI, the product was crystallized from ethanol. Obtained: 0.7 g, $T_{mp}$ 300°C.

For the 6-isomer XIX obtained, the filtrate obtained after crystallization of the mixture of selenones from ethanol was evaporated to dryness. The residue, containing ~70% compound XIX, was separated on a chromatographic column. The packing was silica gel; the eluent, chloroformethylacetate (3:1). The selenone XIX obtained was recrystallized from 30% ethanol. Obtained: 0.15 g dark reddish brown selenone XIX. $T_{mp}$ > 300°C.

## REFERENCES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