# REACTION OF PROPIOLIC ACID ESTERS WITH DITHIOLS AND β-MERCAPTOETHANOL

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UDC 547.77.07'738.
07'892:543.422

2-Alkoxycarbonylmethyl-1,3-oxathiolane and -dithiolane, 3-methyloxycarbonylmethyl-7,8-dimethyl-1,5-dihydrobenzo[e]-1,3-dithiepine, and 2-methoxycarbonylmethyl-1,3-dithiolo[4,5-b]quinoxaline were synthesized on the basis of the reaction of esters of propiolic acid with β-mercaptoethanol, 1,2-dimercaptoethanol, 1,2-dimethyl-4,5-di(mercaptomethyl)benzene, and 2,3-dimercaptoquinoxaline in chloroform medium in the presence of $K_2CO_3$ or in DMSO medium.

Earlier we studied the reactions of certain 1,2-dinucleophilic reagents (β-mercaptoethanol, 1,2-dimercaptoethanol, 1,2-dimercaptobenzene, 2,3-dimercaptoquinoxaline) with acylacetylenes and obtained various cyclic products, arising as a result of double addition to the triple bonds [1-6].

In this work we investigated the reaction of β-mercaptoethanol (II), 1,2-dimercaptoethanol (III), 1,2-dimethyl-4,5-di(mercaptomethyl)benzene (IV), and 2,3-dimercaptoquinoxaline (V) with methyl and ethyl esters of propiolic acid. The reaction of the dinucleophiles II-V with esters of propiolic acid (Ia, b) evidently proceeds through an intermediate step of formation of the corresponding S-monoadducts VIa, VIII, X, and XII (addition of one mercapto group to the acetylenic bond) and cyclization of the latter to the corresponding compounds VIIIa, IXa, b, XIa, and XIVa (scheme). We succeeded in isolating the intermediate vinyl sulfide VIa only in the interaction of β-mercaptoethanol II with the methyl ester of propiolic acid (Ia) at an equimolar ratio of the reagents in chloroform medium at 60°C in the presence of $K_2CO_3$. Such a difference in the behavior of β-mercaptoethanol and dithiols III-V in the reaction with esters of propiolic acid can be explained by the fact that the mercapto group is a stronger nucleophile than the hydroxyl group [7, 8], as a result of which intermediate vinyl sulfides VIII, X, and XII are more inclined to intramolecular cyclization than the vinyl sulfide VIa.

The reaction of 1,2-dimercaptoethanol with the methyl and ethyl esters of propiolic acid (Ia, b) proceeded at an equimolar ratio of the reagents in chloroform medium at 60°C in the presence of $K_2CO_3$ and led to the formation of 2-methoxycarbonyl-(IXa) and 2-ethoxycarbonylmethyl-1,3-dithiolanes (IXb). The reaction of dithiol IV with methyl propiolate Ia, 3-methoxycarbonylmethyl-7,8-dimethyl-1,5-dihydrobenzo[e]-1,3-dithiepine (XIa) was isolated in a yield

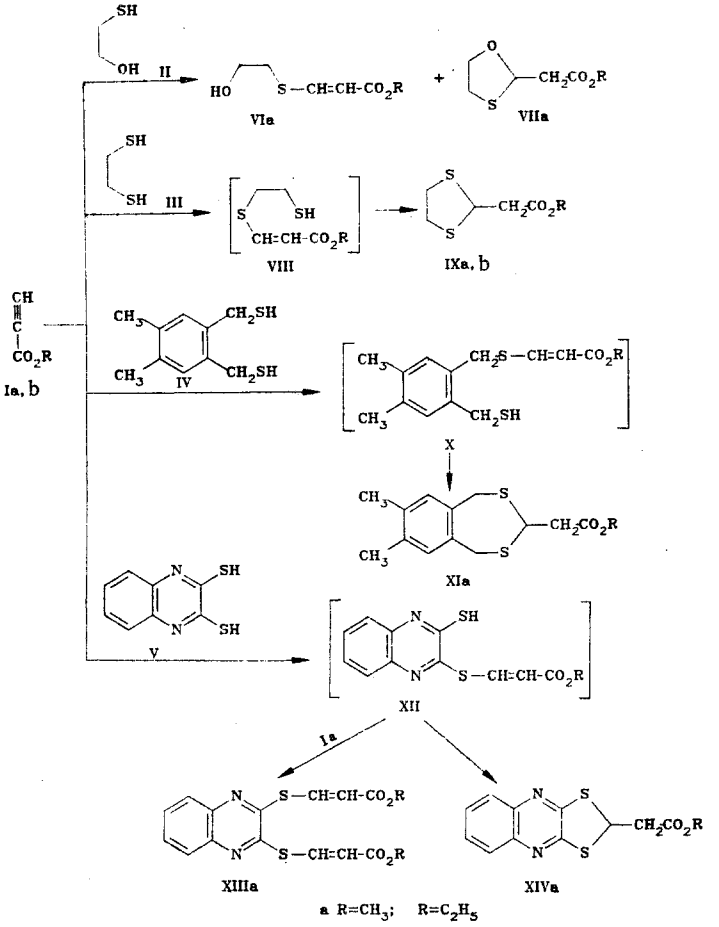
TABLE 1. Characteristics of the Compounds Synthesized

| Compound | bp, °C (hPa), mp, °C | Found, % | | | | Empirical formula | Calculated, % | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | S | | C | H | N | S | |
| VIa | 125—127 (2,6) | 44,6 | 6,4 | — | 20,0 | $C_6H_{10}O_3S$ | 44,4 | 6,2 | — | 19,8 | 59 |
| VIIa | 70 (1,3) | 44,5 | 6,3 | — | 20,1 | $C_6H_{10}O_3S$ | 44,4 | 6,2 | — | 19,8 | 12 |
| IXa | 112—113 (1,3) | 40,6 | 5,7 | — | 36,6 | $C_6H_8O_2S_2$ | 40,4 | 5,6 | — | 36,4 | 78 |
| IXb | 110—112 (1,3) | 44,0 | 6,4 | — | 33,3 | $C_7H_{12}O_2S_2$ | 43,8 | 6,3 | — | 33,3 | 76 |
| XIa | 126—127 | 59,4 | 6,6 | — | 22,6 | $C_{14}C_{18}O_2S_2$ | 59,6 | 6,4 | — | 22,7 | 79 |
| XIIIa | 175—176 | 53,0 | 3,9 | 7,8 | 17,7 | $C_{16}H_{14}N_2O_4S_2$ | 53,0 | 3,9 | 7,7 | 17,7 | 19 |
| XIVa | 108—109 | 51,7 | 3,6 | 10,1 | 22,9 | $C_{12}C_{10}N_2O_2S_2$ | 51,8 | 3,6 | 10,1 | 23,0 | 34 |
| XV | 110—112 | 32,9 | 4,8 | — | 24,7 | $C_7H_{12}O_6S_2$ | 32,8 | 4,7 | — | 25,0 | 46 |
| XVI | 230—232 | 48,7 | 5,2 | — | 18,3 | $C_{14}H_{18}O_6S_2$ | 48,6 | 5,2 | — | 18,5 | 52 |

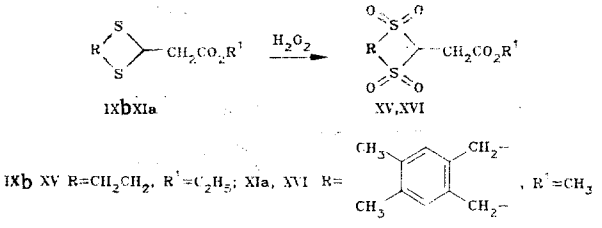
Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsilicheskikh Soedinenii, No. 8, pp. 1062-1065, August, 1984. Original article submitted August 30, 1983; revision submitted December 14, 1983.

 0009-3122/84/2008-0862$08.50 

of 79% as the sole reaction product. In the interaction of 2,3-dimercaptoquinoxaline with compound Ia in DMSO medium at 80-90°C in the absence of a catalyst at an equimolar ratio of the reagents, the following are formed: 2-methoxycarbonylmethyl-1,3-dithiolo[4,5-b]quinoxaline (XIVa) (yield 34%), 2,3-di(methoxycarbonylvinylthio)quinoxaline (XIIIa) (yield 19%), and the side product diquinoxalino-1,2,5,6-tetracyclooctane (yield 39%). When this reaction was conducted under the same conditions at a 1:2 ratio of V and Ia, the yield of compound XIIIa was increased to 31% (Table 1). The structure of the compounds obtained was confirmed by the IR and PMR spectra (Table 2).




In the oxidation of compounds IXb and XIVa with 30% hydrogen peroxide in glacial acetic acid medium, the corresponding disulfones XV and XVI were obtained (Table 1).




## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in tablets with KBr or in a microlayer for liquid samples; the PMR spectra were recorded on a Tesla-487B spectrometer (80 MHz) in $CCl_4$ or $CDCl_3$, internal standard HMDS.

2-Methoxycarbonylmethyl-1,3-oxathiolane (VIIa) and 1-Methoxycarbonyl-3-thia-1-penten-5-ol (VIa). To a solution of 2.52 g (30 mmoles) of methyl propiolate Ia in 30 ml of chloroform we added 2.34 g (30 mmoles) of the ethanol II, 2 g of freshly calcined $K_2CO_3$, and heated for 2 h at 60°C. The mixture was cooled to 20°C, $K_2CO_3$ filtered off, the solvent evaporated, and the

TABLE 2. PMR Spectra

| Compound | Chemical shifts, δ, ppm | | | | | | | | SSIC, J, Hz | |
|---|---|---|---|---|---|---|---|---|---|---|
| | S–$CH_2$ | O–$CH_2$ | S–CH= | CO–CH= | $CO_2CH_2$ | $CO_2CH_3$ | >CH– | Ar | CH=CH | CH–$CH_2$ |
| VIa* | 2,96 t | 3,77 t | 7,51 d | 5,73 d | — | 1,42 s | — | — | 15,0 | — |
| VIIa | 2,92 t | 4,22 m | — | — | 3,05 d | 1,45 s | 5,25 t | — | — | 6,5 |
| IXa | 3,40 s | — | — | — | 2,75 d | 1,44 s | 4,74 t | — | — | 7,5 |
| IXb | 3,18 s | — | — | — | 2,73 d | — | 4,70 t | — | — | 7,5 |
| XIa | 3,93 m | — | — | — | 3,08 d | 1,42 s | 4,65 t | 6,93 s | — | 7,5 |
| XIIIa | — | — | 7,42 d | 5,92 d | — | 2,20 s | — | 7,70 m | 14,5 | — |
| XIVa | — | — | — | — | 3,12 d | 2,22 s | 5,20 t | 7,55 m | — | 7,0 |

*4.21 ppm (c, OH).

residue distilled under vacuum. Yield 0.86 g (12%) of a fraction with bp 70°C (1.3 hPa) – compound VIIa. IR spectrum (microlayer): 675 (C–S), 1140, 1210, 1265 (C–O), 1448 ($\delta CH_2$), 1740 $cm^{-1}$ (C=O).

We also isolated 2.9 g (59%) of a fraction with bp 125-127°C (2.7 hPa) – compound VIa.

2-Methoxycarbonylmethyl-1,3-dithiolane (IXa). Produced analogously from 2.52 g (30 mmoles) of the methyl propiolate Ia and 2.82 g (30 mmoles) of 1,2-dimercaptoethanol III. Yield 4.07 g (78%). IR spectrum (microlayer): 708 (C–S), 1180, 1240, 1265 (C–O), 1420 ($\delta CH_2$), 1720 $cm^{-1}$ (C=O).

2-Ethoxycarbonylmethyl-1,3-dithiolane (IXb). Produced analogously from 2.49 g (25 mmoles) of the ethyl propiolate Ib and 2.35 g (25 mmoles) 1,2-dimercaptoethane. Yield 3.68 g (76%). IR spectrum (microlayer): 708 (C–S), 1185, 1240, 1265 (C–O), 1425 ($\delta CH_2$), 1722 $cm^{-1}$ (C=O).

3-Methoxycarbonylmethyl-7,8-dimethyl-1,5-dihydrobenzo[e]-1,3-dithiepine (XIa). To a solution of 0.84 g (10 mmoles) of methyl propiolate in 30 ml of dry chloroform we added 2 g of freshly calcined $K_2CO_3$, and with vigorous mixing at 20°C we slowly added 1.98 g (10 mmoles) of the benzene IV. The mixture was heated to 60°C, mixed for 2 h, and cooled to 20°C, $K_2CO_3$ was filtered off, the solvent partially evaporated under vacuum, and the compound XIa precipitated with ether with cooling (5°C). Yield 2.06 g (79%). Mp 126-127°C (from alcohol). IR spectrum (KBr): 695 (C–S), 1190, 1220, 1275 (C–O), 1420 ($CH_2$), 760, 1490, 1520 (ortho-substituted benzene ring), 1745 $cm^{-1}$ (C=O).

2-Methoxycarbonylmethyl-1,3-dithiolo[4,5-b]]quinoxaline (XIVa). To a solution of 4.65 g (24 mmoles) of the quinoxaline V in 30 ml of DMSO we added 2 g (24 mmoles) of the methyl propiolate Ia, heated to 80-90°C, and mixed for 2 h. The mixture was cooled to 20°C, the precipitate formed was filtered off and recrystallized from xylene. Yield 1.8 g (39%) diquinoxalino-1,2,5,6-tetracyclooctane with mp 283-285°C (subl.). IR spectrum (KBr): 708 (C–S), 765, 1490, 1580 (ortho-substituted benzene ring), 1630 $cm^{-1}$ (C=N). Found: C 50.3; H 2.1; N 14.7; S 33.5%. $C_{16}H_8N_4S_4$. Calculated: C 50.0; H 2.1; N 14.6; S 33.3%.

The DMSO solution remaining was poured out into water with ice with vigorous mixing. The precipitate formed was filtered off and recrystallized from a 1:1 alcohol-acetone mixture. Yield 2.23 g (34%) of compound XIVa. IR spectrum (KBr): 705 (C–S), 1110, 1210, 1260 (C–O), 1430 ($\delta CH_2$), 760, 1490, 1540 (ortho-substituted benzene ring), 1625 (C=N), 1715 $cm^{-1}$ (C=O).

2-Ethoxycarbonylmethyl-1,3-dithiolane Tetraoxide (XV). To a solution of 1.46 g (7 mmoles) of the compound IXb in 2 ml of glacial acetic acid, 4.74 ml of 30% hydrogen peroxide was slowly added dropwise with mixing, it was mixed for 2 h, and the mixture was left at room temperature for two days. The reaction mixture was poured out into water with ice; the precipitate formed was filtered off, washed with water, and recrystallized from ethanol. Yield 0.9 g (46%). Mp 110-112°C. IR spectrum (KBr): 712 (C–S), 1130, 1180 ($\nu_s SO_2$), 1320 ($\nu_{as} SO_2$), 1220, 1260 (C–O), 1450 ($CH_2$), 1720 $cm^{-1}$ (C=O).

3-Methoxycarbonylmethyl-7,8-dimethyl-1,5-dihydrobenzo[e]-1,3-dithiepine Tetraoxide (XVI) was produced analogously to compound XV from 0.5 g (2 mmoles) of compound XIVa and 1.2 ml (30%) of hydrogen peroxide. Yield 0.3 g (52%). Mp 230-232°C (from alcohol). IR spectrum (KBr): 708 (C–S), 1140, 1175 ($\nu_s SO_2$), 1230, 1280 (C–O), 1315 ($\nu_{as} SO_2$), 760, 1495, 1580 (ortho-substituted benzene ring), 1440 ($CH_2$), 1745 $cm^{-1}$ (C=O).

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# STRUCTURE OF 2-AMINO-4-THIAZOLINONE

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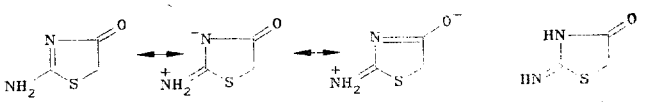
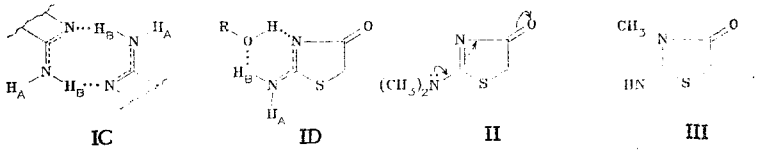
UDC 547.789.1.0:543.25'4:541.623

It was shown by the methods of IR and NMR spectroscopy that 2-amino-4-thiazolinone ("pseudothiohydantoin") exists in an amino form in the crystalline state and in solutions in dimethyl sulfoxide, water, and trifluoroacetic acid, and in this amino form all the nitrogen-carbon bonds are partially double. In dimethyl sulfoxide and trifluoroacetic acid there is an autoassociation with the formation of dimers. Inhibited rotation of the amino group around the exocyclic nitrogen-carbon bond was detected. The results of a calculation of the IR spectrum of 2-amino-4-thiazolinone according to the force-field method agrees with the experimental data.

Earlier [1] we showed that in aqueous solution 2-amino-4-thiazolinone (I, "pseudothiohydantoin") exists in the amino form IA. The reports on the predominant tautomeric form of compound I in the crystalline state, based on the results of a study of the IR spectra, are contradictory [1]. A structural peculiarity of the cyclic analogs, 2-aminoazolines and 2-aminoazines, which hinders the interpretation of the data of x-ray crystallographic analysis and IR spectroscopy, is the ability of the molecules of these compounds to dimerize as a result of the formation of short hydrogen contacts N–H...N between the amidine fragments [2-4]. Such contacts enhance the conjugation already present in the monomer molecules, and as a result, the double bonds are delocalized to a substantial degree over the amidine fragments, the N–H bonds are lengthened, and the N...H hydrogen bonds in the contacts N–H...N are shortened, i.e., cyclic dimers IC are mesomeric "hybrids" of the tautomeric forms [5].



IA IB



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For such potential tautomeric systems it is insufficient, while knowing the localization of the hydrogen atoms, to establish in which "classic" flow-through tautomeric form the com-

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1066-1070, August, 1984. Original article submitted June 22, 1983.

0009-3122/84/2008-0865$08.50  