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SYNTHESIS AND PROPERTIES OF β-OXO SULFIDES OF THE DIOXOTHIOLANE SERIES

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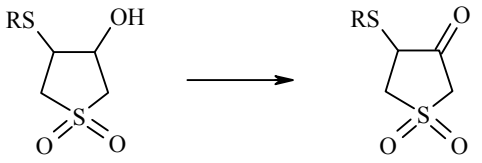
It was shown that the hydroxy group in β-hydroxy sulfides of the dioxothiolane series can be oxidized selectively to a carbonyl group in the presence of a sulfide group. A sequence of transformations leading to the final β-oxo sulfides was proposed and was confirmed experimentally. A new original method was developed for the production of β-oxo sulfides. Some characteristics of the synthesized compounds were studied.

Keywords: β-hydroxy sulfides, β-oxo sulfides, five-membered cyclic sulfones, selective oxidation, chemical properties.

Five-membered cyclic sulfones are extremely reactive compounds and are of interest both in synthetic chemistry and in the design of substances with useful properties [1]. A notable position among such compounds is occupied by the carbonyl derivatives. The presence of the carbonyl group in conjunction with the thiolane ring significantly extends the synthetic possibilities of this type of compound. They have found use in peptide synthesis [2] and in the synthesis of hormonal products [3], heterocyclic analogs of steroids [4, 5], insectoacaricides [6], and herbicides [7]. In addition, they can be used as convenient intermediates for the production of various types of cyclic sulfones [8].

Earlier [9] we demonstrated the basic possibility of selectively oxidizing a hydroxyl group to a carbonyl group in the presence of a sulfide group in the β-hydroxy sulfide **1** (R = Me) of the dioxothiolane series using chlorinating agents (elemental chlorine, sulfuryl chloride) with the formation of the keto sulfides **2** [9].



1 **2 a–d**

1, 2a R = Me; **2 b** R = Et, **c** R = *p*-MeC_6H_4, **d** R = *p*-BrC_6H_4

Further investigation of this reaction showed that direct oxidation of the hydroxyl group does not occur [10]. Initially, substitutive chlorination occurs at the C(4) atom with the formation of the chloride **3**, accompanied by elimination of hydrogen chloride and the formation of the sulfolene **4**. Migration of the double bond then occurs in the acidic medium, and this leads to the enol **5** and to the ketone **2** as final product.

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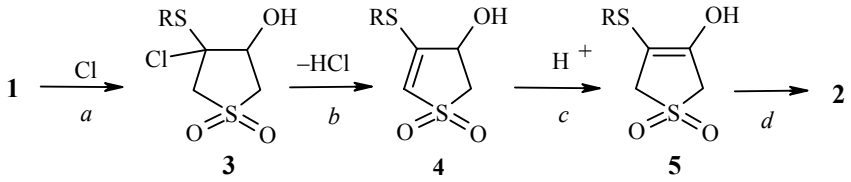
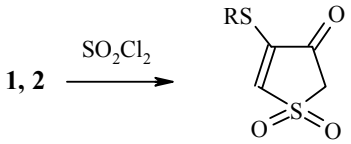


Isomerization at the double bond in compound **4** (R = *p*-C_6H_4), which was isolated by fractional crystallization from the crude product of the reaction of the hydroxy sulfide **1** with SO_2Cl_2, was established by IR spectroscopy from the disappearance of the absorption band of the hydroxyl group and the appearance of the carbonyl group in a methylene chloride solution saturated with hydrogen chloride.

As a rule, migration of the double bond in a dioxothiolane ring is carbanionic in nature, i.e., takes place in an alkaline medium [11]. There are isolated examples of isomerization in an acidic medium, e.g., [12], but their nature was not studied. It was noticed that the double bond in 4-hydroxy-2-thiolene 1,1-dioxide does not isomerize either in an alkaline or in an acidic medium [13].

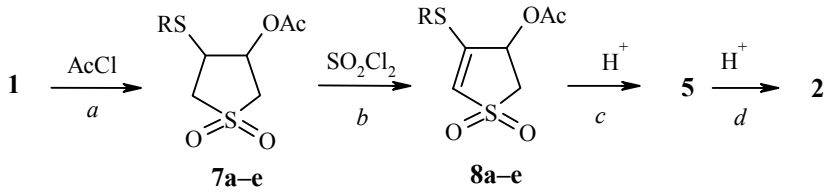
The composition of the products of the investigated reaction depends on the ratio of the rates of the individual stages, which in turn depend to a considerable degree on the electronic and steric characteristics of the substituent at the sulfur atom. The process takes place sufficiently smoothly if the rates of the first two stages (a and b) are higher than the rates of the last two stages (c and d). Otherwise, difficultly separated mixtures, from which compounds **3**, **4**, and **6** can be isolated together with the initial and final products, are formed.



6 a R = Me, **b** R = Ph

Thus, in the reaction of the hydroxy sulfide **1c** (R = Ph) with sulfuryl chloride the unsaturated ketone **6b** was isolated from the mixture of compounds with a 17% yield instead of the expected ketone **2**. The rate of stages a and b is clearly lower than the rate of the concluding stages, and the unreacted chlorinating agent reacts with the saturated ketone that forms, giving the unsaturated ketone. This is confirmed by the fact that the oxo sulfide **6a** is readily produced during chlorination of the oxo sulfide **2a**.

From the established sequence of reactions, leading to transformation of the hydroxyl group into a carbonyl group, we proposed a new original approach to the synthesis of β-oxo sulfides of the dioxothiolane series making it possible to avoid the formation of side products and to increase considerably the yield of the final products. The method involves prior protection of the hydroxyl group with the formation of the acetate **7** (a), its oxidative chlorination to the sulfolene **8** (b), removal of the protection, and isomerization at the double bond (c and d) (Table 1).



7,8 a R = Me, **b** R = Et, **c** R = Ph, **d** R = *p*-MeC_6H_4, **e** R = *p*-BrC_6H_4

TABLE 1. The Physicochemical Characteristics of Compounds **2a-d**, **7a**,**c-e**, and **8a-e**

Compound*	Empirical formula	Found, % / Calculated, %			mp, °C*[2]	Yield, %
		C	H	S		
2a	$C_5H_8O_3S_2$	33.00 / 33.30	4.50 / 4.48	35.50 / 35.58	80-82	70
2b	$C_6H_{10}O_3S_2$	37.56 / 37.10	5.21 / 5.19	32.71 / 33.01	87-88	80
2c	$C_{11}H_{12}O_3S_2$	51.75 / 51.54	5.08 / 4.72	24.68 / 25.01	129-132	89
2d	$C_{12}H_{13}BrO_4S_2$	37.58 / 37.39	3.13 / 2.82	19.91 / 19.56	146-147.5	70
7a	$C_7H_{12}O_4S_2$	37.84 / 37.49	5.47 / 5.39	28.26 / 28.59	53-56*[3]	86
7c	$C_{12}H_{14}O_4S_2$	50.29 / 50.33	4.94 / 4.93	22.14 / 22.39	92-93.5	95
7d	$C_{13}H_{16}O_4S_2$	51.73 / 51.98	5.35 / 5.37	21.25 / 21.35	84-85	89
7e	$C_{12}H_{13}BrO_4S_2$	39.54 / 39.46	3.57 / 3,59	17.15 / 17.56 (21.77) / (21.87)*[4]	123-125	70
8a	$C_7H_{10}O_4S_2$	37.98 / 37.83	4.54 / 4.54	28.79 / 28.75	121-122	68.5
8b	$C_8H_{12}O_4S_2$	41.02 / 40.66	5.19 / 5.12	27.08 / 27.13	109-111	84.6
8c	$C_{12}H_{14}O_4S_2$	50.17 / 50.69	4.16 / 4.25	22.35 / 22.55	125-127	88
8d	$C_{13}H_{16}O_4S_2$	52.42 / 52.33	4.78 / 4.73	21.69 / 21.49	94-97	60.7
8e	$C_{12}H_{13}BrO_4S_2$	40.01 / 39.67	3.25 / 3.05	(21.38) / (21.72)*[4]	117-118	70.7

* Compound **7b**: bp 144-146°C (0.03 mm Hg), yield 80%.

*[2] Solvents: isopropyl alcohol (compounds **2a-c**, **7c**,**d**, and **8b**,**e**), benzene (compounds **2d** and **8a**,**c**), and methanol (compounds **7e** and **8d**).

*[3] bp 126-128°C (0.05 mm Hg), solidifies on storage. Crystallized by introducing a seed into the freshly distilled product.

*[4] Data from analysis for bromine.

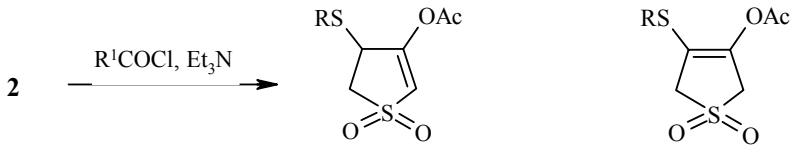
Preparatively, the last two processes are carried out in one stage. The protecting group is removed first, and the rearrangement then occurs, as confirmed by the fact that as the hydrochloric acid concentration at stage (c) decreases the unsaturated hydroxy sulfide **4** is also found in the reaction products together with the final product.

The synthesis of the analogous oxo sulfides **2** (R = Alk, C_4, C_6, C_8) by the reaction of the corresponding hydroxy sulfoxides with thionyl chloride was described in [12]. The authors state that the process can be realized in sulfoxides with the *trans* arrangement of the substituents at positions 3 and 4 of the dioxothiolane ring; in the case of the *cis* isomers the final product is the hydroxy sulfide **4**. In view of our discovered transformation of the hydroxy sulfide **4** into the oxo sulfide **2** it is difficult to agree with such statements.

According to data in [14], the 3-oxosulfolane is present to a significant degree in the enolic form. There are no signs of the enolic form in the IR and NMR spectra of freshly obtained compounds **2**. However, the oxo sulfide **2c** probably isomerizes gradually into the enolic form during prolonged storage. (Absorption bands characteristic of the hydroxyl group and the C=C bond appear in the IR spectra.)

The obtained substances are polyfunctional compounds with many reaction centers. It can be assumed that during the action of bases the anion can form at any of the carbon atoms and also at the oxygen atom. The products from O- or C-alkylation or acylation can therefore be expected to form during their reaction with alkyl or acyl halides.

We studied the reaction of some β-oxo sulfides with acid chlorides in the presence of triethylamine. The reactions were conducted under mild conditions at room temperature in an inert solvent. The O-acylation products **9a-j** were formed (Table 2).



9 a–j **10**

9 a-e R = Me, **f-i** R = Et, **j** R = p-C_6H_4Br; **a, f, j** R^1 = Me, **b** R^1 = Et, **c, g** R^1 = Pr, **d, h** R^1= Ph, **e, i** R^1 = C_2H_4COOMe

The position of the double bond is confirmed by the data from the IR spectra. In the spectra of the investigated compounds there is fairly strong absorption at 1610-1630 cm^{-1}. This favors structure **9**, in which the double bond occupies position 2 of the dioxothiolane ring. In compounds **8**, which we obtained by the action of SO_2Cl_2 on the acylated hydroxy sulfides **7** where the double bond occupies position 4, the $\nu_{C=C}$ absorption bands are significantly lower (1570-1580 cm^{-1}) while those in the 3-sulfolenes **10** are weak.

TABLE 2. 4-Alkyl(aryl)thio-3-carboxy-1,1-thiolene 1,1-Dioxides **9a-j**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C*	IR, ν, cm^{-1}		Yield, %
		C	H	S		$\nu_{C=C}$	$\nu_{C=O}$	
9a	$C_7H_{10}O_4S_2$	37.91 / 37.83	4.56 / 4.54	29.26 / 28.85	90-92	1626	1788	66.0
9b	$C_8H_{12}O_4S_2$	40.67 / 40.66	5.17 / 5.12	27.20 / 27.14	84-85	1610	1783	76.1
9c	$C_9H_{14}O_4S_2$	43.15 / 43.18	5.60 / 5.64	25.61 / 25.61	76-78	1610	1783	71.4
9d	$C_{12}H_{22}O_4S_2$	50.78 / 48.95	4.54 / 4.79	22.44 / 21.78	94-96	1624	1750	49.4
9e	$C_{10}H_{14}O_6S_2$	40.90 / 40.81	4.74 / 4.79	21.80 / 21.78	85-86	1620	1725 1760	89
9f	$C_8H_{12}O_4S_2$	40.82 / 40.66	5.13 / 5.12	27.16 / 27.14	81-83	1626	1782	66.7
9g	$C_{10}H_{16}O_4S_2$	45.51 / 45.43	6.10 / 6.10	24.27 / 24.25	70-71	1620	1782	58.9
9h	$C_{13}H_{14}O_4S_2$	52.37 / 52.33	4.76 / 4.73	21.41 / 21.47	116-117.5	1612	1750	71.4
9i	$C_{11}H_{16}O_6S$	42.85 / 42.85	5.06 / 5.23	20.78 / 20.79	69.5-70.5	1621	1730 1780	76
9j*[2]	$C_{12}H_{11}BrO_4S$	39.69 / 39.67	3.04 / 3.05	17.54 / 17.65	114-117	77.4	1780	77.4

* Solvents: methanol (compounds **9a**,**b**,**e-g**,**i**), isopropyl alcohol (compound **9c**), benzene (compounds **9d**,**h**), and carbon tetrachloride (compound **9j**).

*[2] Found, %: Br 22.70. Calculated, %: Br 21.99.

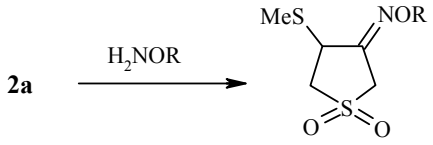
In the reaction of the ketones **2a** and **11** with unsymmetrical dimethylhydrazine the enehydrazines **12** are formed instead of the expected hydrazones.

2a, 11 **12a,b**

2a, 12a R = SMe; **11, 12b** R = H

The structure of these compounds was established by IR and ^{13}C NMR spectroscopy. The presence of an absorption band at 3240 cm^{-1} (ν_{NH}) favors the enehydrazine structure and makes it possible to assign the band at 1628 cm^{-1} to the vibrations of the C=C bond and not the C=N bond. In addition, the ^{13}C NMR spectrum contains signals for two sp^2-hybridized $C_{(2)}$ and $C_{(3)}$ atoms and not one as in the supposed hydrazone.

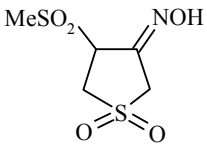
Unlike dimethylhydrazine, hydroxylamine and O-alkylhydroxylamines react with the oxo sulfide **2a** to form the respective oximes **13a-g** (Table 3).



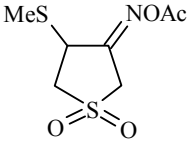
13a–g

13 a R = H, **b** R = Me, **c** R = Et, **d** R = Pr, **e** R = Bu, **f** R = CH_2–CH=CH_2; **g** R = CH_2Ph

The structure of the oximes **13** is confirmed by data from the ^{13}C NMR spectra and chemical transformations. The IR spectra do not contradict the proposed structure, but they do not contain absorption characteristic of the C=N bond. Since, according to the selection rules, vibrations accompanied by change in dipole moment do not appear in the IR spectra, it can be supposed that change in the electronic nature of substituents close to the above-mentioned bond will affect the character of its vibrations, and it will appear in the spectrum. In fact, although the spectrum of the oxidized substance **14** also does not contain the relevant absorption, in the spectrum of the acetyl derivative **15** there is a weak band at 1640 cm^{-1}.



14



15

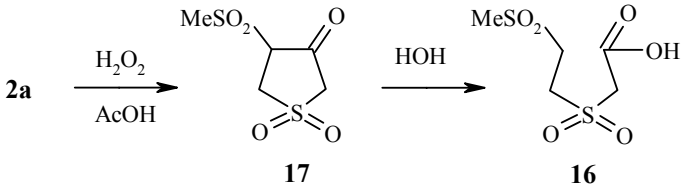
Oxidation of the methylthio group in the oxime **13a** with hydrogen peroxide takes place readily without complications. Oxidation of this group in the oxo sulfide **2a** under analogous conditions leads to a complex mixture of compounds, from which 2-(methylsulfonyl)ethylsulfonylacetic acid **16** was isolated with a 26% yield.

At first sight this unusual opening of the sulfothiolane ring in an acidic medium is reminiscent of Baeyer–Villiger oxidation [15], in which the corresponding lactones or ω-hydroxy acids are formed from cyclic ketones. We suppose that in the investigated case sulfide group is initially oxidized, thereby facilitating subsequent nucleophilic substitution at the carbonyl carbon atom with cleavage of the C=C bond. This is supported by the fact that compound **17** is formed during oxidation under anhydrous conditions.

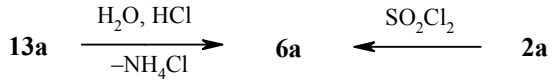
TABLE 3. 3-(O-Alkoxyimino)-4-methylthiothiolane 1,1-Dioxides **13a-g**

Compound	Empirical formula	Found, % / Calculated, %		mp, °C*	^{13}C NMR spectrum, δ, ppm						Yield, %
		N	S		C_5	C_4	C_3	C_2	S–$\underline{C}H_3$	=N–O–$\underline{C}$	
13a	$C_5H_3NO_3S_2$	7.32 / 7.20	32.73 / 32.80	150-153 (dec.)	57.68	150.42	44.13	50.32	14.93	—	71
13b	$C_6H_{11}NO_3S_2$	6.57 / 6.69	30.60 / 30.64	129-132	57.34	150.49	43.92	50.52	14.92	62.94	54
13c	$C_7H_{13}NO_3S_2$	6.19 / 6.27	28.62 / 28.72	98-99.5	57.17	149.96	43.79	50.36	14.67	70.64	63
13d	$C_8H_{15}NO_3S_2$	5.79 / 5.90	26.78 / 27.02	87-89	57.35	150.11	43.99	50.58	14.94	77.04	41
13e	$C_9H_{17}NO_3S_2$	5.78 / 5.57	25.22 / 24.52	51-53	57.13	149.89	43.74	50.34	14.63	75/07	52
13f	$C_8H_{13}NO_3S_2$	5.87 / 5.95	27.53 / 27.25	80-81	57.09	150.62	43.70	50.47	14.56	76.03	40
13g	$C_{12}H_{15}NO_3S_2$	4.77 / 4.91	22.35 / 22.47	88-90	57.10	150.84	43.72	50.37	14.56	7.17	63

* Solvents: isopropyl alcohol (compounds **13a-c**,**e**,**f**), methanol (compounds **13d**,**g**).



The reverse reaction to the production of the oxime (acid hydrolysis) is accompanied by dehydrogenation with the formation of the unsaturated oxo sulfide **6**. The nitrogen-containing part was identified in the form of ammonium chloride.



With aliphatic and aromatic isocyanates in the presence of dibutyldiacetyltin the oxime **13a** is converted into the corresponding carbamoyloximes **18a-n** (Table 4). Aliphatic carbamoyloximes **18a-g**, unlike the aromatic compounds, are thermally unstable, and they cannot therefore be purified by recrystallization. They

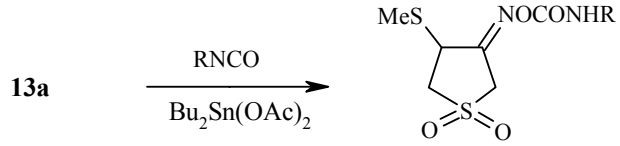
TABLE 4. 3-Carbamoyloxyimino-4-methylthiothiolane 1,1-Dioxides **18a-n**

Compound	Empirical formula	Found, % / Calculated, %				mp, °C*	Yield, %
		C	H	N	S		
18a	$C_7H_{12}N_2O_4S_2$	33.10 / 33.31	4.71 / 4.79	11.15 / 11.10	25.11 / 25.40	99-100	76.9
18b	$C_8H_{14}N_2O_4S_2$	35.92 / 36.08	5.36 / 5.30	10.45 / 10.52	24.05 / 24.08	90-92	86.6
18c	$C_9H_{16}N_2O_4S_2$	38.55 / 38.56	5.79 / 5.75	10.00 / 9.99	22.93 / 22.87	85-86	85
18d	$C_9H_{16}N_2O_4S_2$	—	—	—	23.03 / 22.87	70-73	69.4
18e	$C_{10}H_{18}N_2O_4S_2$	40.89 / 40.80	6.10 / 6.16	9.67 / 9.52	21.86 / 21.78	72-74	22
18f	$C_{12}H_{20}N_2O_4S_2$	44.85 / 44.98	6.35 / 6.29	8.33 / 8.74	20.01 / 20.01	84-86	67
18g	$C_{13}H_{16}N_2O_4S_2$	47.04 / 47.55	4.85 / 4.90	8.06 / 8.53	19.50 / 19.52	105-106	67.8
18h	$C_{12}H_{14}N_2O_4S_2$			8.94 / 8.95	20.59 / 20.39	122-124	80
18i	$C_{12}H_{13}ClN_2O_4S_2$				(10.39)*2 / (10.16)	128-130	84
18j	$C_{13}H_{16}N_2O_4S_2$		8.50 / 8.53	19.50 / 19.53	(10.18)*2 / (10.16)	123-125	74
18k	$C_{12}H_{13}ClN_2O_4S_2$		—	—		126-127	22
18l	$C_{12}H_{13}FN_2O_4S_2$	—	—	—	19.15 / 19.29	131-133	38
18m	$C_{12}H_{13}N_3O_6S_2$	—	—	11.41 / 11.69	17.51 / 17.84	141-142	87
18n	$C_{12}H_{13}N_3O_6S_2$	—	—	—	17.50 / 17.84	136-137	67.4

* Solvents: benzene (compounds **18h**,**j**,**k**), benzene + isopropyl alcohol (compound **18i**), dichloroethane (compound **18l**,**n**).

*2 Data from analysis for Cl.

can be obtained in the analytically pure state with the use of pure starting compounds, accurate proportioning of the reagents, and treatment under mild conditions. With the exception of **18g** these compounds are converted into dark-red resinous substances after storage for 2-3 months.



18a–n

18 a R = Me, **b** R = Et, **c** R = Pr, **d** R = *i*-Pr, **e** R = *sec*-Bu, **f** R = *cyclo*-C_6H_{11}, **g** R = CH_2Ph, **h** R = Ph, **i** R = *p*-ClC_6H_4, **j** R = *p*-MeC_6H_4, **k** R = *o*-ClC_6H_4, **l** R = *m*-FC_6H_4, **m** R = *p*-$NO_2C_6H_4$, **n** R = *m*-$NO_2C_6H_4$

EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on a Specord M-80 spectrometer in tablets with potassium bromide. The ^{13}C NMR spectra were recorded on a Bruker SXR-200 instrument at 50 MHz in acetone-d_6. The signal of the CD_3 group was taken as 29.2 ppm. The ^1H NMR spectrum for **6b** was recorded on a Bruker SXR-200 instrument at 200 MHz in acetone-d_6 with TMS as internal standard.

The initial β-hydroxy sulfides **1** were obtained by the described methods from 3-chloro-4-hydroxythiolane 1,1-dioxide **1a** [16] or 3,4-epoxythiolane 1,1-dioxide **1b** [17] and the corresponding sodium thiolates, using mixtures of the *cis* and *trans* isomers.

3-Hydroxy-4-methylthiothiolane 1,1-Dioxide (1a). Yield 85%; mp 152-154°C (0.05 mm Hg).

3-Hydroxy-4-(*p*-tolylthio)thiolane 1,1-Dioxide (1c). To a solution of sodium (0.130 g) in absolute methanol (400 ml) we added 3,4-epoxythiolane 1,1-dioxide (14 g, 104.4 mmol) and *p*-methylthiophenol (13 g, 104.4 mmol). The mixture was boiled with stirring for 2 h and neutralized with hydrochloric acid solution, and the volatile products were removed under vacuum. A small amount of water was added to the residue (a yellowish oily liquid). The precipitate was filtered off, dried, and recrystallized from 2-propanol. The product formed colorless prisms, yield 16.9 g (63%); mp 93-96°C. Found, %: C 50.98; H 5.60; S 24.96. $C_{11}H_{14}O_3S_2$. Calculated, %: C 51.16; H 5.43; S 24.80.

4-(*p*-Bromophenylthio)-3-hydroxythiolane 1,1-Dioxide (1d). To a solution of sodium hydroxide (2.33 g, 52.9 mmol) in water (34 ml) we added in portions with stirring over 45 min *p*-bromothiophenol (10 g, 52.9 mmol) and then dioxane (34 ml). After this over 2 h at room temperature we added 3-hydroxy-4-thiolene 1,1-dioxide (9.02 g, 52.9 mmol). The mixture was stirred for 2 h and was then concentrated to a third of the initial volume under vacuum. The precipitate was filtered off, washed with water (2×30 ml), and dried. The yield of the crude product was 15.68 g (92%); mp after threefold recrystallization from benzene, isopropyl alcohol, and trichloroethylene 122-124.5°C. The product formed colorless plates. Found, %: C 37.48; H 3.41; Br 24.36 S 19.64. $C_{11}H_{14}BrO_3S_2$. Calculated, %: C 37.16; H 3.43; Br 24.72; S 19.84.

3-Acetoxy-4-alkyl(aryl)thiothiolane 1,1-Dioxides 7a-e. We dissolved the respective hydroxy sulfide (20-30 mmol) in ten times the amount of acetyl chloride and left the solution at room temperature for 10-15 h. The excess of acetyl chloride was removed under vacuum, and the residue was purified either by recrystallization or by distillation at reduced pressure.

3-Acetoxy-4-alkyl(aryl)thio-2-thiolene 1,1-Dioxides 8a-e. To a 20-30% solution of the respective compound **7a-e** in methylene chloride we added dropwise with stirring an equimolar amount (up to a 10% excess) of sulfuryl chloride. The mixture was stirred at room temperature until the release of gas had stopped (2-3 h). The volatile products were removed under vacuum, and the residue was recrystallized. During storage without protection against atmospheric moisture the substances were converted into oily products of undetermined structure.

4-Alkyl(aryl)thio-3-oxothiolane 1,1-Dioxides 2. A. To a solution of the hydroxy sulfide **1a**,**b** (80 mmol) in methylene chloride (400 ml) with stirring and cooling (-10°C) we added sulfuryl chloride (80 mmol) in methylene chloride (90 ml) over 2 h 30 min. The mixture was stirred without cooling for a further 1 h, most of the solvent was removed at atmospheric pressure, the residue and the gaseous products were removed under vacuum (15 mm Hg), and the product was left overnight. The mixture was then again treated under vacuum until the heating had stopped and the gaseous products were released. A 30-ml portion of isopropyl alcohol was added to the residue, and the precipitate was separated, dried, and recrystallized. The yield was ~70%. An additional quantity of the product can be obtained by partial evaporation of the mother solution.

B. A sample of the acetate **8** was boiled with 10-20 times the amount of hydrochloric acid until the mixture was completely homogeneous (2-3 h). The product separated in the form of an oily liquid, which solidified with time. The solid substance was filtered off, washed with water, dried, and recrystallized from a suitable solvent.

4-Methylthio-3-oxo-4-thiolene 1,1-Dioxide (6a). To a solution of the oxo sulfide **2a** (5.4 g, 30 mmol) in methylene chloride (25 ml) with stirring and cooling (-10°C) we added sulfuryl chloride (4.05 g, 30 mmol) in methylene chloride (8 ml) over 45 min, after which the mixture was stirred without cooling for 3 h. The volatile products were removed under vacuum, and the residue was recrystallized from dichloroethane and then from isopropyl alcohol. Yield 0.34 g (63%); mp 174-176°C, and the product formed colorless prisms. IR spectrum, ν, cm^{-1}: 1152, 1316 (ν_{SO_2}); 1556 ($\nu_{C=C}$); 1720 ($\nu_{C=O}$). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 13.89 ($\underline{C}H_3$, q, $^1J_{CH}$ = 142.9); 56.29 ($\underline{C}H_2$, t, $^1J_{CH}$ = 149.5); 137.44 ($\underline{C}H$, d, $^1J_{CH}$ = 191.2); 153.0 (s, $\underline{C}$–S); 187.7 (s, $\underline{C}$=O). Found, %: S 35.55. $C_5H_6O_3S_2$. Calculated, %: S 35.98.

3-Oxo-4-phenylthio-4-thiolene 1,1-Dioxide (6b). To a solution of compound **1c** (3 g, 12.3 mmol) in methylene chloride (150 ml) at room temperature with cooling we added dropwise sulfuryl chloride (1.66 g) in methylene chloride (15 ml) over 2 h. The mixture was stirred for 2 h and left overnight. The next day isopropyl alcohol (15 ml) was added to the mixture, and the precipitate was filtered off, washed with the same solvent, and dried. After recrystallization from isopropyl alcohol 0.5 g of compound **6b** (17%) was obtained; mp 127-147°C. It gradually decomposed during storage. IR spectrum (0.1 M in methylene chloride), ν, cm^{-1}: 1146, 1328 (ν_{SO_2}); 1558 ($\nu_{C=C}$); 1732 ($\nu_{C=O}$). ^1H NMR spectrum (solution in acetone-d_6), δ, ppm: 4.30 (2H); 6.99 (1H); 7.59-7.64 (5H). ^{13}C NMR spectrum, δ, ppm: 57.285 (CH_2); 128.350, 132.000, 132.144, 176.120 (C_{arom}); 139.890, 139.926 (=CH); 153.534 (C–S); 188.572 (C=O).

3-O-Acyl-4-alkyl(aryl)thio-2-thiolene 1,1-Dioxides (9a-j). To a solution of the oxo sulfide **2** (~30 mmol) and an equimolar amount of acyl chloride in dioxane (15 ml) we added dropwise with stirring and without cooling an equivalent amount of triethylamine in dioxane (5 ml). The mixture was stirred at room temperature for 2 h and filtered, and the filtrate was evaporated under vacuum. The residue was recrystallized from a suitable solvent.

3-(N,N-Dimethylhydrazino)-2-thiolene 1,1-Dioxide (12b). To a solution of 3-oxothiolane 1,1-dioxide (5 g, 37.3 mmol) in methylene chloride (50 ml) with stirring at room temperature we added dropwise a solution of N,N-dimethylhydrazine (2.24 g, 37.3 mmol) in methylene chloride (10 ml). The mixture was stirred for 1 h and filtered. The filtrate was evaporated under vacuum, and the residue was recrystallized from dichloroethane. The product formed colorless prisms; mp 131-135°C. Yield 4.72 g (71.8%). An additional quantity of the product can be extracted by partial evaporation of the mother solution. ^{13}C NMR spectrum, δ, ppm: 98.35 (C-2); 152.353 (C-3); 39.979 (C-4); 57.03 (C-5); 10.457 (SCH_3); 6.522 ($N(CH_3)_2$). Found, %: S 17.94. $C_6H_{12}N_2O_2S$. Calculated, %: S 18.19.

3-(N,N-Dimethylhydrazino)-4-methylthio-2-thiolene 1,1-Dioxide (12a). Similarly to the previous method from the oxo sulfide **2a** (1.0 g) and N,N-dimethylhydrazine (0.36 g) we obtained the corresponding enehydrazine (0.2 g). The product formed slightly yellowish prisms; mp 111-114°C. ^{13}C NMR spectrum, δ, ppm: 95.133 (C-2); 154.389 (C-3); 24.752 (C-4); 49.632 (C-5); 48.712 ($N(CH_3)_2$). Found, %: S 28.46. $C_7H_{14}N_2O_2S_2$. Calculated, %: S 28.84. After prolonged storage the substance decomposes.

(2-Methylsulfonylethylsulfonyl)acetic Acid (16). A mixture of compound **2a** (0.27 g, 1.5 mmol) and 30% hydrogen peroxide (0.7 ml, 7.5 mmol) in glacial acetic acid (5 ml) was kept at room temperature for 3 days. The mixture was evaporated under vacuum, filtered, and washed with isopropyl alcohol. Yield 0.09 g; mp 164-165°C. IR spectrum, ν, cm^{-1}: 1120, 1304 (ν_{SO_2}), 1712 ($\nu_{C=O}$), 3108 (ν_{OH}). Found, %: C 26.59; H 4.00; S 27.50. $C_5H_{10}O_6S_2$. Calculated, %: C 26.08; H 4.38; S 27.85.

4-Methylsulfonyl-3-oxothiolane 1,1-Dioxide (17). To a solution of compound **2a** (0.5 g, 2.7 mmol) in anhydrous methylene chloride (10 ml) while stirring and cooling with iced water we added dropwise *m*-chloroperbenzoic acid (1.0 g, 5.8 mmol) in methylene chloride (17 ml) over 1 h. The mixture was stirred without cooling for 3 h 30 min. The precipitate was separated, washed with methylene chloride, dried, and recrystallized from dichloroethane. Yield 0.2 g (34%); mp 164-166°C. IR spectrum, cm^{-1}: 1123, 1145, 1308, 1332 (ν_{SO_2}); 1750 ($\nu_{C=O}$). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 42.00 (CH_3); 50.85, 59.23 (C_2, C_6); 70.13 (C_3); 193.81 (C_4). Found, %: C 28.26; H 4.07; S 30.28. $C_5H_8O_5S_2$. Calculated, %: C 28.30; H 3.80; S 30.21.

4-Hydroxyimino-3-methylthiothiolane 1,1-Dioxide (13a). A mixture of compound **17** (5.4 g, 30 mmol), hydroxylamine hydrochloride (6.25 g, 90 mmol), and sodium acetate (7.38 g, 90 mmol) in 2-propanol (125 ml) was boiled for 5 h. After cooling the reaction mixture was evaporated to dryness under vacuum, water (5 ml) was added to the residue, the mixture was filtered, and the product was dried and recrystallized from 2-propanol. Yield 3.4 g. A further 0.5 g of the substance was isolated by extraction of the aqueous filtrate with ethyl acetate. The total yield 67%. IR spectrum, cm^{-1}: 1140, 1320 (ν_{SO_2}), 32.60 (ν_{OH}). Found, %: C 31.17; H 4.66; N 7.32; S 32.73. $C_5H_9NO_3S_2$. Calculated, %: C 30.80; H 4.60; N 7.20; S 32.80.

3-Hydroxyimino-4-methylsulfonylthiolane 1,1-Dioxide (14). A mixture of the oxime **13a** (2 g, 10 mmol), 30% hydrogen peroxide (2.5 ml, 25 mmol), and acetic acid (30 ml) was stirred at 70°C for 3 h. The reaction mixture was evaporated to dryness under vacuum, and the residue was recrystallized from ethanol. Yield 1.0 g (43%); mp 193-196°C (decomp.). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 46.62 (CH_3, $^1J_{CH}$ = 136.7); 53.42 (C_2, $^1J_{CH}$ = 147.6); 52.54 (C_5, $^1J_{CH}$ = 146.3); 64.74 (C_3, $^1J_{CH}$ = 144.9); 146.32 (C_4). Found, %: N 6.06; S 27.93. $C_5H_9NO_5S_2$. Calculated, %: N 6.16; S 27.92.

3-Acetoxyimino-4-methylthiothiolane 1,1-Dioxide (15). To a solution of the oxime **13a** (2.0 g, 10 mmol) and acetyl chloride (0.83 g, 11 mmol) in dioxane (40 ml) with stirring and cooling with iced water we added triethylamine (1.06 g, 11 mmol) in dioxane (15 ml) over 30 min. The mixture was stirred at room temperature for 2 h and filtered. the filtrate was evaporated under vacuum, and the residue was recrystallized from methanol. Yield 1.56 g (64%); mp 103-105°C, and the product formed colorless prisms. Found, %: N 6.28; S 26.85. Calculated, %: N 6.90; S 27.02.

3-Alkoxyimino-4-methylthiothiolane 1,1-Dioxides (13b-g). A mixture of compound **2a** (12.0 mmol), the respective O-alkylhydroxylamine hydrochloride (15.0 mmol), and sodium acetate (15.0 mmol) in 2-propanol (30 ml) was boiled for 5 h. The solvent was distilled under vacuum, and water (15 ml) was added to the residue. The mixture was filtered, and the product was washed with water, dried, and recrystallized from alcohol.

3-[N-Alkyl(aryl)carbamoyloxyimino-4-methylthiothiolane 1,1-Dioxide (18). To a solution of the oxime **13a** (1.0 g) in dioxane (15 ml) we added an equimolar amount of the respective isocyanate and 2-3 drops of tin dibutyldiacetate, and we left the mixture overnight. The residue in the form of a slightly colored viscous mass was crystallized by rubbing with 2-propanol or ether. The aromatic carbamoyloximes were purified by recrystallization, and the aliphatic compounds were obtained in the analytically pure state after washing with ether. The latter decompose after prolonged storage.

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