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Dedicated to Full Member of the Russian Academy of Sciences M.G. Voronkov on the 80th Anniversary of His Birth

Reactions of 2-Alkoxypropenals with Thiols in Neutral and Acid Media*

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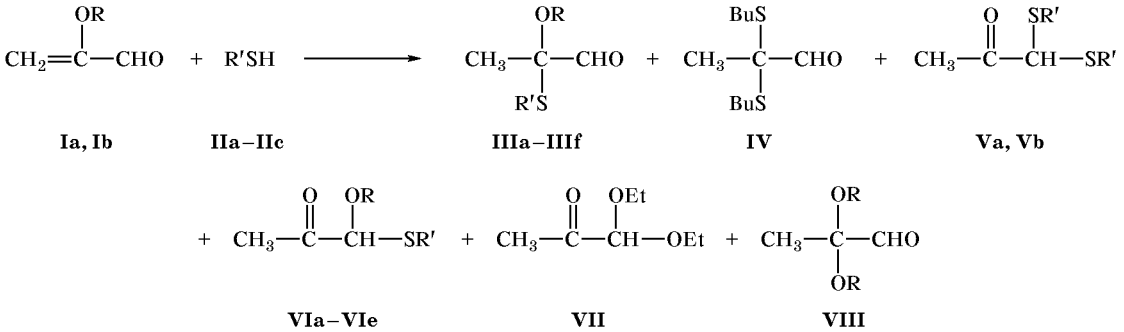
Abstract—Addition of thiols to 2-alkoxypropenal in neutral medium at 20°C in the absence of a catalyst occurs regioselectively, following the Markownikoff pattern. The resulting 2-alkoxy-2-R-thiopropanals are capable of undergoing spontaneous isomerization to 1-alkoxy-1-R-thiopropanones. The addition and isomerization processes are accelerated by heating to 60°C or in the presence of acid catalysts (TsOH, HCl). The reaction is also accompanied by partial disproportionation of 2-oxopropanal *O,S*-acetals to give *O,O*- and *S,S*-acetals.

Biochemical activity of α,β-unsaturated carbonyl compounds is explained by nucleophilic addition at the double bond of thiol groups of some enzymes, coenzymes, and mercapto amino acids [1]. Just that reaction is responsible for biological activity of acrylic compounds having an alkoxy group in the α-position [2].

With the goal of establishing the regioselectivity of the reaction of 2-alkoxypropenals with thiols under various conditions, in the present work we examined their reactions in neutral and acid media at room temperature and on heating. It is known that acrolein reacts with methanethiol with heat evolution even in the absence of a catalyst to afford 3-(methylthio)propanal in 94–99% yield [3]. Michael addition of butanethiol [4] and benzenethiol [5] occurs also readily. Unlike acrolein, the reaction of α-ethoxyacrolein with butanethiol at 20°C is very slow, and

Scheme 1.



Ia, Ib **IIa–IIc** **IIIa–IIIf** **IV** **Va, Vb** **VIa–VIe** **VII** **VIII**

I, R = Et (**a**), Me (**b**); **II**, R′ = Bu (**a**), CH_2=$CHCH_2$ (**b**), Ph (**c**), $PhCH_2$ (**d**); **III**, R = Et, R′ = Bu (**a**), CH_2=$CHCH_2$ (**b**), Ph (**c**), $PhCH_2$ (**d**); R = Me, R′ = Bu (**e**), Ph (**f**); **V**, R′ = Bu (**a**), Ph (**b**); **VI**, R = Et, R′ = Bu (**a**), CH_2=$CHCH_2$ (**b**), Ph (**c**), $PhCH_2$ (**d**); R = Me, R′ = Ph (**e**).

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Reactions of 2-alkoxypropenals with thiols at 20°C

Run no.	Initial compounds	Solvent (catalyst, mol %)	Time, days	Composition of the reaction mixture,[a] mol %				
				IIIa–IIIf	**IV**	**Va, Vb**	**VIa–VIe**	**VII**
1	**Ia** + **IIa**	–	5	75	10	5		
2	**Ia** + **IIb**	–	4	53			7	
3	**Ib** + **IIa**	–	17	50				
4	**Ia** + **IIc**	–	7	100				
5	**Ib** + **IIc**	–	17	33			22	
6	**Ia** + **IId**	–	5	77			10	
7	**IIIc**	–	55	78		11	11	1[b]
8[c]	**IIIa**	$CDCl_3$	3 h	54		16	30	1[b]
9[c]	**IIIa**	$CDCl_3$	5 h			40	40	1[b]
10[c]	**IIIc**	$CDCl_3$	3 h			25	50	1[b]
11[c]	**IIIc**	–	3 h	10		49	40	2[b]
12	**IIIa**	(TsOH, 1)	1			14	71	14
13	**IIIc**	(TsOH, 1)	1	10		6	70	4
14	**Ia** + **IIa**	(HCl, 1)	2	18		20	57	6[b]
15	**Ia** + **IIa**	(TsOH, 1)	6	14	42		42	
16	**Ia** + **IIa**	Et_2O (TsOH, 0.5)	6[d]	80	10			
17	**Ia** + **IIc**	(TsOH, 5)	5	20		20	60	
18[e]	**Ia** + **IIa**	Et_2O (TsOH, 5)	7		22	11	67	
19[e]	**Ia** + **IIc**	Et_2O (TsOH, 5)	7	46		19	35	
20	**VII** + **IIc**	–	5				70	29
21	**VII** + **IIa**	–	5				80	14

[a] According to the ^{1}H NMR data.
[b] According to the GC–MS data.
[c] At 60°C.
[d] Compound **VIII**, 10 mol %, was identified by GC–MS.
[e] Reactant ratio **I**:**II** = 1:1.5.

almost no change could be observed over the first 24 h [6]. Therefore, in the previous studies the mixture was heated (90°C, 11 h), and 2-butylthio-2-ethoxypropanal was then isolated in 30% yield.

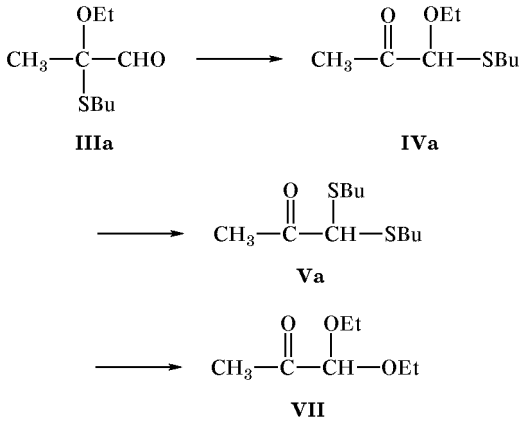
We now performed ^{1}H NMR monitoring of the reactions of 2-alkoxypropenals with thiols at 20°C. Even at that temperature and in the absence of a catalyst the addition follows the Markownikoff rule, and the yields of 2-alkoxy-2-R-thiopropanals **III** attain 50–100% in several days (see table, run nos. 1–6; Scheme 1).

Examination of the product mixtures by GC–MS showed that in the reaction of 2-ethoxypropenal (**Ia**) with butanethiol (**IIa**), apart from the major adduct **IIIa**, products of its disproportionation, 2,2-bis(butylthio)propanal (**IV**) and 1,1-bis(butylthio)-2-propanone (**Va**), were formed (run no. 1). The addition of benzenethiol to 2-ethoxypropenal at 20°C in the absence of a catalyst is regioselective, and 2-ethoxy-2-phenylthiopropanal (**IIIc**) is formed in quantitative yield (run no. 4). On storage, the latter gradually undergoes isomerization to 1-ethoxy-1-phenylthio-2-propanone (**VIc**) (run no. 7). Another minor isomerization product is 1,1-bis(phenylthio)-2-propanone (**Vb**); presumably, it appears as a result of disproportionation of monothioacetal (**VIc**). After storage of this mixture for 2 months at room temperature, the ratio **IIIc**:**VIc**:**Vb** became 8:1:1. One more disproportionation product, acetal **VII**, was difficult to detect by ^{1}H NMR spectroscopy, but it was identified by GC–MS. The formation of acetals **Va**, **Vb**, and **VIc** prompted us to investigate their origin and determine the sequence and the rate of thiol attack on particular reaction centers of the substrate. Compounds **Va**, **Vb**, and **VIc** are structurally related to 2-oxopropenal thioacetals which play an important role in biochemical transformations of the glyoxalase enzymatic system in cells of all living bodies [7].

A possible way of formation of dithioacetals **V** via thioacetalization of initial aldehyde **I** and subsequent hydrolysis of the vinyloxy group with liberated water was ruled out, for the reactions were carried out in the absence of acids. Moreover, in none of the experiments intermediate product having a vinyloxy group was detected.

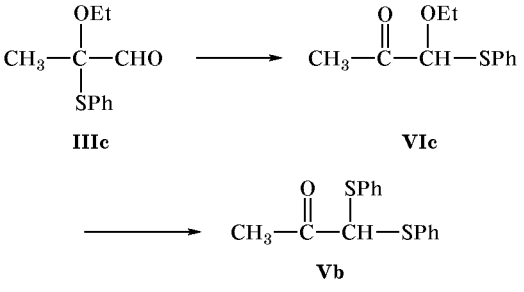
We have found that heating of pure monothioacetal **IIIa** in $CDCl_3$ results in its spontaneous isomerization into thermodynamically more stable 1-butylthio-1-ethoxy-2-propanone (**VIa**). Partial disproportionation of the latter gives rise to dithioacetal **Va** and 1,1-diethoxy-2-propanone (**VII**) (run no. 8, Scheme 2).

Scheme 2.



Further heating of the reaction mixture leads to complete transformation of monothioacetal **IIIa** to dithioacetals **VIa** and **Va** at a ratio of 1:1 (run no. 9). Analogous reaction sequence was observed on heating of pure monothioacetal **IIIc** having an aromatic group (run no. 10, Scheme 3).

Scheme 3.



In the reactions with arenethiols considerable amounts (8–30%) of diaryl disulfides are formed as a result of thermally induced radical decomposition of aryl thioacetals and subsequent combination of $ArS^{\cdot}$ radicals.

The rate of isomerization of sulfur-containing compounds sometimes depends on the solvent nature [8]. Therefore, we specially examined thermal isomerization of *S*,*O*-acetal **IIIc** in the absence of a solvent (run no. 11). After heating for 3 h at 60°C, the ratio **IIIc**:**VIc**:**Vb** was equal to 1:4:5. In this case the degree of isomerization of monothioacetal **IIIc** is slightly lower than in $CDCl_3$ (cf. run no. 10), as follows from the fact that a small amount of initial compounds **IIIc** remains unchanged; the degree of disproportionation of *S*,*O*-acetal **VIc** is twice as high. It should be emphasized that both reactions occur in the absence of a solvent and catalyst.

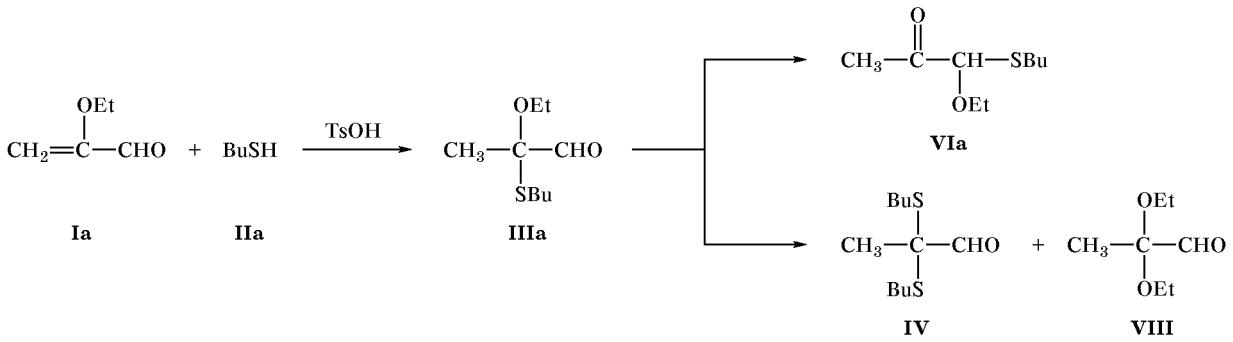
The isomerization of individual *S*,*O*-acetals **III** in the presence of catalytic amounts of acids occurs even more readily than on heating. By the action of *p*-toluenesulfonic acid (1 mol %) acetals **IIIa** and **IIIc** are converted into acetals **VI**, **V**, and **VII** in 24 h at 20°C (run nos. 12 and 13). Here, the major products are *O*,*S*-acetals **VIa** and **VIc**. The ratio **VIa**:**Va**:**VII** is 5:1:1. The ratio of 1-ethoxy-1-phenylthio-2-propanone (**VIc**) to products of its isomerization **Vb** and **VII** is equal to 14:1:1, the fraction of diphenyl disulfide reaching 10% (run no. 13).

In order to accelerate the Markownikoff addition of butanethiol (**IIa**) to 2-ethoxypropenal (**Ia**), a catalytic amount of hydrochloric acid (1 mol %) was added to an equimolar mixture of the reactants (run. no. 14). The reaction was exothermic. According to the ^1H NMR data, after 48 h, the molar ratio **IIIa**:**VIa**:**Va** was 1:3:1. These data indicate that hydrochloric acid not only accelerates primary addition at the double bond but also strongly favors isomerization of 2-butylthio-2-ethoxypropanal (**IIIa**) into 1-butylthio-1-ethoxy-2-propanone (**VIa**) whose disproportionation yields dithioacetal (**Va**). On the other hand, the latter can also be formed (in the presence of an acid) via direct thioacetalization of the initial aldehyde and hydrolysis of the vinyloxy group.

p-Toluenesulfonic acid as catalyst acts somewhat differently. Addition of a catalytic amount (1 mol %) of TsOH to an equimolar mixture of reactants **Ia** and **IIa** leads to formation of *O*,*S*-acetal **IIIa** which undergoes (during the process; 6 days, 20°C) both isomerization to monothioacetal **VIa** and appreciable disproportionation to 2,2-bis(butylthio)propanal (**IV**) and 2,2-diethoxypropanal (**VIII**) (Scheme 4, run no. 15). No formation of compounds **IV** was observed for aromatic derivatives.

The reaction between compounds **Ia** and **IIa** in diethyl ether, catalyzed by TsOH (run no. 16), is more selective. Here, monothioacetal **IIIa** is formed in

Scheme 4.

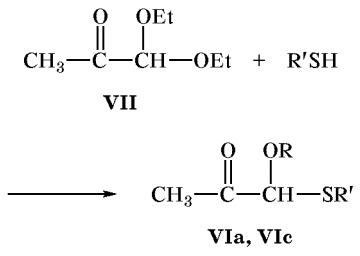


80% yield; in addition, disproportionation products **IV** and 2,2-diethoxypropanal (**VIII**) were detected.

The addition of benzenethiol (**IIc**) to an equimolar amount of 2-ethoxypropenal was carried out in the presence of 5 mol % of TsOH. After 5 days, a mixture of acetals **IIIc**, **VIc**, and **Vb** was obtained (run no. 17). The yield of semithioacetal **VIc** may be raised to 70% by performing the reaction for 3 h at 50°C. In order to increase the yield of dithioacetals **Va** and **Vb**, the reactions of 2-ethoxypropenal with butanethiol and benzenethiol were carried out at a substrate-to-reagent molar ratio of 1:1.5 with a considerable amount of the catalyst (TsOH, 5 mol %) in diethyl ether at 20°C (reaction time 7 days; runs nos. 18 and 19). However, no significant increase in the product yield was attained. This result indirectly indicates that dithioacetals **Va** and **Vb** are not formed by direct condensation at the aldehyde group with subsequent hydrolysis of the vinyloxygroup. Presumably, these products appear as a result of some reaction sequence (see Schemes 2 and 3) which inhibits the effect of excess reagent on the formation of dithioacetal **V**.

The structure of compounds **VIa** and **VIc** was proved by independent synthesis from 1,1-diethoxy-2-propanone (**VII**) and the corresponding thiols (Scheme 5). The yields of mixed acetals **VIa** and **VIc** attain 70–80% (runs nos. 20 and 21) when the reactions were carried out at room temperature in the presence of 4-Å molecular sieves as catalyst and ethanol acceptor.

Scheme 5.



Our results convincingly showed that *O,S*-acetals **III** derived from 2-oxopropanal are capable of undergoing spontaneous isomerization into *O,S*-acetals **VI**. The transformation is accelerated by heating or adding an acid catalyst.

Some examples of deacetalization of ketone acetals with other ketones are known, but these reactions occur intermolecularly in the presence of acids [9]. Removal of monothioacetal protection from α-dicarbonyl compounds having a ketone and an aldehyde group (which exchange RS and RO groups) has not been reported. However, the reaction of 2-chloro-2-phenylthio aldehydes with methanol is known to give 1-methoxy-1-phenylthio-2-alkanones rather than the expected ketone acetals [10]. It should be noted that the above reaction occurred in the presence of an equimolar amount of hydrogen chloride, i.e., under conditions of acid catalysis.

Analysis of the transformations of ketone *O,S*-acetals **III** to *O,S*-acetals **VI** led us to conclude that the mechanism of catalytic effect of acids involves intermolecular transfer of RO and RS fragment between the reacting centers (isomerization and disproportionation). Also, we can presume that in the absence of a catalyst the isomerization of α-formylketone monothioacetals into α-oxoaldehyde monothioacetals occurs intramolecularly.

The high yields of *O,S*-acetals **III** and **VI** and also dithioacetals **V** suggest that some experimental conditions can be utilized in preparative syntheses of such compounds. Previously, some of these were obtained from α-alkyl(aryl)thio-α-chloromethylketones [10, 11] or could be obtained from 2,2-dichloropropanal [12] or, probably, by methylation of enamines derived from bis(ethylthio)acetaldehyde [13].

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$ using HMDS as internal reference. The IR spectra were

measured on a Specord 75IR instrument. Gas chromatographic–mass spectrometric analysis was performed on an HP 5971A mass-selective detector (70 eV) coupled with an HP 5890 chromatograph; Ultra-2 column (5% of phenylmethylsilicone), injector temperature 250°C, oven temperature 70–280°C (at 20 deg/min), carrier gas helium.

Reaction of 2-ethoxypropenal (Ia) with butanethiol (IIa). *a.* (See table, run no. 1). Butanethiol, 0.436 g (4.85 mmol), was added to 0.48 g (4.85 mmol) of 2-ethoxypropenal stabilized by 0.001 g of hydroquinone. The mixture was kept for 5 days at 20°C, and the substrate disappearance was monitored by ^{1}H NMR spectroscopy.

b. (Run nos. 8 and 9). A half of the reaction mixture obtained as described in *a* was diluted with a twofold volume of $CDCl_3$, and the mixture was refluxed for 3 h.

c. (Run no. 12). *p*-Toluenesulfonic acid, 0.004 g (1 mol %), and hydroquinone, 0.001 g, were added to a half of the reaction mixture obtained in run no. 1. The mixture was kept for 24 h at room temperature.

Reaction of 2-ethoxypropenal (Ia) with benzenethiol (IIc) (run no. 4). Hydroquinone, 0.001 g, and benzenethiol, 0.53 g (4.85 mmol), were added to 0.45 g (4.85 mmol) of 2-etoxypropenal (**Ia**). After 7 days, the yield of acetal **IIIc** was quantitative; purity 95.5% (GC–MS).

Thermal decomposition of 2-ethoxy-2-(phenylthio)propanal (IIIc). A mixture of 0.5 ml of acetal **IIIc** and 1 ml of $CDCl_3$ was refluxed for 3 h, the composition of the mixture being monitored by ^{1}H NMR spectroscopy (run no. 10). Taking into account that chloroform can contain traces of HCl which catalyzes the isomerization, pure acetal **IIIc** was also heated for 3 h (without a solvent; run no. 11).

Isomerization of 2-ethoxy-2-(phenylthio)propanal by the action of *p*-toluenesulfonic acid (run no. 13). *p*-Toluenesulfonic acid, 0.008 g (1 mol %), and hydroquinone, 0.001 g, were added to 0.5 ml of acetal **IIIc**.

Reaction of 2-ethoxypropenal with butanethiol in the presence of acids. *d.* (Run no. 14). Butanethiol, 0.87 g (1.04 ml, 9.7 mmol), and concentrated hydrochloric acid, 1 drop (1 mol %), were added to 0.97 g (9.7 mmol) of 2-ethoxypropenal (**Ia**). The mixture spontaneously warmed up to 50°C and was kept at 20°C.

e. (Run no. 15). Butanethiol, 0.87 g (1.04 ml, 9.7 mmol), *p*-toluenesulfonic acid, 0.016 g (1 mol %), and freshly calcined 4-Å molecular sieves, 3 g, were added to 0.97 g (9.7 mmol) of 2-ethoxypropenal (**Ia**). Heat evolution was observed, and the mixture was kept at 20°C.

f. (Run no. 16). Butanethiol, 3.81 g (4.54 ml, 42.4 mmol), *p*-toluenesulfonic acid, 0.04 g (0.5 mol %) in 2 ml of ether, and freshly calcined 4-Å molecular sieves, 3 g, were added to a solution of 4.24 g (42.4 mmol) of 2-ethoxypropenal (**Ia**) in 31 ml of ether. Heat evolution was observed, and the mixture was kept for 6 days at 20°C.

Reaction of 2-ethoxypropenal (Ia) with benzenethiol in the presence of *p*-toluenesulfonic acid. A mixture of 0.485 g (4.85 mmol) of aldehyde **Ia**, 0.5 ml (4.85 mmol) of benzenethiol, 0.04 g (5 mol %) of TsOH, and 2 g of 4-Å molecular sieves was kept for 5 days at 20°C (run no. 17). When the same mixture containing 0.001 g of hydroquinone instead of 4-Å molecular sieves was heated for 3 h at 50°C, the yield of semithioacetal **VIc** was 70% (according to the ^{1}H NMR data).

Reaction of 2-ethoxypropenal (Ia) with excess thiols. Butanethiol, 2.91 mmol (run no. 18), or benzenethiol (run no. 19), *p*-toluenesulfonic acid, 0.0025 g (5 mol %), and hydroquinone, 0.001 g, were added to a solution of 0.2 g (1.94 mmol) of compound **Ia** in 2 ml of ether.

Reaction of 1,1-diethoxy-2-propanone (VII) with thiols. Benzenethiol, 4.85 mmol (run no. 20), or butanethiol (run no. 21), and 4-Å molecular sieves, 3 g, were added to 0.7 g (4.85 mmol) of acetal **VII**.

Below are given the propeties of the compounds prepared.

2-Butylthio-2-ethoxypropanal (IIIa) was obtained in run no. 16 by neutralization of the catalyst with potassium carbonate, removal of the solvent, and vacuum distillation. Yield 4.48 g (56%), bp 67°C (1 mm), n_D^{20} = 1.4640. ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3 in Bu, ^3J = 7.3 Hz), 1.26 t (3H, CH_3 in Et), 1.35 m (2H, C**H**$_2$CH$_3$ in Bu), 1.45 m (2H, SCH_2CH_2), 1.53 s (3H, CH_3CO), 2.35 t (2H, SCH_2, ^3J = 7.35 Hz), 3.55 d.q and 3.77 d.q (2H, OCH_2, ^2J = 9.09, ^3J = 7.04 Hz), 9.07 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 190 (1) M^+, 161 (100) $[M-CHO]^+$, 133 (45) $[M-Bu]^+$, 101 (14) $[M-SBu]^+$, 73 (46), 59 (24). 43 (78). IR spectrum (film), ν, cm^{-1}: 2955 s, 2925 s, 2870, 2820, 1725 v.s (C=O), 1445, 1380, 1200, 1145–1155, 1100, 1070, 1045 s. Found, %: C 57.60; H 9.70; S 16.48. $C_9H_{18}O_2S$. Calculated, %: C 56.80; H 9.53; S 16.85.

2-Allylthio-2-ethoxypropanal (IIIb) (run no. 2). ^{1}H NMR spectrum, δ, ppm: 1.27 t (3H, CH_3 in Et, ^3J = 7.0 Hz), 1.53 s (3H, CH_3), 3.06 d.d (2H, SCH_2, J = 6.5 Hz), 3.58 d.q and 3.80 d.q (2H, OCH_2, ^2J =

9.0, ^3J = 7.0 Hz), 5.06 d (1H, CH_2=, ^3J = 9.6 Hz), 5.16 d (1H, CH_2=, ^3J = 16.8 Hz), 5.58 d.d.t (1H, CH=, ^3J = 16.8, ^3J = 9.6, ^3J = 6.5 Hz), 9.12 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 145 (88) [*M*–CHO]$^+$, 129 (2) [*M*–OEt]$^+$, 117 (3), 101 (15) [*M*–SCH_2–CH=CH_2]$^+$, 75 (32), 73 (71) [SCH_2–CH=CH_2]$^+$, 59 (18) (CH_3CS), 45 (62) [OEt]$^+$, 43 (100) [CH_3CO]$^+$.

2-Ethoxy-2-(phenylthio)propanal (IIIc) was isolated by vacuum distillation of the reaction mixture obtained in run no. 4. bp 120–124°C (3 mm), n_D^{22} = 1.5560. ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, OCH_2CH_3, ^3J = 7.0 Hz), 1.55 s (3H, CH_3CO), 3.7 d.q (1H, OCH_2, ^2J = 7.3, ^3J = 7.0 Hz), 4.05 d.q (1H, OCH_2, ^2J = 7.3, ^3J = 7.0 Hz), 7.29 m (3H, *p*-H, *m*-H), 7.43 d (2H, *o*-H, ^3J = 8.0 Hz), 9.17 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.06 (CH_3), 19.44 (CH_3), 58.81 (CH_2), 128.92 (C^p), 128.87 (C^o), 135.42 (C^m), 193.47 (CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 210 (1) M^+, 181 (100) [*M*–CHO]$^+$, 165 (2) [*M*–OEt]$^+$, 153 (8), 137 (3), 123 (6), 110 (50) [HSPh]$^+$, 109 (66) [SPh]$^+$, 101 (34) [*M*–SPh]$^+$, 73 (100), 65 (43), 45 (67) [OEt]$^+$, 43 (70). Found, %: C 62.64; H 6.3; S 15.66. $C_{11}H_{14}O_2S$. Calculated, %: C 62.83; H 6.71; S 15.25.

2-Benzylthio-2-ethoxypropanal (IIId) (run no. 6). ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, CH_3 in Et, ^3J = 7.0 Hz), 1.54 s (3H, CH_3), 3.71 d.q and 3.78 d.q (2H, OCH_2, ^2J = 9.0, ^3J = 7.0 Hz), 7.24 m (5H, Ph), 9.09 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 195 (49) [*M*–CHO]$^+$, 179 (1) [*M*–OEt]$^+$, 167 [*M*–$CHOC_2H_5$]$^+$ (1), 123 (3) [*M*–SCH_2Ph]$^+$, 108 (1), 101 (3) [*M*–SCH_2Ph]$^+$, 91 (100) [$PhCH_2$]$^+$, 77 (9) [Ph]$^+$, 73 (27), 59 (7), 45 (44) [C_2H_5]$^+$.

2-Butylthio-2-methoxypropanal (IIIe) (run no. 13). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3 in Bu), 1.39 m (2H, C**H**$_2$$CH_3$), 1.50 s (3H, CH_3), 1.55 m (2H, C**H**$_2$$CH_2S$), 2.53 m (2H, SCH_2), 3.40 s (3H, OCH_3), 9.06 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 147 (100) [*M*–CHO]$^+$, 91 (73), 87 (32), 73 (3), 59 (93), 43 (47).

2-Methoxy-2-(phenylthio)propanal (IIIf) (run no. 5). ^{1}H NMR spectrum, δ, ppm: 1.56 s (3H, CH_3), 3.59 s (3H, OCH_3), 7.28 m and 7.41 m (5H, Ph), 9.15 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 196 (27) [*M*]$^+$, 167 (16) [*M*–CHO]$^+$, 152 (1) [PhSCOMe]$^+$, 135 (100) [*M*–CHO–MeOH], 123 (60), 110 (74) [PhSH]$^+$, 109 (60) [PhS]$^+$, 91 (12), 77 (16), 65 (25), 59 (11), 45 (35), 39 (12).

2,2-Bis(butylthio)propanal (IV) (run no. 1). ^{1}H NMR spectrum, δ, ppm: 0.89 t (6H, CH_3 in Bu), 1.4 m (2H, SCH_2CH_2C**H**$_2$), 1.55 m (2H, SCH_2C**H**$_2$), 1.63 s (3H, CH_3), 2.5 m (2H, SCH_2), 9.05 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 234 (1) M^+, 205 (100) [*M*–CHO]$^+$, 149 (11), 103 (7), 93 (10), 59 (74), 41 (30), 29 (42) [CHO]$^+$.

1,1-Bis(butylthio)-2-propanone (Va) (run no. 9). ^{1}H NMR spectrum, δ, ppm: 0.9 t (6H, CH_3 in Bu), 1.4 m (4H, SCH_2CH_2C**H**$_2$), 1.53 m (4H, SCH_2C**H**$_2$), 2.35 s (3H, CH_3), 2.35 m (4H, CH_2S), 5.28 s (1H, SCHS). Mass spectrum, *m*/*z* (I_{rel}, %): 234 (1) M^+, 205 (2) [*M*–CHO]$^+$, 191 (100), 135 (27), 89 (6) [SBu]$^+$, 79 (21), 43 (81), 41 (37).

1,1-Bis(phenylthio)-2-propanone (Vb) (run no. 11). ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, CH_3), 5.45 s (1H, SCHS), 7.29 m and 7.44 m (10H, Ph). Mass spectrum, *m*/*z* (I_{rel}, %): 231 (41) [*M*–CH_3CO]$^+$, 165 (28) [*M*–SPh]$^+$, 121 (46), 109 (41) [SPh]$^+$, 77 (31) [Ph]$^+$, 43 (100) [CH_3CO]$^+$, 28 (87) [CO]$^+$.

1-Butylthio-1-ethoxy-2-propanone (VIa) was obtained as described above in *e* (run no. 15) from 2.75 g (27.5 mmol) of 2-ethoxypropenal. The mixture was neutralized by passing it through a layer of potassium carbonate. The product was isolated by vacuum distillation. Yield 1.25 g (23%), bp 75°C (3 mm), n_D^{20} = 1.4510. ^{1}H NMR spectrum, δ, ppm: 0.84 t (3H, CH_3 in Bu, *J* = 7.3 Hz), 1.21 t (3H, CH_3 in Et, *J* = 7.0 Hz), 1.33 m (2H, C**H**$_2$$CH_3$ in Bu, ^3J = 7.5 Hz), 1.48 m (2H, SCH_2C**H**$_2$), 2.21 s (3H, CH_3CO), 2.45 m (2H, SCH_2), 3.45 d.q and 3.84 d.q (2H, OCH_2, ^2J = 9.0, ^3J = 7.0 Hz), 4.80 s (1H, CH). Mass spectrum, *m*/*z* (I_{rel}, %): 190 (1) M^+, 147 (69) [*M*–CH_3CO]$^+$, 119 (48) [*M*–CH_3CO–C_2H_4]$^+$, 101 (2), 91 (6), 73 (19), 57 (39), 43 (100) [CH_3CO]$^+$, 29 (58) [Et]$^+$, 27 (50). Found, %: C 56.62; H 9.52; S 16.11. $C_9H_{18}O_2S$. Calculated, %: C 56.84; H 9.47; S 16.85.

1-Ethoxy-1-phenylthio-2-propanone (VIc) was obtained by keeping the reaction mixture from run no. 17 for 3 h at 50°C, neutralization of the catalyst (K_2CO_3), and vacuum distillation. A considerable amount of diphenyl disulfide was formed during distillation. bp 120°C (2 mm), n_D^{20} = 1.5515. ^{1}H NMR spectrum, δ, ppm: 1.29 t (3H, OCH_2C**H**$_3$, ^3J = 7.0 Hz), 2.07 s (3H, CH_3CO), 3.54 d.q (1H, OCH_2, ^2J = 7.3 Hz, ^3J = 7.0 Hz), 4.05 d.q (1H, OCH_2, ^2J = 7.3, ^3J = 7.0 Hz), 5.03 s (1H, OCHS), 7.29 m and 7.44 m (5H, Ph). Mass spectrum, *m*/*z* (I_{rel}, %): 210 (4) M^+, 167 (100) [*M*–CH_3CO]$^+$, 139 (84) [*M*–CH_3CO C_2H_4]$^+$, 111 (65), 109 (40) [SPh]$^+$, 77 (41) [Ph]$^+$, 73 (26), 45 (69) [OEt]$^+$, 43 (85). Found, %: C 62.45; H 7.18; S 15.68. $C_{11}H_{14}O_2S$. Calculated, %: S 62.83; H 6.71; S 15.25.

1,1-Diethoxy-2-propanone (VII) (run no. 12). ^{1}H NMR spectrum, δ, ppm: 1.24 t (6H, $2CH_3$, ^3J =

7.0 Hz), 2.18 s (3H, CH_3CO), 3.69 q and 3.56 q (4H, *AB* system, $2OCH_2$, ^2J = 9.5, ^3J = 7.0 Hz), 4.52 s (1H, CH). Mass spectrum, *m*/*z* (I_{rel}, %): 103 (24) $[M-MeCO]^+$, 75 (31) $[M-MeCO-C_2H_4]^+$, 73 (29), 47 (100), 45 (42), 43 (89). The spectra of acetal **VII** were identical to those reported in [14]. Compounds **VIb**, **VId**, and **VIe** (runs nos. 2, 5, and 6, respectively), by analogy with *O*,*S*-acetals **VIa** and **VIb** were identified by the appearance of singlets in the regions 2.07–2.21 (CH_3CO) and 4.8–5.03 ppm [CH(OR)(SR)] with an intensity ratio of 3 : 1.

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