Russian Journal of Organic Chemistry, Vol. 41, No. 4, 2005, pp. 517–522. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 4, 2005, pp. 529–534.

Reaction of 2-Alkoxypropenals with 2-Aminoethanethiol and Ring–Chain Tautomerism of the Resulting 2-(1-Alkoxyvinyl)-1,3-thiazolidines

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Received July 9, 2004

Abstract—2-Alkoxypropenals react with 2-aminoethanethiol to give tautomeric mixtures of the corresponding 2-(1-alkoxyvinyl)-1,3-thiazolidines and 2-(2-alkoxy-2-propenylideneamino)ethanethiols in quantitative yield. The state of the ring–chain tautomeric equilibrium depends on the polarity and acidity of the medium and initial reactant ratio, and it does not change on raising the temperature and is only slightly affected by microwave irradiation.

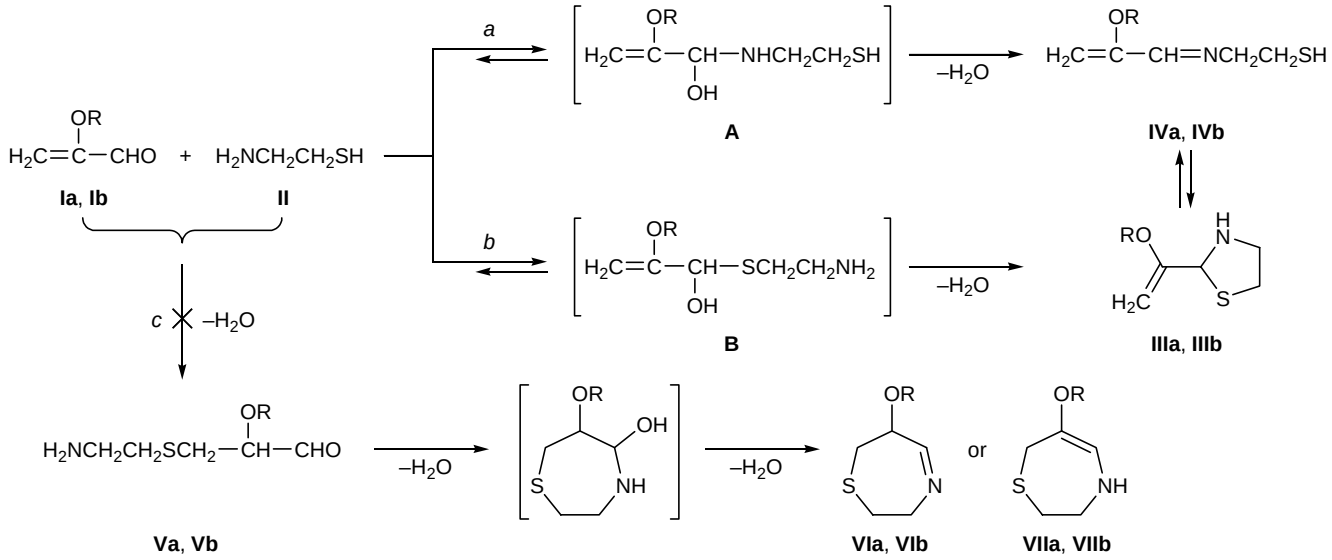
Functionalized thiols, such as 2-sulfanylethanol [1] and 1,2- and 1,3-dithiols [2], are known to add to 2-alkoxypropenals in neutral medium according to the Markownikoff rule to give methylglyoxal *O*,*S*-acetals. However, in the presence of bases (K_2CO_3, Et_3N) the addition of thiols to 2-alkoxypropenals occurs at the 1,4-positions with formation of 3-alkylsulfanyl-2-alkoxypropanals in 75–100% yield [3]. Primary amines react with 2-ethoxypropenal to afford Schiff bases [4]; as noted in [5], in the reaction of acrolein with nucleosides, the primary amino groups of cytosine and thymine can add to the 1,4-position. The above data suggest that nucleophilic attack on 2-alkoxypropenal can be directed at the double C=C bond or aldehyde group, depending on the nucleophile nature, catalyst, and reaction medium.

The goal of the present work was to elucidate regio- and chemoselectivity in the addition of a difunctional nucleophile, 2-aminoethanethiol (cysteamine [6]), to 2-alkoxypropenals, depending on the reaction conditions (solvent nature, polarity and acidity of the medium, temperature, microwave activation) and to study ring–chain tautomerism of the resulting Schiff bases and thiazolidines. A considerable interest in the chemistry [7] and pharmacology of thiazolidine derivatives [8, 9] stimulates studies on the synthesis of new compounds of this series. 2-Alkyl-1,3-thiazolidines are especially important, for they exhibit radioprotective and antimutagenic activity [6]. Furthermore, thiazolidine ring is a structural fragment of a number of natural compounds and biologically active substances [10]; therefore, studies on the dynamics of ring–chain equilibrium of thiazolidine derivatives are important for understanding biochemical processes [11].

The reactions of 2-alkoxypropenals **Ia** and **Ib** with 2-aminoethanethiol (**II**) were expected to follow pathway *a* (Scheme 1) which involves 1,2-addition of the amino group. Elimination of water from intermediate **A** could give rise to vinylthiazolidine **III** or Schiff base **IV**. Isomers **III** and **IV** are interconvertible; it is known that even in neutral aqueous medium thiazolidine ring exists in equilibrium with the open-chain iminothiol structure [12] or initial reagents (from which it was synthesized) [13]. An alternative initial stage is sometimes considered to be attack on the carbonyl carbon atom by the SH group of 2-aminoethanethiol with formation of monothio semiacetals (pathway *b*) [14]. This reaction sequence was observed in reactions of α,β-unsaturated ketones with β-amino thiols [15]. By analogy with the data of [3], one more reaction pathway may be 1,4-addition of the SH group in weakly basic medium (pathway *c*). The subsequent cyclization of adduct **V** could give rise to aminothiacyclohexenes **VI** and **VII**.

We found that 2-alkoxypropenals react with an equimolar amount of 2-aminoethanethiol, like with 2-aminoethanol [16], in the absence of a catalyst according to pathway *a*, via addition of the amino group

Scheme 1.



R = Et (**a**), Me (**b**).

to the carbonyl group. The progress of the reaction was monitored by ^{1}H NMR spectroscopy; the concentration of iminothiol **IV** in $CDCl_3$ was determined from the intensities of the singlet at δ 7.59 ppm (CH=N) and two doublets at δ 4.57 and 4.65 ppm (H_2C=); the thiazolidine ring clearly appeared as a singlet at δ 4.99 ppm from 2-H and two doublets at δ 4.02 and 4.26 ppm (H_2C=).

In order to eliminate the effect of liberated water, the reaction of 2-ethoxypropenal (**Ia**) with amino thiol **II** was carried out in the presence of 4-Å molecular sieves. The reaction occurred at room temperature and was accompanied by heat evolution (the mixture warmed up to 30–50°C). The complete conversion of the initial compounds was attained in 10 h in methylene chloride or in more than 24 h in benzene. According to the ^{1}H NMR data, the reaction mixture contained tautomers **IIIa** and **IVa** at a ratio of 2:1 in the first case, and 1.3:1, in the second. In chloroform in the presence of molecular sieves, the reaction rate was comparable with that in benzene. In all cases, by distillation of the mixture we succeeded in isolating only the cyclic tautomer. Presumably, the open-chain tautomer has a higher boiling point, and it undergoes tarring during distillation. Thiazolidines **IIIa** and **IIIb** isolated by distillation are stable at 20°C; after 16–20 days, no linear tautomer was detected by ^{1}H NMR spectroscopy in $CDCl_3$ or DMSO-d_6.

It is known that the state of the thiazolidine–iminothiol equilibrium depends on the solvent polarity [8]. In order to elucidate the effect of the solvent polarity on the tautomer ratio we performed the reaction in benzene, $CDCl_3$, CD_3OD, DMSO-d_6, and D_2O directly in an NMR ampule without binding the liberated water. The reaction in the absence of molecular sieves occurred at a considerably higher rate and was complete in 0.5–1 h in most solvents. After 3 h, the tautomer ratio **IIIa**:**IVa** was 2.5:1 ($CDCl_3$, ε = 4.81), 1.7:1 (CD_3OD, ε = 32.7), 1.3:1 (DMSO-d_6, ε = 46.45), and 1.35:1 (D_2O, ε = 78.3). In the recent years, the role of water as solvent in nucleophilic addition to carbonyl group is extensively revised [17]. A very strong acceleration of Michael addition reactions in going from nonpolar solvents to water was observed in [18]. In our case, liberated water is likely to strongly increase the polarity of the medium; therefore, the reaction rate increases.

The ratio of tautomers **III** and **IV** also depends on the initial reactant ratio. The reaction of aldehyde **Ia** in D_2O with 2 equiv of aminothiol **II** in 1 h gives only cyclic tautomer **IIIa** (yield 100%); after 3 h, the fraction of the linear tautomer rises, and the ratio **IIIa**:**IVa** becomes 1.35:1. Analogous shift of the equilibrium toward linear tautomer was observed in the reaction with excess aminothiol **II** in $CDCl_3$: after 1 h, the ratio **IIIa**:**IVa** was 7:1, after 5 days, 3.5:1, and after 12 days, 2:1. By contrast, in the presence of excess aldehyde **Ia** (D_2O), only iminothiol **IVa** was detected in the reaction mixture in 1 h. Presumably, these results are explained by variation of pH during the

process. As shown in [19] while studying the mechanism of formation of thiazolidine having no substituent on C^2, variation of pH could change the rate-determining stage.

The ^{1}H NMR spectrum of thiazolidine **IIIa** obtained by the reaction in D_2O differs from the spectrum of a sample of **IIIa** isolated by distillation and dissolved in D_2O. The latter contained two sets of signals **C** and **D**, the latter being located more upfield, with an intensity ratio of 2:1. The difference in the chemical shifts was $\Delta\delta \approx 0.1$–0.15 ppm. In the ^{1}H NMR spectrum of **IIIa**, recorded from the reaction mixture (which is alkaline due to excess 2-aminoethanethiol), all signals appeared in a stronger field ($\Delta\delta = 0.15$ ppm) relative to the corresponding signals of the predominant compound **C**. Insofar as unpurified D_2O has a pH value of ~5, we presumed that thiazolidine **IIIa** in such medium exists in two forms: as free base and ammonium salt with carbonate ion as counterion. To verify this assumption we performed the reaction of aldehyde **Ia** with aminothiol **II** in D_2O preliminarily passed through a layer of K_2CO_3. In fact, the ^{1}H NMR spectrum of the resulting thiazolidine contained only signal set **D**. The possibility for protonation of thiazolidine **IIIa** was checked as follows. A sample of distilled compound **IIIa** was dissolved in DMSO-d_6, and an equimolar amount of trifluoromethanesulfonic acid was added. In the ^{1}H NMR spectrum of the resulting solution, signals from all protons were displaced downfield by 0.1 ppm relative to their position before acidification. Analogous downfield shift of signals from the neighboring groups upon protonation of the amino group was observed previously [20].

When the reaction of ethoxypropenal **Ia** with 2-aminoethanethiol (**II**) was performed in benzene at 80°C in the absence of molecular sieves, the conversion reached 98% in 15 min, and the tautomer ratio **IIIa**:**IVa** was 1:1. After cooling, the tautomer ratio remained unchanged. The position of the tautomeric equilibrium (1:1) did not change when the reactants were heated in benzene at 80°C for 30 or 60 min. Open-chain tautomer **IVa** obtained in C_6D_6 in 100% yield in an NMR ampule remained intact on heating for 40 min at 80°C and subsequent cooling to 20°C. These data indicate that the tautomeric equilibrium **IIIa** $\rightleftharpoons$ **IVa** is not affected by temperature.

We also examined the effect of microwave irradiation with a view to change the reaction regioselectivity or accelerate formation of one of the tautomers. In the reactions performed under microwave activation (2–9 min, 20–40% of the maximal power, 750 W), regardless of the solvent (benzene, CH_2Cl_2, $CDCl_3$, or no solvent), the conversion of initial aldehyde **Ia** or **Ib** attained 71–100%. No appreciable effect of microwave irradiation on the tautomer ratio **III**:**IV** was observed, but the rate of the process increased 5–10-fold.

We also tried to minimize (or eliminate) the effect of autoprotolysis of aminothiol **II** by carrying out the reaction in triethylamine. At 20°C, the conversion was complete in 30 min, and the tautomer ratio **IIIa**:**IVa** was 1:1.6 (according to the ^{1}H NMR data, $CDCl_3$). After 48 h, the tautomer ratio changed to 1.1:1. In the reaction of ethoxypropenal **Ia** with thiol **II** in triethylamine under microwave activation, the conversion was 99% in 4 min (7-fold acceleration), and a mixture of cyclic and linear tautomers **IIIa** and **IVa** at a ratio of 1.67:1 was obtained. It should be noted that, in contrast to the data of [3], no products corresponding to pathway *c* were detected even when the reaction was carried out in triethylamine.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz for ^{1}H) using $CDCl_3$, DMSO-d_6, CD_3OD, and D_2O as solvents and HMDS as internal reference. The IR spectra were measured on a Specord IR75 instrument. Reactions under microwave activation were performed in an LG MS-1904H multivariant microwave furnace (700 W).

2-Alkoxypropenals **Ia** and **Ib** were prepared according to the procedure described in [21]. ^{1}H NMR spectrum of 2-ethoxypropenal (**Ia**) (D_2O), δ, ppm: 9.23 s (1H, CHO), 5.60 d (1H, $=CH_2$, ^2J = 3.07 Hz), 5.38 d (1H, $=CH_2$, ^2J = 3.07 Hz), 3.95 q (2H, OCH_2, ^3J = 7.0 Hz), 1.35 t (3H, CH_3, ^3J = 7.0 Hz).

Condensation of alkoxypropenals Ia and Ib with 2-aminoethanethiol (II). 2-Aminoethanethiol (**II**), 9.74 mmol, was added to a solution of 9.74 mmol of 2-alkoxypropenal **Ia** or **Ib** in 5 ml of appropriate solvent (benzene or chloroform). The mixture was kept for 1 h at 22°C, dried with $MgSO_4$, filtered from the drying agent, and evaporated under reduced pressure. Before distillation, the yield was determined by ^{1}H NMR spectroscopy. 2-(1-Alkoxyvinyl)thiazolidines **IIIa** and **IIIb** were isolated by vacuum distillation.

Reaction of 2-ethoxypropenal (Ia) with 2-aminoethanethiol (II). The ratio **IIIa**:**IVa** was 1.2:1 (30 min) and 1.1:1 (1 h), the conversion being 98%.

2-(1-Ethoxyvinyl)thiazolidine (IIIa). Yield 32% (after distillation), bp 87°C (2 mm), n_D^{20} = 1.5267. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.99 s (1H, SCHN), 4.26 d (1H, =CH_2, ^2J = 2.4 Hz), 4.02 d (1H, =CH_2, ^2J = 2.4 Hz), 3.82 q (2H, OCH_2, ^3J = 7.0 Hz), 3.56 m (1H, NCH_2), 2.99 m (2H, SCH_2), 2.90 m (1H, NCH_2), 1.31 t (3H, CH_3, ^3J = 7.0 Hz). Found, %: C 52.77; H 7.98; N 8.48; S 20.01. $C_7H_{13}NOS$. Calculated, %: C 52.79; H 8.23; N 8.80; S 20.14.

2-(2-Ethoxy-2-propenylideneamino)ethanethiol (IVa). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.59 t (1H, CH=N, ^4J = 1.1 Hz), 4.65 d (1H, =CH_2, ^2J = 2.3 Hz), 4.57 d (1H, =CH_2, ^2J = 2.3 Hz), 3.90 q (2H, OCH_2, ^3J = 7.0 Hz), 3.79 d.d.d (2H, NCH_2, ^3J = 7.0, ^4J = 1.1 Hz), 2.98 t (2H, SCH_2, ^3J = 7.0 Hz), 1.38 t (3H, CH_3, ^3J = 7.0 Hz).

In the presence of 4-Å molecular sieves as drying agent (in benzene), the conversion of aldehyde **Ia** was 75% in 16 h and 86% in 24 h.

The reaction of ethoxypropenal Ia with thiol II on heating was performed following the general procedure using 4 ml of benzene. The mixture was heated at 80°C for 30 or 60 min, cooled, and evaporated. According to the ^{1}H NMR data ($CDCl_3$), after 30 min, the ratio of tautomers **IIIa** and **IVa** was 1:1, and it remained unchanged after 60 min.

The reaction of methoxypropenal Ib with thiol II was performed following the general procedure. Overall yield 100%; tautomer ratio **IIIb**:**IVb** = 0.26:1.

2-(1-Methoxyvinyl)thiazolidine (IIIb). Yield 34% (after distillation), bp 94°C (4 mm), mp 50°C. IR spectrum (KBr), ν, cm^{-1}: 3210, 2930, 1650, 1610, 1450, 1300, 1280, 1180, 1170, 1050, 960, 920, 880, 820, 790. ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 4.99 s (1H, NCHS), 4.28 d (1H, =CH_2, ^2J = 2.5 Hz), 4.06 d (1H, =CH_2, ^2J = 2.5 Hz), 3.61 s (3H, OCH_3), 3.80 t (2H, NCH_2, J = 7.0 Hz), 2.98 t (2H, SCH_2, J = 7.0 Hz); in DMSO-d_6: 4.91 s (1H, NCHS), 4.24 d (1H, =CH_2, ^2J = 2.0 Hz), 3.98 d (1H, =CH_2, ^2J = 2.0 Hz), 3.50 s (3H, OCH_3), 3.20 m (1H, NCH_2), 2.96 m (1H, NCH_2), 2.76 m (2H, SCH_2). Found, %: C 49.79; H 7.82; N 10.12; S 21.82. $C_6H_{11}NOS$. Calculated, %: C 49.62; H 7.63; N 9.64; S 22.08.

2-(2-Methoxy-2-propenylideneamino)ethanethiol (IVb). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 7.72 s (1H, CH=N), 4.71 d (1H, =CH_2, ^2J = 2.5 Hz), 4.58 d (1H, =CH_2, ^2J = 2.5 Hz), 3.80 t (2H, NCH_2, J = 7.0 Hz), 3.69 s (3H, OCH_3), 2.99 t (2H, SCH_2, ^3J = 7.0 Hz); in DMSO-d_6: 7.75 s (1H, CH=N), 4.71 d (1H, =CH_2, ^2J = 2.2 Hz), 4.68 d (1H, =CH_2, ^2J = 2.2 Hz), 3.70 t (2H, NCH_2, ^3J = 6.4 Hz), 3.57 s (3H, OCH_3), 2.97 m (2H, SCH_2).

Reactions of alkoxypropenals Ia and Ib with 2-aminoethanethiol (II) in an NMR ampule. An NMR ampule was charged with 0.6 ml of appropriate solvent ($CDCl_3$, CD_3OD, DMSO-d_6, D_2O), 0.12 mmol of alkoxypropenal **Ia** or **Ib** and 0.12 mmol of 2-aminoethanethiol (**II**). The mixture was stirred, and the ratio of products **III** and **IV** was determined by ^{1}H NMR spectroscopy at definite time intervals.

a. In chloroform: after 3 h, the yield of **IIIa** and **IVa** was 97%, ratio **IIIa**:**IVa** = 2.5:1.

b. In DMSO-d_6: yield 100%, **IIIa**:**IVa** = 1.3:1 (after 3 h). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: **IIIa**: 4.90 s (1H, NCHS), 4.22 d (1H, =CH_2, ^2J = 1.8 Hz), 3.94 d (1H, =CH_2, ^2J = 1.8 Hz), 3.73 q (2H, OCH_2, ^3J = 7.0 Hz), 3.21 m (1H, NCH_2), 2.88 m (1H, NCH_2), 2.76 m (2H, SCH_2), 1.22 t (3H, CH_3, ^3J = 7.0 Hz); **IVa**: 7.72 s (1H, CH=N), 4.65 d (1H, =CH_2, ^2J = 1.8 Hz), 4.68 d (1H, =CH_2, ^2J = 1.8 Hz), 3.78 q (2H, OCH_2, ^3J = 7.2 Hz), 3.69 t (2H, NCH_2, ^3J = 6.6 Hz), 2.98 t (2H, SCH_2, ^3J = 6.6 Hz), 1.26 t (3H, CH_3, ^3J = 7.2 Hz).

c. In CD_3OD: yield 72%, **IIIa**:**IVa** = 1.7:1 (after 3 h). ^{1}H NMR spectrum (CD_3OD), δ, ppm: **IIIa**: 4.91 s (1H, NCHS), 4.24 d (1H, =CH_2, ^2J = 2.3 Hz), 4.03 d (1H, =CH_2, ^2J = 2.3 Hz), 3.86 q (2H, OCH_2, ^3J = 7.0 Hz), 2.91 m (1H, NCH_2), 2.85 m (3H, NCH_2, SCH_2), 1.29 t (3H, CH_3, ^3J = 7.0 Hz); **IVa**: 7.74 s (1H, CH=N), 5.00 s (1H, =CH_2), 4.86 s (1H, =CH2), 3.86 q (2H, OCH_2, ^3J = 7.2 Hz), 3.77 m (2H, NCH_2), 2.91 m (2H, SCH_2), 1.33 t (3H, CH_3, ^3J = 7.2 Hz).

d. In C_6D_6: The reaction of aldehyde **Ia** with 2-aminoethanethiol (**II**) at 20°C in 5 min afforded linear tautomer **IVa** in 100% yield. The composition of the reaction mixture did not changed on heating for 40 min at 80°C and subsequent cooling to 20°C. ^{1}H NMR spectrum (C_6D_6), δ, ppm: **IVa**: 7.42 s (1H, CH=N), 4.53 d (1H, =CH_2, ^2J = 2.0 Hz), 4.18 d (1H, =CH_2, ^2J = 2.0 Hz), 3.53 t (2H, NCH_2, ^3J = 6.2 Hz), 3.36 q (2H, OCH_2, ^3J = 7.0 Hz), 2.74 t (2H, SCH_2, ^3J = 6.2 Hz), 1.01 t (3H, CH_3, ^3J = 7.0 Hz).

e. In D_2O: The ^{1}H NMR spectrum of thiazolidine **IIIa** isolated by vacuum distillation and dissolved in D_2O contained two sets of signals **C** and **D** with an intensity ratio of 2:1.

2-(1-Ethoxyvinyl)thiazolidinium hydrocarbonate (C). ^{1}H NMR spectrum (D_2O), δ, ppm: 4.96 s (1H, NCHS), 4.32 d (1H, =CH_2, ^2J = 2.0 Hz), 4.17 d (1H,

=CH_2, ^2J = 2.0 Hz), 3.83 q (2H, OCH_2, ^3J = 7.0 Hz), 3.48 m (1H, NCH_2), 2.95 m (3H, NCH_2, SCH_2), 1.26 t (3H, CH_3, ^3J = 7.0 Hz).

2-(1-Ethoxyvinyl)thiazolidine (IIIa-D). ^{1}H NMR spectrum (D_2O), δ, ppm: 4.9 s (1H, NCHS), 4.21 s (1H, =CH_2), 3.93 s (1H, =CH_2), 3.72 q (2H, OCH_2, ^3J = 7.0 Hz), 3.36 m (1H, NCH_2), 2.81 m (1H, NCH_2), 2.81 m (2H, SCH_2), 1.26 t (3H, CH_3, ^3J = 7.0 Hz).

f. The reaction of 0.24 mmol of ethoxypropenal **Ia** with 0.48 mmol (2 equiv) of 2-aminoethanethiol (**II**) in D_2O in 1 h gave exclusively cyclic tautomer **IIIa**. ^{1}H NMR spectrum (D_2O), δ, ppm: 4.81 s (1H, NCHS), 4.17 d (1H, =CH_2, ^2J = 2.2 Hz), 4.02 d (1H, =CH_2, ^2J = 2.2 Hz), 3.68 q (2H, OCH_2, ^3J = 7.0 Hz), 3.33 m (1H, NCH_2), 2.80 m (3H, NCH_2, SCH_2), 1.12 t (3H, CH_3, ^3J = 7.0 Hz). The chemical shifts corresponded to those found for tautomer **D**.

g. The reaction of 0.097 g (0.97 mmol) of ethoxypropenal **Ia** with 0.75 g (0.97 mmol) of 2-aminoethanethiol (**II**) was performed in D_2O at pH ≈ 11 (in an NMR ampule). The ^{1}H NMR spectrum of the product coincided with that given above for tautomer **D**.

h. Ethoxypropenal **Ia**, 0.012 g (0.12 mmol), was added to a solution of 0.018 g (0.24 mmol) of 2-aminoethanethiol (**II**) in 0.6 ml of $CDCl_3$, and the mixture was kept for 1 h at room temperature. According to the ^{1}H NMR data, the ratio of tautomers **IIIa** and **IVa** was 7:1, the conversion being 96%. After 5 days, the ratio changed to 3.5:1, and after 12 days, to 2:1.

i. Distilled thiazolidine **IIIa**, 0.016 g (0.1 mmol), was dissolved in 0.6 ml of DMSO-d_6, an equimolar amount (0.015 g, 0.1 mmol) of trifluoromethanesulfonic acid was added, and the mixture was kept for 5 h at room temperature. ^{1}H NMR spectrum of 2-(1-ethoxyvinyl)thiazolidinium trifluoromethanesulfonate (DMSO-d_6), δ, ppm: 4.99 s (1H, NCHS), 4.28 s (1H, =CH_2), 4.02 s (1H, =CH_2), 3.73 q (2H, OCH_2, ^3J = 7.0 Hz), 3.30 m (1H, NCH_2), 3.10 m (1H, NCH_2), 2.87 m (2H, SCH_2), 1.23 t (3H, CH_3, ^3J = 7.0 Hz).

j. Excess ethoxypropenal **Ia**, 0.067 g (0.80 mmol), was added to a solution of 0.025 g (0.32 mmol) of 2-aminoethanethiol (**II**) in 0.6 ml of $CDCl_3$, and the mixture was kept for 1 h at room temperature. According to the ^{1}H NMR data, only tautomer **IVa** was formed, the conversion being 88%.

k. Excess ethoxypropenal **Ia**, 0.05 g (0.48 mmol), was added to a solution of 0.035 g (0.37 mmol) of 2-aminoethanethiol (**II**) in 1 ml of D_2O, and the mixture was kept for 3 h at room temperature. According to the ^{1}H NMR data, only tautomer **IVa** was formed, the conversion being 100%.

Reaction of 2-ethoxypropenal (Ia) with 2-aminoethanethiol (II) in triethylamine. 2-Ethoxypropenal (**Ia**), 0.48 g (4.85 mmol), was added to a solution of 0.37 g (4.85 mmol) of 2-aminoethanethiol (**II**) in 4 ml of triethylamine. The mixture was kept for 30 min at room temperature and evaporated. According to the ^{1}H NMR data, the ratio of tautomers **IIIa** and **IVa** was 1:1.6, the conversion being complete. When the mixture was kept for 48 h, the tautomer ratio was 1.1:1.

Reaction of 2-ethoxypropenal (Ia) with 2-aminoethanethiol (II) under microwave activation. Ethoxypropenal **Ia**, 0.097 g (0.97 mmol), was added to a solution of 0.076 g (0.97 mmol) of 2-aminoethanethiol (**II**) in 0.5 ml of triethylamine, and the mixture was subjected to microwave irradiation over a period of 4 min (4×1 min) at a power of 300 W. According to the ^{1}H NMR data, the ratio of tautomers **IIIa** and **IVa** was 1.67:1, the conversion being 99%.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 03-03-33143).

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