Multicomponent condensation of aliphatic amines with formaldehyde and hydrogen sulfide

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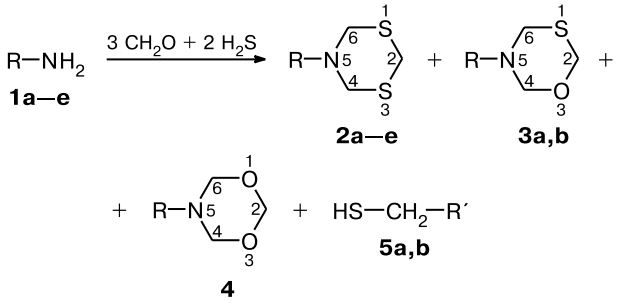
Cyclothiomethylation of primary aliphatic amines with the reagent $H_2S—CH_2O$ (2 : 3) in aqueous medium mainly gave substituted dithiazines; oxathiazines and dioxazines were obtained from butylamine and ethanolamine. Under the chosen reaction conditions, ethylenediamine was converted into 5-[2-(perhydro-1,3,5-dithiazin-5-yl)ethyl]perhydro-1,3,5-dithiazine or substituted thiazetidine and oxazetidine, depending on the order of mixing of the starting reagents.

Key words: cyclothiomethylation, aliphatic amines, O,N,S-containing heterocycles, formaldehyde, hydrogen sulfide, 1,3,5-dithiazines, 1,3,5-oxathiazines.

The literature data on thiomethylation of amines with hydrogen sulfide and formaldehyde to give the simplest dithiazines are scarce.[1—4] Recently,[5] dithiazines were obtained by thiomethylation of amino acids. Dithiazines can also be synthesized by thiomethylation of imines[6] or by reactions of amines with sodium hydrosulfide and formaldehyde.[7,8] Such N,S-containing heterocycles are biologically active[9] and exhibit the properties of complexones for precious metals.[10]

To further investigate multicomponent condensation of various amines with formaldehyde and hydrogen sulfide and develop an efficient method for the synthesis of N,S-containing heterocycles (substituted dithiazines and oxathiazines), we studied cyclothiomethylation of aliphatic mono- and diamines with formaldehyde and hydrogen sulfide. *n*-Butyl- (**1a**), *n*-hexyl- (**1b**), cyclohexyl- (**1c**), *n*-nonyl- (**1d**), and ethanolamines (**1e**) were used as the starting monoamines (Scheme 1). The reaction conditions were optimized with *n*-hexylamine as an example by varying the temperature, the concentrations of the starting compounds, and the order of addition of the substrates and the reagents to the reaction mixture. The yields and ratios of the products are given in Table 1. It was found that the heterocyclization of amine **1b** with sodium hydrosulfide and formaldehyde according to a known method[7] gave dithiazine **2b** in a somewhat lower yield than that attained in a hydrogen sulfide—formaldehyde system (see Table 1). In addition, use of the less expensive and more accessible H_2S makes this method preferred for practical application.

Scheme 1



R = Bu^n (**1a**, **2a**, **3a**, **4**), *n*-C_6H_{13} (**1b**, **2b**), *cyclo*-C_6H_{11} (**1c**, **2c**), *n*-C_9H_{19} (**1d**, **2d**), $HO(CH_2)_2$ (**1e**, **2e**, **3b**); R′ = OH (**5a**), SH (**5b**)

Cyclothiomethylation was carried out in two ways. According to the first method (method *A*), hydrogen sulfide was bubbled through a mixture of an amine and formaldehyde. According to the second one (method *B*), the starting amine was added to a thiomethylating mixture prepared by bubbling gaseous H_2S through an aqueous solution of formaldehyde (see Scheme 1).

The first method (at 80 °C) proved to be more efficient for the preparation of dithiazines **2** (see Table 1).

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Table 1. Effects of the structure of the aliphatic amine, the reaction temperature T, and the order of mixing of the starting reagents (methods *A* and *B*) on the total yield (Y) and ratio of the reaction products

Starting reagent	R	K_b*	T/°C	Method	Y (wt.%)	Ratio of the reaction products (%)			
						2	**3**	**4**	**5a,b**
1a	Bu^n	$4.0 \cdot 10^{-4}$	20	*A*	45	73	15	12	—
	Bu^n	$4.0 \cdot 10^{-4}$	40	*A*	50	60	40	—	—
1b	*n*-C_6H_{13}	$4.4 \cdot 10^{-4}$	20	*A*	10	35	—	—	65
	n-C_6H_{13}	$4.4 \cdot 10^{-4}$	40	*A*	24	42	—	—	58
	n-C_6H_{13}	$4.4 \cdot 10^{-4}$	80	*A*	60	60	—	—	40
	n-C_6H_{13}	$4.4 \cdot 10^{-4}$	20	*B*	51	27	—	—	73
	n-C_6H_{13}	$4.4 \cdot 10^{-4}$	40	*B*	26	39	—	—	61
	n-C_6H_{13}	$4.4 \cdot 10^{-4}$	80	*B*	56	55	—	—	21
	n-C_6H_{13}	$4.4 \cdot 10^{-4}$	20	—**	11	100	—	—	—
1c	*cyclo*-C_6H_{11}	$4.4 \cdot 10^{-4}$	20	*A*	27	100	—	—	—
	cyclo-C_6H_{11}	$4.4 \cdot 10^{-4}$	80	*A*	43	100	—	—	—
1d	*n*-C_9H_{19}	$4.4 \cdot 10^{-4}$	20	*A*	24	40	—	—	60
1e	$HO(CH_2)_2$	$3.1 \cdot 10^{-5}$	20	*A*	48	86	14	—	—
	$HO(CH_2)_2$	$3.1 \cdot 10^{-5}$	80	*A*	60	94	6	—	—

* The basicity constant K_b was taken from Ref. 11.

** Heterocyclization in the formaldehyde—sodium hydrosulfide system according to a known method.[7]

Along with dithiazine **2b**, the reaction mixture contained a mixture of mercaptomethanol **5a** and methanedithiol **5b** (GC-MS data), which seem to be intermediate products involved in amine thiomethylation. Analogous compounds **5a,b** were obtained by thiomethylation of *n*-nonylamine (**1d**) according to method *A*.

The reactions of amines **1a—e** with formaldehyde and H_2S afford dithiazines **2a—e** (GC-MS data); in the case of butylamine (**1a**) and ethanolamine (**1e**), individual oxathiazines **3a,b** and dioxazine **4** were isolated and identified by ^{13}C and ^1H NMR spectroscopy.

The formation of three products in the thiomethylation of *n*-butylamine (**1a**) was also confirmed by ^1H and ^{13}C NMR spectra. The major product was *n*-butyldithiazine **2a**; this is evident from the ^{13}C NMR spectrum containing a signal at δ 53.6 for two magnetically equivalent C atoms of the methylene groups of the NCH_2S fragment in the dithiazine ring and a signal at δ 34.6 for the C atom of the methylene group between two S atoms. The ^1H NMR spectrum shows, along with the signals for the protons of the Bu^n group, broadened singlets at δ 4.14 and 4.50 in the 1 : 2 ratio corresponding to the methylene protons of the dithiazine ring at the C(2), C(4), and C(6) atoms, respectively. The mass spectrum of product **2a** contains the peak of the molecular ion $[M]^+$ with m/z 177 and peaks of fragmentation ions produced by successive detachment from $[M]^+$ of fragments containing the methylene groups and the S atoms.

In *n*-butyloxathiazine **3a**, all the C atoms of the ring are magnetically nonequivalent and manifest themselves in the ^{13}C NMR spectrum as three signals at δ 72.1, 81.7, and 55.2. They were assigned, with consideration of the increments of the heteroatoms, to the C(2), C(4), and C(6) atoms, respectively. The ^1H NMR spectrum of product **3a** shows signals for the methylene protons at δ 4.22, 4.71, and 4.00 with an integrate intensity ratio of 1 : 1 : 1. The mass spectrum of compound **3a** contains the peak of the molecular ion $[M]^+$ with m/z 161 and peaks of characteristic fragmentation ions produced by successive detachment from $[M]^+$ of fragments containing the methylene groups and the S and O atoms. Based on these data, we formulated compound **3a** as 5-*n*-butylperhydro-1,3,5-oxathiazine.

In the ^{13}C NMR spectrum of product **4**, signals are shifted downfield. The signal at δ 94.6 was assigned to the C(2) atom between two O atoms, while the signal at δ 78.8 belongs to the C atoms between the N and O atoms in the dioxazine ring. The ^1H NMR spectrum of compound **4** shows singlet signals for the methylene protons at δ 4.74 and 5.07 in the 1 : 2 ratio. The mass spectrum of product **4** contains the peak of the molecular ion $[M]^+$ with m/z 145 and peaks of fragmentation ions produced by successive detachment from $[M]^+$ of fragments containing the methylene groups and the O atoms. Based on these data, the structure of 5-*n*-butylperhydro-1,3,5-dioxazine was assigned to compound **4**.

The structures of dithiazines **2b—e** were determined analogously.

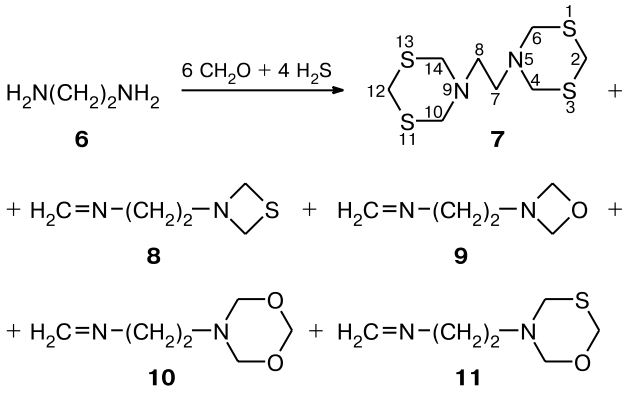
The fairly selective thiomethylation of ethylenediamine (**6**) by method *A* predominantly gave 5-[2-(perhydro-1,3,5-dithiazin-5-yl)ethyl]perhydro-1,3,5-dithiazine (**7**) (Scheme 2, Table 2). Its content in the reaction mixture at 80 °C was ~90%, the overall conversion of the starting reagents being ~50%. In each experiment, 1,3-thiazetidine **8** was detected in the reaction mixture along with dithiazine **7**. The thiomethylation of ethylene-

Table 2. Effects of the reaction temperature T and the order of mixing of the starting reagents (methods *A* and *B*) on the total yield (Y) and ratio of the cyclothiomethylation products from ethylenediamine (**6**) ($K_b = 1.15 \cdot 10^{-4}$)[11]

T /°C	Method	Y (wt.%)	Ratio of the reaction products (%)				
			7	**8**	**9**	**10**	**11**
60	*A*	46	53	25	22	—	—
80	*A*	49	90	10	—	—	—
20	*B*	24	12	62	5	6	15
60	*B*	27	18	66	4	4	8

diamine by method *B* reduced the selectivity of the reaction. The reaction products were 1,3-thiazetidine **8**, 1,3-oxazetidine **9**, 1,3,5-dioxazine **10**, and 1,3,5-oxathiazine **11** (see Scheme 2, Table 2).

Scheme 2



The thiomethylation of ethylenediamine (**6**) by method *B* with formaldehyde and hydrogen sulfide in the 1 : 6 : 4 ratio mainly gave thiazetidine **8** (GC-MS data). Minor products were heterocycles **7** and **9**—**11** (see Table 2). The mass spectra of compounds **9**—**11** contain the molecular ion peaks and peaks of fragmentation ions produced by successive detachment from $[M]^+$ of fragments containing the methylene groups and the S, O, and N atoms.

For some of the heterocycles obtained, Kováts[12] retention indices (I) were determined by GC-MS analysis.

Heterocycles **7** (method *A*) and **8** (method *B*) were isolated by fractional recrystallization from chloroform. The ^{13}C NMR spectrum of compound **7** shows, apart from the characteristic signals for the dithiazine ring (δ 33.9 and 58.4), a signal at δ 46.1 belonging to the C(7) and C(8) atoms of the ethylene fragment. In the ^1H NMR spectrum of compound **7**, the chemical shifts and intensity ratio of the signals observed (δ 3.20, 4.09, and 4.45) confirmed the structure proposed. The mass spectrum of product **7** contains the peak of the molecular ion $[M]^+$ with m/z 268 and peaks of fragmentation ions with m/z 235, 222, 190, 176, and 130 ($[M - HS]^+$, $[M - SCH_2]^+$, $[M - SCH_2S]^+$, $[M - SCH_2SCH_2]^+$, and $[M - SCH_2SCH_2SCH_2]^+$, respectively).

The mass spectrum of compound **8** contains the peak of the molecular ion $[M]^+$ with m/z 130 and peaks of fragmentation ions with m/z 98, 84, and 56 ($[M - SCH_2]^+$ and $[M - SCH_2NCH_2]^+$). In the ^{13}C NMR spectrum, three signals at δ 54.9, 55.2, and 128.1 correspond to the thiazetidine, ethylene, and imino fragments, respectively. According to these data, we assigned the 3-(2-methylideneaminoethyl)-1,3-thiazetidine structure to compound **8**.

As can be seen from Table 1, the yields of cyclothiomethylation products increase with a decrease in the basicity of the starting amine. The highest yields of dithiazines were attained with ethanolamine (**1e**) (56%) and ethylenediamine (**6**) (44%). The yields of dithiazines from *n*-butyl- (**1a**), *n*-hexyl- (**1b**), and cyclohexylamines (**1c**) were somewhat lower (33, 36, and 43%, respectively). *n*-Nonylamine (**1d**) proved to be least reactive in cyclothiomethylation (10%).

Thus, the optimum conditions for the synthesis of dithiazines from aliphatic amines were found to arise at 80 °C in the presence of a triple molar excess of the thiomethylating mixture CH_2O—H_2S. We found that with a decrease in the basicity of the primary aliphatic amine, it becomes more reactive in cyclothiomethylation.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90 Q spectrometer (89.55 and 22.50 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. IR spectra were recorded on a Specord 75IR spectrophotometer (Nujol). GC-MS analysis was carried out with a Finnigan 4021 instrument (glass capillary column 50 000×0.25 mm, HP-5 stationary phase, helium as a carrier gas, temperature rise from 50 to 300 °C at a rate of 5 deg min^{-1}, evaporator temperature 280 °C, ion source temperature 250 °C, 70 eV). Compounds **2a**—**e**, **3a,b**, **4**, **7**, and **8** were isolated by fractional recrystallization from chloroform.

Cyclothiomethylation of aliphatic amines (general procedure *A*). A three-neck flask fitted with a stirrer, a reflux condenser, and a bubbler and controlled at a given temperature was charged with formalin (5.5 mL, 0.075 mol) and an amine (0.025 mol). After two hours, gaseous hydrogen sulfide (1.12 L, 0.05 mol) was added for 1 h. The products were extracted from the resulting mixture with chloroform.

General procedure *B*. Gaseous hydrogen sulfide (1.12 L, 0.05 mol) was bubbled through formalin (5.5 mL, 0.075 mol) for 2 h. Then, an amine (0.025 mol) was added dropwise for 1 h. The products were extracted from the resulting mixture with chloroform.

5-*n*-Butylperhydro-1,3,5-dithiazine (2a) was obtained according to procedure *A* (20 °C). The yield of compound **2a** was 1.46 g (33%), m.p. 95—96 °C, $I = 1443$. Found (%): C, 47.71; H, 8.24; N, 8.12; S, 35.93. $C_7H_{15}NS_2$. Calculated (%): C, 47.46;

H, 8.47; N, 7.91; S, 36.16. IR, ν/cm^{-1}: 720 (C—S), 1120—1190 (C—N), 1460 (CH_3), 1470 (CH_2), 2830 (CH_2). ^{1}H NMR, δ: 1.07 (s, 3 H, C(10)H_3); 1.17—1.29 (m, 4 H, C(8)H_2, C(9)H_2); 3.68—3.91 (m, 2 H, C(7)H_2); 4.14 (s, 2 H, C(2)H_2); 4.50 (s, 4 H, C(4)H_2, C(6)H_2). ^{13}C NMR, δ: 27.5 (q, C(10)); 29.5 (t, C(9)); 29.7 (t, C(8)); 34.6 (t, C(2)); 50.9 (t, C(7)); 53.6 (t, C(4), C(6)). MS, *m/z* (I_{rel} (%)): 177 $[M]^+$ (60); 162 $[M - Me]^+$ (24); 131 $[M - CH_2S]^+$ (23); 99 $[M - SCH_2S]^+$ (56); 57 $[M - SCH_2S(CH_2)_3]^+$ (100).

5-*n*-Hexylperhydro-1,3,5-dithiazine (2b) was obtained according to procedure *A* (80 °C). The yield of compound **2b** was 1.84 g (36%), m.p. 84—85 °C, *I* = 1720. Found (%): C, 52.49; H, 9.39; N, 6.68; S, 31.44. $C_9H_{19}NS_2$. Calculated (%): C, 52.68; H, 9.27; N, 6.83; S, 31.22. IR, ν/cm^{-1}: 690—720 (C—S), 1090 (C—N), 1380 (CH_3), 1470 (CH_2), 2900 (CH_2). ^{1}H NMR, δ: 0.85 (s, 3 H, C(12)H_3); 1.20—1.35 (m, 6 H, C(9)H_2, C(10)H_2, C(11)H_2); 1.35—1.50 (t, 2 H, C(8)H_2, ^3J = 7.1 Hz); 2.97 (t, 2 H, C(7)H_2, ^3J = 7.1 Hz); 4.19 (s, 2 H, C(2)H_2); 4.52 (s, 4 H, C(4)H_2, C(6)H_2). ^{13}C NMR, δ: 14.2 (q, C(12)); 23.0 (t, C(11)); 27.3 (t, C(9)); 27.3 (t, C(8)); 32.1 (t, C(10)); 33.6 (t, C(2)); 49.0 (t, C(7)); 58.2 (t, C(4), C(6)). MS, *m/z* (I_{rel} (%)): 205 $[M]^+$ (88); 173 $[M - S]^+$ (8); 159 $[M - CH_2S]^+$ (16); 127 $[M - SCH_2S]^+$ (100); 112 $[M - SCH_2SCH_3]^+$ (24); 98 $[M - SCH_2SCH_3CH_2]^+$ (24); 84 $[M - SCH_2SCH_3(CH_2)_2]^+$ (56).

5-Cyclohexylperhydro-1,3,5-dithiazine (2c) was obtained according to procedure *A* (80 °C). The yield of compound **2c** was 2.2 g (43%), m.p. 58 °C, *I* = 1814. Found (%): C, 53.25; H, 8.24; N, 6.73; S, 31.78. $C_9H_{17}NS_2$. Calculated (%): C, 53.20; H, 8.37; N, 6.90; S, 31.53. IR, ν/cm^{-1}: 670—720 (C—S), 1120—1180 (C—N), 1370 (S—CH_2), 1450 (CH_2), 2850 (CH_2). ^{1}H NMR, δ: 0.40—1.50 (m, 10 H, C(8)H_2, C(9)H_2, C(10)H_2, C(11)H_2, C(12)H_2); 3.15 (m, 2 H, C(7)H_2); 3.45 (s, 4 H, C(4)H_2, C(6)H_2); 3.77 (s, 2 H, C(2)H_2). ^{13}C NMR, δ: 24.5 (t, C(9), C(11)); 25.1 (t, C(10)); 28.9 (t, C(8), C(12)); 30.1 (t, C(2)); 53.0 (t, C(7)); 57.2 (t, C(4), C(6)). MS, *m/z* (I_{rel} (%)): 203 $[M]^+$ (98); 171 $[M - S]^+$ (6); 157 $[M - CH_2S]^+$ (30); 125 $[M - SCH_2S]^+$ (100); 111 $[M - SCH_2SCH_2]^+$ (12); 97 $[M - SCH_2SCH_2CH_2]^+$ (12); 83 $[M - SCH_2SCH_2CH_2N]^+$ (51).

5-*n*-Nonylperhydro-1,3,5-dithiazine (2d) was obtained according to procedure *A* (20 °C). The yield of compound **2d** was 0.5 g (10%), m.p. 60—61 °C, *I* = 2055. Found (%): C, 58.14; H, 10.23; N, 5.49; S, 26.14. $C_{12}H_{25}NS_2$. Calculated (%): C, 58.30; H, 10.12; N, 5.67; S, 25.91. IR, ν/cm^{-1}: 700 (C—S), 1180 (C—N), 1380 (CH_3), 1420 (S—CH_2), 1450 (CH_2), 2840 (CH_2). ^{1}H NMR, δ: 0.20—0.80 (m, 17 H, C(15)H_3, C(8)H_2—C(14)H_2); 3.25 (m, 2 H, C(7)H_2); 3.65 (s, 4 H, C(4)H_2, C(6)H_2); 4.01 (s, 2 H, C(2)H_2). ^{13}C NMR, δ: 14.1 (q, C(15)); 22.6 (t, C(14)); 27.0 (t, C(13)); 27.2 (t, C(12)); 29.2 (t, C(11)); 29.5 (t, C(10)); 29.5 (t, C(9)); 31.8 (t, C(8)); 34.0 (t, C(2)); 48.8 (t, C(7)); 58.2 (t, C(4), C(6)). MS, *m/z* (I_{rel} (%)): 247 $[M]^+$ (42); 215 $[M - S]^+$ (12); 169 $[M - SCH_2S]^+$ (100); 154 $[M - SCH_2SCH_3]^+$ (36); 140 $[M - SCH_2SCH_3CH_2]^+$ (36).

2-(Perhydro-1,3,5-dithiazin-5-yl)ethan-1-ol (2e) was obtained according to procedure *A* (80 °C). The yield of compound **2e** was 2.36 g (56%), m.p. 44—45 °C. Found (%): C, 36.42; H, 6.55; N, 8.59; S, 38.83. $C_5H_{11}NOS_2$. Calculated (%): C, 36.36; H, 6.67; N, 8.48; S, 38.79. IR, ν/cm^{-1}: 580—650 (C—S), 1170 (C—N), 1420 (S—CH_2), 2850 (CH_2), 3610 (OH). ^{1}H NMR, δ: 1.95 (t, 2 H, C(7)H_2, ^3J = 7.1 Hz); 2.75 (s, 2 H, C(2)H_2); 3.41 (s, 4 H, C(4)H_2, C(6)H_2); 3.60 (t, 2 H, C(8)H_2, ^3J = 7.1 Hz). ^{13}C NMR, δ: 33.5 (t, C(2)); 51.5 (t, C(7)); 58.7 (t, C(4), C(6)); 59.2 (t, C(8)). MS, *m/z* (I_{rel} (%)): 165 $[M]^+$ (84); 133 $[M - S]^+$ (12); 119 $[M - SCH_2]^+$ (48); 87 $[M - SCH_2S]^+$ (100).

5-*n*-Butylperhydro-1,3,5-oxathiazine (3a) was obtained according to procedure *A* (40 °C). The yield of compound **3a** was 0.8 g (20%), m.p. 88—89 °C, *I* = 1217. Found (%): C, 51.84; H, 9.50; N, 8.51; S, 20.02. $C_7H_{15}NOS$. Calculated (%): C, 52.17; H, 9.32; N, 8.69; S, 19.87. IR, ν/cm^{-1}: 580—650 (C—S), 1170 (C—N), 1460 (CH_3), 1470 (CH_2), 2850 (CH_2). ^{1}H NMR, δ: 1.07 (s, 3 H, C(10)H_3); 1.17—1.29 (m, 4 H, C(8)H_2, C(9)H_2); 3.68—3.91 (m, 2 H, C(7)H_2); 4.00 (s, 2 H, C(6)H_2); 4.22 (m, 2 H, C(2)H_2); 4.71 (s, 2 H, C(4)H_2). ^{13}C NMR, δ: 28.0 (q, C(10)); 29.4 (t, C(9)); 29.6 (t, C(8)); 50.7 (t, C(7)); 55.2 (t, C(6)); 72.1 (t, C(2)); 81.7 (t, C(4)). MS, *m/z* (I_{rel} (%)): 161 $[M]^+$ (15); 146 $[M - CH_3]^+$ (13); 114 $[M - CH_3 - S]^+$ (9); 100 $[M - CH_3SCH_2]^+$ (9); 70 $[M - CH_3S(CH_2)_2O]^+$ (100).

2-(Perhydro-1,3,5-oxathiazin-5-yl)ethan-1-ol (3b) was obtained according to procedure *A* (20 °C). The yield of compound **3b** was 0.26 g (7%), m.p. 41—42 °C. Found (%): C, 40.26; H, 7.43; N, 9.31; S, 21.59. $C_5H_{11}NO_2S$. Calculated (%): C, 40.27; H, 7.38; N, 9.40; S, 21.48. IR, ν/cm^{-1}: 650—730 (C—S), 1170 (C—N), 1420 (S—CH_2), 2850 (CH_2), 3610 (OH). ^{13}C NMR, δ: 48.8 (t, C(7)); 48.9 (t, C(8)); 57.5 (t, C(6)); 65.0 (t, C(2)); 89.0 (t, C(4)). MS, *m/z* (I_{rel} (%)): 149 $[M]^+$ (100); 103 $[M - CH_2S]^+$ (36); 70 $[M - CH_2SOOH]^+$ (72).

5-*n*-Butylperhydro-1,3,5-dioxazine (4) was obtained according to procedure *A* (20 °C). The yield of compound **4** was 0.18 g (5%), m.p. 45—46 °C, *I* = 996. Found (%): C, 58.08; H, 10.12; N, 9.47. $C_7H_{15}O_2N$. Calculated (%): C, 57.93; H, 10.34; N, 9.66. IR, ν/cm^{-1}: 1170 (C—N), 1460 (CH_3), 1470 (CH_2), 2850 (CH_2). ^{1}H NMR, δ: 1.07 (s, 3 H, C(10)H_3); 1.17—1.29 (m, 4 H, C(8)H_2, C(9)H_2); 3.68—3.91 (m, 2 H, C(7)H_2); 4.74 (s, 2 H, C(2)H_2); 5.07 (s, 4 H, C(4)H_2, C(6)H_2). ^{13}C NMR, δ: 28.5 (q, C(10)); 29.5 (t, C(9)); 29.7 (t, C(8)); 54.6 (t, C(7)); 78.8 (t, C(4), C(6)); 94.6 (t, C(2)). MS, *m/z* (I_{rel} (%)): 145 $[M]^+$ (10); 130 $[M - CH_3]^+$ (19); 84 $[M - CH_3OCH_2O]^+$ (8); 70 $[M - CH_3O(CH_2)_2O]^+$ (100).

Mercaptomethanol (5a). MS, *m/z* (I_{rel} (%)): 62 $[M - H_2]^+$ (51); 46 $[M - H_2O]^+$ (100).

Methanedithiol (5b). MS, *m/z* (I_{rel} (%)): 80 $[M]^+$ (100); 78 $[M - H_2]^+$ (38); 46 $[M - H_2S]^+$ (90); 34 $[H_2S]^+$ (78).

5-[2-(Perhydro-1,3,5-dithiazin-5-yl)ethyl]perhydro-1,3,5-dithiazine (7) was obtained according to procedure *A* (80 °C). The yield of compound **7** was 2.9 g (44%), m.p. 179—180 °C, *I* = 2600. Found (%): C, 36.07; H, 5.73; N, 10.26; S, 47.94. $C_6H_{12}N_4S_2$. Calculated (%): C, 35.82; H, 5.97; N, 10.45; S, 47.76. IR, ν/cm^{-1}: 670—690 (C—S), 1090 (C—N), 1450 (S—CH_2), 2840—2900 (CH_2). ^{1}H NMR, δ: 3.20 (s, 4 H, C(2)H_2, C(12)H_2); 4.09 (s, 4 H, C(7)H_2, C(8)H_2); 4.45 (s, 8 H, C(4)H_2, C(6)H_2, C(10)H_2, C(14)H_2). ^{13}C NMR, δ: 33.9 (t, C(2), C(12)); 46.1 (t, C(7), C(8)); 58.4 (t, C(4), C(6), C(10), C(14)). MS, *m/z* (I_{rel} (%)): 268 $[M]^+$ (12); 222 $[M - SCH_2]^+$ (30); 190 $[M - SCH_2S]^+$ (54); 176 $[M - SCH_2SCH_2]^+$ (54); 130 $[M - SCH_2SCH_2SCH_2]^+$ (100).

3-(2-Methylideneaminoethyl)-1,3-thiazetidine (8) was obtained according to procedure *B* (60 °C). The yield of compound **8** was 0.6 g (18%), m.p. 153—154 °C. IR, ν/cm^{-1}: 670—680 (C—S), 1110 (C—N), 1450 (S—CH_2), 2840—2900 (CH_2). ^{1}H NMR, δ: 3.10 (s, 4 H, C(5)H_2, C(6)H_2); 4.93 (s, 4 H, C(2)H_2, C(4)H_2); 7.28 (s, 2 H, C(8)H_2). ^{13}C NMR, δ: 54.9 (t, C(2), C(4)); 55.2 (t, C(5), C(6)); 128.1 (t, C(8)). MS,

m/z (I_{rel} (%)): 130 $[M]^+$ (100); 98 $[M - S]^+$ (16); 84 $[M - SCH_2]^+$ (16); 56 $[M - SCH_2CH_2N]^+$ (90).

3-(2-Methylideneaminoethyl)-1,3-oxazetidine (9) was obtained according to procedure *A* (60 °C). The yield of compound **9** was 0.28 g (10%). MS, *m/z* (I_{rel} (%)): 114 $[M]^+$ (82); 84 $[M - OCH_2]^+$ (96); 56 $[M - OCH_2CH_2N]^+$ (100).

5-(2-Methylideneaminoethyl)perhydro-1,3,5-dioxazine (10) was obtained according to procedure *B* (20 °C). The yield of compound **10** was 0.04 g (1%). MS, *m/z* (I_{rel} (%)): 144 $[M]^+$ (57); 114 $[M - OCH_2]^+$ (100); 100 $[M - CH_2OCH_2]^+$ (62); 84 $[M - CH_2OCH_2O]^+$ (12); 70 $[M - CH_2OCH_2OCH_2]^+$ (33).

5-(2-Methylideneaminoethyl)perhydro-1,3,5-oxathiazine (11) was obtained according to procedure *B* (20 °C). The yield of compound **11** was 0.16 g (4%). MS, *m/z* (I_{rel} (%)): 160 $[M]^+$ (40); 128 $[M - S]^+$ (5); 114 $[M - SCH_2]^+$ (28); 100 $[M - CH_2SCH_2]^+$ (10); 84 $[M - CH_2SCH_2O]^+$ (28); 70 $[M - CH_2SCH_2OCH_2]^+$ (100).

References

1. A. Wohl, *Ber.*, 1886, **19**, 2344.
2. D. Collins and J. Graymore, *J. Chem. Soc.*, 1953, 4089.
3. D. Collins and J. Graymore, *J. Chem. Soc.*, 1957, 9.
4. R. S. Aleev, Yu. S. Dal´nova, Yu. N. Popov, R. M. Masagutov, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR*, 1988, **303**, 873 [*Dokl. Chem.*, 1988 (Engl. Transl.)].
5. R. V. Kunakova, S. R. Khafizova, Yu. S. Dal´nova, R. S. Aleev, L. M. Khalilov, and U. M. Dzhemilev, *Neftekhimiya*, 2002, **42**, 382 [*Petroleum Chemistry*, 2002, **42**, 347 (Engl. Transl.)].
6. D. Collins and J. Graymore, *J. Chem. Soc.*, 1953, 143.
7. E. Juaristi, E. Gonzalez, B. Pinto, B. Johnston, and R. Nagelkerke, *J. Am. Chem. Soc.*, 1989, **111**, 6745.
8. A. N. Kurchan and A. G. Kutateladze, *Org. Lett.*, 2002, **4**(23), 4129.
9. RF Pat. 2 160 233; *Byull. Izobret.*, 2000, 34.
10. Yu. I. Murinov, V. N. Maistrenko, and N. G. Afzaletdinova, *Ekstraktsiya metallov S,N-organicheskimi soedineniyami* [*Extraction of Metals with S,N-Containing Organic Compounds*], Nauka, Moscow, 1993, 192 (in Russian).
11. *Spravochnik khimika* [*The Chemist´s Reference Book*], Ed. B. P. Nikol´skii, Khimiya, Moscow—Leningrad, 1964, **3**, 98 pp. (in Russian).
12. M. S. Vigdergauz, L. V. Semenchenko, V. A. Ezrets, and Yu. N. Bogoslovskii, *Kachestvennyi gazokhromatograficheskii analiz* [*Qualitative Analysis by Gas Chromatography*], Nauka, Moscow, 1978, 244 (in Russian).

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