C, 63.39; H, 5.19; N, 5.19. $C_{13}H_{13}NO_2S$. Calculated (%): C, 63.14; H, 5.30; N, 5.66.

3-(2-Nitrophenylthio)tricyclo[2.2.1.0^{2,6}]heptane (5). R_f 0.82. ^{1}H NMR (CCl_4), δ: 8.00 (d, 1 H, H arom., J = 8.8 Hz); 7.50—7.00 (m, 3 H, H arom.); 3.01 (br.s, 1 H, HCS); 2.10—1.10 (m, 8 H). Found (%): C, 63.13; H, 5.29; N, 5.50. $C_{13}H_{13}NO_2S$. Calculated (%): C, 63.14; H, 5.30; N, 5.66.

***trans*-2-(4-Nitrophenylthio)cyclohexanol (6).** R_f 0.60. ^{1}H NMR ($CDCl_3$), δ: 8.10 (d, 2 H, H arom., J = 8.8 Hz); 7.32 (d, 2 H, H arom., J = 8.8 Hz); 3.48 (q, 1 H, HCO, J = 10.8 Hz); 3.48 (q, 1 H, HCS, J = 10.8 Hz); 2.12 (m, 2 H); 1.75—1.15 (m, 6 H). IR, ν/cm^{-1}: 3120 (OH). MS, m/z: 253 $[M]^+$.

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Synthesis of diaminohydroxyethers *via* 3-(ω-haloalkoxy)-2-hydroxypropyl sulfamates

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Reactions of 3-(ω-haloalkoxy)-2-hydroxypropyl sulfamates with amines or ammonia followed by acid hydrolysis give the corresponding diaminohydroxyethers.

Key words: sulfamates, 1-amino-3-(ω-aminoalkoxy)propan-2-ols.

Functional amino derivatives and in particular amino alcohols are widely used in organic synthesis, in chemistry of polymers, and as biologically active substances.[1—5] In this connection, synthesis of new representatives of amino derivatives and perfection of methods for their preparation remain urgent problems. The use of sulfamic acid and oxiranes as the starting reagents makes it possible to obtain (with rather high selectivity) several previously unknown or hardly accessible functionalized amino alcohols.

Previously,[6] we reported on the synthesis of some diaminoethers by the reactions of sulfamates with diglycidyl ether. However, this method gives only symmetrical diaminodihydroxyethers. In the present work, for the purpose of extending the series of diamines, we propose another method for the synthesis of diaminohydroxyethers, *viz.*, by the reaction of *N*-(3-(ω-haloalkoxy)-2-hydroxypropyl) sulfamates with amines or ammonia in an aqueous medium followed by acid hydrolysis (Scheme 1).

We have previously[7] described the preparation of the starting sulfamate **1**; synthesis of compound **1n** was performed similarly. The reactions of halides **1** with R^1R^2NH were performed at 90—95 °C for 1 h in an aqueous medium with a 5—10-fold excess of an amine. The substitution of halogen by nitrogen was almost quantitative. Then the aminosulfamates **2** were converted by acid hydrolysis (according to the previously used procedure[6]) without purification into diaminohydroxyethers (**3**), which were additionally purified by fractional distillation. The overall yields of **3** (purity 90—95%) are within 70—90%, the yields after distillation and other parameters of the products obtained are presented in Table 1.

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Table 1. Parameters of 1-amino-3-(ω-aminoalkoxy)propan-2-ols (**3a—n**)

Compound	Yield (%)	B.p. /°C (*p*/Torr)	Found / Calculated (%) C	H	N	Molecular formula	^{1}H NMR, δ
3a	54.4	103—104 (0.2)	43.91 / 44.76	10.66 / 10.52	—	$C_5H_{14}N_2O_2$	2.41—2.89 (m, 4 H, 2 CH_2N); 3.48—3.70 (m, 4 H, 2 CH_2O); 3.80—3.92 (m, 1 H, CHO)
3b	54.7	106—107 (0.2)	48.71 / 48.63	10.90 / 10.88	18.96 / 18.90	$C_6H_{16}N_2O_2$	2.30 (s, 3 H, MeN); 2.53—2.73 (m, 4 H, 2 CH_2N); 3.40—3.66 (m, 4 H, 2 CH_2O); 3.71—3.81 (m, 1 H, CHO)
3c	57.0	155—157 (0.2)	—	—	—	$C_7H_{18}N_2O_3$	2.91—3.18 (m, 4 H, 2 CH_2N); 3.18—3.32 (t, 2 H, NCH_2CH_2OH); 3.45—3.62 (t, 2 H, NCH_2CH_2O); 3.65—3.83 (m, 4 H, CH_2O, CH_2OH); 3.95—4.04 (m, 1 H, CHO)[a]
3d	57.7	93—94 (0.2)	—	—	18.79 / 18.90	$C_6H_{16}N_2O_2$	2.28 (s, 3 H, MeN); 2.46—2.62 (m, 2 H, CH_2N); 2.70—2.78 (t, 2 H, CH_2N); 3.38—3.62 (m, 4 H, 2 CH_2O); 3.82—3.94 (m, 1 H, CHO)
3e	54.7	101—102 (0.2)	51.86 / 51.83	11.20 / 11.18	17.40 / 17.27	$C_7H_{18}N_2O_2$	2.33 (s, 6 H, 2 MeN); 2.56—2.72 (m, 2 H, CH_2N); 2.68—2.76 (t, 2 H, CH_2N); 3.41—3.68 (m, 4 H, 2 CH_2O); 3.87—3.98 (m, 1 H, CHO)
3f	66.7	97 (0.2)	—	—	17.42 / 17.27	$C_7H_{18}N_2O_2$	1.09—1.14 (t, 3 H, Me); 2.59—2.76 (m, 4 H, 2 CH_2N); 2.80—2.86 (t, 2 H, CH_2N); 3.48—3.66 (m, 4 H, 2 CH_2O); 3.92—4.02 (m, 1 H, CHO)
3g	55.5	94 (0.2)	54.30 / 54.52	11.30 / 11.44	15.88 / 15.89	$C_8H_{20}N_2O_2$	1.02—1.11 (t, 3 H, Me); 2.31 (s, 3 H, MeN); 2.51—2.66 (m, 4 H, 2 CH_2N); 2.66—2.73 (t, 2 H, CH_2N); 3.40—3.68 (m, 4 H, 2 CH_2O); 3.84—3.97 (m, 1 H, CHO)
3h	59.6	112—113 (0.2)	48.43 / 48.63	10.71 / 10.88	19.02 / 18.90	$C_6H_{16}N_2O_2$	1.67—1.80 (t, 2 H, $OCH_2CH_2CH_2N$); 2.54—2.77 (m, 4 H, 2 CH_2N); 3.40—3.67 (m, 4 H, 2 CH_2O); 3.73—3.83 (m, 1 H, CHO)
3i	56.6	101—102 (0.2)	51.73 / 51.83	11.21 / 11.18	—	$C_7H_{18}N_2O_2$	1.70—1.85 (t, 2 H, $OCH_2CH_2CH_2N$); 2.31 (s, 3 H, MeN); 2.56—2.76 (m, 4 H, 2 CH_2N); 3.41—3.68 (m, 4 H, 2 CH_2O); 3.72—3.84 (m, 1 H, CHO)
3j	60.4	152—153 (0.2)	62.15 / 62.57	11.19 / 11.38	12.15 / 12.16	$C_{12}H_{26}N_2O_2$	0.93—1.10 (d, 3 H, Me); 1.20—2.18 (m, 9 H, CH_2CHCH_2, $OCH_2CH_2CH_2N$); 2.40—3.10 (m, 6 H, 3 CH_2N); 3.44—3.76 (m, 4 H, 2 CH_2O); 3.76—3.90 (m, 1 H, CHO)
3k	63.7	109 (0.2)	51.80 / 51.83	11.11 / 11.18	17.15 / 17.27	$C_7H_{18}N_2O_2$	1.63—1.74 (t, 2 H, $OCH_2CH_2CH_2N$); 2.30 (s, 3 H, MeN); 2.50—2.60 (m, 2 H, CH_2N); 2.62—2.70 (t, 2 H, CH_2N); 3.39—3.64 (m, 4 H, 2 CH_2O); 3.85—3.94 (m, 1 H, CHO)
3l	54.1	106 (0.2)	53.63 / 54.52	11.46 / 11.44	16.07 / 15.89	$C_8H_{20}N_2O_2$	1.61—1.76 (t, 2 H, $OCH_2CH_2CH_2N$); 2.22 (s, 3 H, MeN); 2.27 (s, 3 H, MeN); 2.46—2.58 (m, 4 H, 2 CH_2N); 3.32—3.58 (m, 4 H, 2 CH_2O); 3.78—3.91 (m, 1 H, CHO)
3m	56.8	114—116 (0.2)	—	—	15.96 / 15.89	$C_8H_{20}N_2O_2$	1.10—1.20 (t, 3 H, Me); 1.73—1.90 (t, 2 H, $OCH_2CH_2CH_2N$); 2.59—2.80 (m, 6 H, 3 CH_2N); 3.49—3.78 (m, 4 H, 2 CH_2O); 3.92—4.04 (m, 1 H, CHO)
3n	58.7	89—90 (0.2)	—	—	15.79 / 15.89	$C_7H_{18}N_2O_2$	1.06—1.13 (d, 3 H, Me); 2.25 (s, 3 H, MeN); 2.27 (s, 3 H, MeN); 2.48—2.61 (m, 4 H, 2 CH_2N); 3.27—3.69 (m, 3 H, $CHOCH_2$); 3.78—3.89 (m, 1 H, CHO)

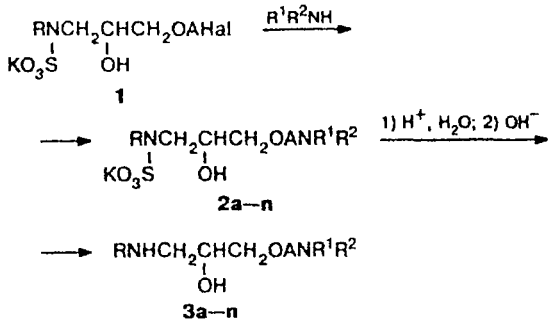
[a] Data for dihydrochloride.

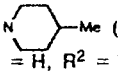
Experimental

^{1}H NMR spectra were recorded on a Bruker WH-250 spectrometer (250.13 MHz) in D_2O (HMDS as the external standard).

1-(2-Aminoethoxy)-3-ethylaminopropan-2-ol (3f). A 21% solution of NH_3 (6.5 mL) was added to a solution of potassium *N*-[3-(2-chloroethoxy)-2-hydroxypropyl]-*N*-ethyl sulfamate (2.4 g, 8 mmol) in water (3 mL), and the mixture was kept in a sealed tube at 90 °C for 1 h. Then the reaction mixture was concentrated, and water (10 mL) and 95% H_2SO_4 (4 g) were added to the reaction mixture, which was then heated at 100 °C for 6 h. The cooled reaction mixture was alkalized to pH 12.2 and concentrated, and the residue was extracted with ethanol (10 mL). The extract was concentrated,

Scheme 1



Hal = Cl; A = $-(CH_2)_2-$; R = R^1 = H, R^2 = H (**a**), Me (**b**), CH_2CH_2OH (**c**); R = Me, R^1 = H, R^2 = H (**d**), Me (**e**); R = Et, R^1 = H, R^2 = H (**f**), Me (**g**);
A = $-(CH_2)_3-$; R = R^1 = H, R^2 = H (**h**), Me (**i**); R = H, R^1 = R^2 = 

(**j**); R = Me, R^1 = H, R^2 = H (**k**), Me (**l**); R = Et, R^1 = H, R^2 = H (**m**);
Hal = Br; A = $-CHMe-CH_2-$, R = Me, R^1 = H, R^2 = Me (**n**)

the residue was extracted with a mixture of ethanol (5 mL) and ether (10 mL), and the extract was concentrated to dryness to obtain compound **3f** (1.21 g, purity ~95%), which was additionally purified by fractional distillation, b.p. 97–98 °C (0.2 Torr).

Compounds **3a–e,g–n** were obtained similarly.

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