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BRIEF COMMUNICATIONS

Synthesis of Methyleneoxyamino Derivatives of 1-Butylthioheptane

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Abstract—The possibility of synthesizing new methyleneoxyamino derivatives of 1-butylthioheptane was investigated. The structure of the synthesized compounds was proved by elemental analysis and IR and ^{1}H NMR spectroscopy. Some representatives of the synthesized compounds were tested as antimicrobial lubricant additives, and also as antiseptic materials against bacteria and funguses.

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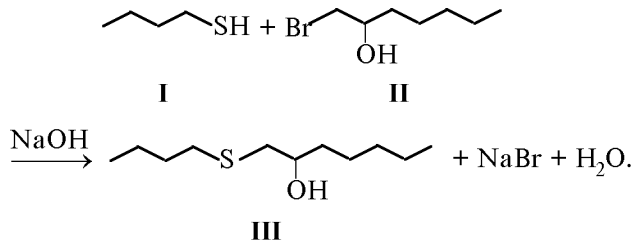
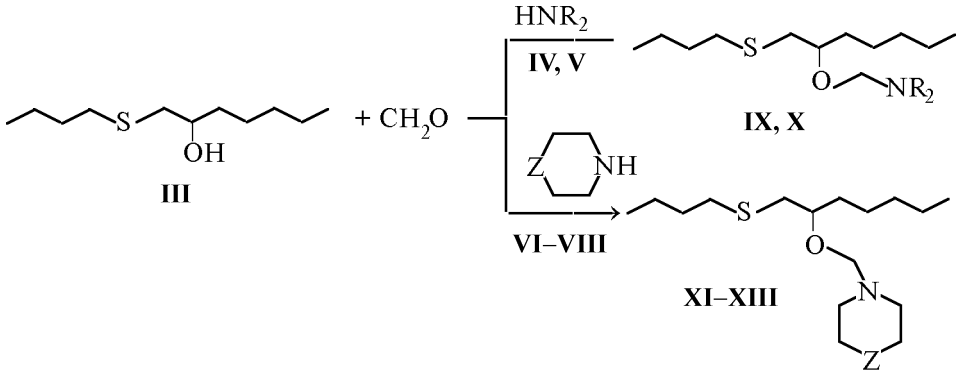
Organic compounds containing simultaneously various functional groups and heteroatoms, such as sulfur and nitrogen, are used for improving quality of lubricants and oils, and also as effective biologically active materials [1–3]. The synthesis of new generations of the specified compounds on the basis of accessible raw materials, and the refinement of the procedures of their preparation always draw attention of researchers [4].

The data on the synthesis and study of properties of methyleneoxyamino derivatives of 1-butylthioheptane are presented in this paper as a prolongation of the studies on alkylthioalkanes [5].

Earlier unknown 1-butylthioheptane-2-ol (**III**) was synthesized by the reaction of 1-butanethiol (**I**) with 1- bromohexane-2-ol (**II**) in an alkaline medium by the scheme:



New representatives of 1-butylthio-2-methyleneoxyaminoheptanes (**IX**)-(**XIII**) were synthesized by a reaction of 1-butylthio-2-heptanol (**III**) with formaldehyde and secondary amines (**IV**)-(**VIII**) by the scheme:



R = C_2H_5 (**IV**), (**IX**); C_4H_9 (**V**), (**X**); Z = O (**VI**), (**XI**); CH_2 (**VII**), (**XII**); CH_2CH_3 (**VIII**), (**XIII**).

Physicochemical properties of amine derivatives **III**, and **IX**–**XIII** of 1-butylthio-2-heptanol

Compd.	Bp, °C/P, mm Hg	n_D^{20}	d_4^{20}	Found MR_D / Calculated MR_D	Yield, %	Found, % /Calculated, %				Gross formula
						C	H	N	S	
III	112–113 / 1	1.4715	0.9164	62.39 62.55	75	64.58 64.64	11.81 11.84	–	15.63 15.69	$C_{11}H_{24}SO$
IX	126–128 / 2	1.4630	0.8917	89.43 89.76	75	66.31 66.38	12.14 12.19	4.81 4.84	11.02 11.07	$C_{16}H_{35}NSO$
X	178–180 / 3	1.4614	0.8784	108.05 108.35	78	69.42 69.50	12.51 12.54	4.02 4.05	9.22 9.28	$C_{20}H_{43}NSO$
XI	162–164 / 1	1.4782	0.9621	89.38 89.53	70	63.28 63.32	10.94 10.96	4.60 4.61	10.52 10.56	$C_{16}H_{33}NSO_2$
XII	161–163 / 2	1.4784	0.9236	92.48 92.46	69	67.62 67.72	11.62 11.70	4.56 4.64	10.54 10.63	$C_{17}H_{35}NSO$
XIII	159–161 / 3	1.4818	0.9282	96.89 97.02	65	68.40 68.51	11.74 11.92	4.36 4.44	10.02 10.16	$C_{18}H_{37}NSO$

Synthesized 1-butylthio-2-heptanol (**III**) and its amino derivatives (**IX**)–(**XIII**) are transparent liquids with a characteristic odor. Physicochemical properties of compounds **III** and **IX**–**XIII** are presented in the table.

The synthesis of 1-butylthio-2-heptanol (**III**) was carried out at 40–50°C within 3–4 h at the mole ratio of components 1:1. The yield of the main product was 75%. Mannich's reaction: the synthesis of amine derivatives **IX**–**XIII** was carried out at 45-55°C within 4-5 h, the yield was 65-78%. It is seen from the table that the introduction of **III** and aliphatic amines in the reaction results in high yields of condensation products. The lowest yield was observed in the synthesis of compound **XIII** (65%).

The composition and structure of resulting compounds **III**, and **IX**–**XIII** were proved by IR and ^{1}H NMR spectra. A wide absorption band in the region of 3400 cm^{-1}, characteristic of the hydroxyl group [6], is observed in the IR spectrum of compound **III**, whereas this band is absent from the IR spectra of compounds **IX**–**XIII**.

For all the compounds absorption bands in the region of 720 cm^{-1} characteristic of C-S bonds were detected. Alongside with it, bands in the region of 2920–2890 and 2880–2840 cm^{-1} characteristic of CH_3 and CH_2 groups, respectively, were detected. Stretching vibrations ν(C–N) for compounds **IX**–**XIII** are observed in the range of 1140–1130 cm^{-1}.

The signals of CH_3-group protons in the ^{1}H NMR spectra of the synthesized compounds are exhibited in the range of 0.9–1.0 ppm as a singlet, those of the CH_2 group (in the range of 1.3–1.5 ppm as a multiplet, of the S–CH_2 group) in the region of 3.1–3.2 ppm as a multiplet. Purity of the initial and synthesized compounds was controlled by the GLC analysis.

The compounds were tested as antimicrobial additions to M-11 lubricant. The tests have shown that compounds **IX**–**XIII** possess bactericidal and fungicidal properties and effectively suppress the growth of microorganisms in M-11 oil at the concentrations of 0.5 and 1.0%, compounds **IX** and **XIII** being more effective than the remaining compounds and than the industrial addition agent Na-pentachlorophenolate taken as the measurement standard. The remaining compounds show the effectiveness close to the standard.

Compounds **IX**, **X**, and **XII** were tested for antimicrobial activity. The study of antimicrobial properties of compounds was carried out in relation to the specimens used in practice: ethanol, carbolic acid (phenol), chloramines, rivanol, and nitrofungin. Antimicrobial activity of the substances was studied by the serial dilution method. As the test-cultures we took gram-negative (coliform and pyocyanic rods), gram-positive (yellow-green staphilococcus), spore-forming (anthracoid) bacteria, and yeast-like funguses (Candid genus).

The study of antimicrobial activity has shown that the compounds under study: 1-butylthio-2-(*N,N*-diethylaminomethyleneoxy)- (**IX**), 1-butylthio-2 (*N,N*-dibutylaminomethyleneoxy)- (**X**), and 1-butylthio-2-(piperidyl-*N*-methyleneoxy)heptane (**XII**) show more strongly pronounced antimicrobial activity than ethanol,

carbolic acid, rivanol, nitrofungin, and nitrofurazone applied in practice. The specified compounds can be recommended as germicides.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer in the range of 4000–400 cm^{-1}, the ^1H NMR spectra on a Tesla BS-48 spectrometer (80 MHz) in CCl_4 with hexamethylenedisiloxane as the internal standard. The chromatographic analysis and purity control of the initial and synthesized compounds were carried out on an LKhM-8MD chromatograph with a thermal conduction detector; a column 300×0.3 cm with 5% PEHS on dinochrome P; rate of the gas-carrier (helium) of 40 cm^3 min^{-1}; temperature of a column 150, of evaporator 240°C. The effect of compounds **IX**–**XIII** as antimicrobial dopes to M-11 oil was studied with the application of their 0.5–1.0% solutions in the oil. Antimicrobial properties were determined in a thermal moisture chamber according to GOSTs 9025-74 and 9052-75, and also by the well method at 28–30°C within 2–3 days. Fungal (*Aspergillus niger and Candida tropicalis*) and bacteriemic (*Mycobacterium lacticola and Pseudomonas aeruginoza*) crops were used as test-organisms.

Antimicrobial activity of compounds (**IX**), (**X**), and (**XII**) was studied by the serial dilution method on several strains of microorganisms. As nutrient agents we used MPA with pH 7.2–7.4 (for bacteria) and Saburo medium (for funguses). The dilution degrees were 1:200, 1:400, 1:800, 1:1600, and 1:3200. As reference standards we used ethanol, phenol, chloramine, rivanol, and nitrofungin equally diluted. Bacteria and funguses were plated after 10, 20, 30, 40, and 60 min.

1-Butylthio-2-heptanol (III). To a mixture of 22.5 g (0.25 mol) of 1-butanethiol (**I**) and 25 g of 40% aqueous solution of NaOH 48.75 g (0.25 mol) of 1-bromo-2-heptanol (**II**) was added dropwise at 50–60°C under vigorous stirring. The stirring was prolonged for 3–5 h. After cooling benzene was added to the mixture, an organic layer was separated and washed out by a 5% NaOH solution, then by water up to a neutral reaction, and dried with anhydrous $MgSO_4$. After distilling off a solvent the residual was distilled in vacuum. Yield of 1-butylthio-2-heptanol (**III**) 38.25 g (75%), bp 112–113°C (1 mm Hg), n_D^{20} = 1.4715, d_4^{20} = 0.9164, MR_D: found 62.39, calculated 62.55. IR spectrum, ν, cm^{-1}: 3500 (OH), 2900 (CH_3), 2880 (CH_2). Found (%): C 64.52, H 11.76, S 15.60. $C_{11}H_{24}SO$. Calculated (%): C 64.64, H 11.84, S 15.69.

Methyleneoxyamino derivatives of 1-butylthio-2-heptanol (IX)-(XIII). A common procedure of the synthesis. To a mixture of 0.2 mol of 1-butylthioheptane-2-ol and 0.2 mol of formaldehyde in 30 ml of benzene 0.2 mol of secondary amine (**IV**)–(**VIII**) was added dropwise at 20–22°C with stirring. The stirring was prolonged for 4–5 h more at 45–55°C. After distilling off benzene the residual was distilled in vacuum.

CONCLUSIONS

(1) The reaction of 1-buthanethiol with 1-bromo-2-heptanol in an alkaline medium at 40–50°C results in 1-butylthio-2-heptanol with a yield of 75%.

(2) 1-Butylthio-2-heptanol condenses with formaldehyde and secondary amines to form within 4–5 h at 45–55°C before unknown condensation products with a yield of 65–78%.

(3) 1-Butylthio-2-methyleneoxyamino derivatives of heptane possess bactericidal and fungicidal properties and effectively suppress growth of microorganisms in M-11 oil at a concentration of 0.5–1.0%.

(4) It has been shown that 1-butylthio-2-(*N,N*-diethylaminomethyleneoxy)-, 1-butylthio-2-(*N,N*-dibutylaminomethyleneoxy)-, and 1-butylthio-2-(piperidyl-*N*-methyleneoxy)heptanes exhibit more strongly pronounced antimicrobial activity than ethanol, carbolic acid, rivanol, etc. applied in a medical practice.

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