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SECTION 9. Chemistry and chemical technology.

SYNTHESIS AND PROPERTIES OF FUNCTIONALLY SUBSTITUTED OXYALKYLS

Abstract: *Reaction of N-chloroamides of sulfonic acids (chloramines or N-bromosuccinimide) with unstaturated compounds in aquatic environment was investigated. Wherein, 1-chloro-2-hydroxoalkyls were obtained. It is found that substitution reactions of chlorine atom with different nucleophiles leads functionally substituted hydroxyalkyls. While conducting biological tests of synthesized compounds, positive effect of N, N-diethyldithiocarbamate and thioamide fragments on their antimicrobial properties.*

Key words: *oxyalkyls, chloroamides of sulfonic acid, hydrohalohydrination, halohydrins, anticorrosive and tribological properties, antimicrobial activity.*

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Introduction

As it is known, the compounds, containing hydroxylic group together with other functional fragments, are biologically active compounds. Therefore, functionally substituted hydroxyalkyls attract the attention of researchers due to their wide range of biological effects. It is determined that functionally substituted oxyalkyls have antibacterial and fungicidal activity [1,2]. It was revealed that 2-hydroxy-3-(diamyl) aminopropyl esters have analgesic and antiarrhythmic effects. Arylmethylpyrrolidin-2-yl ethanolamines are antogonists of calcium receptors. A method for the preparation of aminocyclohexyl esters was worked out.

Experimental part

IR-spectra of the obtained compounds were recorded on a «Nicolet IS-10» spectrometer, and NMR H1-spectra were recorded on a «Tesla-467» spectrophotometer operating at 90 MHz.

1-Chloro-2-hydroxyalkyls (I a, b). General technique. 32.1 g (0.12 moles) of chloramine-B were dissolved in 150 ml of water, 11.2 g (0.1 moles) of octene-1 or 16.8 g (0.1 moles) of dodecene-1 were added. While stirring, 11 ml of concentrated HCl were added dropwise at such a rate that the temperature did not rise above 35-40 °C. The mass was then heated to 75 - 80 °C for 2.5 to 3 hours, then cooled, 50-60 ml of hexane was added, after which benzenesulfonamide was filtered off. The hexane layer was separated, hexane was distilled off, and the residue was distilled under vacuum.

1-Bromo-2-undecanol (I c). 89 g (0.5 moles) of N-bromosuccinimide were dissolved in 250 ml of water. 77 g (0.5 moles) of undecene-1 were added dropwise to the solution. The temperature of the reaction mixture was kept not lower than 50-60 °C during 8-10 hours. Then warm water was added until the yellow color of bromosuccinimide disappeared. The resulting solution was washed with warm water. The lower organic layer was separated, dried, and then distilled under vacuum.

N-2-Hydroxyoctyl-4-methylphenylsulfamide (II a). 8.6 g (0.05 moles) of 4-methylphenylsulfamide were dissolved in 20 ml of ethanol, 3 g (0.08 moles) of sodium hydroxide was added. The mixture was heated until dissolution and 9.1 g (0.055 moles) of 1-chloro-2-hydroxyoctane was added dropwise at a temperature of 80 to 85 °C, after which it was boiled during 8-10 hours. The precipitate was separated, ethanol was distilled off, and the residue was distilled under vacuum.

2-Hydroxyoctyl-s-amidothioacetic acid (II b). 9.1 g (0.1 moles) of amidothioacetic acid, 4.5 g (0.11 moles) of NaOH and 30 ml of ethanol while stirring was heated to a temperature of 50-60 °C until dissolved. At this temperature, 16.5 g (0.1 moles) of

1-chloro-2-hydroxyoctane were added dropwise. The temperature was maintained at 75 - 80 °C for 5-6 hours. The reaction mixture was then filtered off, ethanol was distilled off, and the residue was distilled under vacuum.

1-N,N-Diethyldithiocarbamino-2-phenylcarbamateundecyl (III). 3.19 g (0.01 moles) of the compound (II d) and 50 ml of anhydrous benzene while stirring were heated to a temperature of 80-85 °C. At this temperature, 20 ml of a benzene solution of 1.19 g (0.01 moles) of phenyl isocyanate were added dropwise. This temperature was then maintained for 4-5 hours. Benzene was distilled off, and 20 ml of anhydrous hexane was added to the residue. The precipitated crystals were recrystallized from a mixture of benzene: hexane (1: 3).

Physicochemical characteristics of synthesized compounds are given in Table 1.

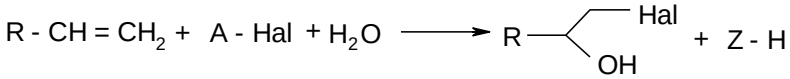
Table 1

Physicochemical properties of synthesized 1,2-functionally substituted alkyls (Ia-c, IIa-d, IIIa-d)

№	Yield, %	Boiling temperature, ^{0}C/ mmHg	n_D^{20}	d_4^{20}	MR_D		Molecular Formula	Elemental analysis, found/calculated		
					found	calculated		N	S	Cl
I a	71.5	85 – 87/1	1.4151	0.9771	45.379	45.536	$C_8H_{17}OCl$			21.9 11.66
I b	65.8	112 - 116/0.6	1.4505	0.9211	64.75	64.01	$C_{12}H_{25}OCl$			19.03 18.66
I c	68.9	136 – 137/5	1.4684	1.238	62.0	62.39	$C_{11}H_{23}OBr$			18.91 18.66
II a	69.9	208 – 211/0.4	1.5048	1.051	84.89	85.41	$C_{15}H_{25}NO_3S$	5.4 4.7		
II b	70.2	167 – 21690.5	1.4679	0.9798	62.24	61.526	$C_{10}H_{21}NO_3S$	15.12 14.61		
II c	69.8	178 – 181/0.4	1.5295	1.0318	83.69	82.87	$C_{13}H_{27}NOS_2$	3.61 3.22		
II d	68.7	211 – 212/2	1.4918	0.9520	97.35	97.82	$C_{16}H_{33}NOS_2$	4.26 4.38	19.98 20.08	
III	67.5	195 – 196 (T_{melt})	-	-	-	-	$C_{23}H_{38}N_2O_2S_2$	6.29 6.38	14.50 14.61	-

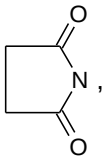
DISCUSSION OF OBTAINED RESULTS

We investigated hydrohalohydrination reaction of unsaturated compounds with monochloroamides of benzenesulfonic acid (chloramine-B), N-bromosuccinimide and calcium hypochlorite in aqueous solution:



$R = C_6H_{13}$, $A = C_6H_5SO_2NNa$, Hal = Cl (Ia);

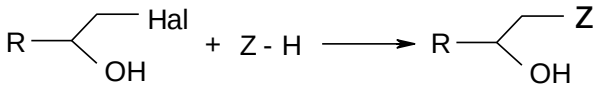
$R = C_{10}H_{21}$, $A = C_6H_5SO_2NNa$, Hal = Cl (IIb);



$R = C_6H_{13}$, $A=Ca(OCl)_2$ (Ia)

Research has shown that regardless of the length of the alkyl radical of the unsaturated compound and the nature of the halogen-containing reagent, the yield of halohydrin is satisfactory (65-72%).

Nucleophilic substitution reactions of halides were carried out and functionally substituted hydroxyalkyls were obtained:

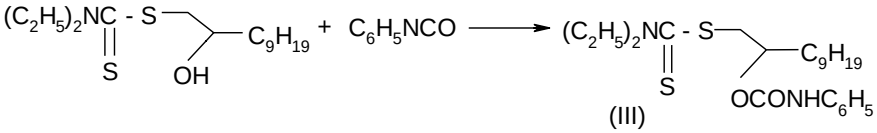


$R = C_6H_{13}$: $Z = n\text{-}CH_3C_6H_4SO_2NH$ (IIa);

$Z = SCH_2CONH_2$ (IIb); $-S-\underset{\underset{S}{\|}}{C}N(C_2H_5)_2$ (IIc);

$R = C_9H_{19}$, $Z = -S-\underset{\underset{S}{\|}}{C}N(C_2H_5)_2$ (IId)

The presence of a hydroxyl group is proved by the reaction of N,N-diethyldithiocarbamino-2-hydroxyundecane with phenyl isocyanate:



The presence of bifunctional groups in the content of synthesized compounds makes them perspective for studying as additives to lubricating oils. The data obtained are shown in Table 2.

Table 2

Effect of synthesized compounds on the properties of M-8 and AK-15 oils

№ comp.	Concentration, %	Corrosion, g/m^2	Critical load, P_{cr}, H	Welding load, P_w, H	Load wear index, LWI	Wear scar diameter, d, mm
Oil M-8	-	180 - 200	-	-	-	-
Oil AK-15	-	-	440	1560	20.1	0.68
I a	1 3	38.5 20.4	820 980	2350 2560	79 61	0.65 0.60
I b	1 3	18.7 14.5	920 1000	2450 2690	65 59	0.60 0.55
II a	1 3	11.6 8.3	1100 1250	2760 2920	52 68	0.56 0.51
II b	1 3	16.8 8.5	1150 1200	2800 3280	65 70	0.50 0.45
II c	1 3 5	13.5 4.8 2.1	1250 1360 1450	3150 3400 3850	71 72 74	0.45 0.41 0.38
ДФ-11	2 5	24.7 6.1	705 820	2590 2870	61 64	0.63 0.40

Among the investigated compound, mercaptoacetamide (II b) and N, N-diethyldithiocarbamate derivatives (IIc) show high anticorrosive properties. Compounds containing a chlorine atom are ineffective.

Studies of anti-wear and anti-seize properties of compounds have shown their high efficiency. The critical load, welding load and load wear index are higher in them than in the industrial additive ДФ-1. Among the synthesized compounds, the highest efficiency is observed in compounds (II b) and (II c). They have high anti-corrosion, anti-seize and anti-wear properties.

Our previous investigations [6 - 9] have shown that compounds containing, in addition to hydroxyl, other functional groups have antimicrobial properties. On this basis, the antimicrobial properties of the synthesized compounds in the M-8 oil solution were investigated.

For investigation of antimicrobial properties the following types of bacteria were used:

Psevdomonas aerugenosa
Mycobacterium

For the investigation of fungicidal properties, the following species of fungi were used:

Aspergillus niger van Tieghem
Penicillium chrysogenium Thom
Scopulariosis brevicanlis (sacc)

Conclusion

The obtained results are provided in Table 3. As it can be seen from the table, compounds containing thioethers have the most effective antimicrobial properties. Among them, the N, N-diethyldithiocarbamate derivatives (II c) showed the best results in terms of inhibiting bacterial growth. 2-Hydroxyoctyl-s-amidoacetic acid has also good fungicidal properties.

Table 3

Test results of some synthesized compounds as antimicrobial additives in the oil M-8

№ compound	Concentration, %	Diameter of the zone of growth inhibition of microorganisms, cm	
		Mixture of bacteria	Mixture of fungi
Ia	0.3 0.5	1.8 2.0	2.3 2.9
Ib	0.3 0.5	2.3 2.6	2.5 3.0
IIa	0.1 0.3 0.5	2.8 3.0 3.3	2.6 2.8 3.0
IIb	0.1 0.3 0.5	3.0 3.3 3.5	2.7 2.9 3.1
IId	0.1 0.3 0.5	3.0 3.3 3.6	2.1 2.5 2.7
Vazin	0.8 - 1	3.0	2.8

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