SYNTHESIS AND PROPERTIES OF FUNCTIONALLY SUBSTITUTED OXYALKYLS

Abstract: Reaction of N-chloroamides of sulfonic acids (chloramines or N-bromosuccinimide) with unsaturated compounds in aquatic environment was investigated. Wherein, 1-chloro-2-hydroxalkyls were obtained. It is found that substitution reactions of chlorine atom with different nucleophiles leads functionally substituted hydroxalkyls. 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, hydroralohydration, halohydrins, anticorrosive and tribological properties, antimicrobial activity.

Language: English

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 antiaarrhythmic effects. Arylmethylpyrrolidin-2-yl ethanolamines are antagonists 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-hydroxalkyls (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

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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-Diethylthiocarbamino-2-phenylcarbamateundecyl (II). 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**

| №  | Yield, % | Boiling temperature, °C/mmHg | nD²⁰ | d²⁰  | MRd found | MRd calculated | Molecular Formula | Elemental analysis, found/calculated |
|----|----------|-----------------------------|------|------|-----------|---------------|------------------|------------------------------------|
| I  |          |                             |      |      |           |               |                  | N   | S   | Cl |
| Ia | 71.5     | 85 – 87/1                   | 1.4151 | 0.9771 | 45.379    | 45.536        | C₁₆H₁₇ClO       | 21.9 | 11.66 |
| Ib | 65.8     | 112 – 116/0.6              | 1.4505 | 0.9211 | 64.75     | 64.01         | C₁₂H₂₅ClO       | 19.03 | 18.66 |
| Ic | 68.9     | 136 – 137/5                | 1.4684 | 1.238  | 62.0      | 62.39         | C₁₁H₂₃Br        | 18.91 | 18.66 |
| II |          |                             |      |      |           |               |                  | N   | S   | Cl |
| IIa| 69.9     | 208 – 211/0.4              | 1.5048 | 1.051  | 84.89     | 85.41         | C₁₅H₂₃NO₃S     | 5.4  | 4.7  |
| IIb| 70.2     | 167 – 216/0.5              | 1.4679 | 0.9798 | 62.24     | 61.526        | C₁₀H₁₀NO₃S     | 15.12 | 14.61 |
| IIc| 69.8     | 178 – 181/0.4              | 1.5295 | 1.0318 | 83.69     | 82.87         | C₁₃H₂₇NOS₂      | 3.61  | 3.22  |
| IId| 68.7     | 211 – 212/2               | 1.4918 | 0.9520 | 97.35     | 97.82         | C₁₆H₃₃NOS₂      | 4.26  | 4.38  | 19.98 | 20.08 |
| III| 67.5     | 195 – 196/T_{min}         | -     | -     | -         | -             | C₁₃H₁₉N₂O₂S₂    | 6.29  | 6.38  | 14.50 | 14.61 |

**DISCUSSION OF OBTAINED RESULTS**

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

\[
\text{R - CH = CH}_2 + \text{A - Hal} + \text{H}_2\text{O} \rightarrow \text{R - Hal} + \text{Z - H}
\]

- \( \text{R = C}_6\text{H}_{13} , \text{A = C}_6\text{H}_5\text{SO}_2\text{NNa} , \text{Hal = Cl} (\text{Ia}); \)
- \( \text{R = C}_{10}\text{H}_{21} , \text{A = C}_6\text{H}_5\text{SO}_2\text{NNa} , \text{Hal = Cl} (\text{Iib}); \)
- \( \text{R = C}_9\text{H}_{19} , \text{A = C}_6\text{H}_5\text{SO}_2\text{NNa} , \text{Hal = Br} (\text{Ic}); \)
- \( \text{R = C}_6\text{H}_{13} , \text{A = Ca(OCl)}_2 (\text{Ia}) \)

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:

\[
R - \text{Hal} + Z - H \rightarrow R - Z
\]

\[
R = C_6H_{13} : Z = n-CH_3C_6H_4SO_2NH \quad (\text{IIa})
\]

\[
Z = \text{SCH}_2\text{CONH}_2 \quad (\text{IIb})
\]

\[
R = C_9H_{19} , Z = - S \cdot \text{CN(C}_2\text{H}_5)_2 \quad (\text{IIc})
\]

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

\[
(C_2\text{H}_5)_2\text{N} - \text{S} - \text{OH} + C_6\text{H}_5\text{NCO} \rightarrow (C_2\text{H}_5)_2\text{N} - \text{S} - \text{CONHC}_6\text{H}_5
\]

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**

| № comp. | Concentration, % | Corrosion, g/m² | Critical load, Pср, H | Welding load, Pw, 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                | 38.5            | 820                  | 2350               | 79                  | 0.65                     |
|         | 3                | 20.4            | 980                  | 2560               | 61                  | 0.60                     |
| I b     | 1                | 18.7            | 920                  | 2450               | 65                  | 0.60                     |
|         | 3                | 14.5            | 1000                 | 2690               | 59                  | 0.55                     |
| II a    | 1                | 11.6            | 1100                 | 2760               | 52                  | 0.56                     |
|         | 3                | 8.3             | 1250                 | 2920               | 68                  | 0.51                     |
| II b    | 1                | 16.8            | 1150                 | 2800               | 65                  | 0.50                     |
|         | 3                | 8.5             | 1200                 | 3280               | 70                  | 0.45                     |
| II c    | 1                | 13.5            | 1250                 | 3150               | 71                  | 0.45                     |
|         | 3                | 4.8             | 1360                 | 3400               | 72                  | 0.41                     |
|         | 5                | 2.1             | 1450                 | 3850               | 74                  | 0.38                     |
| ДФ-11   | 2                | 24.7            | 705                  | 2590               | 61                  | 0.63                     |
|         | 5                | 6.1             | 820                  | 2870               | 64                  | 0.40                     |

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Among the investigated compound, mercaptoacetamide (II b) and N, N-diethylldithiocarbamate 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:

- Pseudomonas aeruginosa
- Mycobacterium

For the investigation of fungicidal properties, the following species of fungi were used:
- Aspergillus niger van Tieghem
- Penicillium chrysogenum 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-diethylldithiocarbamate 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              | 1.8                | 2.3              |
|            | 0.5              | 2.0                | 2.9              |
| Ib         | 0.3              | 2.3                | 2.5              |
|            | 0.5              | 2.6                | 3.0              |
| IIA        | 0.1              | 2.8                | 2.6              |
|            | 0.3              | 3.0                | 2.8              |
|            | 0.5              | 3.3                | 3.0              |
| IIb        | 0.1              | 3.0                | 2.7              |
|            | 0.3              | 3.3                | 2.9              |
|            | 0.5              | 3.5                | 3.1              |
| IId        | 0.1              | 3.0                | 2.1              |
|            | 0.3              | 3.3                | 2.5              |
|            | 0.5              | 3.6                | 2.7              |
| Vazin      | 0.8 - 1          | 3.0                | 2.8              |
Impact Factor:

|               | ISRA (India) | SIS (USA) | ICV (Poland) |
|---------------|--------------|-----------|--------------|
| ISI (Dubai, UAE) | 1.344       | 0.912    | 6.630        |
| GIF (Australia) | 0.829       | 0.156    | 1.940        |
| JIF           | 0.564       | 4.102    | 2.031        |
| SIS (USA)     | 1.500       | 0.912    | 4.260        |
| PIF (India)   | 4.102       | 0.564    | 4.260        |
| ICV (Poland)  | 2.031       | 4.102    | 4.260        |

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