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INVESTIGATION OF THE DIRECTION OF THE REACTIONS OF MERCAPTOACETIC ACID ESTERS WITH EPI- AND THIOEPICHLOROHYDRINS

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The reactions of mercaptoacetic acid esters with epi- and thio-epichlorohydrin in alkaline medium have been investigated. It was found that the reaction of mercaptoacetic acid esters with epichlorohydrin in the presence of an equimolar amount of sodium hydroxide simultaneously produces 2,3-epoxypropylalkoxycarbonylmethyl sulfides and 1-chlor-3-alkoxycarbonylmethylthio-2-propanols. Under using sodium hydroxide is used as a catalyst, only 1-chlorine-3-alkoxycarbonylmethylthio-2-propanols are obtained the reaction of mercaptoacetic acid esters with epichlorohydrin. As a result of the interaction of mercaptoacetic acid esters with thioepichlorohydrin in the presence of equimolar amounts of sodium hydroxide, 2,3-epitiopropylalkoxycarbonylmethyl sulfides are formed as the only products of the reaction.

Keywords: *epichlorohydrin, thioepichlorohydrin, esters of mercaptoacetic acid, thiophenol sodium hydroxide.*

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Introduction

The problem of developing the effective ashless additives for lubricating oils used in modern engines remains relevant today. The solution of this problem is connected with the creation of scientific bases for synthesis of additives with given properties.

There exists a great deal of information in the literature on the synthesis of various derivatives of thiophenols and mercaptans as anti-corrosion additives for lubricating oils. Among them – 2,3-epoxypropyl(aryl) sulfides are of interest, containing both sulfide and epoxy groups, obtained by the reaction of epichlorohydrin with thiols:

This reaction proceeds both in the presence of the catalysts and without them. The direction of the reaction in the presence of catalysts depends on their amount and the ratio of the reacting components. In this case, various compounds can be obtained, since epichlorohydrin, being a bifunctional compound can react, on the one hand, with a halide group, and on the

other, with the opening of the epoxy ring [1]. While the thiophenol reactions with epi- and thioepichlorohydrins have been sufficiently studied [1–4], the ester reactions of mercaptocarboxylic acid with these compounds have not been considered. The aim of the present work is to study the direction this reaction.

Results and discussion

Taking into account the fact previously revealed by us that in sulfides a substitution of the alkyl radical at the sulfur atom by the complex ether fragment $-\text{CH}_2\text{COOR}$ leads to a sharp increase of the anticorrosive activity of the compound, we were interested in study of the direction of the ester reactions of mercaptoacetic acid (EMAA) with epi- and thioepichlorohydrins under various conditions.

It has been established [5] that in the presence of equimolar quantity of the sodium hydroxide EMAA reaction with epichlorohydrin proceeds with formation of 2,3-epoxypropylalkoxycarbonylmethylsulfides and 1-chloro-3-alkoxycarbonylmethylthio-2-propanols simultaneously:

R = C₂H₅, *i*-C₃H₇, C₄H₉.

The yield of each of these products is 25–30%. The low yields of compounds have been apparently connected with partial hydrolysis of EMAA in the alkaline medium.

In the presence of catalytic quantities of the sodium hydroxide or triethylamine, EMAA acts like 2,5-dimethylthiophenol [5] and leads to the formation of only 1-chloro-3-alkoxycarbonylmethylthio-2-propanols with 70–90% yield.

The structure of the synthesized compounds has been studied by a method of PMR. The PMR spectra were recorded on spectrometers T-60 of firm "Varian" with working frequency 60 MHz and firm "Tesla" with working frequency 80 MHz. Hexamethyldisiloxane (HMDS) and tetramethylsilane (TMS) were used as an internal standard, the solvent was carbon tetrachloride. The accuracy of measurement of chemical shifts is 0.05 ppm, scale δ .

In the PMR spectrum of 2,3-epoxypropylisopropoxycarbonylmethyl sulfide a singlet from –SCH₂COO-group is observed at $\delta = 3.17$ ppm.

The resonance signals of protons of fragment are appeared as doublet from –HC–CH₂S– and –CH–CH₂ group with chemical shift $\delta = 2.7$ ppm and from with chemical shift $\delta = 2.6$ ppm, the proton of methine group appears as a quintet at $\delta = 3.0$ ppm.

In the PMR spectrum of 1-chloro-3-isopropoxycarbonylmethylthio-2-propanol the resonance signals of protons of Cl–CH₂–CH(OH)CH₂S-fragment are appeared as two doublets from methylene groups with chemical shifts $\delta_a = 2.8$

ppm and $\delta_b = 3.6$ ppm, as a quintet from methine group at $\delta_c = 3.85$ ppm and a singlet from OH-group at $\delta = 3.8$ ppm. The resonance signal of protons of –S–CH₂–COO-group are observed as a singlet at $\delta = 3.23$ ppm. The resonance signals of protons of –CH(CH₃)₂ in the PMR spectra of above-mentioned compounds are observed as a doublet of two methyl groups at $\delta = 1.22$ ppm and sextet from methine group with chemical shift at $\delta = 4.95$ ppm.

The study of the reaction of compounds containing mercapto- group with sulfurous analog of epichlorohydrin – thioepichlorohydrin is of particular interest. These reactions lead to the formation mainly of thiiranes – sulfurous analogs of epoxy compounds.

A number of works has been devoted to the synthesis and investigation of thiiranes [6–8]. It has been shown that thiophenolate potassium reacts with thioepichlorohydrin to form a single reaction product of 2,3-epithiopropylphenylsulfide [9].

Earlier, a number of alkyl- and aryl-2,3-epithiopropyl sulfides have been synthesized by the reaction of various alkanethiols and thiophenols with thioepichlorohydrin in the presence of an aqueous solution of the sodium hydroxide at 60°C [3].

We have studied the interaction of thioepichlorohydrin with EMAA in alkaline medium [10] and established that the single products of this reaction are 2,3-epithiopropylalkoxycarbonylmethyl sulfides:

R = C₂H₅, C₃H₇, *i*-C₃H₇, C₄H₉, *i*-C₄H₉, C₅H₁₁, C₆H₁₃.

It was known [1] that the oxygen atom of epoxy group is easily exchanged for a sulfur

atom of thiourea with formation of thiirane cycle. It has been shown that as a result of the re-

action of 2,3-epoxypropylethoxycarbonylmethyl sulfide with thiourea 2,3-epithiopropylethoxy-

carbonylmethyl sulfide is formed:

In the IR-spectrum of 2,3-epithiopropylalkoxycarbonylmethyl sulfides there are absorption bands in the field of $1720\text{--}1728\text{ cm}^{-1}$, characteristic for CO group, and also bands at 625 and $670\text{--}673\text{ cm}^{-1}$, indicating the presence of thiirane cycle [11, 12].

In the NMR spectrum of 2,3-epithiopropylpropoxycarbonylmethyl sulfide the chemical shifts in the field of $2.17\text{--}2.92\text{ ppm}$ characterize the protons of propylene sulfide residue. Along with this, there are signals with chemical shifts 0.97 (protons of CH_3 group), 1.58 (protons of CH_2 -group, adjacent to CH_3), 3.98 (protons of $-\text{CH}_2-\text{O}$ -group) and 3.17 (protons of $-\text{CO}-\text{CH}_2$ -group) ppm [13].

It follows from consideration of the above-mentioned material that in the reactions with haloid-containing compounds in the alkaline medium, EMAA acts like thiophenols, excepting EMAA reaction with epichlorohydrin in the presence of an equimolar quantity of the sodium hydroxide, when along with 2,3-epithiopropylalkoxycarbonylmethyl sulfides rather 1-*bis* (alkoxycarbonyltio)-2-propanols, but 1-chlorine-3-alkoxycarbonylmethylthio-2-propanols are formed.

There have been investigated the anticorrosive and anti-wear properties of the synthesized compounds in the mineral oil DS-11 at the end of $0.5\text{--}1\%$. The anticorrosive properties were determined on apparatus DK-2 on a method NAMI (GOST 20502-75 variant 2). The results of tests showed that the obtained 2,3-epoxypropylalkoxycarbonylmethyl sulfides and 1-chloro-3-alkoxycarbonylmethylthio-2-propanols possess high anticorrosive properties and at concentration 0.5% decrease the corrosion of lead plates from $180\text{ gm}^2\text{h}^{-1}$ to 1.3 and $2.4\text{ gm}^2\text{h}^{-1}$. The anti-wear properties of the compounds were studied in the oil solution DS-11 on a friction machine CHSHM-3.3 (GOST 9490-75) at

an axial load of 392 N and the experiment duration for 60 min . The test results showed that these compounds at the same concentration decrease the diameter of the wear spot from 1.01 mm to $0.46\text{--}0.56\text{ mm}$.

It should be noted that the obtained alkoxycarbonylmethylglycidyl- and hydroxy-3-chloropropylalkoxycarbonylmethyl sulfides can also be used as synthons for further synthesis and study of new classes of compounds.

Conclusions

1. It has been established that in the presence of an equimolar quantity of the sodium hydroxide, the reaction of mercaptoacetic acid esters with epichlorohydrin proceeds with the formation of 2,3-epoxypropylalkoxycarbonylmethyl sulfides and 1-chloro-3-alkoxycarbonylmethylthio-2-propanols simultaneously.

2. In the presence of catalytic quantities of the sodium hydroxide or triethylamine the esters of mercaptoacetic acid acts like thiophenols and leads to the formation of 1-chloro-3-alkoxycarbonylmethylthio-2-propanols with $70\text{--}90\%$ yield.

3. The reaction of mercaptoacetic acid esters with thioepichlorohydrin proceeds with the conservation of thiirane cycle and formation of only reaction products – 2,3-epithiopropylalkoxycarbonylmethyl sulfides. The latter ones are also formed as a result of the reaction of 2,3-epoxypropylalkoxycarbonylmethyl sulfides with thiourea.

4. The synthesized compounds have been investigated as additives for lubricating oils. It has been established that 2,3-epoxypropylalkoxycarbonylmethyl sulfides possess high anticorrosive, antimicrobial and anti-wear properties.

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MERKAPTOSİRKƏ TURŞUSU EFİRLƏRİNİN EPİ- VƏ TİOEPIKLORHİDRİNLƏRLƏ REAKSİYALARININ TƏDQİQİ

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Qələvi mühitdə merkaptosirkə turşusu efirlərinin epİ- və tioepixlorhidrinlə reaksiyaları öyrənilmişdir. Müəyyən olunmuşdur ki, ekvimolyar miqdarda natrium hidroksid iştirakı ilə merkaptosirkə turşusu efirlərinin epixlorhidrinlə reaksiyasından eyni zamanda 2,3- epoksipropilalkoksikarbonilmetil sulfidlər və 1- xlor- 3-alkoksikarbonilmetiltio-2-propanollar əmələ gəlir. Natrium hidroksiddən katalizator kimi istifadə etdikdə merkaptosirkə turşusu efirlərinin epixlorhidrinlə reaksiyasından yalnız 1-xlor-3-alkoksikarbonilmetiltio-2-propanollar alınır. Ekvimolyar miqdarda natrium hidroksid iştirakı ilə merkaptosirkə turşusu efirlərinin tioepixlorhidrinlə qarşılıqlı təsiri nəticəsində reaksiyanın yeganə məhsulu kimi 2,3- epitiopropilalkoksikarbonilmetilsulfidlər əmələ gəlir.

Açar sözlər: epixlorhidrin, tioepixlorhidrin, merkaptosirkə turşunun efirləri, tiofenol, natrium hidroksid

ИССЛЕДОВАНИЕ НАПРАВЛЕНИЯ РЕАКЦИИ ЭФИРОВ МЕРКАПТОУКСУСНОЙ КИСЛОТЫ С ЭПИ- И ТИОЭПИХЛОРИДИНАМИ

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Изучены реакции эфиров меркаптоуксусной кислоты с эпи- и тиоэпихлоргидринами в щелочной среде. Установлено, что в присутствии эквимольного количества едкого натра реакция эфиров меркаптоуксусной кислоты с эпихлоргидрином протекает с образованием смеси 2,3-эпоксипропилалкокенилсульфидов и 1-хлор-3-алкоксикарбонилметилтио-2-пропанолов. В присутствии каталитических количеств едкого натра реакции эфиров меркаптоуксусной кислоты с эпихлоргидрином приводят к образованию лишь 1-хлор-3-алкоксикарбонилметилтио-2-пропанолов. В присутствии эквимольного количества едкого натра эфиры меркаптоуксусной кислоты реагируют с тиоэпихлоргидрином с образованием в качестве продуктов реакции только 2,3-эпителиопропилалкокенил-метилсульфидов.

Ключевые слова: эпихлоргидрин, тиоэпихлоргидрин, эфиры меркаптоуксусной кислоты, тиофенол, гидроксид натрия.