

UDC 547.279(088.8)

SYNTHESIS OF ALKOXYCARBONYLMETHYL ESTERS OF THIOACETIC AND THIOBENZOIC ACIDS AND THEIR INVESTIGATION AS ADDITIVES TO LUBRICATING OILS

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Received 18.05.2023

Accepted 27.07.2023

Abstract: The method for obtaining alkoxy carbonylmethyl esters of thioacetic acid, based on the interaction of mercaptoacetic acid esters with acetic anhydride in an alkaline medium was proposed. It showed that an alternative way to obtain alkoxy carbonylmethyl esters of thioacetic acid is the reaction of mercaptoacetic acid esters with acetyl chloride in the presence of equimolar quantities of triethylamine. The interaction of mercaptoacetic acid esters with benzoyl chloride in the presence of equimolar amounts of triethylamine was used to synthesize appropriate alkoxy carbonylmethyl esters of thioacetic and thiobenzoic acids. Study into synthesized compounds as additives to lubricating oils revealed that addition of butoxycarbonyl methyl ester of thioacetic acid at a concentration of 1% in M-8 oil practically eliminated its corrosibility, while butoxycarbonyl methyl esters of thioacetic and thiobenzoic acids also had some lubricating and antimicrobial properties.

Keywords: esters of mercaptoacetic, thioacetic and thiobenzoic acids, acetic anhydride, acetyl chloride, lubricating oils, corrosibility, lubricating properties, antimicrobial additives

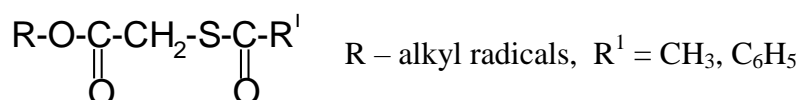
DOI: 10.32737/2221-8688-2023-3-294-300

Introduction

As the mechanical engineering and the tightening of requirements for lubricating oils develops, there is a need to develop more effective additives for them. In this aspect, any study related to the directed synthesis of new multifunctional additives and the identification of the relationship between their structure and properties is undoubtedly relevant.

Previously, we studied the effect of the ester group on the functional properties of

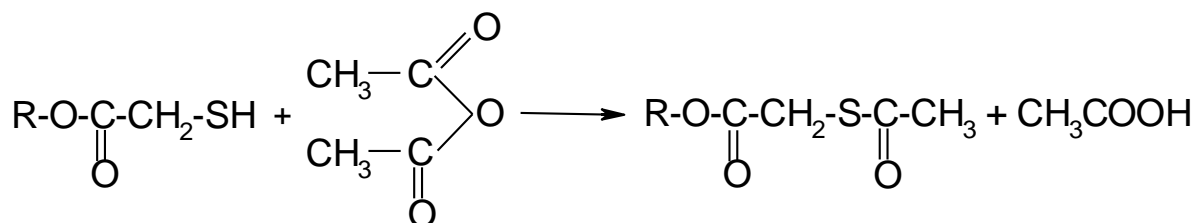
various sulfides and found that just alkoxy carbonylmethylthio fragment largely contributed to enhancing the anticorrosion activity of the compounds [1–3]. In order to study the effect of the acyl group attached to a sulfur atom, on the properties of the compound, there were studied alkoxy carbonylmethyl esters of thioacetic and thiobenzoic acids with the following formula



As compared to the alkyl esters of thiocarboxylic acids, their alkoxy carbonyl methyl esters are poorly studied compounds [4,5].

There is no information in the literature on the interaction of alkyl esters of mercaptoacetic

acid with acetic anhydride. We revealed that in an alkaline medium, this reaction leads to the formation of alkoxy carbonyl methyl derivatives of thioacetic acid, which are of interest both as additives to lubricating oils and biologically active substances [6,7].



R = *i*-C₃H₇ (I), C₄H₉ (II)

The structure of the synthesized compounds was confirmed by the data of IR and NMR spectra [8, 9], as well as chemically. So, in the IR spectrum of isopropoxycarbonylmethyl ester of thioacetic acid (comp.I), the absence of a band with a frequency of 2600-2500 cm⁻¹ indicates the interaction of the mercapto-group of the isopropyl ester of mercaptoacetic acid with acetic anhydride. The IR spectrum of comp.I

contains absorption bands at 1740 and 1136 cm⁻¹, indicating the presence of C=O and C-S bonds, respectively.

¹H NMR spectrum of comp.I (CDCl₃, δ, ppm): 1.28 d. (6H, 2CH₃), 2.35 s. (3H, CH₃), 3.78 s. (2H, CH₂), 4.96 m. (1H, CH).

¹³C NMR spectrum of comp.I (CDCl₃, δ, ppm): 22.3 (2CH₃), 33.6 (CH₂), 70.2 (CH), 169.9 (COO), 195.3 (CO).

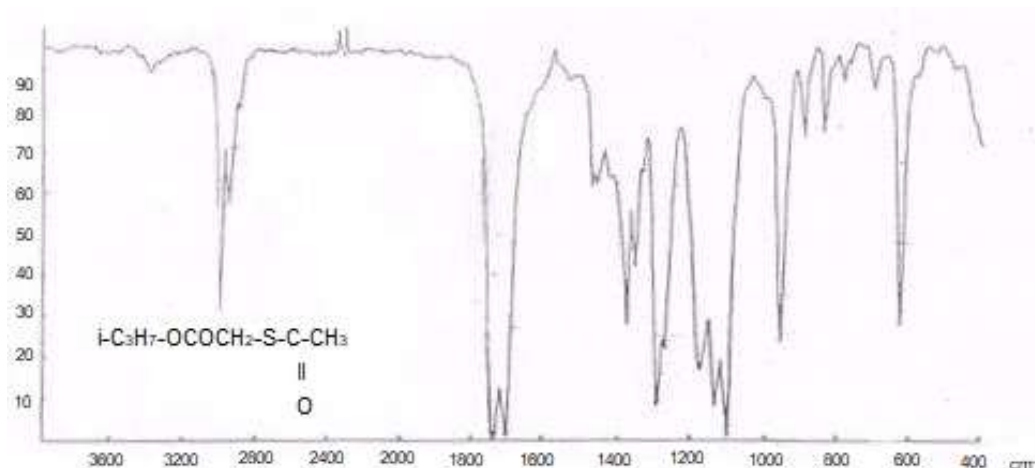


Fig.1. IR spectra of isopropoxycarbonylmethyl ester of thioacetic acid

Experimental Part

The starting esters of mercaptoacetic acid were obtained by the well-known method [10].

The IR spectra of substances were taken on a Specord M-80 spectrophotometer in a thin layer of 4000-400 cm⁻¹.

The NMR spectra were taken on AS-200 spectrophotometers (Bruker ¹H-200 MHz, ¹³C-50 MHz). Internal standard was TMS. 1-5%

solutions of the studied compounds in CDCl₃ were used.

Butoxycarbonylmethyl ester of thioacetic acid (II). A mixture of 4 g of NaOH, 8 ml of water and 17.76 g (0.12 g-mol) of mercaptoacetic acid butyl ester was poured onto 50 g of finely crushed ice, and 12.75 g (0.125 g-mol) of acetic anhydride was quickly added

with vigorous stirring. Stirring continued for another 1 hour at a temperature of 40-50°C. Then the reaction mixture is extracted with benzene, washed with water to neutral, dried

over calcium chloride, and after distillation of benzene, comp.II was isolated by vacuum distillation, yield is 14.8 g (65%).

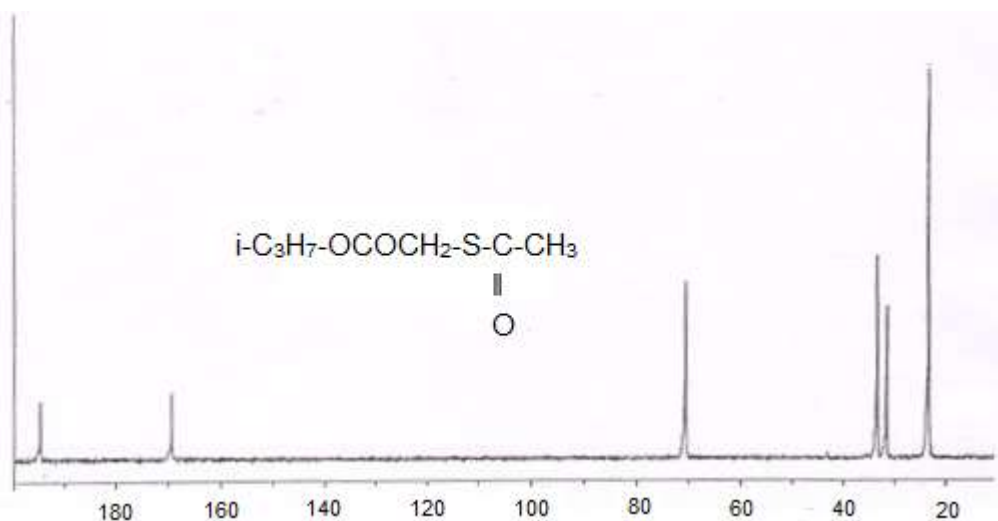
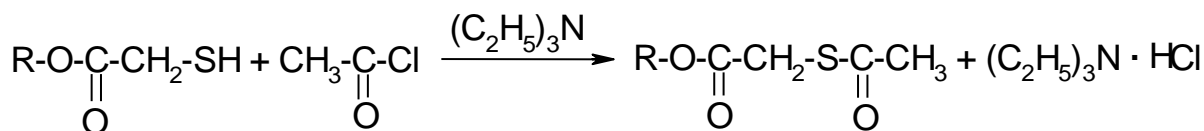


Fig.2. NMR spectra of isopropoxycarbonylmethyl ester of thioacetic acid

The isopropoxycarbonylmethyl ester of thioacetic acid comp.I was obtained by a similar procedure with yield of 64%. By interaction of isopropyl and butyl esters of

mercaptoacetic acid with acetyl chloride in the presence of equimolar amounts of triethylamine compounds identical to comp.I and II, respectively were obtained:

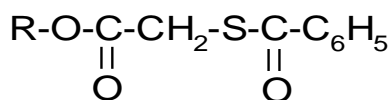


R = i-C₃H₇ (I), C₄H₉ (II)

Isopropoxycarbonylmethyl ester of thioacetic acid (I). 3.93 g (0.05 g-mol) of acetyl chloride was added dropwise to cooled to -5°C solution of 6.7 g (0.05 g-mol) of isopropyl ester of mercaptoacetic acid and 5.1 g (0.05 g-mol) of triethylamine in 50 ml of anhydrous benzene, so that the mixture temperature didn't rise above 5°C. The reaction mixture was stirred for

1 hour at 50-60°C. The separated precipitate of the hydrochloric acid salt of triethylamine was filtered off, after distillation of benzene, comp.I was isolated by vacuum distillation, yield was 6.6 g (75%).

Alkoxy carbonylmethyl esters of thiobenzoic acid were obtained by a similar procedure (74-80%)



R = C₂H₅ (III) i-C₃H₇ (IV), C₄H₉ (V)

The synthesized compounds (I - V) (Table1) are liquids that are readily soluble in

organic solvents and lubricating oils, insoluble in water.

Table 1. Characterization of alkoxy carbonylmethyl esters of thioacetic and thiobenzoic acids

Comp.	R	R'	B.p., °C (P, mm Hg)	d_4^{20}	n_D^{20}	MR _D		Found, %			Calculated, %		
						found	cal.	C	H	S	C	H	S
I	i-C ₃ H ₇	CH ₃	126-127 (20)	1.0990	1.4670	44.49	44.19	47.38	7.04	17.98	47.71	6.86	18.09
II	C ₄ H ₉	CH ₃	115-117 (5)	1.0738	1.4716	49.58	48.81	50.84	7.30	16.66	50.50	7.42	16.85
III	C ₂ H ₅	C ₆ H ₅	192-193 (20)	1.1966	1.5613	60.72	59.06	60.16	5.54	14.12	58.91	5.39	14.30
IV	i-C ₃ H ₇	C ₆ H ₅	155-156 (3)	1.1493	1.5343	64.48	63.68	60.31	6.18	13.65	60.48	5.92	13.45
V	C ₄ H ₉	C ₆ H ₅	190-191 (5)	1.1413	1.5389	69.25	68.30	61.54	6.52	12.54	61.88	6.39	12.71

Results and Discussions

The influence of the synthesized compounds on the anticorrosive, lubricating and antimicrobial properties of M-8 oil was studied.

The anticorrosive properties of derivatives of thioacetic and thiobenzoic acids were determined by the rigorous NAMI method in the presence of 0.02% copper naphthenate for 25 hours at 140°C (lead plates). As a result of the

tests, it was found that the addition of 1% of comp.II practically eliminated the corrosiveness of M-8 oil.

The lubricating properties of the studied compounds were studied on a four-ball friction machine according to GOST 9490-75. The test results are shown in Table 2.

Table 2. Lubricating properties of synthesized compounds

Comp.	Formula of compounds	Concentration, %	I_s	P_w, H	P_c, H	D_{ws}, mm
II	$C_4H_9-O-C(=O)-CH_2-S-C(=O)-CH_3$	1	38	784	1568	0.49
V	$C_4H_9-O-C(=O)-CH_2-S-C(=O)-C_6H_5$	1	38	784	1568	0.44
	M-8 oil	-	32	617	1235	0.62

The lubricating properties of the compounds are characterized by the scuffing index (I_s), the welding load (P_w), the critical seizing load (P_c) and the wear spot diameter (D_{ws}). The anti-wear property index is determined at a load of 392 Newton and test duration of 30 minutes.

According to Table 2, butoxycarbonyl methyl esters of thioacetic and thiobenzoic acids significantly improve the lubricating properties

of M-8 oil. So, introducing 1% of these compounds into M-8 oil decrease the wear scar diameter from 0.62 mm to 0.44 - 0.49 mm.

The antimicrobial properties of the synthesized compounds (II, V) are established by the method MEC - 1954 under conditions simulating tropical atmosphere (in a thermostat at 28-32°C and relative air humidity 90-100%). Fungal and bacterial cultures were used as test microbes. The test results are shown in Table 3.

Table 3. Antimicrobial properties of synthesized compounds

Comp.	Formula	Concentration, %	Zone of microbial growth inhibition, cm		
			Bacteria	Fungi	
			<i>Pseudomonas aeruginosa</i>	<i>Candida tropicalis</i>	<i>Aspergillus niger</i>
II	$C_4H_9-O-C(=O)-CH_2-S-C(=O)-CH_3$	0.5	++	0.1 - 0.2	0.7 - 0.9
		1.5	++	0.3 - 0.4	1.5 - 1.7
V	$C_4H_9-O-C(=O)-CH_2-S-C(=O)-C_6H_5$	0.5	++	0.1 - 0.2	0.6 - 0.8
		1.5	0.1 - 0.2	0.2 - 0.3	0.8 - 1.5

+ Abundant growth of microorganisms around the well in the Petri dish

As can be seen from Table 2, the studied compounds (II, V) show a certain antifungal activity: the inhibition zone of fungi is 1.5-1.7 cm.

Thus a one-stage method for the synthesis of alkoxy carbonylmethyl esters of thioacetic and thiobenzoic acids was developed, which consists in the interaction of alkyl esters of mercaptoacetic acid with acetic anhydride in an alkaline medium.

It found that the interaction of

mercaptoacetic acid esters with acetyl and benzoyl chlorides in the presence of equimolar amounts of triethylamine leads to the formation of alkoxy carbonylmethyl esters of thioacetic and thiobenzoic acids, respectively.

It was established that alkoxy carbonylmethyl esters of thioacetic and thiobenzoic acids had some anticorrosive, lubricating and antimicrobial properties in relation to lubricating oils.

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TİOSİRKƏ VƏ TİOBENZOY TURŞULARININ ALKOKSİKARBONİLMETİL EFİRLƏRİNİN SİNTEZİ VƏ ONLARIN SÜRÜTKÜ YAĞLARINA AŞQAR KİMİ TƏDQIQI

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Xülasə: Tiosirkə turşusunun alkoksikarbonilmetil efirlərinin alınması üçün qələvi mühitdə merkaptosirkə turşusu efirlərinin sirkə anhidridi ilə qarşılıqlı təsirinə əsaslanan üsul təklif edilmişdir. Göstərilmişdir ki, tiosirkə turşusunun alkoksikarbonilmetil efirlərini almaq üçün alternativ üsul merkaptosirkə turşusu efirlərinin ekvimolyar miqdarda trietilaminin iştirakı ilə asetilxloridlə reaksiyasıdır. Tiosirkə və tiobenzoy turşularının müvafiq alkoksikarbonilmetil efirlərinin sintezi üçün ekvimolyar miqdarda trietilaminin iştirakı ilə merkaptosirkə turşusu efirlərinin benzoilxloridlə qarşılıqlı təsirindən istifadə edilmişdir. Sintez edilmiş birləşmələrin sürtkü yağlarına aşqar kimi tədqiqi nəticəsində müəyyən edilmişdir ki, tiosirkə turşusunun butoksikarbonilmetil efirinin 1% qatılıqda M-8 yağına əlavə edilməsi onun korroziyasını praktiki olaraq aradan qaldırır, tiosirkə və tiobenzoy turşularının butoksikarbonilmetil efirləri həm də müəyyən yağlayıcı və antimikrob xassələr göstərir.

Açar sözlər: merkaptosirkə-, tiosirkə- və tiobenzoy turşularının efirləri, sirkə anhidridi, asetilxlorid, sürtkü yağları, korroziyaya uğrama, yağlayıcı xassələr, antimikrob aşqarlar

СИНТЕЗ АЛКОКСИКАРБОНИЛМЕТИЛОВЫХ ЭФИРОВ ТИОУКСУСНОЙ И ТИОБЕНЗОЙНОЙ КИСЛОТ И ИССЛЕДОВАНИЕ ИХ В КАЧЕСТВЕ ПРИСАДОК К СМАЗОЧНЫМ МАСЛАМ

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Аннотация: Предложен способ получения алкоксикарбонилметилового эфира тиоуксусной кислоты, основанный на взаимодействии эфиров меркаптоуксусной кислоты с уксусным ангидридом в щелочной среде. Показано, что альтернативным путем получения алкоксикарбонилметилового эфира тиоуксусной кислоты являются реакции эфиров меркаптоуксусной кислоты с хлористым ацетилом в присутствии эквимольных количеств триэтиламина. Взаимодействием эфиров меркаптоуксусной кислоты с хлористым бензоилом в присутствии эквимольных количеств триэтиламина синтезированы соответствующие алкоксикарбонилметилловые эфиры тиоуксусной и тиобензойной кислот. В результате исследования синтезированных соединений в качестве присадок к смазочным маслам установлено, что добавление бутоксикарбонилметилового эфира тиоуксусной кислоты в концентрации 1% в масло М-8 практически устраняет его коррозионность, бутоксикарбонилметилловые эфиры тиоуксусной и тиобензойной кислот также обладают определенными смазывающими и антимикробными свойствами.

Ключевые слова: эфиры меркаптоуксусной, тиоуксусной и тиобензойной кислот, уксусный ангидрид, ацетилхлорид, смазочные масла, коррозионность, смазывающие свойства, антимикробные присадки.