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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

1-Heptylthio-3-(2'-chlorophenoxy)-2-propanol Derivatives as Additives to Lubricating Oils

M. A. Mirzoeva, V. S. Gasanov, V. A. Abbasova, and M. A. Allakhverdiev

Baku State University, Baku, Republic of Azerbaijan
Azerbaijani State Pedagogical University, Baku, Republic of Azerbaijan

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Abstract—Possibility to obtain 1-heptylthio-3-(2'-chlorophenoxy)-2-propanol by reacting 1-heptylthio-3-chloro-2-propanol with o-chlorophenol in an alkaline medium and synthesize its carbamates, thiocarbamates, and acetyl, alkoxymethyl, and amino methyl derivatives was studied. The compounds synthesized were examined as anticorrosion and antimicrobial additives to lubricating oils

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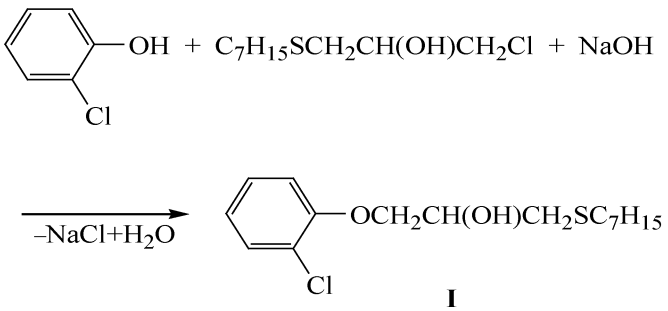
It is known that various nitrogen- and sulfur-containing phenol derivatives are widely used as antioxidant and anticorrosion additives. Joint presence of these elements improves these anticorrosion properties, compared with compounds containing only nitrogen and sulfur [1]. Proceeding with studies in the field of synthesis of various classes of nitrogen- and sulfur-containing compounds and analysis of their functional properties [2–5], we synthesized and examined 1-heptylthio-3-(2'-chlorophenoxy)-2-propanol and its various derivatives.

1-Heptylthio-3-(2'-chlorophenoxy)-2-propanol (**I**) was synthesized in 71% yield by reacting 1-heptylthio-3-chloro-2-propanol with 2-chlorophenol in an alkaline medium (Scheme 1).

1-Heptylthio-3-(2'-chlorophenoxy)-2-propanol (**I**) is a transparent fluid with a characteristic odor and purity of 99.5% (determined by GLC). Its IR spectra contain broad absorption bands at 3430–3450 cm^{-1}, characteristic of hydroxy groups.

Scheme 1.



I

1-Heptylthio-3-(2'-chlorophenoxy)-2-propanol (**I**) was reacted with aromatic isocyanates, isothiocyanates, α-chloroesters, chloranhydrides, and secondary amines in the presence of formaldehyde to give the corresponding derivatives by Scheme 2.

Carbamates **II**–**VII** are colorless crystals well soluble in acetone and chloroform. Thiocarbamates **VIII**–**IX** are yellowish crystals soluble in various organic solvents (Table 1).

Alkoxymethyl, acetyl, and alkylaminomethyl derivatives **X**–**XVI** are transparent liquids with a characteristic odor, soluble in various organic solvents (Table 2).

The IR spectra of compounds **II**–**IX** contain no absorption bands at 2250–2390, 1990–2140, and 3430–3450 cm^{-1}, which are characteristic of the isocyanate, isothiocyanate, and hydroxy groups, but show absorption at 1715–1725, 1480–1510, and 3300–3330 cm^{-1}, which indicates the presence of carbamate, thiocarbamate, and NH groups, respectively [6].

In the 1H NMR spectrum of 1-heptylthio-3-(2'-chlorophenoxy)-2-propanol (**I**), protons of the terminal

Scheme 2.

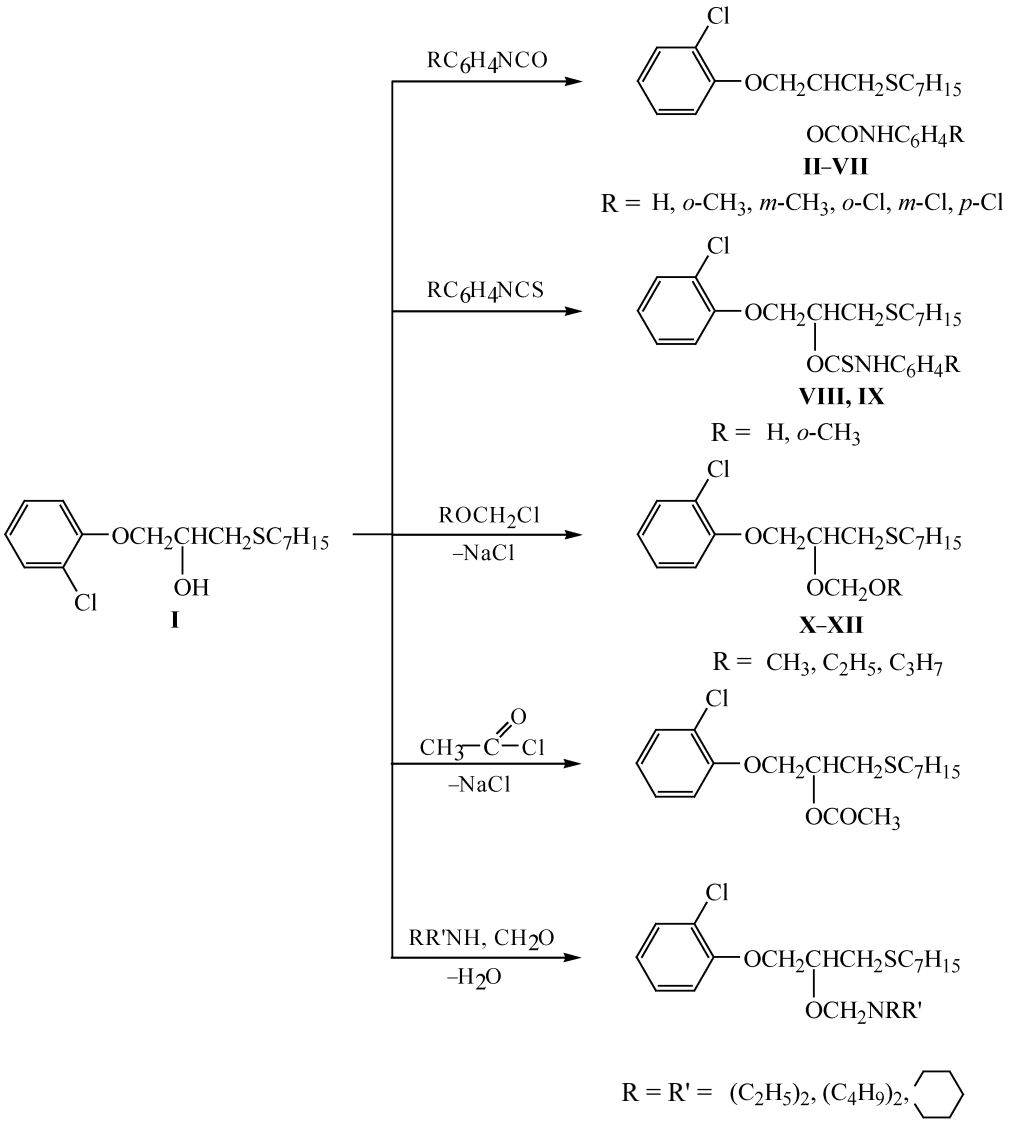


Table 1. Physicochemical constants of 1-heptylthio-2-phenylcarbamato(2-phenylthiocarbamato)-3-(2'-chlorophenoxy)propanes **II–IX**

Compound	R	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
				N	S		N	S
II	H	65	69–70	3.16	7.29	$C_{23}H_{30}ClNSO_3$	3.21	7.35
III	*o*-CH_3	65	70–71	3.03	7.04	$C_{24}H_{32}ClNSO_3$	3.11	7.12
IV	*m*-CH_3	66	71–72	3.04	7.07	$C_{24}H_{32}ClNSO_3$	3.11	7.12
V	*o*-Cl	64	78–79	2.83	6.73	$C_{23}H_{29}Cl_2NSO_3$	2.97	6.81
VI	*m*-Cl	63	77–78	2.84	6.70	$C_{23}H_{29}Cl_2NSO_3$	2.97	6.81
VII	*p*-Cl	62	80–81	2.81	6.71	$C_{23}H_{29}Cl_2NSO_3$	2.97	6.81
VIII	H	61	130–131	3.00	14.11	$C_{23}H_{30}ClNSO_3$	3.09	14.18
IX	*o*-CH_3	60	135–136	2.93	13.68	$C_{24}H_{32}ClNS_2O_2$	3.00	13.75

Table 2. Physicochemical constants of alkoxymethoxy, acetyloxy, and dialkylaminomethoxy derivatives of 1-heptylthio-3-(2'-chlorophenoxy)-2-propanol **X–XVI**

Compd.	R	mp, °C	n_D^{20}	d_4^{20}	MR_D		Found		Calculated		Formula
							%				
					found	calculated	N	S	N	S	
X	CH_3O	220–221	1.5286	1.1102	100.20	100.23	–	8.81	–	8.88	$C_{18}H_{29}ClSO_3$
XI	C_2H_5O	224–225	1.5252	1.1010	104.40	104.87	–	8.49	–	8.55	$C_{19}H_{31}ClSO_3$
XII	C_3H_7O	230–231	1.5220	1.0882	109.02	109.51	–	8.18	–	8.24	$C_{20}H_{33}ClSO_3$
XIII	CH_3CO	192–193	1.5278	1.0987	100.56	100.84	–	8.84	–	8.93	$C_{18}H_{27}ClSO_3$
XIV	$(C_2H_5)_2N$	221–222	1.5290	1.0658	116.13	116.18	3.27	7.88	3.048	7.97	$C_{21}H_{36}ClNSO_2$
XV	$(C_4H_9)_2N$	231–232	1.5262	1.0439	134.54	134.76	3.21	6.88	3.06	6.99	$C_{25}H_{44}ClNSO_2$
XVI		212–213	1.5370	1.0924	118.37	118.77	3.56	7.65	3.38	7.74	$C_{22}H_{36}ClNSO_2$

methyl group appear as a triplet at strong fields, centered at 0.91 ppm. The multiplet at 2.30–3.00 ppm belongs to signals of two methylene groups bonded to a sulfur atom. The broad singlet centered at 4.17 ppm corresponds to resonant absorption by a proton of the hydroxy group. A multiplet associated with the methine proton lies at chemical shifts of about 3.67 ppm. The existence of secondary hydroxy groups in the molecule of compound **I** was confirmed by ^{1}H NMR spectroscopy of the product of its acylation. The ^{1}H NMR spectrum of 1-heptylthio-2-acetyloxy-3-(2'-chlorophenoxy)propane (**XIII**) contains a signal corresponding to the methine group, shifted downfield by 1.6 ppm relative to the starting **I**. Published data [7] on the nature of primary and secondary hydroxy groups indicate that, upon acetylation, the signal of the proton bonded to the carbon atom is shifted downfield, compared with the starting alcohol, by 0.5 ppm for primary alcohols and 1.00–1.15 ppm for secondary alcohols. In the case in question, the shift is by 1.6 ppm. This indicates that the hydroxy group in compound **I** synthesized in this study is at the secondary carbon atom. Nonequivalent protons of the aromatic ring appear as a multiplet in a weak field at 7.4–7.8 ppm.

The ^{1}H NMR spectra of the rest of the compounds are similar to those already considered.

The carbamates and thiocarbamates **II–IX** we synthesized were tested as anticorrosion additives to the M-11 lubricating oil and the data obtained were compared with the properties of the IKhP-21 additive. The results of these tests (Table 3) demonstrate that compounds **II–IX** possess good anticorrosion properties. The carbamates synthesized, and especially thiocarbamates, surpass the IKhP-21 additive in efficiency as anticorrosion additives.

The alkoxymethyl, acyl, and alkylaminomethyl derivatives **X–XVI** we synthesized were tested as antimicrobial additives to the M-11 lubricating oil. The results of these tests (Table 4) demonstrate that compounds **X–XVI** possess bactericide and fungicide properties and effectively suppress growth of microorganisms in the M-11 oil when added in concentrations of 0.5 and 1.0%.

EXPERIMENTAL

The IR spectra were measured on a Specord 75-IR spectrometer in a thin layer for liquid substances and in Vaseline oil for solids; the ^{1}H NMR spectra were measured on a Bruker-300 MHz instrument.

The analysis by the GLC method was made on an LKhM-8MD chromatograph model 5 (190°C, 1000 × 3 mm column, immobile phase Lukopren G-1000, 5% on Chromaton N-AW-HMDS support, 0.25–0.31 μm).

The effect of compounds **II–IX** on the anticorrosion properties of the M-11 oil was studied with solutions of substances **II–IX** in the M-11 oil in concentrations of 0.5 and 1.0%. The anticorrosion properties were determined on a DK-NAMI instrument at 140°C in the course of 25 h [GOST (State Standard) 20502–75].

The effect of compounds **X–XVI** on the antimicrobial properties of the M-11 oil was studied with solutions of substances **X–XVI** in the M-11 oil in concentrations of 0.5–1.0%. The antimicrobial properties were determined in a hygrothermal chamber in conformity with GOST

9.023–74 and GOST 9.052–75 and by the well method. The experiments were carried out at 28–30°C in the course of 2–3 days. As test-organisms served fungal (*Candida tropicalis, Aspergillus niger*) and bacterial (*Mycobacterium lacticola, Pseudomonas aerruginosa*) cultures.

1-Heptylthio-3-(2'-chlorophenoxy)-2-propanol (I). To a mixture of 12.85 g of *o*-chlorophenol and 10 g of a 40% aqueous solution of NaOH was added, dropwise at 75–80°C under vigorous stirring, 22.48 g of 1-heptylthio-3-chloro-2-propanol. Then, the mixture was agitated at the same temperature for 4–5 h. The mixture was cooled, diluted with benzene, washed first with a 5% aqueous solution of the alkali and then with water to a neutral reaction, and dried with anhydrous sodium sulfide. After the solvent was evaporated, the residue was distilled in a vacuum to give 22.5 g (71%) of 1-heptylthio-3-(2'-chlorophenoxy)-2-propanol (**I**) with the following physicochemical characteristics: bp 222–223°C/1 mm Hg, n_D^{20} 1.5342, d420 1.1150; MR_D: found 88.37,calculated 88.92. Found, %: C 60.61, H 7.81, Cl 11.09, S 10.04. Calculated, %:C 60.64, H 7.94, Cl 11.18, S 10.11.

1-Heptylthio-2-phenylcarbamato-3-(2'-chlorophenoxy)propane (II). To a mixture of 6.34 g of compound **I** and 25 ml of anhydrous benzene was added dropwise, at 80–85°C, 2.38 g of phenylisocyanate dissolved in 20 ml of anhydrous benzene. The mixture was agitated for additional 6–8 h, cooled, 2/3 of benzene was evaporated, and 25 ml of anhydrous hexane was added. The colorless crystals precipitated in the process were determined and recrystallized from a 3 : 1 hexane–benzene mixture.

Table 3. Effect of the compounds synthesized on the anticorrosion properties of the M-11 oil

Additive	Content of an additive in the oil, wt %	Corrosion, g m^{-2}
M-11 oil without additives	–	180–200
II	0.5	60.4
	1.0	47.5
III	0.5	59.9
	1.0	47.2
IV	0.5	59.4
	1.0	47.0
V	0.5	64.6
	1.0	51.3
VI	0.5	63.6
	1.0	50.1
VII	0.5	61.2
	1.0	50.0
VIII	0.5	31.3
	1.0	20.6
IX	0.5	30.1
	1.0	19.8
ИХП-21	0.5	61.2
	1.0	48.2

Table 4. Results of tests in the M-11 oil of the antimicrobial properties of the compounds synthesized

Additive	Content of an additive in the oil	Growth depression zone of microorganisms, cm			
		fungi		bacteria	
		Candida tropicalis	*Aspergillus niger*	*Mycobacterium lacticola*	*Pseudomonas aeruginosa*
X	0.5	0.4	0.4	0.4	0.4
	1.0	0.8	0.8	0.8	0.7
XI	0.5	0.3	0.3	0.3	0.3
	1.0	0.6	0.6	0.6	0.6
XII	0.5	0.3	0.2	0.2	0.3
	1.0	0.6	0.5	0.5	0.6
XIII	0.5	0.2	0.2	0.3	0.3
	1.0	0.4	0.4	0.5	0.5
XIV	0.5	0.5	0.5	0.5	0.5
	1.0	1.0	1.0	1.0	1.0
XV	0.5	0.5	0.5	0.5	0.4
	1.0	0.9	0.9	0.9	0.8
XVI	0.5	0.5	0.5	0.4	0.4
	1.0	1.0	1.0	0.9	0.8
M-11 oil without additives	0	+	+	+	+

Compounds **III–VII** were synthesized and purified similarly in 62–66% yield (Table 1).

1-Heptylthio-2-phenylthiocarbamato-3-(2'-chloro-phenoxy)propane (VII). To a mixture of 5.64 g (0.02 mol) of compound **I**, 25 ml of anhydrous benzene, and 2.02 g (0.02 mol) of freshly distilled triethylamine was added dropwise, at 80–85°C, 2.70 g (0.02 mol) of phenylisocyanate dissolved in 25 ml of anhydrous benzene. Then, the mixture was agitated for additional 10–12 h and cooled, 2/3 of benzene was evaporated, 25 ml of anhydrous hexane was added, and the mixture was kept for 20–24 h. The precipitated crystals of **VIII** were separated, many times decanted with benzene, and recrystallized from hexane.

Compound **IX** was synthesized and purified similarly in 60% yield (Table 1).

1-Heptylthio-3-(2'-chlorophenoxy)-2-methoxy-methyleneoxypropane (X). To a mixture of 6.34 g of compound **I**, 25 ml of anhydrous benzene, and 3.63 g of freshly distilled dimethylaniline was added, at a temperature of 15–20°C in the course of 1 h, 2.41 g of a freshly distilled α-chloromethyl ether. After the whole amount of α-chloromethyl ether was added. The mixture was agitated for 1 h at the same temperature and then for 4–5 h at 40–50°C. The mixture was cooled and washed with a 5% aqueous solution of hydrochloric acid and then with water to a neutral reaction. Then it was dried with anhydrous sodium sulfide. After the solvent was evaporated, the remaining mass was subjected to a vacuum distillation.

Compounds **XI–XII** were synthesized similarly in 60–65% yield (Table 2).

1-Heptylthio-2-acetoxy-3-(2'-chlorophenoxy)-propane (XIII). To a mixture of 6.34 g of compound **I**, 25 ml of anhydrous benzene, and 3.63 g of freshly prepared dimethylaniline was added, at a temperature of 15–20°C in the course of 1 h, 2.25 g of acetyl chloride. After the whole amount of acetyl chloride was added, the mixture was agitated for 1 h at the same temperature and then for 4–5 h at 40–50°C. The mixture was cooled and washed first with a 5% aqueous solution of hydrochloric acid and then with water to a neutral reaction. Then it was dried with anhydrous sodium sulfide. After the solvent was evaporated, the remaining mass was subjected to a vacuum distillation. 1-Heptylthio-2-acetoxy-3-(2'-chlorophenoxy)propane (**XIII**) was obtained in 66% yield (Table 2).

1-Heptylthio-2-(*N,N*-diethylaminomethoxy)-3-(2'-chlorophenoxy)propane (XIV). To a mixture of 6.34 g of compound **I**, 0.6 g of paraform, and 30 ml of anhydrous benzene was added dropwise, at room temperature under agitation for 0.5 h, 1.46 g of diethylamine. The agitation was continued for additional 1 h at the same temperature and for 2 h at 40–50°C. After benzene was evaporated, 1-heptylthio-2-(*N,N*-diethylaminomethoxy)-3-(2'-chlorophenoxy)propane (**XIV**) was isolated from the remaining mass by vacuum distillation.

Compounds **XV–XVI** were synthesized similarly in 65–70% yield (Table 2).

CONCLUSIONS

(1) The reaction of 1-heptylthio-3-chloro-2-propanol with *o*-chlorophenol in the presence of an alkali was used to obtain 1-heptylthio-3-(2'-chlorophenoxy)-2-propanol, which is a key compound for synthesis of carbamates, thiocarbamates, and alkoxymethyl and aminomethyl derivatives.

(2) Owing to their anticorrosion properties, some of the arylcarbamates and arylthiocarbamates synthesized improve the M-11 lubricating oil and surpass the industrial additive IKhP-21 in efficiency.

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