gasometer through drying traps filled with calcium chloride and potassium hydroxide, after which the mixture was heated to 110°, and oxygen was bubbled through it. The oxidation was carried out at 110° with vigorous stirring for 2 h. At the end of the reaction, the precipitate was separated. The reaction products were analyzed by GLC and acetic acid and I and III-VII were detected. The contact solution was diluted with water and extracted immediately with ether. The ether extracts were dried with calcined calcium chloride, the ether was removed by distillation, and the residue was vacuum distilled to give ketone III with mp 87° (4 mm) and n_D^{20} 1.5623. UV spectrum in ethanol, λ_{max}, nm (log ε): 208 (3.37), 265 (4.00), 296 (4.09). IR spectrum: 1670 (C=O), 1365 cm^{-1} (CH_3). The 2,4-dinitrophenylhydrazone had mp 246°C (from ethanol).

LITERATURE CITED

1. T. V. Shchedrinskaya, P. A. Konstantinov, V. P. Litvinov, É. G. Ostapenko, I. V. Zakharov, and M. N. Volkov, Zh. Obshch. Khim., 44, 837 (1974).
2. T. V. Shchedrinskaya, V. P. Litvinov, P. A. Konstantinov, Ya. L. Gol'dfarb, and É. G. Ostapenko, Khim. Geterotsikl. Soedin., No. 8, 1026 (1973).
3. P. A. Konstantinov, T. V. Shchedrinskaya, I. V. Zakharov, and M. N. Volkov, Zh. Org. Khim., 8, 2590 (1972).
4. A. V. Ryazanova, A. V. Bondarenko, I. A. Maizlakh, and M. I. Farberov, Neftekhimiya, 6, 227 (1966).
5. N. M. Émanuél', E. T. Denisov, and Z. K. Maizus, Stepwise Oxidation Reactions of Hydrocarbons in the Liquid Phase [in Russian], Nauka, Moscow (1965).
6. B. V. Aivazov, S. M. Petrov, V. R. Khairullina, and V. G. Yapryntseva, Physicochemical Constants of Organic Sulfur Compounds [in Russian], Khimiya, Moscow (1967).
7. P. Cagniant and P. Cagniant, Bull. Soc. Chim. France, No. 5, 713 (1952).
8. Ya. L. Gol'dfarb and Ya. L. Danyushevskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 4, 540 (1963).
9. E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Manion, J. Am. Chem. Soc., 91, 7381 (1969).
10. D. S. Noyce, C. A. Lipinski, and R. W. Nichols, J. Org. Chem., 37, 2615 (1972).
11. Ya. L. Gol'dfarb and Yu. B. Vol'kenshtein, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 11, 2238 (1960).
12. S. N. Godovikova and Ya. L. Gol'dfarb, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1434 (1965).

REACTION OF 2,3-DICHLOROBENZO[b]THIOPHENE 1,1-DIOXIDE WITH CYCLIC AMINES

V. É. Udre and É. Ya. Lukevits

UDC 547.735.07

The corresponding p-amino derivatives, which have psychotropic activity, were obtained by reaction of 2,3-dichlorobenzo[b]thiophene 1,1-dioxide with cyclic amines. Their IR and PMR spectra are presented.

Pesticides and compounds with psychotropic and cardiovascular effects have been found among benzo[b]-thiophene derivatives in recent years. In order to obtain biologically active compounds – sulfones of condensed thiophene systems – and study their reactions with nucleophilic reagents [3] we investigated the reaction of 2,3-dichlorobenzo[b]thiophene 1,1-dioxide (I) with cyclic amines.

N-Aryl and N-alkyl derivatives of piperazine react with sulfone I in refluxing ethanol to give 2-chloro-3-piperazinobenzo[b]thiophene 1,1-dioxides (II) (Table 1) and the hydrochloride of the corresponding amine (reagent ratio 1 : 2). The reaction of sulfone I with excess aziridine, pyrrolidine, piperazine, and perhydroazepine, which leads to 2-chloro-3-aminobenzo[b]thiophene 1,1-dioxides (III) (Table 1), proceeds similarly.

The reaction of sulfone I with an equimolar amount of aziridine proceeds with opening of the aziridine ring to give 2-chloro-3-(β-chloroethylamino)benzo[b]thiophene 1,1-dioxide (IV) in low yield. The latter was also

---

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 56-57, January, 1977. Original article submitted January 19, 1976.

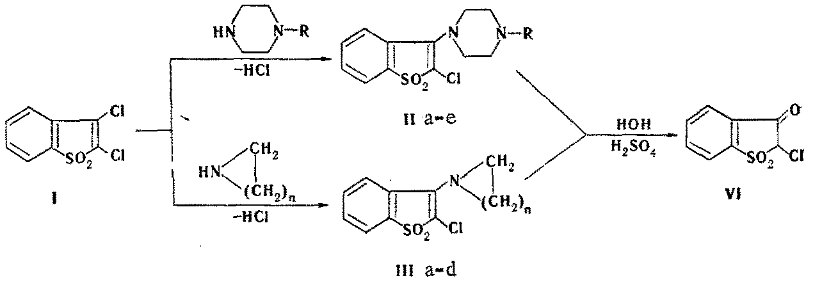
TABLE 1. 2-Chloro-3-R-benzo[b]thiophene 1,1-Dioxides II-V

Compound	R	Reaction time, h	mp, °C (from ethanol)	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
IIa	N-Phenylpiperazino	2	177—178	59,9	4,8	7,6	$C_{18}H_{17}ClN_2O_2S$	59,6	4,8	7,7	90
IIb	p-Methoxyphenylpiperazino	2	164—165	58,6	4,7	7,2	$C_{19}H_{19}ClN_2O_3S$	58,4	4,9	7,2	86
IIc	o-Methoxyphenylpiperazino	2	198—199	58,7	4,8	7,0	$C_{19}H_{19}ClN_2O_3S$	58,4	4,9	7,2	87
IId	m-Chlorophenylpiperazino	2	175—176	54,8	4,1	6,9	$C_{18}H_{16}Cl_2N_2O_2S$	54,7	4,1	7,1	86
IIe	N-(β-Hydroxyethyl)piperazino	2,5	172—173	50,9	5,2	8,7	$C_{14}H_{17}ClN_2O_3S$	51,1	5,2	8,5	85
IIIa	Aziridino	7	162—163	49,3	3,4	5,6	$C_{10}H_8ClNO_2S$	49,6	3,3	5,8	49
IIIb	Pyrrolidino	1,5	153	53,1	4,4	5,3	$C_{12}H_{12}ClNO_2S$	53,4	4,5	5,2	98
IIId	Perhydroazepino	1,5	139	56,5	5,5	4,7	$C_{14}H_{16}ClNO_2S$	56,4	5,4	4,7	98
IV	β-Chloroethylamino	4,5	198—199	43,3	3,4	4,7	$C_{10}H_9Cl_2NO_2S$	43,3	3,3	5,0	13; 90*
Va	2-(Morpholino)-ethylamino	1	163—164	50,9	5,0	8,3	$C_{14}H_{17}ClN_2O_3S$	51,1	5,2	8,5	83
Vb	2-(Piperidino)-ethylamino	1	156	54,8	6,0	8,4	$C_{15}H_{19}ClN_2O_2S$	55,1	5,9	8,6	84

* From IIIa.

obtained by the action of an alcohol solution of HCl on derivative IIIa. The PMR spectrum of IV contains signals of protons of methylene groups in the form of an AA'BB' system at 3.66 and 3.87 ppm, the signal of an NH proton at 7.2 ppm, and signals of aromatic protons at 7.6 ppm.

Tertiary cyclic amines do not react with I; N-aminoalkyl-substituted morpholines and piperidines react with I through the primary amino group to give 3-cycloaminoalkylamino derivatives Va, b.



II a R=C_6H_5, b R=$C_6H_4OCH_3$-*p*, c R=$C_6H_4OCH_3$-*o*, d R=C_6H_4Cl-*m*, e R=CH_2CH_2OH; III a n=1, b n=3, c n=4, d n=5

The yields of II, III, and V increase as the basicity of the reacting amine increases. The weakest bases — 2-carbethoxy- and carbomethoxyaziridines — do not react at all with I.

The position of the nitrogen-containing substituent in II-V was established by acid hydrolysis to the known 2-chloro-3-oxo-2,3-dihydrobenzo[b]thiophene 1,1-dioxide (VI) [4]; intense absorption bands of a sulfonyl group are present in the IR spectra of II-V at 1335-1340 and 1160 cm^{-1}.

A pharmacological study of the effect of the synthesized amino derivatives of benzo[b]thiophene 1,1-dioxide on the central nervous system (CNS) showed that, depending on the substituent in the 3 position, they are either CNS tranquilizers or stimulators [5].

EXPERIMENTAL

The PMR spectra of $CDCl_3$ solutions of the compounds were recorded with an R-12A spectrometer (60 MHz) with hexamethyldisiloxane and tetramethylsilane as the internal standards.

2-Chloro-3-aminobenzo[b]thiophene 1,1-Dioxide (IIa-e, IIIb, d). A solution of 4 mmole of sulfone I [6] and 8 mmole of the corresponding amine in 50 ml of 85% ethanol was refluxed, after which it was cooled, and the resulting precipitate was removed by filtration, washed with water, and recrystallized from alcohol. In the case of IIIe, the solution was evaporated to isolate the crystals.

2-Chloro-3-(2-morpholinoethylamino)- and -(2-piperidinoethylamino)benzo[b]thiophene 1,1-Dioxides (Va, b). A solution of 4 mmole of I and 8 mmole of the appropriate amine in 40 ml of dry benzene was refluxed, after which it was filtered, and the solvent was removed from the filtrate by partial distillation. The residual amine V was washed with water and recrystallized from alcohol.

2-Chloro-3-aziridinobenzo[b]thiophene 1,1-Dioxide (IIIa). This compound was obtained by the method used to prepare amine V. It was isolated by complete removal of the solvent by distillation and addition of 5 ml of ethanol to the residue.

2-Chloro-3-(β-chloroethylamino)benzo[b]thiophene 1,1-Dioxide (IV). A 1-g sample of aziridine derivative IIIa was dissolved in ethanol, and 10 ml of alcohol saturated with HCl was added. The solvent was removed by distillation, and the residue was washed with water and recrystallized from ethanol.

3-Oxo-2-chloro-2,3-dihydrobenzo[b]thiophene 1,1-Dioxide (VI). This compound was obtained by hydrolysis of II-V in 6 N H_2SO_4 and had mp 154-155°. IR spectrum: 1740 cm^{-1} (CO).

LITERATURE CITED

1. Z. S. Aryan and S. Ma, US Patent No. 3790600 (1974); Chem. Abstr., 80, 83632 (1974).
2. J. H. Hess and R. P. Nelson, West German Patent No. 2106038 (1971); Chem. Abstr., 76, 3856 (1972).
3. V. É. Udre, É. Ya. Lukevits, and Yu. Yu. Popelis, Khim. Geterotsikl. Soedin., No. 1, 45 (1975).
4. V. É. Udre and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 12, 1602 (1972).
5. S. K. Germane and V. É. Udre, 13th Scientific Session on the Chemistry and Technology of Organic Sulfur Compounds. Summaries of Papers [in Russian], Dushanbe (1974), p. 71.
6. M. G. Voronkov, V. É. Udre, and É. P. Popova, Khim. Geterotsikl. Soedin., No. 6, 1003 (1967).

ORGANIC COMPOUNDS OF SELENIUM AND TELLURIUM

I. REACTION OF SELENIUM TETRAHALIDES WITH 1,5- AND 1,6-DIOLEFINS AND THEIR DERIVATIVES

Yu. V. Migalina, V. I. Staninets,
V. G. Lendel, I. M. Balog,
V. A. Palyulin, A. S. Koz'min,
and N. S. Zefirov

UDC 547.739

Heterocyclic compounds containing a selenium(IV) atom as the heteroatom were obtained by the action of selenium tetrahalides on 1,5- and 1,6-diolefins and their derivatives.

One of the methods for the synthesis of selenium-containing heterocyclic compounds is cyclization of diolefins under the influence of selenium monochloride [1]. The literature does not contain data on the use of selenium tetrahalides in these reactions, whereas it is known [2] that selenium tetrachloride, as an electrophilic reagent, is capable of adding to olefinic carbon atoms to give bis(β-chloroalkyl)selenium dichlorides.

In the present research we studied the addition of selenium tetrahalides to diolefins 1,5-hexadiene – (I), diallyl ether (IIa), diallyl sulfide (IIb), diallylamine (IIc), ethyldiallylamine (IId), and phenyldiallylamine (IIe). It was found that the addition of selenium tetrahalide to the appropriate hydrohalic acid in an ether solution of I under mild conditions is accompanied by the formation of a crystalline substance, in which, according to the IR

Uzhgorod State University, Uzhgorod 294000. M. V. Lomonosov Moscow State University, Moscow 117234.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 58-62, January, 1977. Original article submitted March 15, 1976.