1-Methyl-2-(5'-bromofuryl-2')benzimidazole (XI). To a solution of 1.98 g (10 mmoles) of compound III in 20 ml of dichloroethane at 80°C a solution of 1.6 g (10 mmoles) of bromine in 10 ml of dichloroethane was added gradually and heating continued at the same temperature for 2 h 30 min. The precipitate of the hydrobromide of compound (XI) was separated, recrystallized from water and converted to the base. Yield 1.69 g (61%), mp 123-124°C (from alcohol). Literature value mp 123-124°C [7].

1-Methyl-2-(4',5'-dibromothienyl-2')benzimidazole (XII). A). To a solution of 2.14 g (10 mmoles) of compound IV in 20 ml dichloroethane at 80°C was added gradually a solution of 3.2 g (20 mmoles) bromine in 20 ml dichloroethane and kept at this temperature for 8 h. The reaction mixture was left at 3-5°C for 12 h, the precipitate of the hydrobromide of compound XII was separated, converted to the base, and recrystallized from alcohol. Yield 1.45 g (39%), mp 178-179°C. PMR spectrum: 6.95 ppm (3-H, s). Found, %: 39.0; H 2.5; N 7.2. $C_{12}H_8Br_2N_2S$. Calculated, %: C 38.7; H 2.2; N 7.6.

B). Prepared in the same way as compound I from 4.32 g (40 mmoles) o-phenylenediamine, 6 g (80 mmoles) of copper acetate and 6.8 g (40 mmoles) of 4,5-dibromo-2-thiophenaldehyde with subsequent methylation of the product by the same reaction as for compound III.

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PHOSPHORYLATION OF THE POTASSIUM SALT OF BENZOTHIAZOLINE-2-THIONE BY DIAMIDOCHLOROPHOSPHATES

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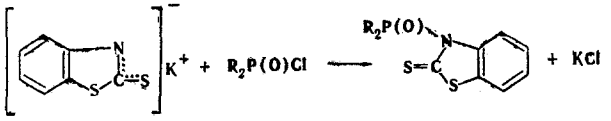
UDC 547.789.6

In order to phosphorylate benzothiazoline-2-thione (I) at the hard donor atom, we have employed diamidochlorophosphates as the phosphorylation agents. The latter, as a result of the negative inductive effect of the chlorine radical and the positive mesomeric effect of the amide groups, which generate an effective positive charge on the phosphorus atom, effect phosphorylation at the hard donor nitrogen atom [7]. This is also facilitated by carrying out the reaction with salts of the thione (I) with a cation of large radius (potassium) in polar aprotic solvents (e.g., acetonitrile) [7].

Phosphorylation of the potassium salt of I by diamidochlorophosphates, using equimolecular amounts of the reactants, results in the preferential formation of the N-derivatives:



I II–VII

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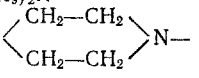
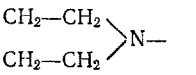
TABLE 1. N-(Diamidophosphoryl)benzothiazolinethiones

Compound	R	d_4^{20} g/cm²	R_f	Found, %			Mol. formula	Calc., %			Mol. wt.		Yield, %
				N	P	S		N	P	S	found	calc.	
II	$(CH_3)_2N-$	1,120	0,61	13,6	10,5	20,1	$C_{11}H_{16}N_3OPS_2$	13,9	10,3	21,3	295,0	301,4	80
III	$(C_2H_5)_2N-$	1,129	0,74	11,5	8,9	17,6	$C_{15}H_{24}N_3OPS_2$	11,8	8,7	17,9	341,0	357,5	87
IV	$(C_3H_7)_2N-$	1,189	0,78	9,7	7,4	14,9	$C_{19}H_{32}N_3OPS_2$	10,2	7,5	15,5	427,8	413,6	86
V	$(C_4H_9)_2N-$	1,240	0,81	8,7	6,9	13,3	$C_{23}H_{40}N_3OPS_2$	8,9	6,6	13,6	445,0	469,8	84
VI		1,375	0,64	10,9	8,4	16,4	$C_{17}H_{24}N_3OPS_2$	11,0	8,1	16,8	354,0	381,5	93
VII		1,445	0,71	10,7	8,3	16,2	$C_{15}H_{20}N_3O_3PS_2$	10,9	8,0	16,6	360,0	385,5	90

The reaction is complete within 1-2 h. Compounds II and III are liquids, and IV-VII are oils soluble in most organic solvents. The purity of the compounds was confirmed by thin layer chromatography, and their constants are shown in Table 1.

That the new compounds are correctly formulated as N-derivatives of the thione I was shown by their electronic absorption spectra. The spectra of II-VII exhibit absorption at λ_{max} 325-330 nm (lg ε 4.3-4.4), indicating that the heterocyclic moiety possesses the thione structure [8-10]; S-derivatives of the thione (I) show absorption at λ_{max} 278 nm [10]. Confirmation of the phosphorylation of the thione (I) at the nitrogen atom is provided by the presence in the IR spectra of all the compounds of thioamide bands ("thioamide I") at 1320-1324 cm^{-1}, and of "thioamide II" bands at 1080-1090 cm^{-1} due to $-\overset{|}{N}-\overset{|}{C}=S$ group vibrations [11]. Also noteworthy in the IR spectra of II-VII are absorption bands due to vibrations of the C=C skeleton of the benzene ring at 1600-1605 cm^{-1} [12], and to valence vibrations of the P—N bond at 920-926 cm^{-1} [13]. Further confirmation of the N-substituted structure of the products is provided by the chemical shift of 30-33.3 ppm in the ^{31}P NMR spectra [14].

EXPERIMENTAL

TLC of all the compounds was carried out on Silufol UV-254 or alumina, as in [15], using as eluent system acetone–hexane (1:2). R_f values were determined by ascending adsorption chromatography under standard conditions [17], the adsorbent layers being without binder. Spots were visualized by UV in a "Chromatoscope" apparatus using a 320-nm filter.

Electronic spectra were obtained using a Specord UV-Vis spectrophotometer, for $4 \cdot 10^{-2}$ molar solutions of II-VII in dioxan. IR spectra were recorded in CCl_4 solution on a UR-20 spectrophotometer. ^{31}P NMR spectra were obtained on an HX-90 spectrometer with a working frequency of 90 MHz (for protons), using 85% H_3PO_4 as external standard, compounds II-VII being in the form of 3 mole/liter solutions in nitromethane. The diamidochlorophosphates were prepared according to [17]. Molecular weights were determined by reverse ebullioscopy [18].

N-[(NN-Tetrabutyldiamido)phosphoryl]benzothiazolinethione (V). To 0.1 mole of NN-tetrabutyldiamidochlorphosphate in 60 ml of anhydrous acetonitrile was added at room temperature dropwise 0.1 mole of I potassium salt dissolved in 150 ml of anhydrous acetonitrile. The reaction mixture was heated to 55-60°C, and kept at this temperature for 1.5-2 h. The precipitate was filtered off, the filtrate shaken with activated charcoal, and the reaction product extracted with hexane. Compounds II-IV (Table 1) were obtained similarly.

N-(NN-Dimorpholidophosphoryl)benzothiazolinethione (VII). To 0.1 mole of NN-dimorpholidochlorophosphate in 60 ml of anhydrous acetonitrile was added at room temperature 0.1 mole of the potassium salt of I, dissolved in 150 ml of anhydrous acetonitrile. The reaction mixture was heated to 55-60°C, and kept at this temperature, for 1-1.5 h. The precipitate was filtered off, the filtrate was evaporated, and the resulting oil was reprecipitated by adding a solution in chloroform to light petroleum.

N-(NN-Dipiperidinophosphoryl)benzothiazolinethione (VI) was prepared and isolated in a similar way.

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BENZOXAZINES AND RELATED COMPOUNDS

6.* NITRATION OF 2,4,4-TRISUBSTITUTED 4H-1,3-BENZOTHIAZINES

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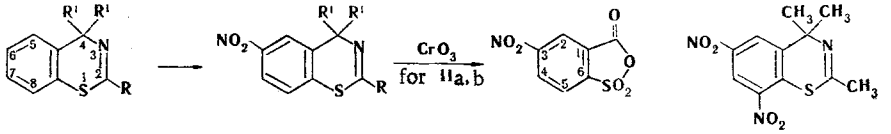
UDC 547.869.1:543.422.25

4H-1,3-Benzothiazines have so far been little-investigated compounds [1, 2] (see also [3]), and there are no data on electrophilic substitution reactions in this system.

In order to synthesize 2,4,4-trisubstituted 4H-1,3-benzothiazines (Ia-k) with a nitro group in the aromatic ring we realized the nitration of compounds (Ia-k) with a mixture of equimolar amounts of nitric acid (d = 1.5) and concentrated sulfuric acid at room temperature. In all cases the mononitro derivatives (IIa-k) were isolated (Table 1).



Ia-k IIa-k III IV

I, II a R=R¹=CH₃; b R=CH₃, R¹=C₂H₅; c R=CH₃, R¹=p-C₃H₇; d R=C₂H₅, R¹=CH₃; e R=R¹=p-C₃H₇; f R=p-C₄H₉, R¹=CH₃; g R=p-C₄H₉, R¹=C₂H₅; h R=p-C₄H₉, R¹=p-C₃H₇; i R=i-C₄H₉, R¹=CH₃; j R=C₆H₅, R¹=CH₃; k R=4-ClC₆H₄, R¹=CH₃

*For Communication 5, see [1].

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