LITERATURE CITED

1. L. V. Éktova and E. P. Fokin, Zh. Org. Khim., 20, No. 4, 805 (1984).
2. Methoden der Organischen Chemie (Houben-Weyl), Vol. 7/3a, Thieme, Stuttgart (1979), a) pp. 27-35, b) p. 385, c) Vol. 7/3b, p. 235.
3. D. Bailey and L. W. Williams, in: The Chemistry of Synthetic Dyes, K. L. Venkataraman (ed.) [Russian translation], Vol. 4, Khimiya, Moscow (1975), p. 320.
4. C. Grundmann, Synthesis, No. 9, 644 (1977).
5. A. J. Fatiadi, in: Synthetic Reagents, J. S. Pizey (ed.), Vol. 4, Wiley, New York (1981), p. 147.

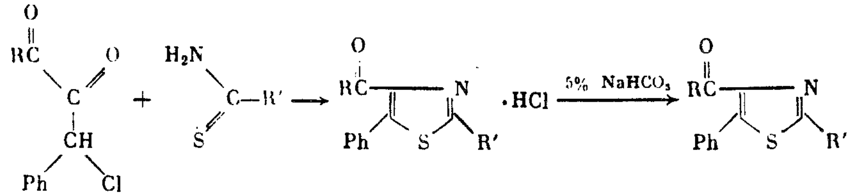
SYNTHESIS OF FUNCTIONALLY SUBSTITUTED 5-PHENYLTHIAZOLES

V. A. Mamedov, I. A. Nuretdinov,
and D. N. Sadkova

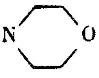
UDC 542.91:547.789.5

The reaction of esters and amides of 3-phenyl-3-chloro-2-oxopropionic acid with thioamides and thiourea gave new 5-phenylthiazoles.

Since thiazoles are found in many biologically active preparations [1,2], we attempted to obtain various **functionally substituted** derivatives of these compounds, which might be useful in organic synthesis. In a continuation of previous work [3], we studied the reactions of derivatives of 3-phenyl-3-chloro-2-oxopropionic acid [4] with thioamides and thiourea. These reactions proceed with the formation of hydrochloride salts of functionally-substituted 5-phenylthiazoles (III), which, after treatment with 5% aqueous sodium bicarbonate, give free thiazole bases (IVa)-(IVℓ) in good yields.



(I) (II) (III) (IVa — ℓ)

R = OMe, R′ = Me (IVa); R = OMe, R′ = Ph (IVb); R = OEt, R′ = Me (IVc); R = OEt, R′ = NH₂ (IVd); R = N(Me)₂, R′ = Me (IVe); R = N(Me)₂, R′ = NH₂ (IVf); R = N(Et)₂, R′ = Ph (IVg). R = N(Et)₂, R′ = NH₂ (IVh); R = N(iso-Bu), R′ = NH₂ (IVi); R = N, R′ = NH₂ (IVj); R = N, R′ = NH₂ (IVk); R = NO, R′ = NH₂ (IVℓ).

The structures of these products were supported by elemental analysis (Table 1) and IR and PMR spectroscopy (Table 2). The IR spectra of (IVd) and (IVi) have three amino group bands at 3140-3410 cm^{-1}. The spectra of (IVf), (IVh), and (IVj)-(IVℓ) have only two bands in this region. The -C(O)N< group probably more strongly binds the NH_2 protons in a hydrogen bond than the -C(O)OEt group. The appearance of a free NH_2 group band in (IVi) is apparently a consequence of the two bulky isobutyl groups which hinder hydrogen bonding between the carbonyl oxygen and amino group.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in vaseline mull. The PMR spectra were taken on a Varian T-60 spectrometer with TMS as the internal standard.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2854-2856, December, 1990. Original article submitted January 16, 1990.

0568-5230/90/3912-2591$12.50

TABLE 1. Physicochemical Indices of 5-Phenyl-2,4-Substituted Thiazoles (IVa)-(IVℓ)

Compound	Mp, °C	Yield %	Recrystallization solvent	Found/calculated, %				Empirical formula
				C	H	N	S	
(IV a)	80–81,5	82	Hexane	61,71/61,80	4,72/4,71	5,90/6.00	13,71/13,74	$C_{12}H_{11}NO_2S$
(IV b)	90–91,5	81	»	69.49/67,17	4,44/4,40	4,83/1.72	10,74/10.84	$C_{17}H_{13}NO_2S$
(IV c)	56	78	»	63,41/63,16	5,30/5,25	5,59/5,66	12.78/12,96	$C_{13}H_{13}NO_2S$
(IV d)	177–178	86	Methanol	58,02/58,07	4,76/4,83	11,12/11.28	12,50/12,81	$C_{12}H_{12}N_2O_2S$
(IV e)	78,5	84	Hexane	63,36/63,41	5,66/5,68	11,12/11,37	12,52/13,02	$C_{13}H_{14}N_2OS$
(IV f)	232	86	Acetone-water(10:1	58,41/58,30	5,41/5,25	16,65/16,99	12,81/12.97	$C_{12}H_{13}N_3OS$
(IV g)	143–144	84	Hexane	71,52/71,43	6.07/5.94	8,43/8,32	9,47/9,53	$C_{20}H_{20}N_2OS$
(IV h)	225–226	91	Acetone	61,14/61,08	6,19/6,17	15.23/15.26	11,44/11,64	$C_{14}H_{17}N_3OS$
(IV i)	128–129	87	»	65,12/65,26	7,61/7,54	12,60/12,67	9.41/9.67	$C_{18}H_{25}N_3OS$
(IV j)	262–263	83	»	61.42/61,54	5.42/5,49	15,32/15,37	11,27/11,73	$C_{14}H_{15}N_3OS$
(IV k)	243–244	81	Chloroform	62,70/62,72	5.87/5,91	14.59/14,62	10,93/11,16	$C_{15}H_{17}N_3OS$
(IVℓ)	292–293	85	Acetone	57,91/58,13	5,85/5,18	14.27/14,52	9.87/10,08	$C_{14}H_{15}N_3O_2S$

TABLE 2. Spectral Indices of 5-Phenyl-2,4-Substituted Thiazoles (IVa)-(IVℓ)

Compound	IR spectrum ν, cm^{-1} (vaseline mull)	PMR spectrum, δ, ppm (solvent)
(IVa)	1715(C=O)	2,63 s (CH_3), 3.66 s (OCH_3), 7,10–7,33 m (C_6H_5); CCl_4
(IVb)	1720(C=O)	3,83 s (OCH_3), 7,23–8.00 m ($2C_6H_5$) $CDCl_3$
(IVc)	1715(C=O)	1,16 t (CH_3). 2.50 s (CH_3 ring), 3,93 q (CH_2), 6.76–7,03 m (C_6H_5); CCl_4
(IVd)	1700(C=O), 3140, 3240(NH_2 bound), 3410(NH_2 free)	1.16 t (CH_3). 4.16 q (CH_2). 4.83 br.s (NH_2). 7.40 s (C_6H_5); CD_3OD
(IVe)	1650(C=O)	2.60 s (CH_3). 2.80 d ($N(CH_3)_2$), 6,96–7,40 m (C_6H_5)
(IVf)	1620(C=O), 3120, 3290(NH_2 bound)	2,73 and 2.90 two s ($N(CH_3)_2$) 7,00–7.23 m (NH_2). 7.23 s (C_6H_5); $(CD_3)_2SO$
(IVg)	1640(C=O)	0,96 and 1.23 two t (CH_3), 3,13 and 3,53 2 q (CH_2), 7.10–8,03 m ($2C_6H_5$); $CDCl_3$
(IVh)	1620(C=O). 3160. 3260(NH_2 bound)	0.86 and 1.10 two t ($2CH_3$), 3,10 and 3,33, two partially overlapping q ($2CH_2$), 7,10–7,20 m (NH_2), 7,26 s (C_6H_5); $(CD_3)_2SO$
(IV i)	1625(C=O), 3140, 3280(NH_2 bound) 3395(NH_2 free)	0,70 and 0.90 two d ($4CH_3$), 1.43–2,16 m ($2CH$). 2,76 and 3,20 two d ($2CH_2$), 7,33 s (C_6H_5): $(CD_3)_2SO$
(IV j)	1615(C=O), 3140. 3290(NH_2 bound)	1,50–1,93 m (CH_2CH_2), 2.93–3.86 m ($N(CH_2)_2$). 7,23 s (C_6H_5); $(CD_3)_2SO$
(IV k)	1610(C=O), 3120, 3290(NH_2 bound)	0,96–1,66 m ($CH_2CH_2CH_2$), 2.85–3,80 m ($N(CH_2)_2$), 7,23 s (C_6H_5); $(CD_3)_2SO$
(IVℓ)	1620(C=O). 3230, 3300(NH_2 bound)	3,10 br.s ($N(CH_2)_2$), 3,66 br.s ($O(CH_2)_2$, 7.33 s (C_6H_5); $(CD_3)_2SO$

All the new functionally substituted 5-phenylthiazoles were obtained according to the general procedure described in our previous work [3].

N,N-Diethylamide of 2-Amino-5-phenylthiazole-4-carboxylic acid (IVh). A solution of equimolar amounts of N,N-diethylamide of 3-phenyl-3-chloro-2-oxopropionic acid and thiourea in ethanol was heated at reflux with stirring for 1.5 h. After cooling the reaction mixture to room temperature, the solvent was evaporated. The semicrystalline mass formed was treated with 5% aqueous $NaHCO_3$, washed with water, and (IVh) was recrystallized. The other thiazoles were obtained by analogy. The physicochemical indices, yields, recrystallization solvents, and elemental analysis data are given in Table 1, while the spectral indices are given in Table 2.

LITERATURE CITED

1. N. N. Mel'nikov, K. V. Novozhilov, and T. N. Pylova, Chemical Plant Pesticides [in Russian], Khimiya, Moscow (1980), p. 263.
2. M. D. Mashkovskii, Pharmaceutical Agents, Meditsina, Moscow, Part 1 (1984), p. 202; Part 2 (1984), pp. 8, 9, 291, 346.
3. V. A. Mamedov and I. A. Nuretdinov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2856 (1987).
4. V. A. Mamedov, I. A. Nuretdinov, and F. G. Sibgatullina, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 2172 (1988).

SYNTHESIS AND SOME TRANSFORMATIONS OF O,O-DIETHYL S-(o-CARBORAN-9-YL) THIOPHOSPHITE

V. P. Balema, E. G. Rys, N. N. Godovikov, and M. I. Kabachnik

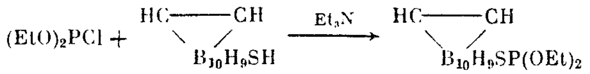
UDC 542.91:547.1'127'118

A synthesis is reported for O,O-diethyl S-(o-carboran-9-yl) thiophosphite and its transformations were studied. A series of new carboranyl esters of seleno- and thioacids of pentavalent phosphorus acids were obtained.

B-Substituted carboranyl esters of phosphorus acids have not been studied extensively. Only a few representatives of B-substituted carboranyl esters of pentavalent phosphorus acids have been reported [1,2]. The analogous trivalent phosphorus compounds have not been reported.

Hence, we undertook the synthesis of O,O-diethyl S-(o-carboran-9-yl) thiophosphite and studied several of its transformations, leading to the corresponding pentavalent phosphorus derivatives.

O,O-Diethyl S-(o-carboran-9-yl) thiophosphite (I) was formed from diethyl chlorophosphite and o-carboran-9-ylthiol in ether in the presence of triethylamine at −30°C in 96% yield. The PMR spectrum of this compound has an ethyl group triplet and quartet (δ 1.23 and 3.81 ppm, J_{HH} = 5.2 Hz) and group of signals at δ 1.9-3.53 ppm, corresponding to the carborane system protons. The ^{31}P NMR spectrum has one signal at $\delta^{31}P$ 188 ppm characteristic for triesters of thiophosphorous acid [3]. The IR spectrum of thiophosphite (I) shows a signal at 2620 cm^{-1}, characteristic for the B–H vibrations of the carboranyl group.



$$(EtO)_2PCl + \underset{B_{10}H_9SH}{HC\text{—}CH} \xrightarrow{Et_3N} \underset{B_{10}H_9SP(OEt)_2}{HC\text{—}CH}$$

(I)

Product (I) is a low-melting crystalline compound, which is stable in the air. Upon passage through a silica gel column, (I) is oxidized to O,O-diethyl S-(o-carboran-9-yl) thiophosphate (II). Product (I) reacts with sulfur and selenium similarly to other known thiophosphites [4] to give the corresponding dithiophosphate (III) in 82% yield and selenothiophosphate (IV) in 70% yield. The addition of both sulfur and selenium does not require heating and proceeds at about 20°C.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2857-2859, December, 1990. Original article submitted February 14, 1990.

0568-5230/90/3912-2593$12.50