1,3-THIAPHOSPHETANE DERIVATIVES

M. M. Gilyazov, T. A. Zyablikova,
É. Kh. Mukhametzyanova, and I. M. Shermergorn

UDC 542.91+661.718.1

We reported previously on the preparation of 1,3-thiaphosphetanes by hydrolysis of bis(chloromethyl)phosphinothioic acid [1]. It was of interest to us to synthesize thiaphosphetane derivatives by the direct condensation of bis(halomethyl)phosphorus derivatives with sodium sulfide. In this paper the preparation of new thiaphosphetane derivatives is described, and detailed procedures for preparing the previously synthesized compounds are presented.

Thus, when sodium bis(chloromethyl)phosphinate reacted with sodium sulfide in an aqueous medium, 3-oxo-3-hydroxy-1,3-thiaphosphetane (I) was obtained in a good yield. The reaction proceeds according to the scheme

When (I) was treated with thionyl chloride, 3-oxo-3-chloro-1,3-thiaphosphetane (II) was obtained, a crystalline substance which hydrolyzes rapidly in air and sublimes freely at 70-80°C (10 mm). When a benzene solution of (II) was allowed to react with methyl, deuteromethyl, ethyl, and decyl alcohols, the corresponding cyclic esters were synthesized. The esters can also be prepared by treating (I) with trialkyl phosphites. However, in this case it is rather difficult to prepare them in a pure state. The properties of the prepared compounds are given in Table 1.

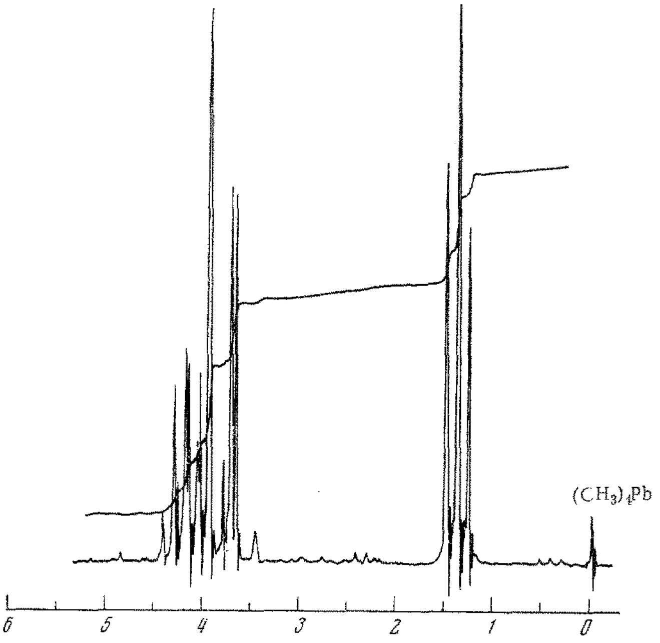
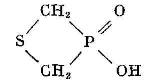
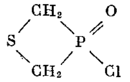
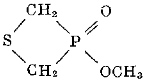
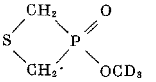
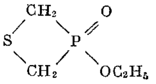
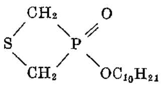
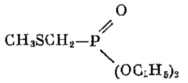


Fig. 1

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1177-1180, May, 1970. Original article submitted October 6, 1969.

TABLE 1

Compound	Yield, %	Bp, °C (p, mm Hg) or mp, °C	n_D^{20}	d_4^{20}	Found / Calculated				Empirical formula
					MR	P, %	C, %	H, %	
	86	142 (benzene)	—	—	—	$\frac{25,26}{24,96}$	$\frac{19,35}{19,35}$	$\frac{4,11}{4,06}$	$C_2H_5O_2PS$
	87,1	76 *	—	—	—	$\frac{22,25}{21,75}$	$\frac{16,90}{16,84}$	$\frac{3,04}{2,80}$	C_2H_4ClOPS
	73,2	58—59 (2,8·10^{-2})	1,5312	1,3612	$\frac{31,38}{31,39}$	$\frac{22,01}{22,40}$	$\frac{26,06}{26,1}$	$\frac{5,13}{5,06}$	$C_3H_7O_2PS$
	71	105—107 (6,5·10^{-2})	1,5320	1,3935	$\frac{31,38}{31,59}$	$\frac{21,92}{21,94}$	$\frac{25,41}{25,52}$	$\frac{5,37\dagger}{5,30}$	$C_3D_3H_4O_2PS$
	90	68 (3·10^{-2})	1,5170	1,2760	$\frac{36,07}{36,21}$	$\frac{19,88}{20,39}$	$\frac{31,55}{31,57}$	$\frac{5,89}{5,92}$	$C_4H_9O_2PS$
	89	133—134 (3·10^{-2}) 26—28	—	—	—	$\frac{11,66}{11,72}$	$\frac{55,53}{54,50}$	$\frac{9,81}{9,48}$	$C_{12}H_{25}O_2PS$
 $CH_3SCH_2{-}P(O)(OC_2H_5)_2$	60	56—57 (2,8·10^{-2})	1,4700	1,1323	$\frac{48,79}{48,79}$	$\frac{15,53}{15,65}$	$\frac{34,88}{36,3}$	$\frac{7,56}{7,60}$	$C_6H_{15}O_3PS$

* The melting point of this product given in [1] is wrong.

†The calculation was made taking into account that two moles of H_2O and 1.5 moles of D_2O are obtained during combustion.

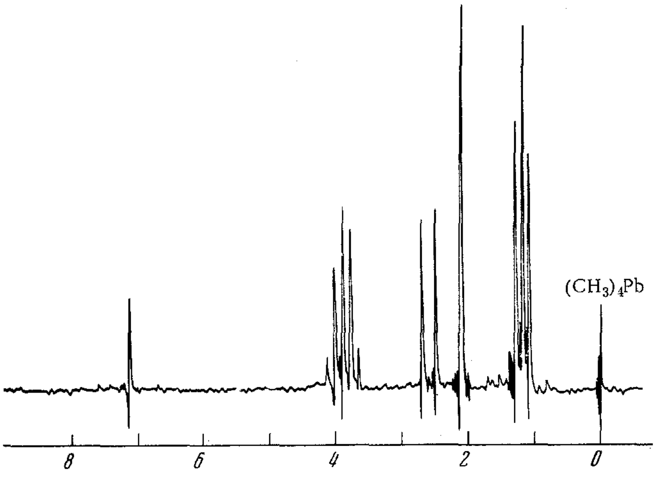
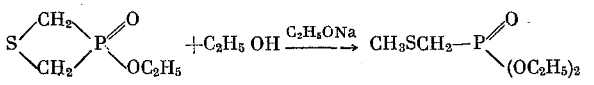


Fig. 2

According to the IR and NMR spectral data, the thiaphosphetane ring is nonplanar, and the obtained esters and acid chloride are mixtures of two isomers (detailed data on the structure of the 1,3-thiaphosphetane derivatives will be published later). As was observed in the case of derivatives of phosphetane [2, 3] and 1,3-phosphetidine [4], four-membered phosphorus-containing rings open relatively easily under the action of nucleophilic reagents. Because of this, it was of interest to us to verify the possibility of opening of the thiaphosphetane ring. Indeed, during the action of sodium ethoxide on 3-oxo-3-ethoxy-1,3-thiaphosphetane (III), the ring opens according to the scheme



Figures 1 and 2 show the PMR spectra of the starting and obtained products when $\nu_0 = 60$ MHz.

Unlike the PMR spectrum of the cyclic product, which contains a triplet of methyl protons of the ethoxyl group in the region of 1.35 ppm and a complex multiplet in the region of 3.40-4.40 ppm belonging to the methylene group of the ethoxyl radical and to the methylene protons of the ring, the PMR spectrum of diethyl methylthiomethylphosphonate contains distinctly visible methyl (a triplet with a center at 1.20 ppm) and methylene (a quintet with a center at 3.90 ppm) protons of the ethoxyl group, a singlet of the methyl group bound to sulfur at 2.10 ppm, and a doublet of the methylene group at the phosphorus with a center at 2.60 ppm and a spin–spin constant of cleavage from the phosphorus nucleus of $J_{PCH} = 18.6$ Hz. Thus, we have shown that the thiaphosphetane ring is unstable in an alkaline medium and opens rather easily under the action of sodium ethoxide.

EXPERIMENTAL

3-Oxo-3-hydroxyl-1,3-thiaphosphetane (I). Sodium sulfide nonahydrate (12.9 g) was added to 10 g sodium bis(chloromethyl)phosphinate dissolved in 40 ml water, and the mixture was heated and stirred at 95°C for 2.5 h. The solution was acidified with conc. HCl, the water was distilled, and the product was extracted from the residue with ethanol. After the ethanol was distilled, the product was recrystallized from benzene.

3-Oxo-3-chloro-1,3-thiaphosphetane (II). A mixture of 3 g (I) and 12 g thionyl chloride was heated at 40°C and stirred for 20 min. After the excess thionyl chloride was distilled, the product was purified by sublimation [75°C (10 mm)].

3-Oxo-3-methoxy-1,3-thiaphosphetane. A benzene solution of 17.2 g (II) was added dropwise to a mixture of 6 g methanol and 12.1 g $(C_2H_5)_3N$ in 10 ml benzene for 45 min with cooling (10°C) and stirring. The reaction mixture was stirred for 20 min at 20°C, $(C_2H_5)_3N \cdot HCl$ was filtered, and the excess methanol and benzene were distilled from the filtrate. The reaction product was distilled under vacuum. The deuteromethyl, ethyl, and decyl esters were similarly prepared.

The Reaction of 3-Oxo-3-ethoxy-1,3-thiaphosphetane with Ethanol in the Presence of Sodium Ethoxide. A mixture of 6.3 g (III) and 80 ml 10% C_2H_5ONa in ethanol was boiled with stirring for 1.5 h. After the excess C_2H_5ONa was neutralized with dry HCl, and the ethanol was distilled, the reaction product was isolated by distillation under vacuum.

CONCLUSIONS

1. Methods of synthesis have been worked out, and 1,3-thiaphosphetane derivatives have been synthesized.

2. It has been shown that the four-membered thiaphosphetane ring can open under the action of basic-type reagents.

LITERATURE CITED

1. N. V. Ivasyuk and I. M. Shermergorn, Izv. Akad. Nauk SSSR, Ser. Khim., 481 (1969).
2. S. E. Cremer and R. J. Chorwat, Tetrahedron Lett., 413 (1968).
3. T. A. Zyablikova, A. R. Panteleeva, and I. M. Shermergorn, Izv. Akad. Nauk SSSR, Ser. Khim., 373 (1969).
4. T. A. Zyablikova, I. M. Magdeev, and I. M. Shermergorn, Izv. Akad. Nauk SSSR, Ser. Khim., 694 (1969).