

## CONCLUSIONS

There is a significant specific geminal interaction of the oxygen and chlorine atom in aryl chloromethyl ethers,  $p\text{-RC}_6\text{H}_4\text{OCH}_2\text{Cl}$ , although this effect is less than in alkyl chloromethyl ethers.

## LITERATURE CITED

1. G. K. Semin, T. A. Babushkina, and G. G. Yakobson, The Application of Nuclear Quadrupole Resonance in Chemistry [in Russian], Khimiya, Leningrad (1972).
2. T. Benneche and Undheim, Acta Chem. Scand., **B37**, 93 (1983).
3. V. P. Feshin, M. G. Voronkov, P. A. Nikitin, M. A. Vasil'eva, A. Kh. Filippova, T. I. Bychkova, and A. V. Kalabina, Dokl. Akad. Nauk SSSR, **239**, 1381 (1978).
4. M. Charton, Progr. Phys. Org. Chem., **13**, 119 (1981).
5. O. Exner, in: Correlation Analysis in Chemistry. Recent Advances, Plenum Press, New York-London (1978), pp. 439-540.
6. B. Yu. Khel'mer, A. T. Shuvaev, O. E. Shelepin, and L. N. Mazalov, X-Ray and Photoelectron Spectra of Organic Oxygen Compounds [in Russian], Izd. Rostovsk. Gos. Univ., Rostov (1983).

## TRANSFORMATIONS OF HYDROXYALKYL ESTERS OF THIOPHOSPHONIC ACIDS CONTAINING A PHENOXY OR DIALKYLAMIDO GROUP AT THE PHOSPHORUS ATOM

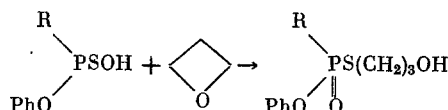
O. N. Nuretdinova and V. G. Novikova

UDC 542.91:547.1'118

Hydroxyalkyl esters of diphenylthiophosphoric acids readily lose phenol with the formation of thiaoxaphospholanes or phosphorinanes [1, 2].

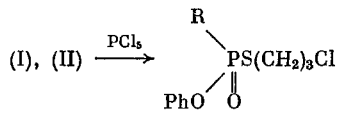
In a continuation of a study of the effect of the environment of the phosphorus atom in hydroxyalkyl esters on their transformations, we synthesized esters of alkylthio- and phenylthiophosphonic acids containing a phenoxy or dialkylamido group at the phosphorus atom.

The reaction of ethyl-O- and phenyl-O-phenylthiophosphonic acid with oxetane gave the S-3-hydroxypropyl esters of these acids (I) and (II), which are oils stable upon storage at 20°C



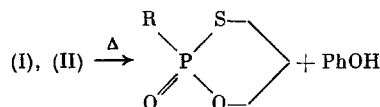
R = Et (I), Ph (II).

The action of  $\text{PCl}_5$  or  $\text{SOCl}_2$  on these esters gave the corresponding 3-chloropropyl esters (III) and (IV).



R = Et (III), Ph (IV).

Heating and distillation of (I) and II) leads to decomposition with loss of phenol and formation of cyclic phosphonates with a thiaoxaphosphorinane ring.

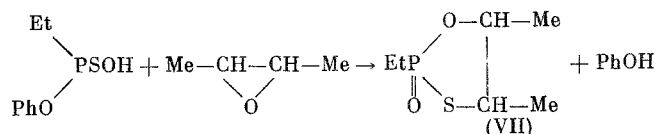


R = Et (V), Ph (VI).

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. 5, pp. 1197-1200, May, 1985. Original article submitted July 10, 1984.

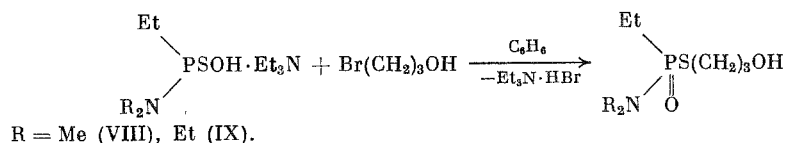
Most of the compounds obtained (especially, derivatives of ethylthiophosphonic acid) are difficult to subject to elemental analysis, although all these compounds, except for (II), which contains the usual small phenol impurity, are pure compounds. The physical constants of the compounds, for which satisfactory elemental analyses were obtained, are given in Experimental section.

The reaction of ethyl-O-phenylthiophosphonic acid with 2,3-butylene oxide directly gives cyclic derivative (VII) which could not be purified to remove phenol, even upon heating at reflux with metallic sodium.



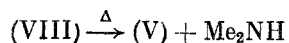
The  $^{31}\text{P}$  NMR spectrum of the product of this reaction has one signal at +73 ppm corresponding to (VII).

The preparation of 3-hydroxypropyl esters of ethyldialkylamidothiophosphonic acids requires a different method due to the instability of these thioacids.



For R = Et, the  $^{31}\text{P}$  NMR spectrum after removal of  $\text{Et}_3\text{N} \cdot \text{HBr}$  and benzene has one signal corresponding to phosphonate (IX). Only a slight impurity of heterocycle (V) is formed upon distillation of (IX).

Hydroxyalkyl ester (VIII) decomposes more rapidly than (IX) upon heating and distillation with the loss of dimethylamine and cyclic phosphonate (V)



Thus, in comparison with the analogous esters of diphenylthiophosphoric acid, 3-hydroxyalkyl esters of ethyl-O- and phenyl-O-phenylthiophosphonic acids and ethyl-O- and phenyl-O-dialkylamidothiophosphonic acids have less tendency to cyclize.

## EXPERIMENTAL

3-Hydroxyalkyl Esters of Alkyl-O- and Phenyl-O-phenylthiophosphonic Acids (I) and (II). Esters (I) and (II) were obtained upon heating the corresponding acids with oxetane in 1:2 ratio at mild reflux for 20-30 min. Then, the excess oxetane was removed at 30-40°C (0.1 mm). The residue contained 3-hydroxyalkyl esters: 1) ethyl-O-phenyl-S-(3-hydroxypropyl) thio-phosphonate (I),  $d_4^{20}$  1.1954,  $n_D^{20}$  1.5540. Found: C 50.86; H 6.43; P 12.27%. Calculated for  $\text{C}_{11}\text{H}_{17}\text{O}_3\text{PS}$ : C 50.76; H 6.54; P 11.92%.  $^{31}\text{P}$  +62 ppm. 2) phenyl-O-phenyl-S-(3-hydroxypropyl) thiophosphonate (II) with  $\delta^{31}\text{P}$  +47 ppm. This compound always contains a slight impurity of phenyl which could not be removed from the starting thiophosphonic acid.

Alkyl-O- and Phenyl-O-phenyl-S-(3-chloropropyl) Thiophosphonates (III) and (IV). A sample of 3.9 g powdered  $\text{PCl}_5$  was added carefully to 4.9 g (I) dissolved in 30 ml  $\text{CH}_2\text{Cl}_2$ . A vigorous reaction ensued. After the addition of all the  $\text{PCl}_5$ , the reaction mixture was heated at reflux for 20 min. Then, the volatile compounds were distilled off at 10 mm and the residue was distilled to yield 2.4 g (45%) ethyl-O-phenyl-S-(3-chloropropyl) thiophosphonate (III), bp 125° (0.08 mm),  $d_4^{20}$  1.2312,  $n_D^{20}$  1.5550. Found: P 11.81; S 11.09%. Calculated for  $\text{C}_{11}\text{H}_{16}\text{ClO}_2\text{PS}$ : P 11.13; S 11.49%.  $\delta^{31}\text{P}$  +60 ppm.

Analogously, 10.3 g (II) and 6.9 g  $\text{PCl}_5$  gave 3.8 g (35%) phenyl-O-phenyl-S-(3-chloropropyl) thiophosphonate (IV), bp 168-160°C (0.1 mm),  $d_4^{20}$  1.2610,  $n_D^{20}$  1.5900. Found: C 55.01; H 4.83; P 9.14%. Calculated for  $\text{C}_{15}\text{H}_{16}\text{ClO}_2\text{PS}$ : C 55.13; H 4.90; P 9.49%.  $\delta^{31}\text{P}$  +43 ppm.

2-Ethyl-2-oxo-1,3,2-thiaoxaphosphorinane (V). Heating and distillation of 19.3 g (I) in vacuum gave 6.6 g (53%) (V) with bp 96-98°C (0.1 mm),  $d_4^{20}$  1.2514,  $n_D^{20}$  1.5315 which contained an impurity of phenol as indicated by IR spectroscopy. A solution of 2 g of this product in 15 ml toluene was prepared and heated at reflux for 15 min. The solution was cooled

and sodium phenolate was filtered off. Toluene was distilled off at 10 mm and the residue was redistilled at yield (V), bp 81-83°C (0.065 mm),  $d_4^{20}$  1.2538,  $n_D^{20}$  1.5295. Found: C 36.75; H 6.60; P 18.54%. Calculated for  $C_5H_{11}O_2PS$ : C 36.14; H 6.63; P 18.67%.  $\delta^{31}P$  +51 ppm.

2-Phenyl-2-oxo-1,3,2-thiaoxaphosphorinane (VI). A sample of 18.6 g (II) was heated at reflux for 1 h in m-xylene. The volatile compounds were distilled off, initially at 10 mm and then at 0.2 mm and the residue was distilled to yield 5 g (38.5%) (VI), bp 152-154°C (0.085 mm),  $d_4^{20}$  1.2991,  $n_D^{20}$  1.5944. Found: P 14.61%. Calculated for  $C_9H_{11}O_2PS$ : P 17.49%.  $\delta^{31}P$  +38 ppm.

Diethylamidoethyl-S-(3-hydroxypropyl) Thiophosphonate (IX). A sample of 7.4 g  $Et_3N$  was added in an argon atmosphere to 10.9 g ethyldiethylamidophosphonite in 30 ml benzene and then 2.35 g sulfur was added. After heating to 60°C until complete dissolution of the sulfur, 10.17 g 1-bromopropanol was added and the reaction mixture was heated for 1 h at reflux. After cooling,  $Et_3N \cdot HBr$  was filtered off. Benzene was distilled off at 10 mm and the viscous brown residue has one  $^{31}P$  NMR signal at +56 ppm corresponding to 3-hydroxypropyl ester (IX). Distillation of the reaction mass gives partial cyclization of (IX) to form cyclic phosphonate (V). A fraction was collected at 130-140°C (0.1 mm) consisting predominantly of (IX) with a slight impurity of (V) as indicated by  $^{31}P$  NMR spectroscopy. This fraction was redistilled, bp 110-112°C (0.08 mm),  $d_4^{20}$  1.1438,  $n_D^{20}$  1.5120. Found: C 44.40; H 8.88; N 5.26; P 12.32; S 14.13%. Calculated for  $C_9H_{22}NO_2PS$ : C 45.18; H 9.20; N 5.85; P 12.96; S 13.39%.  $\delta^{31}P$  +58 ppm (impurity of (V) with  $\delta^{31}P$  +51 ppm).

Distillation of dimethylamidoethyl-S-(3-hydroxypropyl) thiophosphonate (VIII) obtained from 10.96 g dimethylamidoethylphosphonite, 9.15 g  $Et_3N$ , 2.9 g sulfur, and 12.6 g 1-bromopropanol immediately gave 4.4 g (29%) cyclic phosphonate (V), bp 118-121°C (0.1 mm),  $d_4^{20}$  1.2546,  $n_D^{20}$  1.5282. Found: C 35.65; H 6.82; P 18.28%. Calculated for  $C_5H_{11}O_2PS$ : C 36.14; H 6.63; P 18.67%.  $\delta^{31}P$  +50 ppm.

#### CONCLUSIONS

The tendency toward cyclization with the loss of phenol or dialkylamine and formation of compounds with a 1,3,3-thiaoxaphosphorinane ring decreases in the series of 3-hydroxyalkyl esters of diphenylthiophosphoric, alkyl-O-phenylthiophosphonic, phenyl-O-phenylthiophosphonic, and alkylalkylamidothiophosphonic acids.

#### LITERATURE CITED

1. O. N. Nuretdinova and B. A. Arbuzov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1130 (1981).
2. B. A. Arbuzov and O. N. Nuretdinova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 675 (1983).