ESTERS OF THIOACIDS OF TRIVALENT PHOSPHORUS COMMUNICATION 11. REACTION OF ACID HALIDES OF ESTERS OF THIOPHOSPHONOUS ACIDS WITH α_{β} -UNSATURATED KETONES

N. I. Rizpolozhenskii, V. D. Akamsin, R. M. Eliseenkova, and R. R. Shagidullin

UDC 542.91:547.1'118

Previously it was shown that the acid chlorides of the esters of ethylthiophosphonous acid (I, \mathbb{R}^2

 C_2H_5 , Hal = Cl) react with acrylic acid to give the acid chlorides of β -(alkylthioethylphosphinoxido)-propionic acids [1]. As a continuation of the investigation of the properties of (I) we studied the reaction of (I, $R^2 = C_2H_5$, Hal = Cl, Br) and (I, $R^2 = C_6H_5$, Hal = Cl) with unsaturated ketones and obtained the corresponding 2-thiono-1,2-oxa-4-phospholene derivatives (III)



Adduct (II), formed as the result of the 1,4-addition of an α , β -unsaturated compound to (I), undergoes the second step of the Arbuzov rearrangement with the cleavage of alkyl halide and the formation of the (III) derivatives. An opening of the 1,2-oxaphospholene ring fails to occur for the reason that nucleophilic attack by the halogen ion on the carbon at the double bond is hindered. It is known, for example, that the Arbuzov rearrangement of dialkyl vinyl phosphites and alkyl divinyl phosphites always proceeds with a cleavage of the alkyl radical [2].

We assigned the structure of the (III) derivatives to the obtained compounds. The IR spectra and the ³¹P NMR spectra are in agreement with the postulated structure. Quite intense absorption, with a maximum at 1680-1705 cm⁻¹, is observed in the IR spectra, which must be assigned to the vibrations of the C=C bond. The high value of this frequency corresponds to the fact that the double bond is found in a strained ring and has a substituent [3]. The presence of a double bond is also indicated by absorption in the 3060 cm⁻¹ region, which is characteristic for the $\nu_{\rm C-H}$ at a double bond [4]. Only one band of noticeable intensity is observed in the 1100-1300 cm⁻¹ region. The absorption of the $\nu_{\rm C-O}$ at a double bond should appear in this range; other bands, which would indicate the presence of the P=O bond, are not observed. The bands observed in the 600-700 cm⁻¹ region should be associated with the $\nu_{\rm P=S}$ [5]. In addition, as for other compounds with five-membered rings that contain phosphorus and oxygen, very strong bands are observed in the vicinity of 800 cm⁻¹ [3].

The ³¹P NMR spectra have a signal in the region from -114 to -132 ppm relative to 85% H₃PO₄, which is characteristic for compounds that contain a thiophosphoryl group. Rearrangement of the (III) derivatives to 2-oxo-1,2-thia-4-phospholene derivatives, as is postulated for the reaction product of the acid chloride of dithioglycol phosphorus acid with methyl vinyl ketone [6], was not observed by us. If the rearrangement did take place, then the ³¹P signal would be further upfield [7]. For example, the chemical shifts for the

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2765-2768, December, 1972. Original article submitted October 25, 1971.

• 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. two isomeric compounds $(C_2H_5)P(S)OC_2H_5$ and $(C_2H_5)_2P(O)SC_2H_5$ respectively have values of -104 and -65 ppm relative to 85% H₃PO₄.

The data, given in [7] in establishing that the structure of one of the products is $2-(\beta-\text{chloroethyl-thio})-2-\text{oxo-5-methyl-1},2-\text{thia-4-phospholene (IV)}$, evoke doubt. The authors of [6] compare the IR spectra of the reaction product and $2-(\beta-\text{chloroethylthio})-2-\text{oxo-5-methyl-1},2-\text{oxa-4-phospholene (V)}$ and note that both spectra are identical except for the 700-850 cm⁻¹ region. However, the spectra of (IV) and (V) cannot be identical, since, in particular, replacing the oxygen atom in the ring by the sulfur atom should lead to a reduction in the absorption frequency of the double bond [8].

When the synthesized (III) derivatives were treated with P_2S_5 we were able to replace the oxygen atom in the ring by the sulfur atom and obtain 2-thiono-1,2-thia-4-phospholene derivatives. From the IR spectrum of 2-ethyl-2-thiono-3,3,5-trimethyl-1,2-thia-4-phospholene (VI) it can be seen that the $\nu_{C=C}$ actually has a lower value (1630 cm⁻¹) than the $\nu_{C=C}$ for 2-ethyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene (VII) (1680 cm⁻¹). The intense absorption of $\nu_{C-O} \sim 1200$ cm⁻¹ that exists for (VII) is absent in the spectrum of (VI). In turn, in the spectrum of (VI) two intense absorption bands are observed at ~ 600 cm⁻¹

(575 and 665 cm⁻¹), and must be assigned to the P s group; this absorption is absent in the spectrum of

(VII).

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-10 spectrometer as a thin layer between KBr plates, in which connection the crystalline compounds were prepared in advance as Nujol mulls. All of the syntheses described below were carried out in a CO_2 atmosphere.

<u>Reaction of Mesityl Oxide with the Acid Chloride of Ethylthioethylphosphonous Acid.</u> A stirred mixture of 23.5 g of the acid chloride of ethylthioethylphosphonous acid and 14.7 g of mesityl oxide was heated at 135-140°C for 2 h. Vacuum-distillation gave 18.2 g (64%) of 2-ethyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene, bp 62-64° (0.02 mm); n_D^{20} 1.5173; d_4^{20} 1.0656; δ (³¹P)-132 mol. wt. Found: C 50.23; H 7.84; P 16.35%; MR 54.02. C₈H₁₅OPS. Calculated: C 50.52; H 7.95; P 16.28%; MR 53.71.

Reaction of Mesityl Oxide with Acid Bromide of Ethylthioethylphosphonous Acid. To 9.8 g of the acid bromide of ethylthioethylphosphonous acid 4.9 g of mesityl oxide was added in drops. The flask contents were heated for 15 min at 100-115° and then vacuum-distilled. We obtained 5.7 g (60%) of 2-ethyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene; bp 61-63° (0.02 mm); n_D^{20} 1.5182; d_4^{20} 1.0675.

Reaction of Methyl Isopropenyl Ketone with the Acid Chloride of Isobutylthioethylphosphonous Acid. A mixture of 18.5 g of the acid chloride of isobutylthioethylphosphonous acid and 8.4 g of methyl isopropenyl ketone was heated up to 105°, in which connection the temperature in the flask rose to 125°. Then the flask contents were heated at 110° for 1.5 h. The volatile products were removed in vacuo. After distillation we obtained 11 g (62.5%) of 2-ethyl-2-thiono-4,5-dimethyl-1,2-oxa-4-phospholene; bp 69-71° (0.06 mm); n_D^{20} 1.5240; d_4^{20} 1.0977; δ (³¹P)-114 mol. wt. Found: C 47.86; H 7.54; P 17.46%; MR 49.11. C₇H₁₃OPS. Calculated: C 47.73; H 7.43; P 17.58%; MR 49.09.

 $\frac{\text{Reaction of Ethylideneacetone with the Acid Chloride of Butylthioethylphosphonous Acid. A mixture of 11.7 g of the acid chloride of butylthioethylphosphonous acid and 5.3 g of ethylideneacetone was heated at 125-135° in a bath for 2 h, and then vacuum-distilled. We obtained 6.7 g (60.3%) of 2-ethyl-2-thiono-3,5-dimethyl-1,2-oxa-4-phospholene; bp 59-61° (0.09 mm); n_D^{20} 1.5226; d_4^{20} 1.0869; \delta (^{31}\text{P})-121 \text{ ppm.}$ Found: C 47.93; H 7.47; P 17.42%; MR 49.49. C₇H₁₃OPS. Calculated: C 47.73; H 7.43; P 17.58%; MR 49.09.

Reaction of Mesityl Oxide with the Acid Chloride of Propylthiophenylphosphonous Acid. A mixture of 11 g of the acid chloride of propylthiophenylphosphonous acid and 4.9 g of mesityl oxide was heated at 135–150° for 1.5 h. We obtained 7.5 g (63%) of 2-phenyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene; bp 106–107° (0.006 mm); mp. 66–69°. Found: C 60.48; H 6.35; P 13.03%. $C_{12}H_{15}OPS$. Calculated: C 60.48; H 6.35; P 13.0%.

Reaction of Methyl Isopropenyl Ketone with the Acid Chloride of Isopropylthiophenylphosphonous Acid. A mixture of 21.9 g of the acid chloride of isopropylthiophenylphosphonous acid and 8.4 g of methyl isopropenyl ketone was heated at 140-150° for 1.5 h. The isopropyl chloride was distilled off. Vacuum-distillation of the residue gave 14.4 g (64.3%) of 2-phenyl-2-thiono-4,5-dimethyl-1,2-oxa-4-phospholene; bp 125-128° (0.07 mm); mp 83-84° (from benzene). Found: C 58.91; H 5.81; P 13.83; S 14.42%. $C_{11}H_{13}OPS$. Calculated: C 58.89; H 5.84; P 13.81; S 14.30%.

<u>Reaction of Methyl Vinyl Ketone with the Acid Chloride of Ethylthioethylphosphonous Acid.</u> To 7 g of methyl vinyl ketone was added 15.7 g of the acid chloride of ethylthioethylphosphonous acid in drops, at such a rate that the temperature in the flask did not exceed $30-35^{\circ}$. This mixture was heated up to 110° in 2 h, maintained at this temperature until the liberation of C₂H₅Cl ceased, and then vacuum-distilled. We obtained 10.5 g (64.8%) of 2-ethyl-2-thiono-5-methyl-1,2-oxa-4-phospholene; bp 70-72° (0.05 mm); n_D^{20} 5292; d_2^{20} 1.1303; $\delta^{31}P-120$ ppm. Found: C 44.44; H 6.95; P 19.21%; MR 44.27. C₆H₁₁OPS. Calculated: C 44.43; H 6.84; P 19.10%; MR 44.47.

<u>Reaction of P_2S_5 with 2-Ethyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene</u>. A mixture of 14 g of the oxaphospholene and 3.5 g of P_2S_5 in 20 ml of dioxane was heated under reflux for 2 h, and then the dioxane was removed in vacuo. After two distillations in vacuo we obtained 9.4 g (61.8%) of 2-ethyl-2-thiono-3,3,5-trimethyl-1,2-thia-4-phospholene; bp 73-75° (0.025 mm); mp 45-46° (from petroleum ether). Found: P 14.66; S 30.92%. $C_8H_{15}PS_2$. Calculated: P 15.01; S 31.08%.

<u>Reaction of P_2S_5 with 2-Ethyl-2-thiono-4,5-dimethyl-1,2-oxa-4-phospholene</u>. Under the conditions of the preceding experiment, from 13 g of the oxaphospholene and 3.5 g of P_2S_5 was obtained 8.2 g (57.8%) of 2-ethyl-2-thiono-4,5-dimethyl-1,2-thia-4-phospholene; mp 28°. Found: P 16.16; S 33.30%. $C_7H_{13}PS_2$. Calculated: P 16.12; S 33.28%.

CONCLUSIONS

The acid halides of the esters of thiophosphonous acids react with α,β -unsaturated ketones to give 2-thiono-1,2-oxa-4-phospholene derivatives.

LITERATURE CITED

- 1. V. D. Akamsin and N. I. Rizpolozhenskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1976 (1967).
- 2. I. F. Lutsenko and Z. S. Kraits, Dokl. Akad. Nauk SSSR, 132, 612 (1960).
- 3. V. A. Kukhtin, K. M. Kirilova, and R. R. Shagidullin, Zh. Obshch. Khim., 32, 649 (1962).
- L. J. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL (1963), pp. 23, 53, 441.
- 5. R. A. Chittenden and L. C. Thomas, Spectrochim. Acta, 20, 1679 (1964).
- 6. L. S. Kovalev, N. A. Razumova, and N. A. Petrov, Zh. Obshch. Khim., 38, 2277 (1968).
- 7. V. Mark, C. H. Dungan, M. M. Grutechfield, and J. R. Van Wazer, Topics in Phosphorus Chemistry, Vol. 5 (1967), p. 227.
- 8. C. N. R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York-London, (1963).