

Heterocyclic Compounds Containing Phosphorus. I : On the Syntheses of Five Membered Monothio Phosphates

著者	YAMASAKI Taro, SATO Toshiro
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	6
page range	384-389
year	1954
URL	http://hdl.handle.net/10097/26648

Heterocyclic Compounds Containing Phosphorus. I

On the Syntheses of Five Membered Monothio Phosphates

Taro YAMASAKI and Toshiro SATO

The Research Institute of Mineral Dressing and Metallurgy

(Received June 4, 1954)

Synopsis

Cyclic monothio phosphates were prepared by the reaction of glycols and thio phosphoryl chloride. Their characteristics are shown in Table 2, 3 and 4. In order to confirm the structure, a series of cyclic phosphites of known construction were allowed to react with sulfur to give cyclic monothio phosphates, and physical and analytical data show that the products prepared by the both methods were the same ones.

I. Introduction

Many investigations have been published⁽¹⁾ on the formation of primary, secondary or tertiary phosphates or thiophosphates by the reaction between phosphoryl chloride or thio phosphoryl chloride with monohydroxylated alcohols, but none has been reported as to the reaction between glycols and thio phosphoryl chloride. The present paper describes the results obtained by the condensation of the appropriate α,β -hydroxylated glycols with thio phosphoryl chloride.

As glycols have two functional groups of hydroxyl radicals, so the esters obtained may be expected to have numerous structures. Kabachnik⁽²⁾, Arbuzov⁽³⁾ and Lucas⁽⁴⁾ studied the reaction of glycols and phosphorus trichloride and found that the cyclic phosphites could be obtained. Furthermore, Arbuzov described in his work that a cyclic thio phosphate has been prepared by adding sulfur to one of the phosphites prepared by him. We intended to synthesize a series of cyclic thiophosphate directly from the reaction of glycols with thio phosphoryl chloride.

As α,β -glycols we preferred ethylene glycol (Ia), propylene glycol (Ib) and glycerin- α -monomethyl ether (Ic). The general methods of preparing thiophosphates from monohydroxylated alcohols and thio phosphoryl chloride were employed in our procedures. The methods were as follows:

- (A) Dehydrochlorination in the presence of bases.
- (B) Dehydrochlorination by heating the mixtures in solvents.

Attempts were also made at the condensation of sodium glycolates with thio phosphoryl chloride, but their results will be discussed in near future.

(1) G. M. Kosolapoff, "Organophosphorus Compounds" Chapter 9, p. 211 (1950).

(2) P. A. Rossiiskaya, M. I. Kabachnik, Bull. acad. Sci. U. R. S. S. classe sci. chim. **1947**, 509; Chem. Abst. **42** (1948), 2924.

(3) A. E. Arbuzov et al., Bull. Acad. Sci. U. R. S. S. classe sci. chim. **1948**, 208; Chem. Abst. **42** (1948), 4932.

(4) H. J. Lucas et al., J. Am. Chem. Soc. **72** (1952), 5491.

It might be expected that the formation of cyclic chloro thiophosphates by the reaction of glycols and thio phosphoryl chloride in the presence of pyridine would be possible if these three were used in the mole ratio of 2:1:1 respectively. The reaction has been performed at the temperature between 10° to 15°C and products were obtained in liquid state containing chlorine, phosphorus and sulfur. These products were led to colorless crystalline phenylhydrazides and their structures were determined by analyses. Thus, the compounds so obtained from ethylene glycol, propylene glycol and glycerine- α -monomethyl ether were 2-chloro-2-thiono-1,3-dioxo-2-phosphacyclopentan(IIa), its 4-methyl(IIb) and its 4-methoxymethyl(IIc) derivatives respectively. Other compounds could not be found from the reactions. Unsuccessful attempts were made by alternating the mole ratios of the materials as 1:1:2 or 2:2:1 to obtain other compounds which might be expected to have the construction of VI in which one of the hydroxyl groups was substituted by phosphorylation.

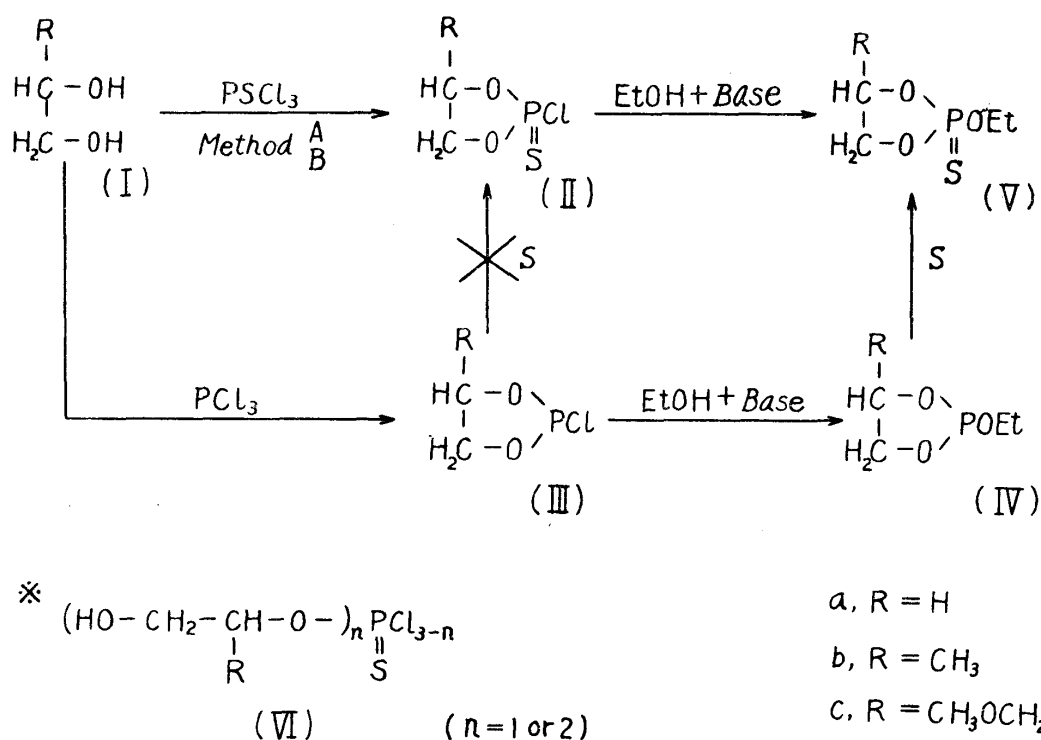


Fig. 1. Reaction Chart.

* Chain isomer may be expected.

The temperature of the reaction should be kept at 10° to 15°C. Under the temperature dropped below this, unreacted starting materials were recovered, and at higher, an amorphous substances were resulted.

B) Another cyclization procedure which we applied was the dehydrochlorination by heating the solution of glycols and thio phosphoryl chloride in inert solvent. As inert solvent we preferred chloroform, because it dissolved glycols. Of the

glycols we used, ethylene glycol was the only one which could not be dissolved in chloroform, while the other two glycols did with the solvent. Trials to find other preferable solvents resulted in failure. Therefore, in the case of ethylene glycol, the reaction was a heterogeneous one, but the reaction proceeded very smoothly for the reason that chloroform went to underlayer and vaporization of it played the part of stirring.

The mole ratio between glycols and thio phosphoryl chloride was fixed at 1 to 1 or 2 to 1, and the reactions always resulted in the formation of cyclic chloro thio phosphate (II). The yields increased remarkably when the excess glycols were used, and also gave better results as compared with the method mentioned previously in part (A).

Table 1. Yields of cyclic secondary chloro thiophosphates.

Product	Method		
	A Glycol : PSCl ₃ : Base 1 : 1 : 2	B Glycol : PSCl ₃ 1 : 1	Glycol : PSCl ₃ 2 : 1
IIa %	36	35	55
IIb %	63	44	74
IIc %	52	32	60

Table 2. Characteristics of cyclic chloro thiophosphate.

Product	C ₂ H ₄ O ₂ PSCl (IIa)	C ₃ H ₆ O ₂ PSCl (IIb)	C ₄ H ₈ O ₃ PSCl (IIc)	
Boiling Point (°C/mmHg)	88/3.5	96-8/3	114/4	
<i>n</i> _D (°C)	—*	1.5112/16	1.5085/18	
Phenylhydrazid	Melting Point (°C)	187	139	
	Molecular Formula	C ₈ H ₁₁ O ₂ N ₂ PS	C ₉ H ₁₃ O ₂ N ₂ PS	C ₁₀ H ₁₅ O ₃ N ₂ PS
	Anal.%	P Calcd. 13.45 Found 13.47 S Calcd. 13.93 Found 14.04 N Calcd. 12.17 Found 12.07	12.68 12.56 13.13 13.26 11.47 11.94	11.29 11.23 11.69 11.74 10.27 10.38

* m. p. 30.5°C

With a view of confirming the structure of the compounds we prepared, unsuccessful attempts were made to synthesize the same compounds by adding sulfur to the cyclic chloro phosphites (III) of known constructions.

As mentioned before, Arbuzov⁽³⁾ prepared 2-ethoxy-2-thiono-4-methoxymethyl-1,3-dioxo-2-phosphacyclopentane (Vc) by adding sulfur to the parent phosphite (IVc). In order to obtain the same compound, we tried to condense the phosphate (IIc) with ethanol in the presence of pyridine. The physical constants and analytical data show that the compound we obtained was the same one as reported by Arbuzov. Table 3 indicates the characteristics of cyclic thio phosphates(V) prepared

by the method mentioned above. Another method of synthesizing the compounds V was tried by following the method demonstrated by Arbuzov. Tertiary phosphites of IVa and IVb were obtained by the method of Lucas⁽⁴⁾, and introduction of sulfur into the phosphites was tried respectively. The results are shown in Table 4.

Table 3. Condensation products of cyclic secondary chloro thio phosphates and ethanol.

Product	Yield (%)	Boiling Point (°C/mmHg)	n_D (°C)	d_4 (°C)	Chemical Formula	Analyses of Sulfur %	
						Calcd.	Found
Va	60	98-99/3	1.4849/21	1.2737/21	C ₄ H ₉ O ₃ PS	19.07	18.94
Vb	94	96/3	1.4759/22	1.2052/22	C ₅ H ₁₁ O ₃ PS	17.60	17.69
Vc	77	119-120/3	1.4790/21.5	1.2310/21.5	C ₆ H ₁₃ O ₄ PS	15.11	15.15

Table 4. Reaction products of cyclic tertiary phosphites with sulfur.

Product	Yield (%)	Boiling Point (°C/mmHg)	n_D (°C)	d_4 (°C)	Chemical Formula	Analyses of Sulfur %	
						Calcd.	Found
Va	43	108/4	1.4842/24	1.2705/24	C ₄ H ₉ O ₃ PS	19.07	18.94
Vb	73	96/3	1.4760/22	1.2043/22	C ₅ H ₁₁ O ₃ PS	17.60	17.53
Vc*	—	121.5-122/2	1.4790/20	1.2359/20	C ₆ H ₁₃ O ₄ PS	15.11	—

* Observed by Arbuzov et al.

Thus it was proved that the formation of cyclic tertiary thio phosphates from cyclic phosphites of known construction was possible. In view of the above facts the most reasonable conclusion to be drawn from the available data is that chloro thiophosphates obtained by us should have a cyclic construction.

II. Experimental

Materials. Commercial ethylene glycol and propylene glycol were subjected to distillation until their physical constants coincided with those given in literature. Glycerin- α -monomethyl ether was prepared according to the method given in literature⁽⁵⁾. A part of the thio phosphoryl chloride used was available through the courtesy of Toyama Chemical Co., and other parts were prepared from phosphorus trichloride and sulfur by the method of Knotz⁽⁶⁾.

1. Condensation of glycols and thio phosphoryl chloride

(A) Reactions in the presence of pyridine

In a four-necked flask equipped with a mercury sealed stirrer, a dropping funnel, a thermometer and a calcium chloride tube was placed a solution consisting of 0.1 mole of thio phosphoryl chloride and 50 ml of anhydrous benzene. The flask was surrounded with ice bath, and the stirrer was started. When the temperature of the solution dropped to 10°C, a mixture of 0.1 mole of glycol and 0.2 mole of pyridine in a dry 20 ml of benzene was added through the dropping funnel at such

(5) "Org. Syntheses", 2, 33 (1922); Ad. Grün, F. Bockisch, Ber. 41, 3471 (1908)

(6) F. Knotz, Oester. Chem. Ztg. 50 (1949), 128; Chem. Abst. 43 (1949), 9396.

a rate that the temperature of the content remained at 10° to 15°C. After the mixture had been added, the mixture was stirred for some time, then allowed to stand at room temperature for several hours. Pyridine hydrochloride precipitated was removed by filtration and the filtrate was washed with cold water, and the organic layer was dried on calcium chloride, then benzene was expelled by distillation under reduced pressure. The residue was subjected to distillation in vacuo. The products were obtained as liquid state and decomposed on standing in air for a long time, but the one from ethylene glycol was crystallized at room temperature, melting at 30.5°C. Phenylhydrazides could be recrystallized from ethanol and subjected to analysis.

(B) Reaction by heating the mixture

In a flask attached to a reflux condenser which was connected to calcium chloride tube to protect moisture were placed 0.1 mole of thio phosphoryl chloride, 50 ml of pure chloroform and 0.1 or 0.2 mole of glycols in the order named. The flask was heated in a water bath for seven hours until the evolution of hydrogen chloride gas ceased. Then chloroform was removed by distillation under reduced pressure. The residue was transferred into water, extracted with benzene, and benzene layer was washed with water and dried over calcium chloride. And after the removal of benzene was completed under reduced pressure, the residue was distilled in vacuo. The distillates were led to their phenylhydrazides, and mixed melting points with the products obtained by the method A showed no depression.

2. Condensation of cyclic chloro thiophosphates and ethanol

A mixture of 0.1 mole of cyclic chloro thiophosphates and 50 ml of benzene was placed in a two-necked flask equipped with a dropping funnel and a calcium chloride tube. The flask was cooled with ice-water, and then 0.1 mole of pyridine was added. After 0.15 mole of anhydrous ethanol was subjected to the reaction in small portion through a dropping funnel, the content was allowed to stand for several hours at room temperature. Pyridine hydrochloride obtained was removed by filtration and the filtrate was washed with cold water, dried over calcium chloride, then benzene was expelled under reduced pressure and the residue was collected by distillation in vacuo. The products were comparatively stable liquids, and the analytical data are shown in Table 3.

3. Preparation of 2-ethoxy-1,3,2-dioxaphosphan (IVa)

2-chloro compound (IIIa) was prepared from ethylene glycol with phosphorous trichloride according to the method of Lucas. IIIa reacted with ethanol in the presence of pyridine to give an expected cyclic phosphite. b.p. 73°C/40 mmHg, n_D^{15} 1.4428.

4. Reaction of 2-ethoxy-1,3,2-dioxaphosphan with sulfur

In a two-necked flask provided with a reflux condenser and a thermometer, was placed 0.15 mole of powdered sulfur and 0.15 mole of IVa was added cautiously. In order to keep the temperature of the reaction at below 140°C, the flask was surrounded with water, with occasional shaking. The reaction ended in a few

minutes. Unless the temperature was kept below 140°C, a vigorous decomposition occurred. Then the product was thrown into ice water and unreacted sulfur was removed by decantation, followed by an extraction with benzene. The benzene extract was washed with water, and the benzene was dried and the solvent removed under reduced pressure. The remainder was distilled in vacuo as colorless liquid.

5. Preparation of 2-ethoxy-4-methyl-1,3,2-dioxaphosporan (IVb)

The method employed was the same as described in part (3). b. p. 83°C/60 mmHg., n_D^{21} 1.4339.

6. Reaction of 2-ethoxy-4-methyl-1,3,2-dioxaphosporan with sulfur

In a two-necked flask equipped with a reflux condenser and a thermometer, was added 0.15 mole of sulfur and 0.1 mole of IVb, and was heated on asbestos at such a rate that the temperature would not exceed over 150°C. The reaction ended in a few minutes. After cooling, the products were treated in the same way as described in part 4.

Acknowledgement

The authors wish to thank to Prof. S. Fujise of Organic Chemistry at the Tohoku University for his precious advices, and Miss T. Kishinami for Nitrogen analyses.