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Abstract

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A NEW METHOD FOR THE SYNTHESIS OF ESTERS OF DIALKYLPHOSPHINIC ACIDS*

Earlier (1) we developed a method for the synthesis of esters of alkylphosphinous acids from dialkyl chlorophosphites $(RO)_2PCl$, readily obtainable from phosphorus trichloride and alcohols in the presence of organic bases. Replacement of the chlorine atoms of dialkyl chlorophosphites by various radicals was carried out by reaction with magnesium-(1), lithium-(2), and sometimes sodium-organic (3) compounds at low temperature, about −60° (see also (4,5))

$$\mathrm{RMe} + \mathrm{ClP(OR')_2} \xrightarrow[-60^\circ]{} \mathrm{RP(OR')_2} + \mathrm{MeCl},$$

$$\mathrm{Me} = \mathrm{MgX},\ \mathrm{Li},\ \mathrm{Na}.$$

It was of interest to extend the indicated method of synthesis to esters of dialkylphosphinic acids, using as starting substances the readily available Menshutkin chlorohydrides, alkyl dichlorophosphites, and the corresponding organomagnesium compounds. This reaction was successfully carried out in quite satisfactory yields in the presence of pyridine at −60°. The reaction scheme is as follows:

$$2\mathrm{RMgX} + \mathrm{Cl_2POR'} \xrightarrow[-60^\circ]{4\mathrm{C_5H_5N}} \mathrm{R_2POR'} + 2[\mathrm{MgXCl} \cdot 2\mathrm{C_5H_5N}].$$

The synthesis can also be performed in the absence of pyridine, with pyridine added after completion of the reaction; however, the yields of the esters of dialkylphosphinic acids are then reduced. The role of pyridine apparently consists in displacing the esters of dialkylphosphinic acids from complex compounds with magnesium halide that are formed during the reaction. In the absence of pyridine, the esters of dialkylphosphinic acids cannot be isolated from the reaction mixture in satisfactory yields. As a complex-forming agent, 8-hydroxyquinoline may be used; in a mixture with pyridine, in some cases it gives better results than pyridine alone. Triethylamine is unsuitable for the stated purposes.

In a recently published work (6), M. Zander used not brominated but chlorinated organomagnesium compounds for the synthesis of esters of dialkylphosphinic acids, on the basis of the lesser tendency of magnesium chloride toward complex formation. In this case it is not necessary to use pyridine; however, the yields of the esters of dialkylphosphinic acids obtained are lower.

All operations for the synthesis of esters of dialkylphosphinic acids are carried out in an atmosphere of purified nitrogen; solvents and reagents are carefully dried. A solution of the organomagnesium compound, prepared in the usual manner from 0.22 gram-atom of magnesium and 0.22 mole of alkyl bromide (the only exception is benzyl chloride) in 100 ml of ether, is added dropwise to 0.1 mole of alkyl dichlorophosphite and 0.44 mole of pyridine in 100 ml of ether at a reaction-mixture temperature of $-60 \pm 5°$

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and vigorous stirring.* Upon completion, 200 ml of petroleum ether is added, and the mixture is left overnight. The precipitate is filtered off and thoroughly washed with petroleum ether (4 × 50 ml), the solvents are removed in vacuo, and the residue is distilled. When 8-hydroxyquinoline is used as the complexing agent, the synthesis is carried out analogously (i.e., in the presence of pyridine), and after completion of the reaction a solution of 0.22 mole of 8-hydroxyquinoline in 50 ml of benzene is added. The yields, constants, and analytical data for the compounds obtained are given in Table 1**.

Table 1

No.	Compound	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	MRD found	MRD calc.	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.
1	$(C_2H_5)_2POCH_2CH_2Cl$	48	27–28°/2	1.4678^{1}	1.0143	46.19	45.96	43.04	42.7	8.3 8.4	8.4	18.11	18.4
2	$(C_2H_5)_2POC_4H_9$	43	70–70.5°/19	^{2}1.4425	0.8479	50.65	50.33	59.05	59.3	11.81	11.8	19.01	19.1
3	$(C_2H_5)_2POC_7H_{15}$	60	62–63°/1	^{2}1.4490	0.8486	64.57	64.18	64.86	64.7	12.31	12.3	15.01	15.2
4	$(C_2H_5)_2POC_8H_{17}$	62	84.5–85°/3	^{2}1.4509	0.8488	69.24	68.80	66.06	66.0	12.51	12.5	14.01	14.2
5	$(C_3H_7)_2POC_4H_9$	66	47–48°/1	1.4470	0.8471	60.02	59.56	63.06	63.1	12.21	12.2	16.01	16.3
6	$(iso\text{-}C_3H_7)_2POC_4H_9$	68	36.5–37°/1	1.4452	0.8510	59.55	59.56	62.86	63.1	12.41	12.2	16.31	16.3
7	$(C_4H_9)_2POC_4H_9$	61	68–69°/1.5	1.4520	0.8479	69.45	68.80	65.96	66.0	12.61	12.5	14.11	14.2
8	$(C_4H_9)_2POC_4H_9\text{-}iso$	72	64–65°/1	1.4469	0.8428	69.21	68.80	65.86	66.0	12.31	12.5	14.01	14.2
9	$(iso\text{-}C_4H_9)_2POC_4H_9$	69	57–58°/1	1.4458	0.8407	69.21	68.80	65.86	66.0	12.51	12.5	14.11	14.2

No.	Compound	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	MRD found	MRD calc.	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.
10	$(C_5H_{11})_2POC_4H_9$	60	84–85°/1	1.4520	0.8475	78.41	78.04	68.16	68.2	12.91	12.7	12.41	12.6
11	$(C_6H_5CH_2)_2POC_2H_5$	27	120–121°/1	1.5737	1.0415	81.81		74.47	74.4	7.4 7.5	7.4	11.91	12.0
12	$(C_6H_5CH_2)_2POC_4H_9$	32	148–149°/2	1.5590[3]	1.0180	90.86		75.57	75.5	8.1 8.1	8.1	10.81	10.8
13	$(C_6H_5)_2POC_4H_9$[4]	42	127–128°/2	1.5733	1.0387	81.98		74.67	74.4	7.4 7.5	7.4	11.61	12.0

[1] Analysis. Found, %: Cl 21.1; 21.5; calculated, %: Cl 21.0. Literature data (9): b.p. 29-30°/2 mm, n_D^{20} 1.4670; d_4^{20} 1.0144. [2] Literature data (10): No. 2 –b.p. 54-55°/10 mm, n_D^{20} 1.4410; d_4^{20} 0.8516. No. 3–b.p. 70-71°/2 mm, n_D^{20} 1.4495; d_4^{20} 0.8547. No. 4–b.p. 82-83°/1 mm, n_D^{20} 1.4520; d_4^{20} 0.8579. [3] When 8-hydroxyquinoline was used as the complexing agent, the yield was 41%. [4] The reaction was carried out in tetrahydrofuran.

As follows from Table 1, the method gives good results in obtaining esters of dialkylphosphinous acids with radicals at the phosphorus atom from C_3 and higher. Esters of diethylphosphinous acid are obtained in satisfactory yields, and the yield increases with increasing number of carbon atoms in the radical of the ester group. It was not possible to carry out the synthesis of esters of dimethylphosphinous acid. Attempts to use methylmagnesium iodide and chloride for this purpose, as well as methyllithium in ether or tetrahydrofuran (7), did not lead to positive results. The butyl ester of diphenylphosphinous acid was obtained only when the reaction was carried out in tetrahydrofuran. In ether, both phenylmagnesium bromide and phenyllithium gave negative results.

* In the synthesis of butyl ester of diisopropylphosphinous acid, per 0.1 mole of butyldiethyl phosphite, 0.25 g-atom of magnesium, 0.25 mole of isopropyl bromide, and 0.5 mole of pyridine are taken.

** In calculating the molecular refractions of esters of dialkylphosphinous acids we used the value of the atomic refraction of phosphorus, 8.44 (15). It should be noted, however, that, as for esters of monoalkylphosphinous acids (1), in all cases there was a constant excess of the found molecular refraction over the calculated one, on average 0.41. The only exception is the butyl ester of diisopropylphosphinous acid.

It should be noted that in the synthesis of the butyl ester of diisopropylphosphinic acid, a by-product was isolated, containing nitrogen and phosphorus and having the composition $C_{15}H_{28}PON$, b.p. 96-97°/1 mm; n_D^{20}1.4909; d_4^{20}0.9317.

Found, %:	C 66.9; 66.8; H 10.6; 10.7; P 11.2; 11.4; N 5.0; 5.2
$C_{15}H_{28}PON$. Calculated, %:	C 66.9; H 10.5; P 11.5; N 5.2

The yield of this product (9–22%) increases with an increase in the amount of pyridine in the reaction mixture. The substance is a derivative of trivalent phosphorus and, on interaction with sulfur, forms an addition product insoluble in hydrochloric acid, with b.p. 124–125°/1 mm; n_D^{20} 1.5140; d_4^{20} 1.0086.

Found, %:	C 60.1; 60.0; H 9.3; 9.4; P 10.8; 10.8
$C_{15}H_{28}PONS$. Calculated, %:	C 59.8; H 9.4; P 10.3

The structure of the substance—possibly an *N*-phosphorylated derivative of dihydropyridine—has not yet been established.

Using the example of the β-chloroethyl ester of diethylphosphinic acid, it was shown that the new method is also suitable for obtaining β-chloroethyl esters of dialkylphosphinic acids. This opens up possibilities for the synthesis of vinylphosphine oxides ([8,9]).

The properties of esters of dialkylphosphinic acids have been studied in the works of B. A. Arbuzov and N. I. Rizpolozhenskii ([10]), and also of A. I. Razumov and N. I. Bankovskaya ([11]), etc., using esters of diethylphosphinic acid as examples. We studied only some reactions of the compounds obtained, in order to confirm their structure as derivatives of trivalent phosphorus.

Thus, by addition of sulfur to two of the esters obtained, the corresponding esters of dialkylthiophosphinic acids, $R_2PS(OR')$, were synthesized. Butyl ester of dibutylphosphinic acid, on interaction with methyl iodide, gave dibutylmethylphosphine oxide.*

Table 2

No.	Compound	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	C, %, found	C, %, calculated	H, %, found	H, %, calculated	P, %, found	P, %, calculated	S, %, found	S, %, calculated
1	$(C_2H_5)_2P(S)OC_8H_{17}$	90	129–130°/3	1.4810	0.9447	75.44	74.85	57.0; 57.1	57.6	10.8; 10.8	10.9	12.5; 12.6	12.4	13.0; 13.0	12.8
2	$(iso\text{-}C_4H_9)_2P(S)OC_4H_9$	82	88–89°/1; 96–97°/2	1.4790	0.9397	75.58	74.85	57.4; 57.4	57.6	11.0; 10.8	10.9	11.9; 12.10	12.4	13.4; 13.2	12.8

No.	Compound	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	C, %, found	C, %, calculated	H, %, found	H, %, calculated	P, %, found	P, %, calculated	S, %, found	S, %, calculated
3	$(C_4H_9)_2P(O)CH_3$	84	(m.p.) 31–33°	–	–	–	–	61.5; 61.3	61.3	12.2; 12.1	12.0	17.3; 17.5	17.6	–	–
4	$(C_6H_5CH_2)_2P(O)OC_4H_9$ [1]	56	m.p. 76.5–77°	–	–	–	–								
5	$(C_6H_5CH_2)_2P(O)H$ [2]	~100	m.p. 108.5–109°	–	–	–	–								
6	$(C_4H_9)_2POCl$ [3]	68	96–97°/1	1.4647	1.0302	52.77	52.48								
7	$(C_4H_9)_2POOH$ [4]	61	m.p. 69.5–70.5°	–	–	–	–								

[1] Literature data (⁵): m.p. 77.5–78°.
[2] Literature data (¹²): m.p. 109.3–110.1°.
[3] Literature data (¹³): b.p. 142–144°/11 mm, n_D^{20}1.4643; d_4^{20}1.0296.
[4] Literature data (¹⁴): m.p. 70.5–71.

By oxidation of the butyl ester of dibenzylphosphinic acid with atmospheric oxygen, the butyl ester of dibenzylphosphinic acid was obtained; it proved identical with the ester synthesized earlier by another route (⁵). Hydrolysis of esters of dibenzylphosphinic acid in a neutral or weakly acidic medium leads to dibenzylphosphinic acid (¹²).

* In the course of the reaction at a temperature of −5°, we observed the formation of a crystalline substance, apparently an intermediate product of the Arbuzov rearrangement, which agrees with the data of A. I. Razumov and N. I. Bankovskaya (¹¹).

By reacting sulfuryl chloride with butyl dibutylphosphinite in petroleum ether (0°, then standing for 1.5 h at 50°), dibutylphosphinous acid chloride (13) was obtained. This reaction may provide a convenient method for the synthesis of dialkylphosphinous acid chlorides. Hydrolysis of dibutylphosphinous acid chloride gave the corresponding acid (14) (the experiment was carried out without isolating intermediate products; yield 61%, calculated on the starting butyl dichlorophosphite). The yields, constants, and analytical data of the compounds obtained are given in Table 2.

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