Chemistry

Corresponding Member of the Academy of Sciences of the USSR
M. I. Kabachnik and E. N. Tsvetkov

1957

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR M. I. Kabachnik and E. N. Tsvetkov

A Method for the Synthesis of Esters of Alkylphosphinic Acids

Esters of alkylphosphinic acids are comparatively difficult-to-obtain substances. Representatives of this class of compounds were synthesized in 1952 from the corresponding alkyldichlorophosphines by B. A. Arbuzov and N. I. Rizpolozhenskii ([1]), and also by A. I. Razumov, O. A. Mukhacheva, and Sim Do Hen ([2], [3]). A series of diphenyl esters of phosphinic acids was obtained by G. Kamaev and E. A. Gerasimova ([4]) by the action of diphenyl chlorophosphite on organomagnesium compounds. Esters of arylphosphinic acids, first described in the works of A. Michaelis ([5]) and A. E. Arbuzov ([6]), have been investigated considerably more fully.

The usual method for obtaining esters of phosphinic acids is based on the interaction of the corresponding dichlorophosphines with alcoholates or with alcohols in the presence of bases. Although satisfactory methods of synthesis have been developed for aryldichlorophosphines ([7], [8]), the preparation of alkyldichlorophosphines still presents considerable preparative difficulties. Synthesis with the aid of organomercury compounds ([9]), which until very recently was the only general method, is associated with the use of toxic substances and is complicated by the difficulty of purifying alkyldichlorophosphines from impurities of organomercury derivatives. The synthesis via organolead compounds proposed in 1949 ([10]) (using ethyldichlorophosphine as an example) has limited possibilities, since practically only tetraethyllead is readily available. The methods developed later for synthesis with the aid of cadmium ([11]) and organozinc ([8]) derivatives are free of the above-mentioned disadvantages, but give comparatively low yields (26–47%) of alkyldichlorophosphines.

In the present work a general method is described for the synthesis of esters of alkyl- and arylphosphinic acids by the action of organomagnesium compounds on dialkyl chlorophosphites at a temperature of −60°:

$$(\mathrm{RO})_2\mathrm{PCl} + \mathrm{R'MgX} \rightarrow (\mathrm{RO})_2\mathrm{PR'} + \mathrm{MgXCl}.$$

Carrying out the reactions under low-temperature conditions makes it possible to effect a selective replacement, not involving the alkoxy groups, of the chlorine atoms of dialkyl chlorophosphites by alkyl or aryl radicals.

A solution of the organomagnesium compound (0.11 mole of alkyl or aryl halide, 0.11 gram-atom of magnesium in 50 ml of ether) was added dropwise (15–20 min) to 0.1 mole of dialkyl chlorophosphite in 50 ml of ether at a temperature of the reaction mixture of $-60 \pm 5°$ and with vigorous stirring. After the addition was complete, the ethereal solution was decanted, the precipitate was washed with dry petroleum ether (3 × 50 ml), the solvents were removed, and the residue was distilled in vacuo. All operations were carried out in an atmosphere of dry nitrogen. The yields, constants, and analytical data of the esters obtained are given in Table 1.

As alkyl and aryl halides, bromo derivatives were used; the exceptions were benzyl chloride and methyl iodide. In the latter case, careful separation of magnesium iodide is useful, which

Table 1

No.	Formula	Yield, %	B.p., °C/pressure, mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	C, found	C, calc.	H, found	H, calc.	P, found	P, calc.
1	$CH_3P(OC_4H_9)_2$	69,5	39–40/1 mm	1,4348	0,8902	56,30	55,89	56,10 56,16	56,22	11,05 10,99	11,02	15,81 15,83	16,12
2	$C_2H_5P(OC_3H_7)_2$	64,3	55–56,5/7 mm	1,4318	0,8935	51,70	51,27	54,00 53,87	53,93	10,89 10,84	10,76	17,60 17,65	17,39
3	$C_2H_5P(OC_4H_9)_2$	70,0	47–48/1 mm	1,4370	0,8871	60,92	60,51	58,18 58,08	58,21	11,07 11,07	11,24	15,38 15,24	15,02
4	$C_3H_7P(OC_4H_9)_2$	66,4	59,8–60,3/1 mm	1,4393	0,8851	65,50	65,12	59,70 59,56	59,96	11,37 11,41	11,45	13,86 14,01	14,06
5	$C_4H_9P(OC_4H_9)_2$	68,4	68–69/1 mm	1,4420	0,8839	70,14	69,74	61,46 61,33	61,51	11,51 11,58	11,61	13,51 13,42	13,22
6	$C_6H_5CH_2P(OC_4H_9)_2$	54,5	103–104/1 mm	1,4972	0,9742	80,62	80,00	66,96 66,87	67,15	9,24 9,49	9,39	11,32 11,55	11,54

No.	Formula	Yield, %	B.p., °C/pressure, mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	C, found	C, calc.	H, found	H, calc.	P, found	P, calc.
7	$C_6H_5P(OC_4H_9)_2$	63,0	97,5–98,5/1 mm	1,4993	0,9769	76,54	75,38	66,12	**66,14**	9,16	9,12	12,40	**12,18**
8	$C_6H_5P(OC_3H_7)_2$	61,5	73–74/1 mm	1,5072	1,0000	67,35	66,14	64,03	**63,70**	8,50	8,46	13,61	**13,70**
9	$C_6H_5P(OC_2H_5)_2$	53,7	62,5–63/1 mm	1,5131	1,0252	58,13	56,91	60,85	**60,59**	7,71	7,63	15,28	**15,63**
10	$HC\equiv C-P(OC_4H_9)_2$	81,5	–83/2 mm	1,4827				64,45	**64,43**	9,47	9,77	12,41	**12,78**

Literature data: No. 2 –b.p. 65–66,5°/11 mm, n_D^{20} 1,4278, d_4^{20} 0,9021 (1). No. 3 –b.p. 63–64°/3 mm, n_D^{20} 1,4353, d_4^{20} 0,8977 (1). No. 5 –b.p. 116,5–118°/10 mm, n_D^{20} 1,4410, d_4^{20} 0,8883 (3). No. 8 –b.p. 137°/15 mm, n_D^{25} 1,4939, d_0^{23} 0,9925 (66). No. 9 –b.p. 235°/237 mm, n_D^{20} 1,5120, d_0^{20} 1,0247 (12).

Table 2

No.	Formula	Yield, %	b.p. (m.p.), °C/pressure in mm	n_D^{20}	d_4^{20}	MR found	MR calc.	C found	C calc.	H found	H calc.	P, $^1/_2$ $Cu_2P_2O_7$ found	P, $^1/_2$ $Cu_2P_2O_7$ calc.	S (I) found	S (I) calc.
1	$CH_3PS(OC_4H_9)_2$	87.3	69–70/1 mm	1.4622	0.9872	62.48	62.12	48.20	48.19	9.51	9.44	13.55	13.81	14.43	14.30
2	$C_2H_5PS(OC_4H_9)_2$	85.4	76–77/1 mm	1.4628	0.9786	67.05	66.74	50.41	50.39	9.84	9.73	13.05	13.02	13.56	13.45
3	$C_2H_5PS(OC_3H_7)_2$	86.6	55–56/1 mm	1.4630	1.0007	57.88	57.50	45.47	45.69	9.15	9.11	14.28	14.73	15.05	15.25
4	$C_3H_7PS(OC_4H_9)_2$	87.5	84–85/1 mm	1.4623	0.9702	71.55	71.35	52.20	52.34	10.02	9.98	12.14	12.27	12.59	12.70

No.	Formula	Yield, %	b.p. (m.p.), °C/pressure in mm	n_D^{20}	d_4^{20}	*MR* found	*MR* calc.	C found	C calc.	H found	H calc.	P, $^1/_2$ Cu$_2$ (I) found	P, $^1/_2$ Cu$_2$ (I) calc.	S (I) found	S (I) calc.
5	$C_6H_5P(OC_2H_5)_2 \cdot CuJ$	71	122-123.5(from alcohol)	—	—	—	—	30.81	30.95	3.91	3.89	38.74	38.73	33.08	32.65
6	$C_6H_5P(OC_3H_7)_2 \cdot CuJ$	72.4	129-130.5(from alcohol)	—	—	—	—	34.47	34.58	4.65	4.60	36.37	36.12	30.77	30.46
7	$C_6H_5P(OC_4H_9)_2 \cdot CuJ$	75	88-89(from alcohol)	—	—	—	—	37.77	37.85	5.39	5.21	34.21	34.83	28.90	28.53

Literature data: No. 1 –b.p. 72-74°/1 mm, n_D^{20} 1.4535, d_4^{20} 0.9848 (13). No. 2 –b.p. 79.5-83°/2 mm, n_D^{20} 1.4533, d_4^{20} 0.9775 (13); b.p. 97-98°/2 mm, n_D^{20} 1.4510, d_4^{20} 0.9768 (14). No. 3 –b.p. 69-70°/1.5 mm, n_D^{20} 1.4622, d_4^{20} 1.0005 (1). No. 4 –b.p. 103-104°/2 mm, n_D^{20} 1.4580, d_4^{20} 0.9772 (14).

is achieved by removing the ester from the reaction mixture and subsequently extracting the residue with petroleum ether.

The obtained esters of alkylphosphinous acids are readily oxidized in air and vigorously add sulfur and cuprous iodide. To confirm the structure of the synthesized substances, some esters of alkylthiophosphinous acids and complex compounds of arylphosphinous esters with cuprous iodide were obtained from them by ordinary methods (see Table 2).

For calculating the molecular refractions of phosphinous acid esters, the value of the atomic refraction of phosphorus proposed by A. I. Razumov and O. A. Mukhacheva (^{3}), equal to 7.74, was used. In the case of esters of alkylphosphinous acids, a constant excess of the found molecular refraction over the calculated one was observed, amounting on average to 0.41; for arylphosphinous esters an exaltation of about 1.20 was noted.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
20 VII 1957

CITED LITERATURE

[1] B. A. Arbuzov, N. I. Rizpolozhenskii, *Izv. AN SSSR, OKhN*, 1952, 854.
[2] A. I. Razumov, O. A. Mukhacheva, Sim Do Khen, *Izv. AN SSSR, OKhN*, 1952, 894; A. I. Razumov, O. A. Mukhacheva, *ZhOKh*, 26, 2463 (1956).
[3] A. I. Razumov, O. A. Mukhacheva, *ZhOKh*, 26, 1436 (1956).
[4] T. K. Mai, E. A. Gerasimova, *Tr. Kazansk. khim.-tekhnol. inst.*, 15, 26 (1951).
[5] H. Köhler; A. Michaelis, *Ber.*, 10, 816 (1877).
[6] A. E. Arbuzov, *ZhRFKhO*, 42, 395 (1910); On catalysis phenomena in the transformations of certain phosphorus compounds, Dissertation, Kazan, 1914; *ZhOKh*, 4, 898 (1934).
[6] A. E. Arbuzov, A. I. Razumov, *Izv. AN SSSR, OKhN*, 1945, 167.
[7] G. M. Kosolapoff, *Organophosphorus Compounds*, N. Y., 1950, p. 43.
[8] Th. Weil, B. Prijs, H. Erlenmeyer, *Helv. Chim. Acta*, 35, 1412 (1952); 36, 1314 (1953).
[9] A. Michaelis, *Ber.*, 13, 2174 (1880); F. Guichard, *Ber.*, 32, 1572 (1899).
[10] M. S. Kharasch, E. V. Jensen, S. Weinhouse, *J. Org. Chem.*, 14, 429 (1949).
[11] R. B. Fox, *J. Am. Chem. Soc.*, 72, 4147 (1950).
[12] B. A. Arbuzov, V. S. Vinogradova, *Izv. AN SSSR, OKhN*, 1947, 459.
[13] M. I. Kabachnik, T. A. Mastryukova, N. I. Kurushkin, *Izv. AN SSSR, OKhN*, 1956, 193.
[14] A. N. Pudovik, K. A. Kavyrzina, *ZhOKh*, 24, 307 (1954).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.