Chemistry

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Abstract

Full Text

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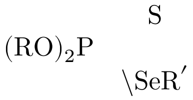
Esters of Selenothiophosphoric Acid

Salts and Neutral Esters of O,O-Diphenylselenothiophosphoric Acid

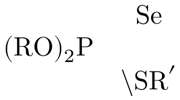
(Presented by Academician M. I. Kabachnik, February 3, 1965)

Salts of acid esters of O,O-diaryl(dialkyl-)selenothiophosphoric acid have not been described in the literature. A method for preparing neutral esters of O,O-diphenylselenothiophosphoric acid with thionic sulfur was recently patented by Lorenz and Schrader (1). By analogy with neutral esters of thiophosphoric acid (2), neutral esters of selenothiophosphoric acid may have structures with thionic (I) and thiol (II) sulfur.



$$(RO)_2P\begin{matrix}S\\ \\ \backslash SeR'\end{matrix}$$

(I)



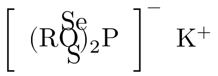
$$(RO)_2P\begin{matrix}Se\\ \\ \backslash SR'\end{matrix}$$

(II)

Neutral esters of selenothiophosphoric acid with thiol sulfur have not been described in the literature.

We have, for the first time, obtained the potassium salt of O,O-diphenylselenothiophosphoric acid. By the method described in the literature (3), we obtained O,O-diphenylchloroselenophosphate. The latter was converted into the potassium salt of O,O-diphenylselenothiophosphoric acid by reaction with potassium hydrosulfide (4).

The structure of the salt may be represented by the formula



$$\left[\ (RO)_2P\begin{matrix}Se\\S\end{matrix}\ \right]^- K^+$$

(5)

The reaction was carried out by adding potassium hydrosulfide to a solution of O,O-diphenylchloroselenophosphate in dry toluene, followed by heating the reaction mixture to the boiling point. The salt, purified by dissolution in dry acetone, was reprecipitated with absolute ether. M.p. 190–191°. Yield 78%.

By alkylation of the potassium salt with alkyl halides, it was possible to obtain neutral esters of O,O-diphenylselenothiophosphoric acid. However, by analogy with salts of thiophosphoric acid (^{6}), the reaction could proceed according to scheme (I) or according to scheme (II).

$$\left[(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{S}\right]^- K^+ + RX \rightarrow (C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SR} + KX \qquad (1)$$

$$\left[(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{S}\right]^- K^+ + RX \rightarrow (C_6H_5O)_2P\genfrac{}{}{0pt}{}{S}{SeR} + KX \qquad (2)$$

In order to establish the direction of the reaction, the neutral esters were synthesized by two methods: a) by reaction of O,O-diphenylchloroselenophosphate with alkyl mercaptides in absolute ether (by this method we obtained, for the first time, neutral esters of selenothiophosphoric acid with thiol sulfur); b) by reaction of the potassium salt of O,O-diphenylselen-

Table 1

Esters of O,O-diphenylselenothiophosphoric acid

Structural formula	B.p., °C (mm Hg)	M.p., °C	n_D^{20}	d_4^{20}	Yield, %	MR found	MR calculated	P, % found	P, % calculated	Se, % found	Se, % calculated
$\left[(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{S}\right]^- K^+$	–	190–191	–	–	83	–	–	8.20 8.36	8.43	20.91 20.50	21.50
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SC_2H_5}$	74–75(0.002)		1.6081	1.2916	32	95.62	95.69	8.34 8.42	8.67	21.38 21.49	22.11
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SC_3H_7}$	82–83(0.002)		1.5678	1.2077	37	100.44	100.31	8.04 7.96	8.24	20.42 20.71	21.28
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SC_3H_7\text{-iso}}$	81–82(0.002)		1.5602	1.1999	42	100.04	100.31	8.14 8.22	8.24	20.53 20.83	21.28
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SC_4H_9}$	100–101(0.02)		1.5790	1.2218	36	104.76	104.93	7.90 7.88	8.04	19.72 19.90	20.50
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SC_5H_{11}}$	105–107(0.004)		1.5580	1.1730	29	109.70	109.55	7.48 7.56	7.75	19.22 19.07	19.78
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SC_5H_{11}\text{-iso}}$	83–84(0.007)		1.5416	1.1404	32	110.09	109.55	7.51 7.63	7.75	19.09 19.14	19.78
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{SC_6H_5}$	140–141(0.04)		1.5961	1.2450	88	110.71	110.56	7.36 7.56	7.64	18.92 18.80	19.48
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{Se}{S-C_6H_4CH_3}$		50–51	–	–	92	–	–	7.38 6.97	7.39	17.94 18.20	18.82

Note. AR_D for the P=Se bond was taken as 13.47 (9).

thiophosphoric acid with alkyl bromides in absolute alcohol.

The physical constants of the neutral esters obtained by method (a) are given in Table 1; those obtained by method (b), in Table 2.

Table 2

Aliphatic esters of O,O-diphenylthioselenophosphoric acid

Structural formula	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	Yield, %	P, % found	P, % calculated	Se, % found	Se, % calculated
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{S}{SeC_2H_5}$	62–64(0.001)	1.5942	1.2221	21	8.398.57	8.67	21.61	22.11
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{S}{SeC_3H_7}$	76–77(0.001)	1.6018	1.1536	31	8.188.13	8.24	20.76	21.28
$(C_6H_5O)_2P\genfrac{}{}{0pt}{}{S}{SeC_5H_{11}\text{-iso}}$	77–79(0.006)	1.5415	1.1407	27	7.527.61	7.75	18.82	19.78

For the compounds obtained, spectra were recorded in the infrared region. The IR absorption spectra were studied on an IKS-11 instrument with a KBr prism in the range 400–800 cm^{-1} and were recorded point by point according to a previously proposed procedure (7). The thickness of the liquid layer under study was determined by the platinum spacer of a demountable cell and was 0.1 mm.

The difference in physical constants and the study of the IR absorption spectra show that the neutral esters obtained by the reaction of the acid chloride of O,O-diphenylselenothiophosphoric acid with alkyl mercaptides have the thiol structure. The neutral esters obtained by the reaction of the potassium salt of O,O-dialkylselenothiophosphoric acid have the thion-

structure. The spectra of some of the compounds synthesized by the two methods are presented in Figs. 1 and 2.

For the compounds obtained by method (a), there is an absorption maximum in the region of 590 cm^{-1}, which is due to $P = Se$ vibrations [8] (Figs. 1a and 2a).

Fig. 1. IR spectra of compounds:

a–$(C_6H_5O)_2P\left(\genfrac{}{}{0pt}{}{Se}{SC_3H_7}\right)$

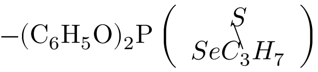
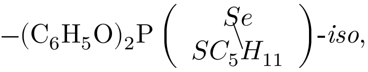
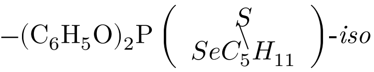
b–
$(C_6H_5O)_2P\left(\begin{matrix}S\\ SeC_3H_7\end{matrix}\right)$

Fig. 2. IR spectra of compounds:

a–
$(C_6H_5O)_2P\left(\begin{matrix}Se\\ SC_5H_{11}\end{matrix}\right)$-*iso*,

b–
$(C_6H_5O)_2P\left(\begin{matrix}S\\ SeC_5H_{11}\end{matrix}\right)$-*iso*

For the same substances obtained by method (b), this maximum is absent, but a maximum appears in the region of 670 cm^{-1}, characteristic of the frequency of the $P = S$ bond [9] (Figs. 1b and 2b).

The results obtained give grounds to consider that the potassium salts of O,O-diphenylseleniophosphoric acid are alkylated by ethyl, propyl, and amyl bromides at sulfur, and not at selenium (equation (2)).

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