

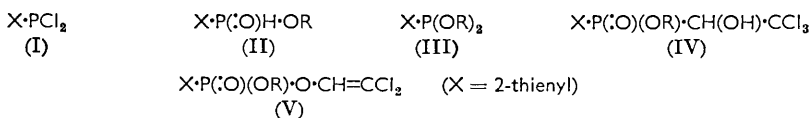
916. Organophosphorus Compounds. Part IV.* Preparation and Reactions of 2-Thienylphosphonous Dichloride.

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In the framework of a systematic study it became interesting to prepare phosphorus derivatives of thiophen as intermediates for the synthesis of potential insecticides; 2-thienylphosphonous dichloride (I) appeared to be a suitable starting point. The classical method of thermal condensation between thiophen and phosphorus trichloride in the gaseous phase gives yields only of the order of 5%, and in the aluminium chloride-catalysed reaction between these two compounds so much polymer is formed that again the yield remains of the same order,¹ although in other cases it is the method of choice, as has recently² been shown for tetralin. For this reason, 2-thienyltrichlorosilane was unsuitable as starting material³ as its reaction with phosphorus halides would again require the presence of aluminium chloride as catalyst.

As Friedel-Crafts reactions of thiophen can be catalysed by stannic chloride⁴ the reaction of thiophen with phosphorus trichloride was studied in the presence of this catalyst. We thus obtained (I) in 40–50% yield, together with small quantities of a crystalline complex with stannic chloride that dissociated into its constituents upon heating. Such complexes are not unknown; a complex of $\text{SnCl}_4 + 2\text{POCl}_3$ has been described only recently.⁵ In the reaction, an excess of phosphorus trichloride was employed as solvent, as the solvents usual in Friedel-Crafts reactions inhibited the desired condensation. It is likely, but not proved, that the 2-position of the thiophen ring is attacked.

In the usual manner,⁶ the reaction of 2-thienylphosphonous dichloride (I) with alcohols gave alkyl 2-thienylphosphinates (II) (Table I), and when the reaction was carried out in the presence of tertiary amines, dialkyl 2-thienylphosphonites (III) (Table 2). The compounds (II) reacted smoothly with chloral to give alkyl *P*-2-thienyl-*P*-(2,2,2-trichloro-1-hydroxyethyl)phosphinates (IV) (Table 3); these compounds, as expected, were unstable in the presence of alkali and were slowly converted into the corresponding alkyl 2,2-dichlorovinyl 2-thienylphosphonates (V). The latter are obtained in excellent yields when the esters (III) are heated with chloral (Table 4), an "abnormal Arbusov rearrangement" taking place.



Infrared Spectra.—2-Thienylphosphonous dichloride (I) shows a distinct band of moderate intensity at 1480 cm^{-1} , due to the thienyl-P bond; it is comparable to the absorption at $1435\text{--}1450\text{ cm}^{-1}$ of the corresponding phenylphosphonous dichloride.

The structure of compounds (II) follows unambiguously from the spectra. Whilst the stretching frequencies ($2560\text{--}2700\text{ cm}^{-1}$) of the P-OH system are absent, the following

* Part III, *J.*, 1961, 856.

¹ Sachs, *Ber.*, 1892, **25**, 1514.

² Houalla, Miguel, and Wolf, *Bull. Soc. chim. France*, 1963, 1152.

³ Yakubovich and Motsarev, *Doklady Akad. Nauk S.S.S.R.*, 1953, **88**, 87; *J. Gen. Chem. (U.S.S.R.)*, 1953, **23**, 805, 1623.

⁴ Johnson and May, *Org. Synth.*, 1943, Coll. Vol. II, 8.

⁵ Braenden, *Acta Chem. Scand.*, 1963, **17**, 759.

⁶ (a) Arbusov and Rizpolozhensky, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 1952, 843; (b) Anand and Todd, *J.*, 1951, 1867; (c) Kosolapoff, *J. Amer. Chem. Soc.*, 1950, **72**, 4292; (d) Pudovik and Yarmukhametova, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 1952, 803; (e) Pudovik, *Doklady Akad. Nauk S.S.S.R.*, 1952, **85**, 349.

TABLE 1.
Alkyl 2-thienylphosphinates (II).

R	Yield (%)	B. p./mm.	n_D (°C)	d (°C)	Formula	M_R		Calc. (%)			Found (%)				
						Calc.	Found	C	H	P	S	C	H	P	S
Me	60	100—101.5 ^a /0.2	1.5535 (14)		C ₅ H ₉ O ₃ PS	40.90	40.50	37.0	4.3	19.1	19.8	37.5	4.1	18.7	19.9
Et	74	113/0.6	1.5369 (14)	1.3377 (27)	C ₆ H ₉ O ₃ PS	45.56	44.80	40.9	5.1	17.6	18.2	40.6	5.1	17.6	18.2 ^a
Pr ⁿ	83	106/0.2	1.5308 (14)	1.3137 (27)	C ₇ H ₁₁ O ₃ PS	45.56	44.50	44.2	5.8	16.3	16.9	44.2	5.8	16.3	16.9
Pr ⁱ	85	100/0.25	1.5271 (14)	1.3184 (28)	C ₈ H ₁₃ O ₃ PS	50.30	49.30	44.2	5.8	16.3	16.9	43.9	6.1	16.6	17.1
Bu ⁿ	80	112/0.15	1.5242 (14)	1.2670 (26)	C ₈ H ₁₃ O ₃ PS	50.30	49.30	47.1	6.3	15.2	15.7	47.3	6.8	15.0	15.7

^a Found: OEt, 25.2. Calc., 25.6%.

TABLE 2.
Dialkyl 2-thienylphosphonites (III).

R	Yield (%)	B. p./mm.	n_D (°C)	d (°C)	Formula	Calc. (%)		Calc. (%)			Found (%)				
						Calc.	Found	C	H	P	S	C	H	P	S
Me	80	57 ^a /0.9	1.5444 (20)	1.1859 (25)	C ₆ H ₉ O ₃ PS	49.4	44.3			17.6	18.2			17.4	18.0
Et	54	81—83 ^b	1.5208 (25)	1.1033 (25)	C ₆ H ₉ O ₃ PS	56.0	56.4			15.2	15.5			15.6	15.9
Pr ⁿ	90	80—82/0.3	1.5092 (24)	1.0698 (25)	C ₁₀ H ₁₇ O ₃ PS	62.9	64.0	51.7	7.3	13.4	13.8	51.5	7.1	13.7	14.0
Pr ⁱ	92	70/0.5	1.5030 (25)	1.0559 (25)	C ₁₀ H ₁₇ O ₃ PS	62.9	63.8	51.7	7.3	13.4	13.8	51.6	7.2	13.6	13.7
Bu ⁿ	88	96—97/0.4	1.5042 (25)	1.0355 (25)	C ₁₂ H ₂₁ O ₃ PS	72.1	72.7	55.4	8.1	12.1	12.3	54.8	7.9	12.1	12.4

TABLE 3.

Alkyl *P*-2-thienyl-*P*-(2,2,2-trichloro-1-hydroxyethyl)phosphinates (IV).

R	Yield (%)	M. p.	Formula	Calc. (%)		Found (%)							
				C	H	Cl	P	S	C	H	Cl	P	S
Me	93	139—140°	C ₇ H ₈ Cl ₃ O ₃ PS	27.2	2.6	34.4	10.0	10.3	27.1	2.7	34.8	10.1	10.6
Et	70	104.5	C ₈ H ₁₀ Cl ₃ O ₃ PS	29.7	3.1	32.9	9.6	9.9	29.6	3.1	32.5	9.9	10.3
Pr ⁿ	87	96.7	C ₉ H ₁₂ Cl ₃ O ₃ PS	32.0	3.6	31.7	9.1	9.5	32.0	3.5	31.6	9.2	10.1
Pr ⁱ	84	139.5	C ₉ H ₁₂ Cl ₃ O ₃ PS	32.0	3.6	31.7	9.1	9.5	32.0	3.5	31.6	9.1	9.5
Bu ⁿ	60	69.7	C ₁₀ H ₁₄ Cl ₃ O ₃ PS	34.1	4.0	30.5	8.8	9.3	33.9	4.0	30.2	8.8	9.1

TABLE 4.

Alkyl 2,2-dichlorovinyl 2-thienylphosphonates (V).

R	Yield (%)	B. p./mm.	n_D (°C)	d (°C)	Formula	M_R		Calc. (%)			Found (%)					
						Calc.	Found	C	H	Cl	P	S	C	H	Cl	P
Me	88	126—127 ^a /0.6	1.5406 (24)	1.4176 (25)	C ₇ H ₇ Cl ₂ O ₃ PS	61.35	61.00	30.8	2.6	26.0	11.4	11.7	31.0	2.9	25.8	12.5
Et	87	118—119/0.4	1.5322 (23)	1.3606 (25)	C ₈ H ₉ Cl ₂ O ₃ PS	66.00	65.60	33.5	3.1	24.7	10.8	11.2	33.8	3.4	24.7	11.2
Pr ⁿ	86	135/0.5	1.5248 (24)	1.3220 (25)	C ₉ H ₁₁ Cl ₂ O ₃ PS	70.65	69.60	35.9	3.7	23.6	10.3	10.9	36.7	4.8	23.2	10.5
Pr ⁱ	83	122/0.35	1.5198 (23)	1.2939 (25)	C ₉ H ₁₁ Cl ₂ O ₃ PS	70.65	70.12	35.9	3.7	23.6	10.3	10.9	36.3	4.1	20.4	10.2
Bu ⁿ	92	144/0.37	1.5198 (24)	1.2790 (24)	C ₁₀ H ₁₃ Cl ₂ O ₃ PS	75.30	75.60	38.1	4.1	22.5	9.8	10.2	39.8	4.8	22.1	10.1

absorptions have been identified: 2380—2420 (P-H),^{7,8} 1470 (thienyl-P), 1230—1250 (P=O), and 1030 (P-O-C).⁹ Also compounds (III) show the absorptions at 1470 and 1030 cm^{-1} .

In the spectra of compounds (IV) we again find absorptions at 1030, 1190 (P=O), and 1470 cm^{-1} and also a broad band at 3140 cm^{-1} representing the hydroxyl group, superimposed on the C-H absorption, whilst compounds (V) exhibit, in addition to the peaks at 980—1030 (P-O-C) and 1275 (P=O) cm^{-1} , absorption due to the C=C double bond at 1650 cm^{-1} .

EXPERIMENTAL

2-Thienylphosphonous Dichloride (I).—Freshly distilled thiophen (1 mole), anhydrous stannic chloride (1 mole), and freshly distilled phosphorus trichloride (6 mole) were refluxed for 40 hr. under anhydrous conditions. The excess of the inorganic chlorides was removed at 20 mm. pressure and the product distilled. The stannic chloride complex of (I) distilled at 48—55°/18 mm. and crystallized. As a second fraction, b. p. 108°/18 mm., *2-thienylphosphonous dichloride* (I) (75—93 g.; 40—50%), n_D^{20} 1.6281 (Found: C, 25.9; H, 1.8; Cl, 38.6. $\text{C}_4\text{H}_3\text{Cl}_2\text{PS}$ requires C, 25.9; H, 1.6; Cl, 38.4%) was obtained.

Ethyl 2-Thienylphosphinate (II; R = Et).—In an atmosphere of carbon dioxide, the dichloride (I) (20 g.) was added, dropwise and with stirring, to ice-cooled ethanol (200 g.). At the end of the addition, the apparatus was evacuated (20 mm.) for 4 hr. and the solution neutralized to pH 7 with sodium hydrogen carbonate. The precipitate was filtered off and washed with small portions of ethanol. The combined filtrates and washings were concentrated under reduced pressure and distilled, after dilution with some dry ether and renewed filtration. The *ethyl ester* (14 g., 74%), had b. p. 113°/0.6 mm.

Methyl P-2-Thienyl-P-(2,2,2-trichloro-1-hydroxyethyl)phosphinate (IV; R = Me).—At room temperature, anhydrous chloral (3.5 g.) in carbon tetrachloride (25 ml.) was added dropwise to methyl 2-thienylphosphinate (II; R = Me) (4 g.) in carbon tetrachloride (75 ml.), and the solution refluxed for 1 hr., cooled, and neutralized to pH 7 with aqueous sodium hydrogen carbonate. The organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure. The methyl ester (7 g., 93%) was purified by crystallization from ether—light petroleum (b. p. 40—60°); it had m. p. 139—140°.

Dialkyl 2-Thienylphosphonites (III).—A solution of the dichloride (I) (1 mole) in dry ether (100 ml.) was added, dropwise and with stirring, at 0° to a solution of the alcohol (2 moles) and dimethylaniline (2 moles) in dry ether (300 ml.). At the end of the addition, stirring was continued (300 ml.). At the end of the addition, stirring was continued for 10 min. at room temperature, and the precipitate washed with small portions of dry ether. The combined filtrates and washings were concentrated under reduced pressure without heating. The residues, obtained in high yields, were oils that distilled almost completely (see Table 2).

Alkyl 2,2-Dichlorovinyl 2-Thienylphosphonates (V).—At 0°, a dialkyl 2-thienylphosphinate (III) (1 mole) in dry ether (100 ml.) was added, dropwise and with stirring, to anhydrous chloral (1 mole) in dry ether (100 ml.). Stirring was continued for 0.5 hr. at room temperature; the ether was then removed *in vacuo* without heating and the residual oil distilled, leaving a small resinous residue (see Table 4).

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