

Phosphinodithioformates

II. *S*-Alkyl *P,P*-Disubstituted Thiophosphinoyldithioformates

OTTO DAHL and OLE LARSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

In part I of this series¹ the preparation of phosphinodithioformates, R_2PCSS^- ($R=C_6H_5$), and phosphoniobisdithioformates, $R_2P(CSS)_2^-$ ($R=C_6H_5$), was described. Because the preparation of esters, R_2PCSSR^2 , from these compounds offered some difficulties, the esters of thiophos-

phinoyldithioformates, $R^1P(S)CSSR^2$, were investigated as potential precursors of derivatives of phosphinodithioformates.

Thiophosphinoyldithioformates, $R_2P(S)CSS^-$, react with alkyl halides to give esters of the general type, $R^1P(S)CSSR^2$ (Table 1). The potassium salts, $R_2P(S)CSSK$ (Ia: $R=C_2H_5$; Ib: $R=C_6H_5$), were found to be more convenient for preparation of the esters, than the previously described tetraphenylphosphonium salts.¹

The infrared (IR) spectra (Table 1) of the potassium salts (I) showed a strong band at *ca.* 1050 cm^{-1} , which was assigned to the CSS^- antisymmetric stretching vibration ($\nu(CSS^-)$) by analogy with the spectra of the corresponding tetraphenylphosphonium salts.¹ In the spectra of the esters (II–III) this band had disappeared and a new strong band was found in the

Table 1. Yields, melting points, and characteristic IR absorption bands (cm^{-1}) for potassium and *S*-alkyl *P,P*-disubstituted thiophosphinoyldithioformates.

No.	Compound	Yield, %	M.p., °C	$\nu(CSS^-)$ or $\nu(CSSR)^b$	$\nu(P=S)^b$	Solvent
Ia	$(C_2H_5)_2P(S)CSSK$	40 (95) ^a	209–210	1049 s ^c	582 s	KBr
Ib	$(C_6H_5)_2P(S)CSSK$	90 ^a	108–109 (decomp.)	1038 vs	646 s 640 s	KBr
IIa	$(C_2H_5)_2P(S)CSSCH_3$	70	29.5–30	1081 s 1078 s	586 m 590 m	CHCl ₃ CS ₂
IIb	$(C_2H_5)_2P(S)CSSC_2H_5$	90 ^a	oil	1087 vs 1083 vs	586 s 588 m	CHCl ₃ CS ₂
IIc	$(C_2H_5)_2P(S)CSSCH_2C_6H_5$	70	50–51	1081 s 1078 s	587 m 591 m	CHCl ₃ CS ₂
IIIa	$(C_6H_5)_2P(S)CSSCH_3$	70	72–74	1079 m 1077 m	648 s 653 s	CHCl ₃ CS ₂
IIIb	$(C_6H_5)_2P(S)CSSC_2H_5$	80 ^a	oil	1085 s 1082 s	649 s 653 s	CHCl ₃ CS ₂
IIIc	$(C_6H_5)_2P(S)CSSCH_2C_6H_5$	30	82–84	1080 s 1077 s	648 s 652 s	CHCl ₃ CS ₂

^a Yield of crude product. ^b For the abbreviations, see text. ^c vs=very strong, s=strong and m=medium.

Table 2. Elemental analyses.

Formula	Analyses (C, H and S)
Ia C ₅ H ₁₀ KPS ₂	Found: 25.32; 4.30; 40.43 Calc.: 25.40; 4.26; 40.69
Ib C ₁₃ H ₁₀ KPS ₂	Found: 44.50; 3.29; 27.06 Calc.: 46.96; 3.03; 28.93
IIa C ₆ H ₁₃ PS ₂	Found: 33.82; 6.25; 45.57 Calc.: 33.94; 6.17; 45.30
IIb C ₇ H ₁₅ PS ₂	Found: 37.10; 6.61; 41.70 Calc.: 37.14; 6.68; 42.50
IIc C ₁₃ H ₁₇ PS ₂	Found: 49.99; 5.94; 32.81 Calc.: 49.96; 5.94; 33.35
IIIa C ₁₄ H ₁₃ PS ₂	Found: 54.50; 4.32; 31.18 Calc.: 54.52; 4.25; 31.20
IIIb C ₁₅ H ₁₅ PS ₂	Found: 56.01; 4.89; 29.55 Calc.: 55.86; 4.69; 29.82
IIIc C ₂₀ H ₁₇ PS ₂	Found: 62.75; 4.63; 24.70 Calc.: 62.47; 4.46; 25.02

region 1077–1088 cm⁻¹, which was accordingly assigned to the CSSR grouping ($\nu(\text{CSSR})$). The positions of the bands are close to those found for the analogous bands exhibited by other tetracoordinated phosphorus compounds of the type R₃P⁺—CSS⁻ and R₃P⁺—CSSR², respectively.^{2,3} A strong band in the region 582–591 cm⁻¹ in the spectra of Ia and II was absent in the spectra of the corresponding *P*-selenides and was consequently assigned to the P=S stretching vibration ($\nu(\text{P}=\text{S})$). The analogous band in the spectra of Ib and III was found at 640–653 cm⁻¹.

The proton magnetic resonance (NMR) spectra of the thiophosphinoyldithioformates are given in Table 3. The spectra (60 MHz) of all the esters showed splitting of the *S*-alkyl signals with a spacing of 0.6–1.5 Hz. This splitting is due to a long-range coupling to phosphorus because the same spacing was found in the 60 and

in the 100 MHz spectra. In the spectra of IIb the CH₃ signals of the *S*-ethyl group partly overlapped one of the triplets exhibited by the CH₃ groups in the *P*-ethyl groups. The assignments of these signals were based on spin decoupling experiments.

The esters react with ammonia and primary and secondary aliphatic amines to give thiophosphinoylthioformamides, and with alkylsubstituted hydrazines containing an NH group to give thiophosphinoylthioformhydrazides. The investigation of these derivatives will be described in forthcoming papers.

Experimental. Conditions and equipment used for physical measurements were those described in part I of this series.¹ Yields, melting points, and analyses are given in Tables 1 and 2.

Potassium diethylthiophosphinoyldithioformate (Ia). Potassium diethylphosphoniobis-dithioformate¹ (2.8 g, 10⁻² mol) was dissolved in a 3:1 acetone-carbon disulfide mixture (20 ml) and a solution of sulfur (0.35 g, 1.1 × 10⁻² mol) in carbon disulfide (5 ml) was added. The solution was stirred for 1 h, evaporated to dryness and the residue extracted with carbon disulfide. The brown-red product (2.2 g) was sufficiently pure for preparation of the esters. For analysis the compound was dissolved in dry acetone and precipitated with methylene chloride. Ia is very soluble in water, ethanol, and acetone, slightly soluble in chloroform and insoluble in carbon disulfide and ether.

Potassium diphenylthiophosphinoyldithioformate (Ib). A solution of sulfur (0.35 g, 1.1 × 10⁻² mol) in carbon disulfide (25 ml) was added to a stirred suspension of potassium diphenylphosphinodithioformate¹ (3.0 g, 10⁻² mol) in methylene chloride (25 ml). The mixture turned deep brown almost at once. Stirring was continued for ½ h, after which the brown-red crystals were filtered off, washed with a 1:1 methylene chloride-carbon disulfide mixture, and dried *in vacuo*. The crude product (3.1 g) was sufficiently pure for preparative use. The solubility of Ib is similar to that of Ia.

S-Alkyl P,P-disubstituted thiophosphinoyldithioformates (II–III). The compounds were prepared by the following general procedure: The appropriate alkyl halide (CH₃I, C₂H₅I, or C₆H₅CH₂Cl, 2–3 × 10⁻² mol) was added to a solution of the potassium salt (I) (2 × 10⁻² mol) in dry acetone (10 ml). The reaction mixture was stirred for 1–3 h, filtered, and evaporated

Table 3. NMR chemical shifts^a (τ , ppm) and coupling constants (J , Hz) of potassium and *S*-alkyl *P,P*-disubstituted thiophosphinoyldithioformates.

No.	CH_3CH_2P	$CH_3CH_2P^c$	CH_3S/RCH_2S	CH_2CH_2S	$J_{HCCH(P)}$	J_{PCCH}	J_{PCSCH}	J_{PCSCCH}	$J_{HCCH(S)}$
Ia	A	8.89 (2×3) ^b	ca. 7.8		ca. 7.4	ca. 17.5			
	B	8.96 (2×3)	ca. 7.9		ca. 7.4	ca. 17.5			
IIa	C	8.83 (2×3)	ca. 7.8	7.29 (2×1)	ca. 7.4	ca. 20.5	0.9		
	D	8.92 (2×3)	ca. 7.9	7.32 (2×1)	ca. 7.4	ca. 20	1.0		
IIb	C	8.83 (2×3)	ca. 7.8	6.72 (2×4)	8.62 (2×3)	ca. 7.3	ca. 20	0.9	1.2
	D	8.92 (2×3)	ca. 7.9	6.78 (2×4)	8.64 (2×3)	ca. 7.3	ca. 19.5	0.9	1.1
IIc ^d	C	8.83 (2×3)	ca. 7.8	5.55 (2×1)	ca. 7.4	ca. 20	1.4		
	D	8.91 (2×3)	ca. 7.9	5.63 (2×1)	ca. 7.4	ca. 20	1.3		
IIIa ^d	C			7.32 (2×1)			0.8		
	D			7.39 (2×1)			0.6		
IIIb ^d	C			6.76 (2×4)	8.67 (2×3)		0.8	1.4	7.5
	D			6.82 (2×4)	8.68 (2×3)		0.9	1.3	7.4
IIIc ^d	C			5.59 (2×1)			1.3		
	D			5.68 (2×1)			1.5		

^a The values given in the table are the centres of the multiplets. ^b Multiplicity of signal. ^c Because the spectra showed second order patterns, first order treatment was not possible for the $CH_2(P)$ signals. ^d The chemical shifts for the aromatic protons have been omitted. The integral showed the correct ratio between aromatic and aliphatic protons.

Solvents: A = $(CD_3)_2CO$; B = $(CD_3)_2SO$; C = $CDCl_3$; D = CS_2 .

to dryness *in vacuo*. The residue was extracted with dry ether, and the resulting solution filtered and evaporated to dryness *in vacuo*. Recrystallization from 90 % aqueous methanol generally afforded the pure products. In the case of IIIe it was most convenient to purify the crude product by preparative layer chromatography on silica gel (PF₂₅₄, Merck) using a 1:1 petroleum ether-benzene mixture as the eluent. The esters are very soluble in most organic solvents and insoluble in water.

- Dahl, O., Gelting, N. C. and Larsen, O. *Acta Chem. Scand.* **23** (1969) 3369.
- Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **17** (1963) 547.
- Jensen, K. A., Dahl, O. and Henriksen, L. E. *Acta Chem. Scand.* **24** (1970). *In press*.

Received November 24, 1969.

Metabolism of Acid Glycosaminoglycans in Granulation Tissue

K. IVASKA, E. HEIKKINEN, A. LEHTONEN and E. KULONEN

Department of Medical Chemistry, University of Turku, Turku 3, Finland

The age-dependent variation of the content of glycosaminoglycans in connective tissues has long been known, and differences have also been reported to exist¹⁻³ in the metabolism of the glycosaminoglycans in growing and mature animals. For investigations of this kind, implantation of viscose sponges^{4,11} can be used to produce connective tissue at different stages of development. The nature and contents of glycosaminoglycans in experimental granulomas⁵ of varying