A Convenient Preparation of Bis(phosphorothioyl) Sulfides

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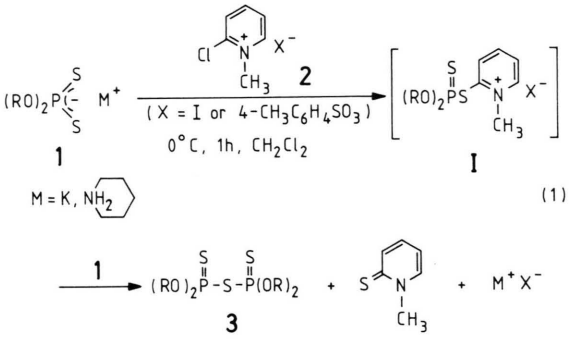
Z. Naturforsch. **44b**, 153–157 (1989); received September 23, 1988

Bis(phosphorothioyl) Sulfides, Piperidinium Phosphorodithioates, Bis(phosphorothioyl) Oxides

The reaction of piperidinium and potassium phosphorodithioates with 2-chloro-1-methylpyridinium salts afforded the corresponding bis(phosphorothioyl) sulfides in good yields. The similar reaction with potassium diphenylphosphorothioate gave exclusively bis(diphenylphosphorothioyl) oxide.

Introduction

In general, bis(phosphorothioyl) sulfides (**3**) which are effective as fungicides [1, 2], cannot be obtained from O,O′-dialkyl or diarylphosphorodithioic acid salts with phosphorochloridothioate [3]. Therefore, several methods have been proposed for the preparation of **3** [4–9], and the following two methods have been employed mainly: a) Reaction of phosphorodithioic acid with aminosulfenyl chloride [5]. b) Desulfurization of bis(phosphorothioyl) disulfides by phosphine [6] or phosphites [8]. These methods, however, have some disadvantages such as limited availability of the starting aminosulfenyl chlorides or the difficult purification of the product **3.** Recently, we have found that piperidinium dithiocarboxylates readily react with 2-chloro-1-methylpyridinium salts to give the corresponding bis(thioacyl) sulfides in good yields [10]. This result stimulated us to develop an alternative, convenient preparation of the title compounds **3** from the reaction of piperidinium phosphorodithioates (**1**) with 2-chloro-1-methylpiperidinium salts (**2**).



No.	R	No.	
3a	C_2H_5	3f	C_6H_5
3b	n-C_3H_7	3g	4-$CH_3C_6H_4$
3c	i-C_3H_7	3h	4-$CH_3OC_6H_4$
3d	n-C_4H_9	3i	4-ClC_6H_4
3e	cyclo-C_6H_{11}		

Results and Discussion

When 2-chloro-1-methylpyridinium *p*-toluenesulfonate was added to a solution of piperidinium O,O′-diphenylphosphorodithioate (**1f**) in dichloromethane, the reaction mixture gradually changed from colorless to yellow. After stirring for 1 h, usual workup of the mixture and then chromatographic separation gave bis(O,O′-diphenylphosphinothioyl) sulfide (**3f**) in 66% yield as colorless crystals. The reactions with other aliphatic and aromatic phosphorodithioates (**1a–e, g–i**) under the same conditions yielded 60–80% of the corresponding bis(phosphorothioyl) sulfides (**3a–e, g–i**). Similar reactions with O,O′-diphenylphosphinodithioic acid potassium salts instead of the piperidinium salts (**1f**) or with the iodides (**2,** X=I) instead of the *p*-toluenesulfonate provided analogous yields of **3,** while the use of the silver and zinc salts led to 5 and 10%, respectively, because of their low solubility and/or reduced reactivity.

It is noted that the reaction of piperidinium diphenylphosphinothioate (**7**) with **2** afforded 40% of bis(diphenylphosphinothioyl) oxide (**8**) (eq. (2)).

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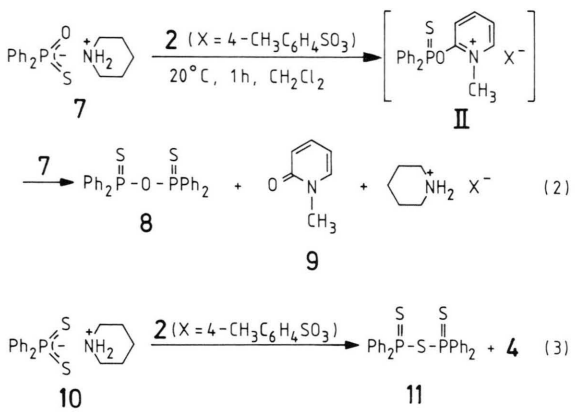
0932–0776/89/0200–0153/$ 01.00/0



No formation of the possible diphenylphosphinothioyl sulfide (**10**) or bis(diphenylphosphinyl) sulfide (**11**) was detected. The reaction would proceed *via* the intermediate **II,** wich is attacked by the oxygen atom of diphenylphosphinothioate anion (**7**).

The structures of the products **3** and **8** were established by spectral data and microanalysis and/or by comparison with authentic samples.

Experimental

Melting points were determined using a Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were measured on a JASCO grating IR spectrometer IR-G. The ^{1}H and ^{31}P NMR spectra were recorded on Hitachi R-20 (90 MHz) and JEOL-JNM-GX270 (270 MHz) with tetramethylsilane as internal standard. Mass spectra were taken by Hitachi RMN-6M mass spectrometer at an ionizing voltage of 20 eV. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

Materials

Piperidinium O,O′-diaralkylphosphorodithioates (**1**) except for the O,O′-diethyl derivative (**1a**) [12] were prepared by slight modification of the method described in literature [13]. Their yields and physical properties are summarized in Table II. Potassium [14], silver [15] and zinc O,O′-diphenylphosphorodithioates [16], and potassium diphenylphosphinothioate [17] and diphenylphosphinodithioate [18] were prepared by the reaction of the corresponding phosphorothioic and -dithioic acids with

Table I. Yields and physical properties of bis(phosphorothioyl) sulfides (**3**).

No.	$(RO)_2P(S)-S-P(S)(OR)_2$ R	Yield [%]	m.p. [°C]	IR (KBr) νP=S [cm^{-1}]	Mass[a] *m/z*	^{31}P NMR[b] [δ]	^{1}H NMR ($CDCl_3$) [δ]
3a	C_2H_5	77	70–72	650	338	+78.4	1.35 (t, 3H, CH_3), 4.00 (qd, J_{POCH} = 10 Hz, 2H, CH_2)
3b	C_3H_7	65	oil	675[c]	394	+77.2	0.96 (t, 3H, CH_3), 1.7 (m, 2H, CH_2), 3.98 (td, J_{POCH} = 9 Hz, 2H, CH_2O)
3c	*i*-C_3H_7	61	oil	635[c]	394	+76.0	1.40 (d, 6H, CH_3), 4.83 (m, J_{POCH} = 10 Hz, 1H, CHO)
3d	C_4H_9	63	oil	645[c]	450	+77.2	0.91 (t, 3H, CH_3), 1.2–1.8 (m, 4H, CH_2), 4.10 (br, 2H, CH_2O)
3e	*cyclo*-C_6H_{11}	86	oil	660[c]	554	+76.3	1.5 and 1.8 (br, 10H, CH_2), 4.6 (m, 1H, CHO)
3f	C_6H_5	66 60[d] 5[e] 10[f]	131–133	645	530	+70.3	7.1–7.4 (m, Ar)
3g	3-$CH_3C_6H_4$	54	oil	645[c]	586	+70.4	2.28 (s, 3H, CH_3), 6.70–7.40 (m, 4H, Ar)
3h	4-$CH_3C_6H_4$	59	91–93	645	586	+71.4	2.28 (s, 3H, CH_3), 7.12 (bs, 4H, Ar)
3i	2-$CH_3OC_6H_4$	30	oil	640[c]	650	+71.8	3.71 (s, 3H, CH_3O), 6.7–7.0 (m, 4H, Ar)
3j	4-$CH_3OC_6H_4$	75	146–148	640	650	+72.9	3.78 (s, 3H, CH_3), 6.80 (d, 2H, Ar), 7.18 (d, 2H, Ar)
3k	4-ClC_6H_4	57	74–76	642	666	+70.1	6.75 (d, 2H, Ar), 7.13 (d, 2H, Ar)

[a] 20 eV, 110 °C; [b] reference 85% H_3PO_4 (slovent: CH_2Cl_2); [c] neat; [d] using potassium O,O′-diphenylphosphinodithioate; [e] using zinc bis(O,O′-diphenylphosphinodithioate); [f] using silver O,O′-diphenylphosphinodithioate.

potassium bicarbonate, silver nitrate, or with zinc diacetate. 2-Chloro-1-methylpyridinium iodide and *p*-toluenesulfonate were commerical grade and used without further purification.

The preparations of bis(O,O'-diethylphosphorothioyl) (**3a**) and bis(O,O'-di-*p*-tolyl(phosphorothioyl)) sulfides (**3h**) are described in detail as typical procedure for the preparation of bis(phosphorothioyl) sulfides **3.** The physical properties of **3** are summarized in Table I.

Bis(O,O'-diethylphosphorothioyl) sulfide (**3a**)

2-Chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) was added to a solution of piperidinium O,O'-diethylphosphorodithioate (**1a**) (271 mg, 1 mmol) in dichloromethane (10 ml), and the reaction mixture was stirred at 30 °C for 1 h. After removal of the solvent by rotary evaporator, thin layer chromatography (TCL) of the residue [dichloromethane/hexane (1:5), R_f = 0.60], gave 130 mg (77%) of **3a** as colorless crystals; m.p. 70–72 °C.

Bis(O,O'-di-propylphosphorothioyl) sulfide (**3b**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-propylphosphorodithioate (**1b**) (299 mg, 1 mmol), followed by TLC [dichloromethane/hexane (1:2), R_f = 0.51], gave 128 mg (65%) of **3b** as a slightly yellow oil. Exact mass (70 eV) calcd for $C_{12}H_{28}O_4P_2S_3$; *m/z* 394.0624; found 394.0629.

Bis(O,O'-di-isopropylphosphorothioyl) sulfide (**3c**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-isopropylphosphorodithioate (**1c**) (299 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:7), R_f = 0.75], gave 120 mg (61%) of **3c** as a slightly yellow oil.

Table II. Yields and physical properties of piperidinium phosphorodithioates (**1**).

No.	Compounds R	Yield [%]	m.p. [°C]	IR (KBr) νPS_2 [cm^{-1}]	^1H NMR ($CDCl_3$) [δ]	Recryst. solvent
1a	C_2H_5	73	55–57 57 [12]	825, 670	1.30 (t, 6H, CH_3), 1.5–2.0 (br, 6H, CH_2), 3.23 (t, 4H, CH_2N), 4.03 (qd, J_{POCH} = 10 Hz, 4H, CH_2), 7.5 (bs, 2H, $^+NH_2$)	Et_2O
1b	C_3H_7	87	50–52	825, 670	0.98 (t, 6H, CH_3), 1.5–2.0 (m, 10H, CH_2), 3.3 (b, 4H, CH_2N), 3.87 (td, J_{POCH} = 9 Hz, 4H, CH_2O), 8.6 (b, 2H, $^+NH_2$)	Et_2O
1c	*i*-C_3H_7	84	114–116	815, 660	1.28 (d, 12H, CH_3), 1.40–2.10 (m, 6H, CH_2), 3.32 (t, 4H, CH_2N), 4.7 (m, J_{POCH} = 10 Hz, 2H, CHO), 7.55 (br, 2H, $^+NH_2$)	AcOEt
1d	C_4H_9	68	62–63	815, 670	0.85 (t, 6H, CH_3), 1.2–1.8 (m, 14H, CH_2), 3.1 (br, 4H, CH_2N), 3.95 (td, J_{POCH} = 9 Hz, 4H, CH_2O), 8.7 (br, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (4:1)
1e	*cyclo*-C_6H_{11}	65	145–147	809, 665	1.2–2.2 (br, 26H, CH_2), 3.35 (br, 4H, CH_2N), 4.4 (br, 2H, CHO), 8.8 (br, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (6:1)
1f	C_6H_5	77	113–115	815, 655	1.4–2.0 (br, 6H, CH_2), 3.0 (br, 4H, CH_2N), 7.0–7.5 (m, 10H, Ar), 8.12 (br, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (6:1)
1g	3-$CH_3C_6H_4$	80	124–127	800, 635	1.3–1.8 (m, 6H, CH_2), 2.30 (s, 6H, CH_3), 2.95 (br, 4H, CH_2N), 6.7–6.9 and 7.0–7.1 (m, 8H, Ar), 8.0 (b, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (6:1)
1h	4-$CH_3C_6H_4$	73	138–140	800, 640	1.3–1.8 (m, 6H, CH_2), 2.38 (s, 6H, CH_3), 2.9 (br, 4H, CH_2N), 6.9–7.3 (m, 8H, Ar), 8.1 (b, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (6:1)
1i	2-$CH_3OC_6H_4$	80	157–159	810, 630	1.0–2.0 (m, 6H, CH_2), 3.20 (br, 4H, CH_2N), 3.78 (s, 6H, CH_3O), 6.5–7.1 and 7.3–7.4 (m, 8H, Ar), 8.0 (br, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (7:1)
1j	4-$CH_3OC_6H_4$	76	93–95	800, 640	1.2–2.0 (m, 6H, CH_2), 3.0 (br, 4H, CH_2N), 3.78 (s, 6H, CH_3O), 6.82 (d, 4H, Ar), 7.27 (d, 4H, Ar), 8.1 (br, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (6:1)
1k	4-ClC_6H_4	71	106–108	810, 630	1.3–1.8 (m, 6H, 2H), 2.7–3.1 (m, 4H, CH_2N), 7.12 (s, 8H, Ar), 8.0 (br, 2H, $^+NH_2$)	CH_2Cl_2/C_6H_{14} (6:1)

Reaction conditions: **1a–e** = 40 °C, 3 h; **1f–k** = 150 °C, 3 h.

Bis(O,O'-di-butylphosphorothioyl) sulfide (**3d**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-butylphosphorodithioate (**1d**) (327 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:7), R_f = 0.80], gave 142 mg (63%) of **3d** as a slightly yellow oil.

Bis(O,O'-di-cyclohexylphosphorothioyl) sulfide (**3e**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-cyclohexylphosphorodithioate (**1e**) (379 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:5), R_f = 0.80], gave 188 mg (68%) of **3e** as a slightly yellow oil. Exact mass (70 eV): calcd for $C_{24}H_{20}O_4P_2S_3$; *m/z* 554.1875; found 554.1891.

Bis(O,O'-diphenylphosphorothioyl) sulfide (**3f**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-diphenylphosphorodithioate (**1f**) (367 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:5), R_f = 0.48] and by recrystallization from dichloromethane/hexane (1:3), gave 175 mg (66%) of **3f** as colorless crystals.

$C_{24}H_{10}P_2O_4S_3$ (553.55)
Found C 53.92 H 3.72,
Calcd C 54.33 H 3.80.

The reaction with potassium O,O'-diphenylphosphorodithioate (320 mg, 1 mmol) gave 320 mg (60%) of **3f.**

The reaction with silver O,O'-diphenylphosphorodithioate) (389 mg, 1 mmol) in THF at 66 °C for 1 h gave 27 mg (10%) of **3f** and 76% of the starting silver salt.

The reaction with zinc bis(O,O'-diphenylphosphorodithioate) (314 mg, 1 mmol) in THF at 66 °C for 1 h gave 13 mg (5%) of **3f** and 84% of the starting zinc salt.

Bis(O,O'-di-m-tolylphosphorothioyl) sulfide (**3g**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-*m*-tolylphosphorodithioate (**1g**) (395 mg, 1 mmol), followed by TLC [dichloromethane/hexane (1:5), R_f = 0.48] and by recrystallization from ether/hexane (1:3), gave 158 mg (54%) of **3g** as colorless crystals.

$C_{28}H_{28}P_2O_4S_3$ (586.55)
Found C 57.47 H 4.78,
Calcd C 57.33 H 4.81.

Bis(O,O'-di-p-tolylphosphorothioyl) sulfide (**3h**)

2-Chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) was added to a solution of piperidinium O,O'-di-*p*-tolylphosphorodithioate (**1h**) (395 mg, 1 mmol) in dichloromethane (10 ml) and the reaction mixture was stirred at 0 °C for 1 h. After removal of the solvent by rotary evaporator, thin layer chromatography of the residue (hexane/ethyl acetate = 5:1, R_f = 0.81) followed by recrystallization of the resulting solid from hexane gave 174 mg (59%) of **3h** as colorless crystals: m.p. 91–93 °C and 38 mg (61%) of 1-methylpyridine-2-thione (**4**) (R_f = 0.57) as yellow crystals: m.p. 81–82 °C. The m.p. and IR, ^{1}H NMR, and mass spectra of **3h** and **4** were consistent with those of the authentic samples, which were prepared by the reaction of O,O'-di-*p*-tolylphosphorodithioic acid with dicyclohexylcarbodiimide [9] or of 4-methylbenzenecarbodithioic acid with 2-chloro-1-methylpyridinium iodide [13], respectively.

Bis(O,O'-di-2-methoxybenzenephosphorothioyl) sulfide (**3i**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-2-methoxybenzenephosphorodithioate (**1i**) (427 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:2), R_f = 0.48], gave 98 mg (30%) of **3i** as pale yellow oil.

Bis(O,O'-di-4-methoxybenzenephosphorothioyl sulfide (**3j**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-3-methoxybenzenephosphorodithioate (**1j**) (427 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:2), R_f = 0.42] and by recrystallization from ether/hexane (1:1), gave 244 mg (75%) of **3j** as colorless crystals.

$C_{28}H_{28}P_2O_8S_3$ (650.65)
Found C 51.26 H 4.20,
Calcd C 51.69 H 4.34.

Bis(O,O'-di-4-chlorobenzenephosphorothioyl) sulfide (**3k**)

The reaction of 2-chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-4-chlorobenzenephosphorodithioate (**1k**) (436 mg, 1 mmol), followed by TLC [dichloromethane/hexane (1:2), R_f = 0.50] and by re-

crystallization from ether/hexane (1:3), gave 192 mg (57%) of **3k** as colorless crystals.

$C_{24}H_{16}P_2O_4S_3Cl_4$ (668.33)
Found C 42.74 H 2.41,
Calcd C 43.13 H 2.41.

Bis(diphenylphosphinothioyl) oxide (**8**)

2-Chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) was added to a solution of piperidinium diphenylphosphorothioate (319 mg, 1 mmol) in dichloromethane (10 ml) at 0 °C, and the reaction mixture was stirred for 30 min. The solvent was evaporated by rotary evaporator. TLC of the residue (hexane/ethyl acetate = 5:1, R_f = 0.57), followed by recrystallization from dichloromethane/hexane, gave 101 mg (45%) of **8** as colorless crystals. M.p. 193–195 °C; MS (20 eV) *m/z* 450 [M^+] (100), 373 [$Ph_2P(S)OP(S)Ph]^+$ (3), 341 [$Ph_2P(S)OPPh]^+$ (30), 201 [$Ph_2PO]^+$ (10); ^{31}P NMR (CH_2Cl_2, reference 85% H_3PO_4) 80.01; IR (KBr): ν (cm^{-1}) 2990, 1470, 1425, 1310, 1270, 1100, 920, 905, 770, 750, 720, 690, 685, 650, 610, 585, 525, 505, 495, 425.

Bis(diphenylphosphinothioyl) sulfide (**11**)

2-Chloro-1-methylpyridinium *p*-toluenesulfonate (150 mg, 0.5 mmol) was added to a solution of piperidinium diphenylphosphinodithioate (335 mg, 1 mmol) in dichloromethane (10 ml). The reaction mixture was evaporated by rotary evaporator. TLC of the residue (hexane/ethyl acetate = 2:1) followed by recrystallization of the resulting solid from hexane gave 145 mg (62%) of **11** (R_f = 0.56) as colorless crystals, m.p. 121–122 °C [lit. [16] 121.5 °C] and 41 mg (65%) of **4.**

11: MS (20 eV) *m/z* 466 (M^+); ^{31}P NMR (CH_2Cl_2, reference 85% H_3PO_4) 61.52; IR (KBr): ν (cm^{-1}) 3010, 1800, 1660, 1570, 1465, 1420, 1290, 1250, 1175, 1155, 1005, 970, 910, 735, 705, 670, 630, 600, 520, 470, 450, 430, 410, 400.

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