A Convenient Preparation of Bis(phosphorothioyl) Sulfides

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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 phosphorochloridithioate [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 phospine [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).

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′-diphenylphosphinothiolyl) 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′-diphenylphosphinothioic 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(diphenylphosphinothiolyl) oxide (8) (eq. (2)).
No formation of the possible diphenylphosphinothioyl sulfide (10) or bis(diphenylphosphinyl) sulfide (11) was detected. The reaction would proceed via the intermediate II, which 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 diphenylphosphinodithioate [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).

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Yield [%]</th>
<th>m. p. [°C]</th>
<th>IR (KBr) vP=S [cm⁻¹]</th>
<th>Massa m/z</th>
<th>$^3$P NMRb [δ]</th>
<th>$^1$H NMR (CDCl₃) [δ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C₅H₅</td>
<td>77</td>
<td>70–72</td>
<td>650</td>
<td>338</td>
<td>+78.4</td>
<td>1.35 (t, 3H, CH₃), 4.00 (qd, JPOCH = 10 Hz, 2H, CH₂)</td>
</tr>
<tr>
<td>3b</td>
<td>C₅H₇</td>
<td>65</td>
<td>oil</td>
<td>675⁴</td>
<td>394</td>
<td>+77.2</td>
<td>0.96 (t, 3H, CH₃), 1.7 (m, 2H, CH₂), 3.98 (td, JPOCH = 9 Hz, 2H, CH₂O)</td>
</tr>
<tr>
<td>3c</td>
<td>i-C₅H₅</td>
<td>61</td>
<td>oil</td>
<td>635⁴</td>
<td>394</td>
<td>+76.0</td>
<td>1.40 (d, 6H, CH₂), 4.83 (m, JPOCH = 10 Hz, 1H, CHO)</td>
</tr>
<tr>
<td>3d</td>
<td>C₆H₁₀</td>
<td>63</td>
<td>oil</td>
<td>645⁴</td>
<td>450</td>
<td>+77.2</td>
<td>0.91 (t, 3H, CH₃), 1.2–1.8 (m, 4H, CH₂), 4.10 (br, 2H, CH₂O)</td>
</tr>
<tr>
<td>3e</td>
<td>cyclo-C₅H₁₀</td>
<td>86</td>
<td>oil</td>
<td>660⁵</td>
<td>554</td>
<td>+76.3</td>
<td>1.5 and 1.8 (br, 10H, CH₂), 4.6 (m, 1H, CHO)</td>
</tr>
<tr>
<td>3f</td>
<td>C₆H₅</td>
<td>66</td>
<td>131–133</td>
<td>645</td>
<td>530</td>
<td>+70.3</td>
<td>7.1–7.4 (m, Ar)</td>
</tr>
<tr>
<td>3g</td>
<td>3-CH₃C₅H₄</td>
<td>54</td>
<td>oil</td>
<td>645⁴</td>
<td>586</td>
<td>+70.4</td>
<td>2.28 (s, 3H, CH₃), 6.70–7.40 (m, 4H, Ar)</td>
</tr>
<tr>
<td>3h</td>
<td>4-CH₃C₅H₄</td>
<td>59</td>
<td>91–93</td>
<td>645</td>
<td>586</td>
<td>+71.4</td>
<td>2.28 (s, 3H, CH₃), 7.12 (bs, 4H, Ar)</td>
</tr>
<tr>
<td>3i</td>
<td>2-CH₃OCC₅H₄</td>
<td>30</td>
<td>oil</td>
<td>640⁶</td>
<td>650</td>
<td>+71.8</td>
<td>3.71 (s, 3H, CH₃O), 6.7–7.0 (m, 4H, Ar)</td>
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<tr>
<td>3j</td>
<td>4-CH₃OC₅H₄</td>
<td>75</td>
<td>146–148</td>
<td>640</td>
<td>650</td>
<td>+72.9</td>
<td>3.78 (s, 3H, CH₃), 6.80 (d, 2H, Ar), 7.18 (d, 2H, Ar)</td>
</tr>
<tr>
<td>3k</td>
<td>4-ClC₅H₄</td>
<td>57</td>
<td>74–76</td>
<td>642</td>
<td>666</td>
<td>+70.1</td>
<td>6.75 (d, 2H, Ar), 7.13 (d, 2H, Ar)</td>
</tr>
</tbody>
</table>

a 20 eV, 110 °C; b reference 85% H₃PO₄ (sloven: CH₃Cl₂); 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 commercial 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 (la) (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 (TLC) of the residue [dichloromethane/hexane (1:5), Rf = 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), Rf = 0.51], gave 128 mg (65%) of 3b as a slightly yellow oil. Exact mass (70 eV) calcd for C12H28O4P2S2: 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), Rf = 0.75], gave 128 mg (61%) of 3c as a slightly yellow oil.

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

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Yield [%]</th>
<th>m.p. [°C]</th>
<th>IR (KBr) vPS2 [cm⁻¹]</th>
<th>'H NMR (CDCl₃)</th>
<th>Recryst. solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>C₂H₅</td>
<td>73</td>
<td>55–57</td>
<td>825, 670</td>
<td>1.30 (t, 6H, CH₃), 1.5–2.0 (br, 6H, CH₃), 3.23 (t, 4H, CH₂N), 4.03 (q, JPOCH = 10 Hz, CH₂), 7.5 (bs, 2H, &quot;NH&quot;)</td>
<td>Et₂O</td>
</tr>
<tr>
<td>1b</td>
<td>C₃H₇</td>
<td>87</td>
<td>50–52</td>
<td>825, 670</td>
<td>0.98 (t, 6H, CH₃), 1.5–2.0 (m, 10H, CH₂), 3.3 (b, 4H, CH₂N), 3.87 (td, JPOCH = 9 Hz, CH₂O), 8.6 (b, 2H, &quot;NH&quot;)</td>
<td>Et₂O</td>
</tr>
<tr>
<td>1c</td>
<td>i-C₃H₇</td>
<td>84</td>
<td>114–116</td>
<td>815, 660</td>
<td>1.28 (d, 12H, CH₂), 1.40–2.10 (m, 6H, CH₂), 3.32 (t, 4H, CH₂N), 4.7 (m, JPOCH = 10 Hz, 2H, CH₂O), 7.55 (br, 2H, &quot;NH&quot;)</td>
<td>AcOEt</td>
</tr>
<tr>
<td>1d</td>
<td>C₆H₆</td>
<td>68</td>
<td>62–63</td>
<td>815, 670</td>
<td>0.85 (t, 6H, CH₃), 1.2–1.8 (m, 14H, CH₂), 3.1 (br, 4H, CH₂N), 3.95 (td, JPOCH = 9 Hz, 4H, CH₂O), 8.7 (br, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (4:1)</td>
</tr>
<tr>
<td>1e</td>
<td>cyclo-C₄H₁₀</td>
<td>65</td>
<td>145–147</td>
<td>809, 665</td>
<td>1.1–2.2 (br, 26H, CH₂), 3.35 (br, 4H, CH₂N), 4.4 (br, 2H, CHO), 8.8 (br, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (6:1)</td>
</tr>
<tr>
<td>1f</td>
<td>C₆H₅</td>
<td>77</td>
<td>113–115</td>
<td>815, 655</td>
<td>1.4–2.0 (br, 6H, CH₂), 3.0 (br, 4H, CH₂N), 7.0–7.5 (m, 10H, Ar), 8.12 (br, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (6:1)</td>
</tr>
<tr>
<td>1g</td>
<td>3-CH₂C₆H₄</td>
<td>80</td>
<td>124–127</td>
<td>800, 635</td>
<td>1.3–1.8 (m, 6H, CH₂), 2.30 (s, 6H, CH₂), 2.95 (br, 4H, CH₂N), 6.7–6.9 and 7.0–7.1 (m, 8H, Ar), 8.0 (br, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (6:1)</td>
</tr>
<tr>
<td>1h</td>
<td>4-CH₂C₆H₄</td>
<td>73</td>
<td>138–140</td>
<td>800, 640</td>
<td>1.3–1.8 (m, 6H, CH₂), 2.38 (s, 6H, CH₂), 2.9 (br, 4H, CH₂N), 6.9–7.3 (m, 8H, Ar), 8.1 (b, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (6:1)</td>
</tr>
<tr>
<td>1i</td>
<td>2-CH₂OC₂H₅</td>
<td>80</td>
<td>157–159</td>
<td>810, 630</td>
<td>1.0–2.0 (m, 6H, CH₂), 3.20 (br, 4H, CH₂N), 3.78 (s, 6H, CH₂O), 6.5–7.1 and 7.3–7.4 (m, 8H, Ar), 8.0 (br, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (7:1)</td>
</tr>
<tr>
<td>1j</td>
<td>4-CH₂OC₂H₅</td>
<td>76</td>
<td>93–95</td>
<td>800, 640</td>
<td>1.2–2.0 (m, 6H, CH₂), 3.0 (br, 4H, CH₂N), 3.78 (s, 6H, CH₂O), 6.82 (d, 4H, Ar), 7.27 (d, 4H, Ar), 8.1 (br, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (6:1)</td>
</tr>
<tr>
<td>1k</td>
<td>4-ClC₆H₄</td>
<td>71</td>
<td>106–108</td>
<td>810, 630</td>
<td>1.3–1.8 (m, 6H, 2H), 2.7–3.1 (m, 4H, CH₂N), 7.12 (s, 8H, Ar), 8.0 (br, 2H, &quot;NH&quot;)</td>
<td>CH₂Cl₂/CH₂Cl₄ (6:1)</td>
</tr>
</tbody>
</table>

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-toluene sulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-butyl phosphorodithioate (1d) (327 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:2), \( R_f = 0.80 \)], 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-toluene sulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-cyclohexyl phosphorodithioate (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 \( C_{66}H_{88}O_{16}P_2S_4 \); found 554.1891.

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

The reaction of 2-chloro-1-methylpyridinium p-toluene sulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-diphenyl phosphorodithioate (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 (68\%) of 3f as colorless crystals.

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

The reaction with silver O,O'-di-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'-di-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-toluene sulfonate (150 mg, 0.5 mmol) with piperidinium O,O'-di-m-tolyl phosphorodithioate (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.

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

2-Chloro-1-methylpyridinium p-toluene sulfonate (150 mg, 0.5 mmol) was added to a solution of piperidinium O,O'-di-p-tolyl phosphorodithioate (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-tolyl phosphorodithioic 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-toluene sulfonate (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-toluene sulfonate (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.

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

The reaction of 2-chloro-1-methylpyridinium p-toluene sulfonate (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.

\[
C_{24}H_{16}P_2O_4S_4Cl_4 \quad (668.33)
\]  
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 \([Pb_2P(S)OP(S)Ph]^+\] (3), 341 \([Pb_2P(S)OPPh]^+\] (30), 201 \([Pb_2PO]^+\] (10); \(^{31}\)P NMR (CH\(_2\)Cl\(_2\), reference 85% H\(_3\)PO\(_4\)) 80.01; IR (KBr): \(\nu (\text{cm}^{-1})\) 2990, 1800, 1660, 1570, 1465, 1420, 1290, 1250, 1175, 1155, 1005, 970, 910, 735, 705, 670, 630, 520, 470, 450, 430, 410, 400.

**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\(_2\)Cl\(_2\), reference 85% H\(_3\)PO\(_4\)) 61.52; IR (KBr): \(\nu (\text{cm}^{-1})\) 3010, 1800, 1660, 1570, 1465, 1420, 1290, 1250, 1175, 1155, 1005, 970, 910, 735, 705, 670, 630, 520, 470, 450, 430, 410, 400.

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