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.

Results and Discussion

When 2-chloro-1-methylpyridinium p-toluenesulfonate was added to a solution of piperidinium O,O'-diphenyolphosphorodithioate (1) 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'-diphenylphosphorothioyl) 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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Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
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, 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.

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>3¹P NMRb</th>
<th>¹H NMR (CDCl₃) [δ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C₂H₅</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>C₆H₅</td>
<td>65</td>
<td>oil</td>
<td>675c</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, CH₂)</td>
</tr>
<tr>
<td>3c</td>
<td>C₆H₅</td>
<td>61</td>
<td>635c</td>
<td>394</td>
<td>+76.0</td>
<td></td>
<td>1.40 (d, 6H, CH₃), 4.83 (m, JPOCH = 10 Hz, 1H, CHO)</td>
</tr>
<tr>
<td>3d</td>
<td>C₆H₅</td>
<td>63</td>
<td>oil</td>
<td>645c</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, CH₂)</td>
</tr>
<tr>
<td>3f</td>
<td>C₂H₅</td>
<td>86</td>
<td>oil</td>
<td>660c</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>3g</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>3h</td>
<td>C₆H₅</td>
<td>60e 10f</td>
<td>oil</td>
<td>645c</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>3i</td>
<td>C₆H₅</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>3j</td>
<td>C₆H₅</td>
<td>30</td>
<td>oil</td>
<td>640c</td>
<td>650</td>
<td>+71.8</td>
<td>3.71 (s, 3H, CH₂O), 6.7-7.0 (m, 4H, Ar)</td>
</tr>
<tr>
<td>3k</td>
<td>C₆H₅</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>3l</td>
<td>C₆H₅</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 (slovent: CH₂Cl₂); c neat; d using potassium O,O'-diphenylphosphinodithioate; e using zinc bis(O,O'-diphenylphosphinodithioate); f using silver O,O'-diphenylphosphinodithioate.

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 ¹H and ³¹P 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...
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 (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 (lb) (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 (lc) (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).

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds</th>
<th>Yield [%]</th>
<th>m.p. [°C]</th>
<th>IR (KBr)</th>
<th>(^1^H \text{NMR (CDCl}_3)</th>
<th>Recryst. solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>C(_2)H(_5)</td>
<td>73</td>
<td>55–57</td>
<td>825, 670</td>
<td>3.10 (t, 6H, CH(_3)), 1.5–2.0 (br, 6H, CH(_3))</td>
<td>Et(_2)O</td>
</tr>
<tr>
<td>1b</td>
<td>C(_3)H(_7)</td>
<td>87</td>
<td>50–52</td>
<td>825, 670</td>
<td>0.98 (t, 6H, CH(_3)), 1.5–2.0 (m, 10H, CH(_3))</td>
<td>Et(_2)O</td>
</tr>
<tr>
<td>1c</td>
<td>i-C(_3)H(_7)</td>
<td>84</td>
<td>114–116</td>
<td>815, 660</td>
<td>1.28 (d, 12H, CH(_3)), 1.40–2.10 (m, 10H, CH(_3))</td>
<td>AcOEt</td>
</tr>
<tr>
<td>1d</td>
<td>C(_4)H(_9)</td>
<td>68</td>
<td>62–63</td>
<td>815, 670</td>
<td>0.85 (t, 6H, CH(_3)), 1.2–1.8 (m, 14H, CH(_3)), 3.1 (br, 4H, CH(<em>3)), 3.95 (td, ( J</em>{POCH} = 9 ) Hz, 4H, CH(_3))</td>
<td>CH(_2)Cl/CH(_3)(_4) (4:1)</td>
</tr>
<tr>
<td>1e</td>
<td>cyclo-C(_4)H(_11)</td>
<td>65</td>
<td>145–147</td>
<td>809, 665</td>
<td>1.2–2.2 (br, 26H, CH(_3)), 3.35 (br, 4H, CH(_3)), 4.4 (br, 2H, CH(<em>3)), 8.8 (br, 2H, ( ^1^H)NH(</em>\text{I} ))</td>
<td>CH(_2)Cl/CH(_3)(_4) (6:1)</td>
</tr>
<tr>
<td>1f</td>
<td>C(_6)H(_6)</td>
<td>77</td>
<td>113–115</td>
<td>815, 655</td>
<td>1.4–2.0 (br, 6H, CH(_3)), 3.0 (br, 4H, CH(<em>3)), 7.0–7.5 (m, 10H, Ar), 8.12 (br, 2H, ( ^1^H)NH(</em>\text{I} ))</td>
<td>CH(_2)Cl/CH(_3)(_4) (6:1)</td>
</tr>
<tr>
<td>1g</td>
<td>3-CH(_3)C(_6)H(_4)</td>
<td>80</td>
<td>124–127</td>
<td>800, 635</td>
<td>1.3–1.8 (m, 6H, CH(_3)), 2.30 (s, 6H, CH(_3)), 2.95 (br, 4H, CH(<em>3)), 6.7–6.9 and 7.0–7.1 (m, 8H, Ar), 8.0 (b, 2H, ( ^1^H)NH(</em>\text{I} ))</td>
<td>CH(_2)Cl/CH(_3)(_4) (6:1)</td>
</tr>
<tr>
<td>1h</td>
<td>4-CH(_3)C(_6)H(_4)</td>
<td>73</td>
<td>138–140</td>
<td>800, 640</td>
<td>1.3–1.8 (m, 6H, CH(_3)), 2.38 (s, 6H, CH(_3)), 2.9 (br, 4H, CH(<em>3)), 6.9–7.3 (m, 8H, Ar), 8.1 (b, 2H, ( ^1^H)NH(</em>\text{I} ))</td>
<td>CH(_2)Cl/CH(_3)(_4) (6:1)</td>
</tr>
<tr>
<td>1i</td>
<td>2-CH(_2)OC(_6)H(_4)</td>
<td>80</td>
<td>157–159</td>
<td>810, 630</td>
<td>1.0–2.0 (m, 6H, CH(_3)), 3.20 (br, 4H, CH(_3)), 3.78 (s, 6H, CH(<em>3)), 6.5–7.1 and 7.3–7.4 (m, 8H, Ar), 8.0 (br, 2H, ( ^1^H)NH(</em>\text{I} ))</td>
<td>CH(_2)Cl/CH(_3)(_4) (7:1)</td>
</tr>
<tr>
<td>1j</td>
<td>4-CH(_2)OC(_6)H(_4)</td>
<td>76</td>
<td>93–95</td>
<td>800, 640</td>
<td>1.2–2.0 (m, 6H, CH(_3)), 3.0 (br, 4H, CH(_3)), 3.78 (s, 6H, CH(<em>3)), 6.82 (d, 4H, Ar), 7.27 (d, 4H, Ar), 8.1 (br, 2H, ( ^1^H)NH(</em>\text{I} ))</td>
<td>CH(_2)Cl/CH(_3)(_4) (6:1)</td>
</tr>
<tr>
<td>1k</td>
<td>4-ClC(_6)H(_4)</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, CH(<em>3)), 7.12 (s, 8H, Ar), 8.0 (br, 2H, ( ^1^H)NH(</em>\text{I} ))</td>
<td>CH(_2)Cl/CH(_3)(_4) (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-butylphosphorodithioate (1d) (327 mg, 1 mmol), followed by TLC [ethyl acetate/hexane (1:5), \( R_f = 0.50 \)], 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-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): calcld for \( \text{C}_{24}\text{H}_{28}\text{O}_{5}\text{P}_{5}\text{S}_{3} \); \( m/z \) 554.1875; 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-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 (59%) of 3f as colorless crystals.

\[ \text{C}_{30}\text{H}_{28}\text{O}_{2}\text{P}_{2}\text{S}_{3} \]

Found C 53.92 H 3.72,
Calcd C 54.33 H 3.80.

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-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.

\[ \text{C}_{28}\text{H}_{28}\text{P}_{2}\text{O}_{2}\text{S}_{3} \]

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-toluene sulfonate (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), \( R_f = 0.80 \), gave 188 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-methoxybenzenesulfonilphosphorothioyl) sulfide (3i)

The reaction of 2-chloro-1-methylpyridinium p-toluene sulfonate (150 mg, 0.5 mmol) with piperidinium O,O′-di-2-methoxybenzenesulfonilphosphorodithioate (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-methoxybenzenesulfonilphosphorothioyl) sulfide (3j)

The reaction of 2-chloro-1-methylpyridinium p-toluene sulfonate (150 mg, 0.5 mmol) with piperidinium O,O′-di-3-methoxybenzenesulfonilphosphorodithioate (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.

\[ \text{C}_{28}\text{H}_{28}\text{P}_{2}\text{O}_{2}\text{S}_{3} \]

Found C 51.26 H 4.20,
Calcd C 51.69 H 4.34.

Bis(O,O′-di-4-chlorobenzenesulfonilphosphorothioyl) sulfide (3k)

The reaction of 2-chloro-1-methylpyridinium p-toluene sulfonate (150 mg, 0.5 mmol) with piperidinium O,O′-di-4-chlorobenzenesulfonilphosphorodithioate (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.

\[ \text{C}_{24}\text{H}_{16}\text{P}_4\text{O}_4\text{S,C}_1 (668.33) } 
\]

*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 \([\text{M}^+] (100), 373 \text{[Ph}_2\text{P(S)OP(S)Ph]}^+ (3), 341 \text{[Ph}_2\text{P(S)OOPh]}^+ (30), 201 \text{[Ph}_2\text{PO]}^+ (10) \); 31P NMR (CH\(_2\)C\(_12\), reference 85% H\(_3\)PO\(_4\) 80.01; IR (KBr): \( v (\text{cm}^{-1}) \) 3010, 1800, 1660, 1570, 1465, 1420, 1290, 1250, 1175, 1155, 1005, 970, 910, 735, 705, 670, 630, 600, 520, 470, 450, 430, 410, 400.

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

2-Chloro-1-methylpyridinium p-toluene sulfonate (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 \([\text{M}^+] \); 31P NMR (CH\(_2\)C\(_12\), reference 85% H\(_3\)PO\(_4\) 61.52; IR (KBr): \( v (\text{cm}^{-1}) \) 3010, 1800, 1660, 1570, 1465, 1420, 1290, 1250, 1175, 1155, 1005, 970, 910, 735, 705, 670, 630, 600, 520, 470, 450, 430, 410, 400.