Preparation and Some Reactions of Phenylmercury Thio- and Dithiocarboxylates

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Phenylmercury Thiocarboxylates

It has been found that the reaction of diphenylmercury with an equimolar amount of thio- or dithio acids gave the corresponding phenylmercury thio- (1) or dithiocarboxylates (2), quantitatively, which further react with thio- or dithio acids to give mercury bis(thio-)(3) or bis(dithiocarboxylates)(4). The phenylmercury dithio salts (2) were found to be the very useful thioacylating agents for primary and secondary amines. The reaction of mercury bis(thiocarboxylates) (3) with dithiocarboxylic acids gave the unsymmetrical thio- and dithiocarboxylic acid mercury salts [RC(0)SHgS(8)R'] (5) in good yields.

Introduction

A vast number of organomercury compounds of types RHgX and R2Hg (R = alkyl and aryl, X = Halogen and CH3CO2) are known and their reactions have been investigated extensively [1]. There are, however, relatively few studies of the sulfur containing compounds such as RSHgR' and RSHgX, especially thio- and dithiocarboxylic acid derivatives. According to our literature survey, very few mercury bis(dithiocarboxylates) have been reported along with spectral data and reactions [2]. The systematic investigations of preparations and reactions of the mercury thio- and dithiocarboxylates are of great importance from the spectroscopical, practical, and biological viewpoints for the chemistry of sulfur containing organomercurials. In this paper, we describe the synthesis of a series of title compounds and their synthetic utility as thioacylating agents, especially for amines.

Results and Discussion

Phenylmercury thio- (1) and dithiocarboxylates (2) were found to be readily obtained in good yields from the reaction of diphenylmercury with thio- or dithio acids (eqs (1) and (2)). In general, the reactions

\[
\begin{align*}
0 & \quad \text{RCSH + PhHgPh} \rightarrow \text{ref. 3 h benzene} \\
0 & \quad \text{RCSHgPh + PhH} \\
\end{align*}
\]

(1)

of diphenyl mercury with dithio acids proceed readily at room temperature, while more drastic conditions, such as refluxing in benzene, are required for the reactions with thio acids except for cyclo-hexane thio carboxylic acid. The yields and physical properties of the products are summarized in Tables I and II. Although yields of the aliphatic derivatives 1a-b and 2a-e are relatively low because of the low stability of these compounds, these reactions proceed almost quantitatively. The structures of 1 and 2 were established on the basis of mass, i.r., u.v. visible and \( ^1H \) n.m.r. spectral data and elemental analyses. Thus, the products 1 and 2 show the molecular ion \( (M^+ \) in the mass spectra. The characteristic carbonyl or thiocarbonyl stretching vibrations are observed at regions 1600–1700 cm\(^{-1}\) or 850–1050 cm\(^{-1}\), respectively. Further, the results of elemental analyses of 3 and 4 are in good agreement with the calculated values, respectively.

Similarly, the reactions with two equivalents of thio- or dithio acids were found to give the bis(thio-)(3) or bis(dithiocarboxylates)(4) in excellent yields (eq. (3)) (Table III). Presumably,

\[
\begin{align*}
0 & \quad 2 \text{RCSH + PhHgPh} \rightarrow (\text{RC})_2\text{Hg} + 2 \text{PhH} \\
0 & \quad 3 (Y = O) \\
0 & \quad 4 (Y = S) \\
\end{align*}
\]

(3)
Table I. Yields and physical properties of phenylmercury thiocarboxylates (1).

<table>
<thead>
<tr>
<th>No.</th>
<th>RC(O)SHgPh</th>
<th>Yield [%]</th>
<th>M.p. [°C]</th>
<th>i.r. [cm⁻¹]¹</th>
<th>¹H n.m.r.²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CH₃</td>
<td>71</td>
<td>86.0-87.5</td>
<td>1629</td>
<td>2.45 (s, 3H, CH₃), 7.34 (s, 5H, Ar)</td>
</tr>
<tr>
<td>1b</td>
<td>cyclo-C₆H₁₁</td>
<td>14</td>
<td>136-137</td>
<td>1660</td>
<td>0.95-2.90 (m, 11H, cyclo-C₆H₁₁), 7.33 (s, 5H, Ar)</td>
</tr>
<tr>
<td>1c</td>
<td>C₆H₅</td>
<td>91</td>
<td>122-123.5</td>
<td>1629</td>
<td>7.20-7.60 (m, 7H, Ar), 7.96-8.20 (m, 3H, Ar)</td>
</tr>
<tr>
<td>1d</td>
<td>2-CH₃C₆H₄</td>
<td>64</td>
<td>108-110</td>
<td>1610</td>
<td>2.50 (s, 3H, CH₃), 7.01-7.70 (m, 8H, Ar), 7.70-8.11 (m, 1H, Ar)</td>
</tr>
<tr>
<td>1e</td>
<td>3-CH₃C₆H₄</td>
<td>82</td>
<td>99-101</td>
<td>1612</td>
<td>2.36 (s, 3H, CH₃), 7.10-7.50 (m, 7H, Ar)</td>
</tr>
<tr>
<td>1f</td>
<td>4-CH₃C₆H₄</td>
<td>80</td>
<td>161-163</td>
<td>1629</td>
<td>2.39 (s, 3H, CH₃), 7.05-8.10 (m, 9H, Ar)</td>
</tr>
<tr>
<td>1g</td>
<td>2-C₂H₅C₂H₄</td>
<td>67</td>
<td>61-65</td>
<td>1610</td>
<td>2.36 (s, 3H, CH₃), 7.10-7.50 (m, 7H, Ar)</td>
</tr>
<tr>
<td>1h</td>
<td>3-CH₃C₆H₄</td>
<td>73</td>
<td>144-145</td>
<td>1610</td>
<td>3.86 (s, 3H, CH₃), 7.38 (s, 5H, Ar), 6.75-8.15 (m, 4H, Ar)</td>
</tr>
<tr>
<td>1i</td>
<td>2-C₆H₄</td>
<td>78</td>
<td>117-120</td>
<td>1610</td>
<td>3.86 (s, 3H, CH₃), 7.38 (s, 5H, Ar), 6.75-8.15 (m, 4H, Ar)</td>
</tr>
<tr>
<td>1j</td>
<td>3-C₆H₄</td>
<td>89</td>
<td>129-132</td>
<td>1613</td>
<td>7.10-8.00 (m, 9H, Ar)</td>
</tr>
<tr>
<td>1k</td>
<td>4-C₆H₄</td>
<td>89</td>
<td>171-173</td>
<td>1602</td>
<td>7.02-7.15 (m, 7H, Ar), 7.80-8.12 (m, 2H, Ar)</td>
</tr>
<tr>
<td>1l</td>
<td>2-NO₂C₆H₄</td>
<td>55</td>
<td>135</td>
<td>1638</td>
<td>7.35 (s, 5H, Ar), 7.50-8.15 (m, 4H, Ar)</td>
</tr>
<tr>
<td>1m</td>
<td>3-NO₂C₆H₄</td>
<td>52</td>
<td>166-169</td>
<td>1620</td>
<td>7.43 (s, 5H, Ar), 8.35-8.97 (m, 4H, Ar)</td>
</tr>
</tbody>
</table>

¹ KBr; ² CDCl₃.

Table I (continued).

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula (mol. weight)</th>
<th>Elemental analyses [%]</th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>C₆H₅OSHg (352.80)</td>
<td>Calcd 27.24 4.53 9.09</td>
<td>27.66 4.21 9.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>C₁₂H₁₂OSHg (420.92)</td>
<td>Calcd 37.10 3.83</td>
<td>37.53 3.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>C₁₂H₁₀OSHg (414.87)</td>
<td>Calcd 37.64 2.43</td>
<td>38.01 2.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>C₁₄H₁₂OSHg (429.92)</td>
<td>Calcd 39.21 2.82</td>
<td>39.55 2.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>C₁₄H₁₀OSHg (428.90)</td>
<td>Calcd 39.21 2.82</td>
<td>39.89 2.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>C₁₄H₁₀OSHg (428.90)</td>
<td>Calcd 39.21 2.82</td>
<td>39.62 2.69 7.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1g</td>
<td>C₁₄H₁₂O₂SHg (444.90)</td>
<td>Calcd 37.80 2.72</td>
<td>37.52 2.90</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

these reactions proceed stepwise via the intermediates 1 or 2, because the stoichiometric reactions of 1 and 2 with thio- or dithio acids give the quantitative yields of 3 and 4, respectively (eqs (4) and (5)) (Table III).

O  O  O
||
RCSH + RCSHgPh → (RCS)₂Hg + PhH (4)

The aromatic derivatives of 1 and 2 are very stable in the solid state and in common protic and aprotic solvents, and no change is observed even in refluxing benzene after 3 days. In contrast, the aliphatic derivatives are relatively unstable, and
Table II. Yields and physical properties of phenylmercury dithiocarboxylates (2).

<table>
<thead>
<tr>
<th>No.</th>
<th>RCS₂HgPh</th>
<th>Yield [%]</th>
<th>M.p. [°C]</th>
<th>i.r. [cm⁻¹]</th>
<th>u.v., vis [nm]</th>
<th>λmax (log e)</th>
<th>¹H n.m.r.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>CH₃</td>
<td>49</td>
<td>140-142 (dec)</td>
<td>865</td>
<td>277 (4.39)</td>
<td>2.90 (s, 3H, CH₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>336 (4.00)</td>
<td>7.20-7.70 (m, 5H, Ar)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>483 (1.60)</td>
<td>7.25-7.80 (m, 5H, Ar)</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>C₂H₅</td>
<td>42</td>
<td>81-82 (dec)</td>
<td>970</td>
<td>282 (4.21)</td>
<td>1.35 (t, 3H, CH₃), 3.15 (q, 2H, CH₂)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>319 (4.01)</td>
<td>7.25-7.80 (m, 5H, Ar)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>478 (1.55)</td>
<td>7.20-7.70 (m, 5H, Ar)</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>n-C₅H₇</td>
<td>53</td>
<td>126-127 (dec)</td>
<td>960</td>
<td>271 (4.46)</td>
<td>1.20 (t, 3H, CH₃), 1.90 (m, 2H, CH₂)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>339 (3.88)</td>
<td>3.20 (t, 2H, CH₃), 7.20-7.70 (m, 5H, Ar)</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>C₄H₅</td>
<td>61</td>
<td>153</td>
<td>1000</td>
<td>310 (4.39)</td>
<td>524 (2.29)</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>4-CH₃C₅H₄</td>
<td>90</td>
<td>160-161</td>
<td>1020</td>
<td>279 (4.38)</td>
<td>330 (4.48)</td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>4-CH₃OC₆H₄</td>
<td>80</td>
<td>180-182</td>
<td>1030</td>
<td>355 (4.57)</td>
<td>516 (2.37)</td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>4-ClC₅H₄</td>
<td>93</td>
<td>176</td>
<td>1005</td>
<td>321 (4.47)</td>
<td>515 (2.44)</td>
<td></td>
</tr>
<tr>
<td>2h</td>
<td>2,4,6-(CH₃)₃C₆H₂</td>
<td>42</td>
<td>112-114</td>
<td>1035</td>
<td>271 (4.57)</td>
<td>506 (2.09)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.30 (s, 3H, CH₃), 2.40 (s, 6H, CH₂), 6.85 (s, 2H, Ar), 7.80-8.05 (m, 5H, Ar)</td>
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<td></td>
</tr>
<tr>
<td>2i</td>
<td>I-C₁₀H₇</td>
<td>77</td>
<td>135-138</td>
<td>1028</td>
<td>278 (4.34)</td>
<td>519 (2.43)</td>
<td></td>
</tr>
</tbody>
</table>

Table II (continued).

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula (mol. weight)</th>
<th>Elemental analyses [%]</th>
<th>¹H n.m.r.</th>
</tr>
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<tbody>
<tr>
<td>2a</td>
<td>C₅H₄S₂Hg (368.86)</td>
<td>Calcd 26.05 2.19 17.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 26.36 2.01 17.63</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>C₅H₁₀S₂Hg (382.89)</td>
<td>Calcd 28.23 2.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 28.56 2.46</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>C₉H₁₂S₂Hg (396.91)</td>
<td>Calcd 30.26 3.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 30.71 3.16</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>C₁₃H₁₄S₂Hg (430.93)</td>
<td>Calcd 36.23 2.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 36.59 2.52</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>C₁₄H₁₂S₂Hg (444.96)</td>
<td>Calcd 37.79 2.72 14.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found 38.10 2.98 14.80</td>
<td></td>
</tr>
</tbody>
</table>

gradually decompose on standing at room temperature to precipitate mercuric sulfide. The thio acid derivatives (1) dissolved in chlorinated solvents such as chloroform and dichloromethane, while the dithio carboxylates (2) except for the dithio-2,4,6-trimethylbenzoate (2h) show low solubility for these solvents.

The unsymmetrical divalent salts (5) possessing both thio- and dithiocarboxyl groups in the molecule have not yet been known. A number of the reactions of phenylmercury thio- (1) or dithiocarboxylates (2) with two different kinds of thio- or dithio acids were carried out in order to obtain the unsymmetrical salts (5 and 5') (eqs (6) and (7)). These reactions, without exception, were found to produce a large amount of the undesirable symmetrical products ([RC(O)S]₂Hg and (R'CS₂)₂Hg from eq. (6), (RCS₂)₂Hg and [R'C(O)S]₂Hg from eq. (7)). The
Table III. Yields and physical properties of mercury bis(thio-) (3) and bis(dithiocarboxylates) (4).

<table>
<thead>
<tr>
<th>No.</th>
<th>Y</th>
<th>Method</th>
<th>Yield [%]</th>
<th>M.p. [°C]</th>
<th>i.r.a [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C₆H₅</td>
<td>O</td>
<td>eq. (3)</td>
<td>89</td>
<td>136–138 (dec)</td>
</tr>
<tr>
<td>3b</td>
<td>4-CH₃C₆H₄</td>
<td>O</td>
<td>eq. (4)</td>
<td>94</td>
<td>177–180 (dec)</td>
</tr>
<tr>
<td>3c</td>
<td>4-ClC₆H₄</td>
<td>O</td>
<td>eq. (3)</td>
<td>90</td>
<td>210–211 (dec)</td>
</tr>
<tr>
<td>4a</td>
<td>C₆H₅</td>
<td>S</td>
<td>eq. (3)</td>
<td>86</td>
<td>155–157 (dec)</td>
</tr>
<tr>
<td>4b</td>
<td>4-CH₃C₆H₄</td>
<td>S</td>
<td>eq. (3)</td>
<td>90</td>
<td>150 (dec)[2a]</td>
</tr>
<tr>
<td>4c</td>
<td>4-ClC₆H₄</td>
<td>S</td>
<td>eq. (3)</td>
<td>90</td>
<td>160–162 (dec)</td>
</tr>
</tbody>
</table>

a KBr; b R = Raman.

The reaction of halomercury thio- (6) or dithiocarboxylates (7) with alkali metal salts of a different kind of thio- or dithiocarboxylic acids provide another possible route of preparation (eq. (9)). At present, however, this route seems to be ruled out because of the preparative difficulty of the starting halomercury salts (6 and 7) [3].

In contrast to the above three methods (A–C), the reactions of mercury bis(dithiocarboxylates) (4) with excess thiocarboxylic acid were found to give the desired unsymmetrical salts (5) in excellent yields (eq. (10)) (Table IV).

```plaintext
Method A
\[
\begin{align*}
\text{RCSHgPh + R'CSH} & \rightarrow \text{RCSHgSCR'} \\
\text{1} & \text{2} & \text{5}
\end{align*}
\]

Method B
\[
\begin{align*}
\text{RCSHgPh + R'CSH} & \rightarrow \text{RCSHgSCR'} \\
\text{1d} & \text{5a}
\end{align*}
\]

Method C
\[
\begin{align*}
\text{RCSHgX + R'CSM} & \rightarrow \text{RCSHgSCR'} + MX \\
6 (Y = O) & \text{M = alkali} \\
7 (Y = S) & \text{metal X = Halogene}
\end{align*}
\]

Method D
\[
\begin{align*}
\text{(R'CS)₂Hg + excess RCSH} & \rightarrow \text{RCSHgSCR'} \\
\text{4} & \text{5}
\end{align*}
\]
Table IV. Yields and physical properties of acylthiomercury dithiocarboxylates (5).

<table>
<thead>
<tr>
<th>No.</th>
<th>RCSHgSCR'</th>
<th>Method</th>
<th>Yield [%]</th>
<th>M.p. [°C]</th>
<th>i.r. [cm⁻¹]a</th>
<th>u.v., vis [nm]b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>νC=O νC=S λmax (log ε)</td>
<td></td>
</tr>
<tr>
<td><strong>O</strong></td>
<td><strong>S</strong></td>
<td><strong>RCSHgSCR'</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>4-CH₃-C₆H₄-CSHgSC-C₆H₄-CH₂-4</td>
<td>A</td>
<td>35</td>
<td>120 (dec)</td>
<td>1628</td>
<td>1172</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1015</td>
<td>330 (4.35), 517 (2.29)</td>
</tr>
<tr>
<td>5b</td>
<td>4-Cl-C₆H₄-CSHgSC-C₆H₄-CH₂-4</td>
<td>B</td>
<td>7</td>
<td>190 (dec)</td>
<td>1615</td>
<td>1172</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1162</td>
<td>330 (4.25), 503 sh (2.23)</td>
</tr>
<tr>
<td>5c</td>
<td>4-Cl-C₆H₄-CSHgSC-C₆H₄-Cl-4</td>
<td>D</td>
<td>84</td>
<td>194–196 (dec)</td>
<td>1620</td>
<td>1172</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1172</td>
<td>330 (4.20), 510 sh (2.23)</td>
</tr>
</tbody>
</table>

a KBr; b CH₂Cl₂.

Table IV (continued).

<table>
<thead>
<tr>
<th>No.</th>
<th>Formula (mol. weight)</th>
<th>Elemental analyses [%]</th>
<th>C</th>
<th>H</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>C₅H₇O₃S₂Hg (519.06)</td>
<td>Calcd 37.02 2.72 18.53</td>
<td>37.32 2.89 18.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found 37.32 2.89 18.89</td>
<td></td>
<td>37.32 2.89 18.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>C₅H₁₁O₃S₂HgCl (539.47)</td>
<td>Calcd 33.40 2.05 17.83</td>
<td>33.73 2.21 18.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found 33.73 2.21 18.06</td>
<td></td>
<td>33.73 2.21 18.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>C₆H₈O₃S₂HgCl₂ (578.35)</td>
<td>Calcd 30.03 1.44 17.18</td>
<td>30.28 1.33 17.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found 30.28 1.33 17.50</td>
<td></td>
<td>30.28 1.33 17.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Carboxymethyl dithiocarboxylates [4], thioacyl chlorides [5] and imidazolides [6], and bis(thioacyl) sulfides [7] have been used practically as thioacylating reagents, although they are characterized by low stability, troublesome preparation procedures or difficulties with the removal of the by-products. Phenylmercury dithiocarboxylates (2), however, proved to be very useful thioacylating reagents, especially for primary and secondary amines, without these disadvantages (eq. (11)). The results are summarized in Table V. The yields of the thioamides

\[
\text{RCSHgPh} + R'\text{NH} \rightarrow \text{RCNR}_{2}' + \text{HgS} + \text{PhH}
\]

Table V. Reaction conditions of eq. (6) and yields of the thioamides (6).

<table>
<thead>
<tr>
<th>Reactants RCS₅HgPh amines</th>
<th>Solv.</th>
<th>Temp. [°C]</th>
<th>Time [h]</th>
<th>Thioamide</th>
<th>Yield [%]</th>
<th>M.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅H₇CS₂H₂Ph (C₅H₁₀) = NH</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>1</td>
<td>C₅H₅CN = (C₅H₁₀)</td>
<td>80</td>
<td>60–62</td>
</tr>
<tr>
<td>4-CH₃C₆H₄CS₂H₂Ph cyclo-C₅H₁₁NH₂</td>
<td>CH₂Cl₂</td>
<td>40</td>
<td>48</td>
<td>4-CH₃C₅H₆CNH₃C₅H₁₁-cyclo</td>
<td>83</td>
<td>105–106</td>
</tr>
<tr>
<td>C₅H₇NH₂</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>1</td>
<td>4-CH₃C₅H₆CNH₃C₅H₆</td>
<td>89</td>
<td>136–138</td>
</tr>
<tr>
<td>(C₅H₁₀)NH</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>1</td>
<td>4-CH₃C₅H₆CN(C₅H₁₀)</td>
<td>78</td>
<td>65–67</td>
</tr>
<tr>
<td>(C₅H₁₀) = NH</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>1</td>
<td>4-CH₃C₅H₆CN = (C₅H₁₀)</td>
<td>96</td>
<td>94–95</td>
</tr>
<tr>
<td>4-ClC₅H₇CS₂H₂Ph (C₅H₁₀) = NH</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>1</td>
<td>4-ClC₅H₆CN = (C₅H₁₀)</td>
<td>91</td>
<td>111.5–112.5</td>
</tr>
</tbody>
</table>
(8) are almost quantitative, but those of the ethyl derivatives are relatively low because of the loss during isolation by preparative T.L.C. The experimental procedures are simple. In addition, the reactions are very clean because the by-product is only mercuric sulfide, which can be easily and completely removed by centrifuging.

Two further thioacylation reactions by using 2 have been attempted for alkoxides and thioalkoxides (eq. (12)). As shown in Table VI, these reactions lead to relatively low yields of the expected thione (9) and dithioesters (10) together with by-products such as sodium dithioates and diphenyl mercury, formed by cleavage of the S–Hg and C–Hg bonds in 2.

Table VI. The reaction condition of phenylmercury dithioate (2) with alkoxides or thioalkoxide and the yields of the products.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CH₃C₆H₄CS₂HgPh</td>
<td>EtONa</td>
<td>1/2</td>
<td>EtOH</td>
<td>24</td>
<td>refl.</td>
<td>4-CH₃C₆H₄C(S)OEt [40], PhHg [25], HgS [20]</td>
</tr>
<tr>
<td>4-CH₃OC₆H₄CS₂HgPh</td>
<td>PhONa</td>
<td>1/20</td>
<td>THF</td>
<td>1</td>
<td>refl.</td>
<td>4-CH₃OC₆H₄C(S)OPh [43], (4-CH₃OC₆H₄CS₂)₂ [11] PhHg [8], HgS [20]</td>
</tr>
<tr>
<td>4-CH₃C₆H₄CS₂HgPh</td>
<td>EtSNa</td>
<td>1/2</td>
<td>EtOH</td>
<td>1</td>
<td>refl.</td>
<td>4-CH₃C₆H₄CS₂Et [23], 4-CH₃C₆H₄CS₂Na [7] PhHg [13], HgS [28]</td>
</tr>
</tbody>
</table>

Experimental

Melting points were determined using a Yanagimoto micro melting point apparatus and are uncorrected. The i.r. spectra were measured on a JASCO grating i.r. spectrophotometer IR–G. The u.v. and visible spectra were obtained from a Hitachi 124 spectrophotometer. The ¹H n.m.r. spectra were recorded on a Hitachi R-24 (60 MHz) with tetramethylsilane as an internal standard. The mass spectra were taken by a Hitachi RMU-6M mass spectrometer. Elemental analyses were performed by the Elemental Analyses Center of Kyoto University and Alfred Bernhardt Analytical Laboratory, Engelskirchen (Germany).

Materials: Diphenylmercury and thioacetic acid were reagent grade without further purification. Other thiocarboxylic acids were prepared according to the literature [8]. Dithiocarboxylic acids were also prepared by conc-HCl acidolysis of the corresponding piperidinium salts [9] and distilled (aliphatics) or dried on anhydrous sodium sulfate before use. The solvents were dried by the use of sodium metal or P₂O₅.

Typical procedures for the preparation of phenylmercury thio- (1) and dithiocarboxylates (2) are described below.

Phenylmercury 4-methylthiobenzoate (1f): Freshly prepared 4-methylthiobenzoic acid (0.084 g, 0.55 mmol) in benzene (30 ml) and the mixture was refluxed for 2.5 h. Evaporation of the solvent from the reaction mixture in vacuo, washing of the resulting residue with n-hexane, and then recrystallization from dichloromethane/n-hexane gave 0.165 g (77%) of phenylmercury 4-methylthiobenzoate (1f) as colorless crystal.

Phenylmercury dithio-4-methylbenzoate (2e): A dichloromethane solution (10 ml) containing phenylmercury (0.35 g, 1 mmol) was added to dithio-4-methylbenzoic acid (0.34 g, 2.2 mmol) in 10 ml of ether and the reaction mixture was stirred at room temperature for 1 h. Filtration of the resulting precipitates and washing with ether and then n-hexane gave 0.32 g (80%) of phenylmercury dithio-4-methylbenzoate (2e). While, evaporation of the solvents from the combined filtrate and then fractional crystallization of the resulting residue from dichloromethane gave 0.08 g (9%) of an additional 2e and 0.016 g of mercury bis(dithio-4-methylbenzoate) (4e).

Typical procedures for the preparation of mercury bis(thio-) (3) and bis(dithiocarboxylates) (4) are described below. The spectral data and elemental analyses of 3 and 4 were summarized in Table IV.

Mercury bis(4-methylthiobenzoate) (3b): Diphenylmercury (0.35 g, 1 mmol) was added to freshly prepared 4-methylthiobenzoic acid (0.34 g, 2.2 mmol)
in benzene (50 ml) and the mixture was refluxed for 3 h. Evaporation of the solvent and then washing of the residue with a small amount of ether and n-hexane gave 0.45 g (90%) of mercury bis(4-methylthiobenzoate) (3b), (m.p. 185 °C), which was identified by comparison of the melting point and i.r. spectra with those of an authentic sample prepared by phenylmercury 4-methylthiobenzoate with 4-methylthiobenzoic acid.

**Mercury bis(dithio-4-methylbenzoate) (4b):** Diphencylmercury (0.18 g, 0.5 mmol) in dichloromethane (10 ml) was added to freshly prepared dithio-4-methylbenzoic acid (1.2 mmol) in 10 ml of ether and the reaction mixture was stirred at room temperature for 1 h. Filtration of the resulting precipitates and washing with a small amount of ether gave 0.225 g (90%) of bis(dithio-4-methylbenzoate) (4b). The melting point and i.r. spectra were exactly consistent with those of an authentic sample, prepared by phenylmercury dithio-4-methylbenzoate with dithio-4-methylbenzoic acid.

**Reaction of phenylmercury 4-methylthiobenzoate (1f) with 4-methylthiobenzoic acid**

Phenylmercury 4-methylthiobenzoate (1f) (0.214 g, 0.5 mmol) and 4-methylthiobenzoic acid (0.09 g, 0.6 mmol) were refluxed in 20 ml of benzene for 1 h. Filtration of the resulting precipitates, followed by washing with n-hexane gave 0.235 g (94%) of mercury bis(4-methylthiobenzoate) (3b). The melting point and i.r. spectrum (Table IV) were exactly consistent with those of an authentic sample.

**Reaction of phenylmercury dithio-4-methylbenzoate (2e) with dithio-4-methylbenzoic acid**

To a suspension of phenylmercury dithio-4-methylbenzoate (2e) (0.223 g, 0.5 mmol) in dichloromethane, dithio-4-methylbenzoic acid (0.1 g, 0.6 mmol) in ether (10 ml) was added and the mixture was stirred for 1 h at room temperature. Filtration of the resulting precipitates, followed by washing with ether and then n-hexane gave 0.256 g (94%) of chemically pure mercury bis(dithio-4-methylbenzoate) (3b). The melting point and i.r. spectrum (Table III) were exactly in agreement with those of an authentic sample.

**Preparation of 4-methylbenzoylthiomercury dithio-4-methylbenzoate (5a) by method A**

An ether solution (10 ml) containing dithio-4-methylbenzoic acid (0.20 g, 1.2 mmol) was added to 0.06 g (0.11 mmol) of mercury bis(dithio-4-methylbenzoate) (4b) in dichloromethane (50 ml) and the mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated to ca. 5 ml. Filtration of the resulting reddish brown crystals, followed by washing with n-hexane and then ethanol, gave 0.05 g (82%) of 4-chlorobenzoylthiomercury dithio-4-chlorobenzoate (5e), which was identified by the spectral data and elemental analyses shown in Table IV.

**Preparation of 4-chlorobenzoylthiomercury dithio-4-methylbenzoate (5b) by method B**

4-Chlorothiobenzoic acid was added to phenylmercury dithio-4-methylbenzoate (2e) in benzene. After refluxing for 2 h under dark, the reaction mixture was evaporated in vacuo. The resulting residue was extracted with n-hexane (20 ml) and then ether (3 ml). The combined extracts were allowed to stand at room temperature for 24 h. Filtration of the resulting plate crystal gave 0.04 g (7%) of 4-chlorobenzoylthiomercury dithio-4-methylbenzoate (5b), which was identified by the spectral data and elemental analyses shown in Table IV.

On the other hand, the n-hexane and ether insoluble solid (0.20 g) was a mixture of 4-chlorothiobenzoate (3e) and bis(dithio-4-methylbenzoate) (4b) (ca. 9:1), which was deduced from mass and i.r. spectra.

**Preparation of 4-chlorobenzoylthiomercury dithio-4-chlorobenzoate (5c) by method C**

4-Chlorothiobenzoic acid (0.26 g, 0.5 mmol) was added to 0.06 g (0.11 mmol) of mercury bis(dithio-4-methylbenzoate) (4b) in dichloromethane (50 ml) and the mixture was stirred at room temperature for 20 h. The reaction mixture was concentrated to ca. 5 ml. Filtration of the resulting reddish brown crystals, followed by washing with n-hexane and then ethanol, gave 0.05 g (82%) of 4-chlorobenzoylthiomercury dithio-4-chlorobenzoate (5e), which was identified by the spectral data and elemental analyses shown in Table IV.

Reactions of phenylmercury dithiocarboxylates (2) with amines. Typical procedures are described below.

**Reaction of phenylmercury dithio-4-methylbenzoate (2e) with piperidine:** Piperidine (0.18 g, 2 mmol) was added to a solution of phenylmercury dithio-4-methylbenzoate (2e) (0.88 g, 2 mmol) in dichloromethane (40 ml) and the mixture was stirred at room temperature for 1 h. Removal of black precipitates (mercuric sulfide) by a centrifuge and
then evaporation of the solvent in vacuo, followed by recrystallization of the resulting residue (solid) from n-hexane/ether (3:1), gave 0.69 g (92%) of N-pentamethylen-4-methylthio- 
amide. 1H n.m.r. (CDCl3): δ = 1.70 (m, 6H, ring- 
CH3); 2.32 (s, 3H, CH3); 3.50-4.38 (m, 4H, ring- 
CH3); 7.14 (s, 4H, Ar). The melting point, and the 
I.r. and 1H n.m.r. spectra were exactly in agreement 
with those of the authentic sample prepared ac-
   cording to the reaction of dithio-4-methylbenzoic 
acid with piperidine.

Reaction of phenylmercury dithiocarboxylates (2) 
with sodium alkoxides and thioalkoxides.

Reaktion of phenylmercury dithio-4-methylbenzoate 
(2f) with sodium phenoxide: Phenylmercury dithio-
4-methylbenzoate (2f) (0.92 g, 2 mmol) and sodium 
phenoxide (2.4 g, 20 mmol) were refluxed in tetra-
hydrofuran (50 ml) for 1 h. After removal of the 
black precipitate [HgS, 0.09 g (20%)], the solvent 
was evaporated. The residue was redissolved in ether
with sodium sulfate and evaporating the ether
(50 ml) and washed with water (30 ml) three times.
The ether layer was concentrated to 5 ml. A small 
amount of n-hexane was added to the concentrate
4-methoxybenzoate (2e) (0.44 g, 1 mmol) and sodium 
thioethoxide (0.17 g, 2 mmol) were refluxed 
in ethanol (30 ml) for 24 h. After removal of mercuric 
sulfide (0.055 g, 28%) by centrifuge the solvent was 
evaporated. The residue was redissolved in ether
(50 ml) and washed with water (30 ml) three times.
The ether layer was concentrated to 5 ml. A 2:1 mixture (20 ml) of ether and n-hexane was added to the result of the resulting reddish solid was filtrate was concentrated 
to 5 ml and allowed to stand at room temperature
overnight. Filtration of the resulting precipitate
gave 0.04 g (8%) of diphenylmercury as colorless 
crystals. Evaporation of the filtrate in vacuo gave 
0.20 g (43%) of 0-phenyl-thione-4-methoxybenzoate 
(9e), which was identified by comparison of the i.r., 
visible and 1H n.m.r. spectra of the authentic 
sample, prepared by the reaction of bis(4-methoxy-
thiobenzoyl) sulfide with sodium phenoxide.

Reaction of phenylmercury dithio-4-methylbenzoate 
(2e) with sodium thioethoxide: Phenylmercury dithio-
4-methylbenzoate (2e) (0.44 g, 1 mmol) and sodium 
thioethoxide (0.17 g, 2 mmol) were refluxed in 
ethanol (30 ml) for 24 h. After removal of mercuric 
sulfide (0.055 g, 28%) by centrifuge the solvent was 
evaporated. The residue was redissolved in ether
(50 ml) and washed with water (30 ml) three times.
The ether layer was concentrated to 5 ml. A small 
amount of n-hexane was added to the concentrate
and the mixture was allowed to stand at —20 °C
for 5 h. Filtration of the resulting crystals gave 
0.025 g (13%) of diphenylmercury. Evaporation of 
the solvent from the filtrate and silica gel column 
chromatography (n-hexane) of the residue gave 
0.047 g (23%) of ethyl dithio-4-methylbenzoate 
(10b). While, the combined washings (aqueous 
layer) were acidolized with conc. HCl (5 ml) to give 
0.012 g (7%) of dithio-4-methylbenzoic acid. The 
i.r. spectra of the ethyl ester (10b) and dithio-
4-methylbenzoic acid were exactly consistent with 
those of the authentic samples, prepared by the 
known method.

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