A Convenient Preparation of Bis(thioacyl) Sulfides

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Bis(thioacyl) sulfides are prepared in 60–90% yield in a one pot reaction of piperidinium or alkali metal dithiocarboxylates with 2-chloro-1-methylpyridinium iodide at room temperature.

In an earlier work, we reported the isolation of bis(thioacyl) sulfides **4** from the reaction of dithiocarboxylic acid with dicyclohexylcarbodiimide.[1] The sulfides **4** have also been shown to be quite useful as thioacylation reagent.[2,3] We now report a more convenient preparation method of **4** from the reaction of ammonium and alkali metal dithiocarboxylates **1** with 2-chloro-1-methylpyridinium iodide **2**.[4–6]

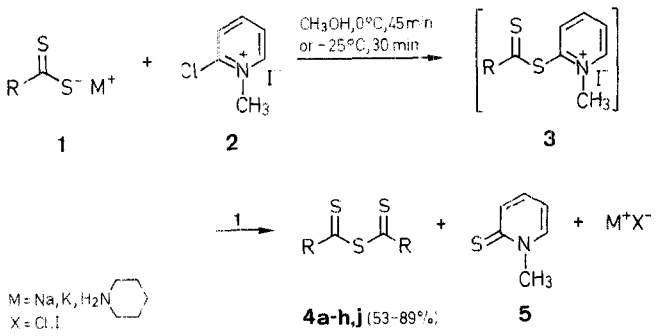

Table. Bis(thioacyl) Sulfides **4** Prepared

Product No.	R	Yield[a] (%)	m.p.[b] (°C)	Molecular Formula[c] or Lit. m.p. (°C)	UV/VIS (CH_2Cl_2)[d] λ_{max}, (log ε)	^{1}H-NMR ($CDCl_3$)[e] δ (ppm)	^{13}C-NMR ($CDCl_3$)[e] δ (ppm)	MS (20 eV, 110 °C)[f] *m/e* (%)
4a	*i*-C_3H_7	75[g]	oil	oil[3]	319, 351, 492, 548	1.34 (d, 12H, CH_3); 3.70 (hept, 2H, CH)	–	206 (M^+, 15); 138 (52); 119 (45); 87 (100)
4b	C_6H_5	83	oil	oil[3]	–	–	224.7 (C=S)	274 (M^+, 6); 121 (100)
4c	2-$CH_3C_6H_4$	83	55–56	$C_{16}H_{14}S_3$ (302.4)	338 (4.46), 368 (4.14), 502 sh (2.46), 616 (2.47)	2.27 (s, 6H, CH_3); 7.0–7.3 (m, 8H_{arom})	20.2 (CH_3), 125.6, 126.9, 130.0, 131.1, 134.6, 147.2 (Ar-ring C) 231.0 (C=S)	302 (M^+, 5); 167 (10); 135 (100)
4d	3-$CH_3C_6H_4$	76	oil	$C_{16}H_{14}S_3$ (302.4)	245, 314, 385, 553, 580 sh, 627	2.37 (s, 6H, CH_3) 7.1–7.8 (s, 8H_{arom})	21.2 (CH_3) 225.1 (C=S)	302 (M^+, 4); 167 (6); 135 (100)
4e	4-$CH_3C_6H_4$	84	80–81	79–80[3]	236 (4.01); 344 (4.43); 559 (2.57); 610–620 sh	2.29 (s, 6H, CH_3); 7.0–7.9 (m, 8H_{arom})	21.6 (CH_3); 127.8, 129.2, 142.6, 144.6, (Ar-ring C); 223.3 (C=S)	302 (M^+, 3); 167 (10); 135 (100)
4f	2,4,6-$(CH_3)_3C_6H_2$	67	136–137	$C_{20}H_{22}S_3$ (358.6)	298 (3.72); 361 (4.12); 500 sh (2.21); 537 (2.21); 585 (2.09); 620 (2.02)	2.21 (s, 12H, CH_3); 2.28 (s, 6H, CH_3); 6.38 (s, 4H_{arom})	19.5 (2,6-CH_3); 21.1 (4-CH_3); 128.7, 132.7, 138.7, 143.1, (Ar-ring C); 231.8 (C=S)	358 (M^+, 2); 195 (0.5); 163 (100)
4g	2-$CH_3OC_6H_4$	62	oil	$C_{16}H_{14}S_3O_2$ (334.4)	250, 318, 385, 531, 580 sh, 616	3.71 (s, 6H, CH_3); 6.5–7.3 (m, 8H_{arom})	55.4 (CH_3O); 110.7, 120.3, 130.3, 132.7, 135.8, 154.1 (Ar-ring C); 228.8 (C=S)	334 (M^+, 4); 183 (6); 151 (100)
4h	4-$CH_3OC_6H_4$	53	70–71	65–66[3]	245 (4.07); 295 sh; 365 (4.51); 548 (2.71); 620 sh	3.81 (s, 6H, CH_3O); 6.7–8.1 (m, 8H_{arom})	55.6 (CH_3O); 113.7, 130.2 138.5, 164.4 (Ar-ring C); 221.0 (C=S)	334 (M^+, 2); 183 (7); 151 (100)
4i	4-ClC_6H_4	–[h]						
4j	1-naphthyl	89	98–99	$C_{22}H_{14}S_3$ (328.2)	258 (4.11); 300 sh; 374 (4.25); 534 (2.59); 597 (2.28); 614 (2.52)	–	124, 124.4, 125.7, 126.2, 127.2, 128.0, 128.4, 130.7, 133.1, 145.1, (Ar-ring C); 230.9 (C=S)	374 (M^+, 5); 203 (3); 171 (100)

[a] Isolated yield.
[b] The solid compounds **4a, e, j** can be recrystallized from dichloromethan/*n*-hexane (1:19), decomposes on melting.
[c] Satisfactory microanalyses obtained: C ±0.23, H ±0.12.
[d] Recorded on a Hitachi 124 and 330 UV spectrophotometers.
[e] Measured on a Jeol JNM-GX-270 NMR spectrometer.
[f] Recorded on a Hitachi RMU-6M Mass spectrometer.
[g] Crude yield.
[h] Bis[4-(chloro)thiobenzoyl] disulfide[13] is obtained as the main product.

The results are summarized in Table 1. The isolated yields of **4** are high except for the 4-methoxy derivative **4h**, which is less crystallizable, and the 4-chloro derivative **4i**, which is thermally very unstable.[7] The starting compounds **1** and **2** are readily obtainable according to literature[8–11] or commercially. The procedures for the preparation of **4** are therefore easy.[12] The structures of **4** were confirmed by comparison of IR, UV, Visible, ^{1}H- and ^{13}C-NMR, mass spectral data and by microanalyses. A number of attempts to isolate the expected intermediates **3**, 2-thioacylthio-1-methylpyridinium iodide, failed.

Bis[2,4,6-(trimethyl)thiobenzoyl] Sulfide (4f); Typical Procedure for 4a–d, f, g:

To a suspension of 2-chloro-1-methylpyridinium iodide (**2**; 256 mg, 1 mmol) in anhydrous methanol (20 ml), a solution of piperidinium 2,4,6-(trimethyl)dithiobenzoate (**1f**[13]; 563 mg, 2 mmol) in the same solvent (60 ml) is added and the mixture is stirred at 0 °C for 45 min. Extraction with *n*-hexane (5 × 50 ml), followed by washing with water (3 × 60 ml), drying with sodium sulfate, and evaporation of the solvent under reduced pressure gives 274 mg (76%) of **4f** as blue violet crystals. Recrystallization from a mixed solvent (20 ml) of *n*-hexane/dichloromethane (20:1) at –25 °C gives chemically pure **4f**; yield: 184 mg (67%).

Bis[4-(methoxy)thiobenzoyl] Sulfide (4h); Typical Procedure for 4e, h, and j:

To a suspension of 2-chloro-1-methylpyridinium iodide (**2**; 256 mg, 1 mmol) in anhydrous methanol (20 ml), a solution of piperidinium 4-(methoxy)dithiobenzoate (**1h**; 534 mg, 2 mmol) in the same solvent (30 ml) is added dropwise and the mixture is stirred at −25 °C for 30 min. Filtration of the resulting precipitate, followed by washing with ice-cold methanol (2 × 2 ml) gives 297 mg (89 %) of **4h** as dark green crystals. Recrystallization from a mixed solvent (100 ml) of *n*-hexane/dichloromethane (20:1) gives chemically pure **4h** as deep violet plates; yield: 157 mg (53 %).

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(4) Mukaiyama, T., Usui, M., Shimada, E., Saigo, K. *Chem. Lett.* **1975**, 1045.
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(6) Saigo, K., Usui, M., Kikuchi, K., Shimada, E., Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1863.
(7) Even below −70 °C, the dark blue solution containing bis[4-(chloro)thiobenzoyl] sulfide **4i** changes, within one minute, to a red solution of bis[4-(chloro)thiobenzoyl] disulfide; yield 46 %; m.p. 171–173 °C (Lit.[13] 173–174 °C).
(8) Kato, S., Mizuta, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3492.
(9) Kato, S., Mitani, T., Mizuta, M. *Int. J. Sulfur Chem.* **1973**, *8*, 359.
(10) Kato, S., Itoh, K., Hattori, R., Mizuta, M., Katada, T. *Z. Naturforsch.* **1978**, *Teil B*, *33*, 976.
(11) Kato, S., Yamada, S., Goto, H., Terashima, K., Mizuta, M. *Z. Naturforsch. Teil B* **1980**, *35*, 458.
(12) Purification of aromatic dithiocarboxylic acids which were used in the previous method[4] is very difficult while the acids cannot be distilled. In addition, determination of the acids by titration using alcoholic potassium hydroxide solution is unpractical, because of interference of their deep red or violet color.
(13) Kato, S., Kato, T., Kataoka, T., Mizuata, M. *Int. J. Sulfur Chem.* **1973**, *8*, 437.