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A Convenient Synthesis of Diacyl Sulfides Using a Novel Sulfur Transfer Reagent

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ABSTRACT: *Various diacyl sulfides were synthesized by reaction of acyl chlorides with LiAlHSH. Reaction of glutaryl chloride with LiAlHSH afforded glutaric thioanhydride.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:633–635, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10217

INTRODUCTION

Some methods for synthesizing diacyl sulfides have been reported [1]. These methods, however, have some disadvantages, such as the use of expensive reagent, the limited availability of the starting materials, severe conditions, and stench and toxicity of the reagents. A more convenient method is required to overcome these disadvantages. Recently, we developed a novel selenating reagent, LiAlHSeH [2], which is generated by stirring selenium powder and $LiAlH_4$ in THF. This reagent is useful for preparing a variety of different selenium-containing compounds [3]. However, application of the same procedure to the sulfur atom, while it seems reasonable, has been been scarcely demonstrated [4]. In the present study, we investigated the preparation of various diacyl sulfides from the corresponding acyl chlorides **1** using LiAlHSH **2**. Herein, we report a new method for preparation of diacyl sulfides **3**, in which we have confirmed the usefulness of LiAlHSH as the reagent for the introduction of sulfur.

RESULTS AND DISCUSSION

Diacyl sulfides **3** were conveniently prepared according to the method shown in Scheme 1. The reaction of 2 equiv. of acyl chlorides **1** with LiAlHSH **2** gave diacyl sulfides in good yields (Table 1). The quantitative formation of low molecular weight products, **3h–3j**, was confirmed by TLC analysis. However, they were lost considerably during concentration process because they were volatile. Both aromatic and aliphatic diacyl sulfides **3** were obtained in excellent yields (Table 1). Moreover, we investigated the reaction of glutaryl chloride with LiAlHSH **2** (Scheme 2). Glutaric thioanhydride **4** was obtained by the reaction in 89% yield.

For the synthesis of diacyl selenides and cyclic selenoanhydrides using LiAlHSeH, the reactions were carried out at 0°C for 2 h in order to avoid decomposition of the resulting selenium-containing compounds [3c]. In contrast, in the present procedure, higher temperatures and longer reaction times could be used because of the stability of LiAlHSH **2** and the products. In conclusion, the synthesis using LiAlHSH **2** can give diacyl sulfides **3** and glutaric thioanhydride **4** in good yields by mere stirring of elementary sulfur and lithium aluminum hydride in THF. It was confirmed that LiAlHSH **2** behaves like LiAlHSeH, and represents an excellent reagent for the introduction of sulfur. The present reaction can be carried out under easier conditions without the use of foul smelling and toxic materials, such as H_2S or thiocarboxylic acid.

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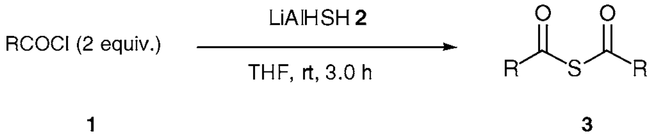
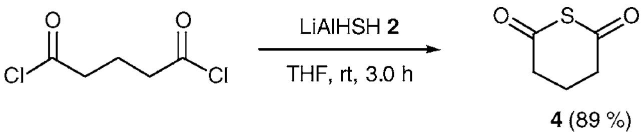


SCHEME 1



SCHEME 2

EXPERIMENTAL

General

Melting points were determined by use of a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer 1600 spectrometer. ^{1}H and ^{13}C spectra were recorded on a JEOL JNM-α400 spectrometer. Mass spectra were obtained on a Shimadzu 9020-DF mass spectrometer. Tetrahydrofuran was distilled from sodium-benzophenone and immediately used.

*Preparation of LiAlHSH **2***: LiAlHSH **2** was prepared in a method similar to that previously reported [2]. To a suspension of sulfur powder (0.80 g, 10.0 mmol) in dry THF (100 ml) was added lithium aluminum hydride (0.38 g, 10.0 mmol) at room temperature under an argon atmosphere. The mixture was stirred for 30 min. The yellow sulfur powder was consumed in less than 10 min. The reaction mixture became a heterogeneous grayish suspension. Compound **2** formed in situ was then ready for further reaction.

*Dibenzoyl Sulfide (**3a**)*

Benzoyl chloride (0.843 g, 6.0 mmol) was added to the suspension of LiAlHSH **2** (3.0 mmol), prepared as described above. The reaction mixture was stirred at room temperature for 3 h. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with dichloromethane:*n*-hexane (1:2) as the eluent to give 0.614 g (84%) **3a** as a white powder. Mp: 102.3–103.8°C; ^{1}H NMR ($CDCl_3$) δ 7.43 (4H, t, $J = 7.8$ Hz, Ar), 7.57 (2H, t, $J = 7.8$ Hz, Ar), 7.88 (4H, d, $J = 7.8$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 127.4, 128.0, 128.7, 134.4, 190.1; IR (KBr): 1718, 1671 cm^{-1}; MS (CI): $m/z = 243$ [$M^+ + 1$] [3d].

TABLE 1 Synthesis of Diacyl Sulfides **3**

R	Yield (%) of **3**	R	Yield (%) of **3**
C_6H_5	**3a** 85	C_2H_5	**3h** 5.4[a]
2-$CH_3C_6H_4$	**3b** 78	C_3H_7	**3i** 9.9[a]
3-$CH_3C_6H_4$	**3c** 89	$(CH_3)_2CH$	**3j** 6.6[a]
4-$CH_3C_6H_4$	**3d** 85	C_5H_{11}	**3k** 81
4-$CH_3OC_6H_4$	**3e** 97	$C_{17}H_{35}$	**3l** 84
4-ClC_6H_4	**3f** 77	$C_6H_5OCH_2$	**3m** 79
4-$NO_2C_6H_4$	**3g** 79		

[a] It was confirmed by TLC analysis that product was formed quantitatively.

*Bis(2-methylbenzoyl) Sulfide (**3b**) [3d,5]*

White powder; Mp: 52.7–53.7°C; ^{1}H NMR ($CDCl_3$) δ 2.40 (6H, s, CH_3), 7.11 (4H, m, Ar), 7.26 (2H, d, $J = 7.6$ Hz, Ar), 7.73 (2H, d, $J = 7.6$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 20.7, 125.7, 129.4, 131.7, 132.5, 136.5, 138.3, 187.1; IR (KBr): 1733, 1677 cm^{-1}; MS (CI): $m/z = 271$ [$M^+ + 1$].

*Bis(3-methylbenzoyl) Sulfide (**3c**) [3d]*

White powder; Mp: 35.0–35.8°C; ^{1}H NMR ($CDCl_3$) δ 2.25 (6H, s, CH_3), 7.20 (2H, t, $J = 7.6$ Hz, Ar), 7.26 (2H, d, $J = 7.6$ Hz, Ar), 7.63 (2H, s, Ar), 7.66 (2H, d, $J = 7.6$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 21.0, 125.5, 128.5, 135.0, 136.8, 138.6, 185.0; IR (KBr): 1714, 1662 cm^{-1}; MS (CI): $m/z = 271$ [$M^+ + 1$].

*Bis(4-methylbenzoyl) Sulfide (**3d**) [3d]*

White powder; Mp: 68.5–70.0°C; ^{1}H NMR ($CDCl_3$) δ 2.04 (6H, s, CH_3), 7.26 (4H, d, $J = 8.4$ Hz, Ar), 7.90 (4H, d, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 21.7, 128.5, 129.6, 134.5, 145.5, 184.8; IR (KBr): 1715 cm^{-1}; MS (CI): $m/z = 271$ [$M^+ + 1$].

*Bis(4-methoxybenzoyl) Sulfide (**3e**) [3d]*

White powder; Mp: 81.7–82.8°C; ^{1}H NMR ($CDCl_3$) δ 3.88 (6H, s, CH_3), 6.94 (4H, d, $J = 8.8$ Hz, Ar), 8.00 (4H, d, $J = 8.8$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 55.6, 114.0, 129.9, 130.9, 164.5, 183.8; IR (KBr): 1716, 1654 cm^{-1}; MS (CI): $m/z = 303$ [$M^+ + 1$].

*Bis(4-chlorobenzoyl) Sulfide (**3f**) [3d]*

White powder; Mp: 72.2–73.2°C; ^{1}H NMR ($CDCl_3$) δ 7.48 (4H, d, $J = 8.4$ Hz, Ar), 7.95 (4H, d, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 129.3, 129.8, 135.1, 141.2, 183.6; IR (KBr): 1713, 1678 cm^{-1}; MS (CI): $m/z = 311$ [$M^+ + 1$].

*Bis(4-nitrobenzoyl) Sulfide (**3g**) [3d]*

White powder; Mp: 167.7–169.0°C; ^{1}H NMR ($CDCl_3$) δ 8.17 (4H, d, $J = 8.0$ Hz, Ar), 8.33 (4H, d, $J = 8.0$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 123.7, 130.7, 136.4, 150.0, 192.4; IR (KBr): 1702 cm^{-1}; MS (CI): $m/z = 333$ [M$^+$ + 1].

*Dipropionyl Sulfide (**3h**) [3d,5]*

Yellow liquid; ^{1}H NMR ($CDCl_3$) δ 1.15 (6H, t, $J = 7.4$ Hz, CH_3), 2.83 (4H, q, $J = 7.4$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 1.97, 41.7, 194.7; IR (neat): 1694 cm^{-1}; MS (CI): $m/z = 147$ [M$^+$ + 1].

*Dibutyryl Sulfide (**3i**) [3d]*

Yellow liquid; ^{1}H NMR ($CDCl_3$) δ 0.90 (6H, t, $J = 7.4$ Hz, CH_3), 1.63 (4H, m, CH_2), 2.66 (4H, t, $J = 7.4$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.2, 18.1, 47.7, 194.6; IR (neat): 1705 cm^{-1}; MS (CI): $m/z = 175$ [M$^+$ + 1].

*Bis(2-methylpropionyl) Sulfide (**3j**) [3d,5]*

Yellow liquid; ^{1}H NMR ($CDCl_3$) δ 1.21 (12H, d, $J = 6.8$ Hz, CH_3), 2.89 (2H, m, CH); ^{13}C NMR ($CDCl_3$) δ 18.6, 44.9, 198.2; IR (neat): 1705 cm^{-1}; MS (CI): $m/z = 175$ [M$^+$ + 1].

*Di-n-hexanoyl Sulfide (**3k**)*

Colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.90 (6H, t, $J = 7.2$ Hz, CH_3), 1.33 (4H, m, CH_2), 1.67 (8H, m, CH_2), 2.75 (4H, t, $J = 7.4$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.2, 24.3, 30.9, 45.9, 194.8; IR (neat): 1764, 1713 cm^{-1}; MS (CI): $m/z = 231$ [M$^+$ + 1]; HRMS $m/z = 230.1335$ for $C_{12}H_{22}O_2S$: found 230.1332.

*Distearoyl Sulfide (**3l**) [3d]*

White powder; Mp: 65.0–65.5°C; ^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, $J = 6.8$ Hz, CH_3), 1.26 (56H, s, CH_2), 1.66 (4H, m, CH_2), 2.74 (4H, t, $J = 7.4$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.8, 29.2, 29.3, 29.5, 29.7, 31.9, 46.0, 195.5; IR (KBr): 1768 cm^{-1}; MS (CI): $m/z = 567$ [M$^+$ + 1].

*Bis(phenoxyacetyl) Sulfide (**3m**)*

Yellow liquid; ^{1}H NMR ($CDCl_3$) δ 4.59 (4H, s, CH_2), 6.92 (4H, d, $J = 8.4$ Hz, Ar), 7.02 (2H, d, $J = 8.4$ Hz, Ar), 7.28 (4H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 114.3, 121.0, 121.5, 129.3, 172.4, 199.7; IR (neat): 1711 cm^{-1}; MS (CI): $m/z = 303$ [M$^+$ + 1]); HRMS $m/z = 302.0609$ for $C_{16}H_{14}O_4S$: found 302.0615.

*Glutaric Thioanhydride (**4**) [6]*

Yellow liquid; ^{1}H NMR ($CDCl_3$) δ 2.09 (2H, m, CH_2), 2.74 (4H, t, $J = 6.0$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 18.4, 40.4, 197.4; IR (neat): 1694 cm^{-1}; MS (CI): $m/z = 131$ [M$^+$ + 1].

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