

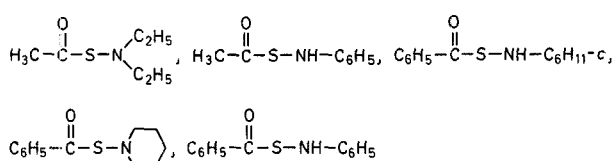
A Convenient, High-Yield Preparation of Novel Unsymmetrical Bis[acyl] Disulfides via *N*-(Aroylthio)-succinimides

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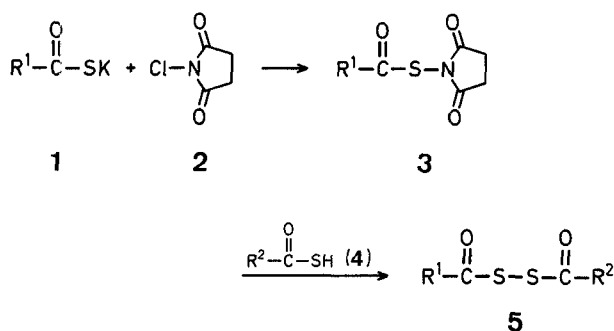
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For the preparation of unsymmetrical bis[acyl] disulfides (**5**; R^2 = alkyl, aryl), which have not been described in the literature, *N*-aroysulfeneamides, $R^1C(O)SN(R^2)_2$, are considered to be an effective starting material. To our knowledge, however, only seven stable *N*-aroysulfeneamides of the structure, $RC(O)SNH_2$, have been reported¹.

Prior to 1972 the following unstable compounds had been described^{2,3}:



In the course of our preparative study of **5**, the reaction of these stable sulfeneamides with aromatic thio acids has been found to afford acylamides as a by-product together with the desired **5**. In order to prevent the formation of these acylamides, we have investigated the preparation of **5** via the previously unknown *N*-(aroylthio)-succinimides (**3**), instead of $RC(O)SNH_2$.



When potassium arenethioates **1** are reacted with *N*-chlorosuccinimide (**2**) in acetonitrile, *N*-(aroylthio)-succinimides (**3**) are obtained in high yields (Table 1). Symmetrical bis[aroyl] disulfides formed as by-products are removed readily by extraction with *n*-pentane using a Soxhlet extractor. Three other preparations of **3** have also been investigated using various solvents (ether, chloroform, dichloromethane, ethyl acetate, tetrahydrofuran and dimethylformamide): (a) triethylammonium arenethioates with **2**, (b) aromatic thio acids with **2** in the presence of tertiary amines, (c) potassium arenethioates **1** with *N*-bromosuccinimide. These methods, however, afforded over 60% of symmetrical bis[aroyl] disulfides.

N-(Aroylthio)-succinimides (**3**) obtained are fairly stable both in the solid state and in solution. For example, no change in **3b** was observed even on refluxing in benzene for a day. The reaction of **3b** with benzylmercaptan does not occur on refluxing in benzene. However, compounds **3** have been found to react readily with thio acids **4** at room

Table 1. *N*-(Aroylthio)-succinimides 3

Product No.	R ¹	Yield [%]	m.p. [°C]	Molecular formula ^a	I.R. (KBr) $\nu_{C=O}$ [cm ⁻¹]	U.V. (CH ₂ Cl ₂) λ_{max} [nm] (log ϵ)	¹ H-N.M.R. (CDCl ₃) δ [ppm]
3a	C ₆ H ₅	72	115–116°	C ₁₁ H ₉ NO ₃ S (235.3)	1682, 1730	246 (4.09); 256 (4.06)	2.98 (s, 4H, CH ₂); 7.15–8.00 (m, 5H _{arom})
3b	3-H ₃ C–C ₆ H ₄	74	61–63°	C ₁₂ H ₁₁ NO ₃ S (249.3)	1690, 1725	249 (4.10); 258 (4.09)	3.02 (s, 4H, CH ₂); 7.20–7.85 (m, 4H _{arom})
3c	4-H ₃ C–C ₆ H ₄	81	159–160°	C ₁₂ H ₁₁ NO ₃ S (249.3)	1683, 1730	266 (4.25)	2.40 (s, 3H, CH ₃); 2.98 (s, 4H, CH ₂); 7.10–7.90 (q, 4H _{arom})
3d	4-H ₃ CO–C ₆ H ₄	69	124–126°	C ₁₂ H ₁₁ NO ₄ S (265.3)	1680, 1735	288 (4.24)	2.98 (s, 4H, CH ₂); 3.82 (s, 3H, CH ₃ O); 6.75–7.95 (q, 4H _{arom})
3e	3-Cl–C ₆ H ₄	78	82–84°	C ₁₁ H ₈ ClNO ₃ S (269.7)	1720	248 (4.14)	3.00 (s, 4H, CH ₂); 7.20–7.90 (m, 4H _{arom})
3f	4-Cl–C ₆ H ₄	76	113–116°	C ₁₁ H ₈ ClNO ₃ S (269.7)	1682, 1720	265 (4.26)	2.98 (s, 4H, CH ₂); 7.30–7.95 (q, 4H _{arom})

^a The microanalyses were in satisfactory agreement with calculated values (C \pm 0.31, H \pm 0.14, N \pm 0.23, S \pm 0.31).

Table 2. Unsymmetrical Bis[acyl] Disulfides 5

Product No.	R ¹	R ²	Yield [%]	m.p. [°C]	Molecular formula ^a	I.R. (KBr) $\nu_{C=O}$ [cm ⁻¹]	U.V. (CH ₂ Cl ₂) λ_{max} [nm] (log ϵ)	¹ H-N.M.R. (CDCl ₃) δ [ppm]
5a	C ₆ H ₅	4-H ₃ C–C ₆ H ₄	98	89–90.5°	C ₁₅ H ₁₂ S ₂ O ₂ (288.37)	1688, 1702	272 (4.42)	2.36 (s, 3H, CH ₃); 7.10–8.20 (m, 9H _{arom})
5b	4-H ₃ C–C ₆ H ₄	4-Cl–C ₆ H ₄	95	113–115°	C ₁₅ H ₁₁ ClS ₂ O ₂ (322.82)	1686, 1705	276 (4.48)	2.33 (s, 3H, CH ₃); 7.05–8.15 (m, 8H _{arom})
5c	4-Cl–C ₆ H ₄	C ₆ H ₅	98	89–91°	C ₁₄ H ₉ ClS ₂ O ₂ (308.79)	1680, 1690	263 (4.37)	7.32–8.35 (m, 9H _{arom})
5d	4-H ₃ CO–C ₆ H ₄	4-Cl–C ₆ H ₄	93	88–90°	C ₁₅ H ₁₁ ClS ₂ O ₃ (338.82)	1671, 1692	261 (4.11)	3.88 (s, 3H, CH ₃); 7.84–8.30 (m, 8H _{arom})
5e	4-H ₃ C–C ₆ H ₄	H ₃ C	96	66–69°	C ₁₀ H ₁₀ S ₂ O ₂ (236.30)	1692, 1734	—	2.32 (s, 3H, CH ₃); 2.38 (s, 3H, CH ₃ CO); 7.10–8.15 (m, 4H _{arom})

^a The microanalyses were in satisfactory agreement with calculated values (C \pm 0.16, H \pm 0.33, S \pm 0.19); exception 5e: C +0.92, S –0.69.

temperature to give the expected unsymmetrical bis[acyl] disulfides (5) in good yield. Yields and physical properties are listed in Table 2. The unsymmetrical disulfides (5) obtained are very stable thermally and to moisture.

N-(4-Methylbenzoylthio)-succinimide (3b):

To a suspension of potassium 4-methylbenzenethioate (3.8 g, 20 mmol) in acetonitrile (40 ml) is added dropwise a solution of *N*-chlorosuccinimide (2.7 g, 20 mmol) in the same solvent (40 ml). The reaction mixture is stirred at room temperature for 2.5 h. After evaporation of acetonitrile in vacuo, the resulting residue is extracted with chloroform (3 \times 30 ml). Washing of the combined extracts with water and subsequent evaporation of the solvent under reduced pressure gives the crude solid 3b. Further extraction of the solid with *n*-pentane using a Soxhlet extractor overnight and recrystallization from dichloromethane of the resulting insoluble solid gives 3b as colorless crystals; yield: 2.8 g (57%).

Benzoyl 4-Methylbenzoyl Disulfide (5a):

A solution of benzenethioic acid (4; R² = C₆H₅; 0.31 g, 2.0 mmol) in tetrahydrofuran (5 ml) is added to *N*-(4-methylbenzoylthio)-succinimide (3b; 0.5 g, 2 mmol) in the same solvent (20 ml) and the reaction mixture is stirred at room temperature for 3 h. After evaporation of the solvent, the resulting residue is extracted with ether (3 \times 20 ml). The combined extracts are washed with water, followed by drying with anhydrous sodium sulfate, and by evaporation of the solvent. Recrystallization of the resulting solid from pe-

troleum ether (b.p. 40–45 °C) gives colorless crystals of 5a; yield: 424 mg (82%).

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