A Convenient Preparation of Acylsulfenyl Chlorides

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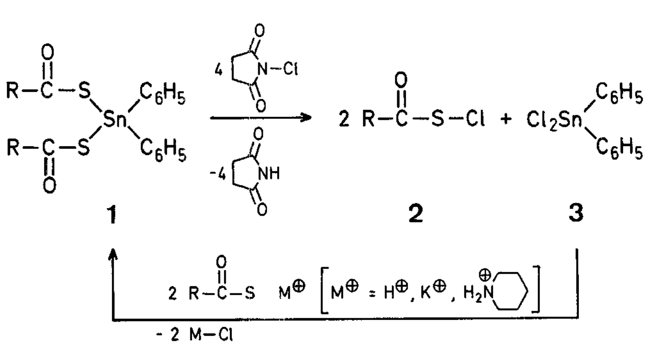
Acylsulfenyl chlorides **2** are considered as effective electrophilic thiocarboxylating reagens. To our knowledge, only acetylsulfenyl chloride[1] has been described in the literature[2]. However, no spectral data have been reported. We now describe a general, convenient preparation of the acylsulfenyl chlorides **2** (Table) by reaction of diphenyltin bis[thiocarboxylates] **1** with *N*-chlorosuccinimide (NCS)[3].

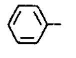
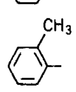
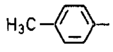
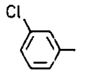
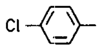
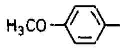


The diphenyltin dichloride (**3**) simultaneously formed can be reconverted to the educt **1** by reaction with thiocarboxylic acids or potassium and piperidinium thiocarboxylates, respectively[4].

The acylsulfenyl chlorides **2** were characterized by spectral data and microanalyses. For example, the mass spectrum of **2f** shows the molecular ion at $m/e = 203$. The I.R. spectrum exhibits a characteristic absorption band at $\nu = 1704$ cm^{-1} assigned to the carbonyl vibration. Its position differs distinctly from that of the corresponding band of the educt **1** (1604 cm^{-1}) and from that of bis[2-methoxybenzoyl] disulfide (1670 cm^{-1}), a possible decomposition product.

The acylsulfenyl chlorides **2** obtained are stable for 4-5 h at room temperature both in the solid state and dissolved in *n*-hexane but they are gradually decomposed by moisture and in protic solvents.

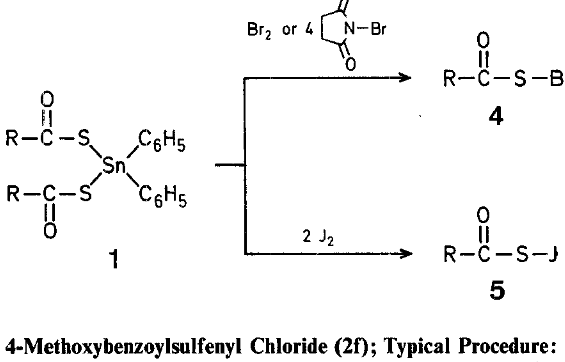
Table. Acylsulfenyl Chlorides **2** prepared

Product No.	R	Yield[a] [%]	m.p. [°C]	Molecular[b] formula	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]
2a		40	20-22.5°	C_7H_5ClSO (172.6)	1688
2b		41	oil	C_8H_7ClSO (186.7)	1706
2c		43	oil	C_8H_7ClSO (186.7)	1700
2d		50	47-49°	$C_7H_4Cl_2SO$ (207.1)	1694
2e		55	43-45°	$C_7H_4Cl_2SO$ (207.1)	1699
2f		see experimental procedure			
2g	n-$C_{17}H_{35}$	53	41-43°	$C_{18}H_{35}ClSO$ (335.0)	1723

[a] Yield of isolated product.

[b] Satisfactory microanalyses obtained: C ±0.39, H ±0.25, except for **2a** and **2b**, which contain a small amount of *n*-hexane.

Analogously, diphenyltin bis[thiocarboxylates] **1** are also suitable for the preparation of both acylsulfenyl bromides **4**[5] and iodides **5**[6].



4-Methoxybenzoylsulfenyl Chloride (2f); Typical Procedure:

To a solution of diphenyltin bis[4-methoxythiobenzoate][4] (**1f**; 0.27 g, 0.44 mmol) in dichloromethane/trichloromethane (2/1; 10 ml), *N*-chlorosuccinimide (0.26 g, 1.95 mmol) is added. The mixture is stirred for 15 min at −20 °C. After evaporation of the solvent under reduced pressure, the residue is dissolved in *n*-hexane (15 ml), the insoluble solid[7] is filtered off, and the filtrate chilled below −70 °C. Filtration of the resulting precipitate gives chemically pure **2f** as pale yellow crystals; yield 0.10 g (57%); m.p. 38-39 °C.

$C_8H_7ClSO_2$	calc.	C 36.55	H 2.88
(202.7)	found	36.62	2.94

M.S. (10 eV): m/e 203 (M^+).

I.R. (KBr): $\nu = 1704$ cm^{-1} (C=O).

Benzoylsulfenyl Bromide (4a); Typical Procedure:

N-Bromosuccinimide (0.36 g, 2 mmol) is added to a solution of diphenyltin bis[thiobenzoate] (**1a**; 0.27 g, 0.5 mmol) in trichloromethane/dichloromethane (3/1; 20 ml) at 0 °C and the mixture is stirred at this temperature for 30 min. The solvent is then evaporated under reduced pressure and the resulting residue is dissolved in *n*-hexane (~20 ml). After removal of the insoluble solid by filtration, the filtrate is concentrated to ~5 ml under reduced pressure, and cooled to −78 °C. Filtration of the resulting solid affords chemically pure **4a** as pale yellow needles; yield 0.09 g (83%); m.p. 52-54 °C. The structure of **4a** was established by comparison of m.p. and the I.R. spectrum of with those of an authentic sample[4].

I.R. (KBr): $\nu = 1686$ cm^{-1} (C=O).

Benzoylsulfenyl iodide (5a); Typical Procedure:

A solution of iodine (0.75 mmol) in *n*-hexane is added to a suspension of diphenyltin bis[thiobenzoate] (**1a**; 0.21 g, 0.37 mmol) in the same solvent (10 ml) and the mixture is stirred for 30 min at room temperature, followed by chilling at −78 °C for ~ 10 sec. The mixture containing black and yellow precipitates is gradually warmed to room temperature with stirring (the black precipitate is dissolved). Filtration of the yellow solid and subsequent recrystallization from a small amount of *n*-hexane gives **5a** as yellow crystals; yield: 0.089 g (45%); m.p. 45–47 °C (dec). The structure of **5a** was established by comparison of m.p. and the I.R. spectrum of with those of an authentic sample[5].

I.R. (KBr): $\nu = 1672$ cm^{-1} (C=O).

Received: April 5, 1983

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[1] H. Böhme, M. Clement, *Justus Liebigs Ann. Chem.* **576**, 61 (1952).

[2] According to Ref.[1], a number of attempts to prepare acylsulfenyl chlorides, especially aromatic substituted derivatives (**2**, R = aryl) by reaction of bis[acyl] sulfides with sulfuryl chloride were unsuccessful due to difficulties with the purification.

[3] A number of the starting thioates such as trimethyl- and triphenyltin thioates, phenyltin tris[thioates], tin tetrakis[thioates], diphenylgermyl bis[thioates], trimethyl- and triphenylgermyl thioates, phenylmercury thioates, and mercury bis[thioates], etc. have been examined. However, the reactions of these thioates with chlorine or NCS give products which are difficult to purify.

[4] Diphenyltin bis[thiocarboxylates] were prepared by the stoichiometric reaction of diphenyltin dichloride with piperidinium or potassium thiocarboxylates. For the reaction conditions, see: S. Kato, W. Akada, M. Mizuta, Y. Ishii, *Bull. Chem. Soc. Jpn.* **46**, 244 (1973).

[5] S. Kato, K. Miyagawa, S. Kawabata, M. Ishida, *Synthesis* **1982**, 1013.

[6] S. Kato, E. Hattori, M. Mizuta, M. Ishida, *Angew. Chem.* **94**, 148 (1982); *Angew. Chem. Int. Ed. Engl.* **21**, 150 (1982).

[7] The detailed composition of this solid is ambiguous, though diphenyltin dichloride and succinimide could be detected by I.R. and ^{1}H-N.M.R. spectra.