A Convenient Preparation of Aromatic Acylsulfenyl Bromides and Iodides via Silver Thiocarboxylates

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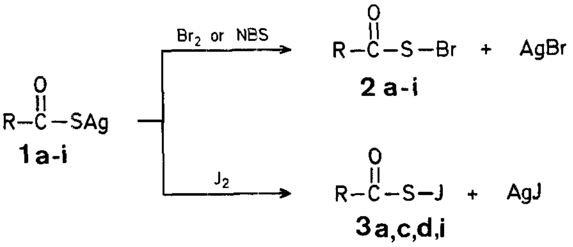
The reaction of silver carboxylates with bromine, leading to alkyl bromide, is well known as the Hunsdiecker reaction and has been investigated extensively[1]. However, no study on the reaction of sulfur analogues such as R—CO—SAg and R—CS—SAg has been described in the literature. In the course of a study concerning dry metallic salts of thio- and dithiocarboxylic acids[2], it has been found that silver thiocarboxylates **1** (Table 1) readily react with bromine, *N*-bromosuccinimide and iodine to give novel acylsulfenyl bromides **2** and iodides **3** in moderate yields (Table 2).



The procedures are very easy and the starting silver thiocarboxylates **1** can be obtained in almost quantitative yields from the aromatic thio acids and silver nitrate, which are readily available. This method is, however, limited to the aromatic derivatives, because of the extreme instability of the starting aliphatic silver thiocarboxylates (**1**, R = aliphatic)[3]. The structures of **2g-i** and **3i** were established by the spectral data and microanalyses and of **2a-f** and **3i** were confirmed by comparison of I.R., U.V.-visible, and ^{1}H-N.M.R. spectra with those of the authentic samples, which were recently isolated in this laboratory[4]. Under these reaction conditions, no aryl bromides and iodides were detected.

Silver 4-Methylthiobenzoate (1c); Typical Procedure:

A solution of piperidinium 4-methylthiobenzoate (1.29 g, 5.5 mmol) in methanol (10 ml) is added to solution of silver nitrate (0.85 g, 5 mmol) in water (10 ml) and the mixture is stirred for 1 h at − 10 to 0 °C. Filtration of the resulting solid, followed by washing with a small amount

Table 1. Compounds **1**, **2**, and **3** prepared

Silver Thiocarboxylate **1**						Acylsulfenyl Halide **2** or **3**					
No.	R	Yield[a] [%]	m.p. [°C]	Molecular formula[b]	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]	No.	X	Yield [%][a] (Method)	m.p. [°C]	Molecular formula[b] or Lit. m.p. [°C]	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]
1a	C_6H_5	~100 (61)	136-138° (dec)	C_6H_5AgOS (245.0)	1605, 1590, 1575	**2a**	Br	57 (A) 61 (B)	37-38° (dec)	37-39° [4b]	— [4b]
						3a	J	60	45-46° (dec)	45-46° [4a]	— [4a]
1b	3-H_3C—C_6H_4	~100	139-142° (dec)	C_8H_7AgOS (259.1)	1613, 1595, 1576 (sh)	**2b**	Br	26 (A) 43 (B)	44-45° (dec)	45-46° [4b]	— [4b]
1c	4-H_3C—C_6H_4	96 (32)	149-152° (dec)	C_8H_7AgOS (259.1)	1608, 1595, 1570	**2c**	Br	36 (A) 61 (B)	30-32° (dec)	30-31° [4b]	— [4b]
						3c	J	40	40° (dec)	40° (dec) [4a]	— [4a]
1d	4-H_3CO—C_6H_4	88[c]	144.5-146° (dec)	$C_8H_7AgO_2S$ (275.1)	1603, 1590, 1565	**2d**	Br	9 (A) 40 (C)[d]	40-41° (dec)	40-41° [4b]	— [4b]
						3d	J	20	31-32° (dec)	32° [4a]	— [4a]
1e	3-Cl—C_6H_4	88	156-158° (dec)	$C_7H_4AgClOS$ (279.5)	1604, 1585, 1566	**2e**	Br	50 (A) 71 (B)	78-80° (dec)	78-79° [4b]	— [4b]
1f	4-Cl—C_6H_4	90	108-110° (dec)	$C_7H_4AgClOS$ (279.5)	1595, 1560	**2f**	Br	24 (B)	50-51° (dec)	49-51° [4b]	— [4b]
1g	2-O_2N—C_6H_4	86	125-127° (dec)	$C_7H_4AgNO_3S$ (290.0)	1567	**2g**	Br	8 (B)	93-95°[c] (dec)	$C_7H_4BrNO_3S$ (262.1)	1710
1h	3-O_2N—C_6H_4	~100	126.5-128° (dec)	$C_7H_4AgNO_3S$ (290.0)	1609, 1605	**2h**	Br	4 (B)	102-104° (dec)	$C_7H_4BrNO_3S$ (262.1)	1692
1i	4-O_2N—C_6H_4	92	130-135° (dec)	$C_7H_4AgNO_3S$ (290.0)	1598	**2i**	Br	23 (B)	117-120° (dec)	$C_7H_4BrNO_3S$ (262.1)	1687
						3i	J	12	—	$C_7H_4JNO_3S$ (309.1)	1685

[a] Yield of isolated product; value in brackets from reaction of thiocarboxylic acid with silver nitrate.
[b] Satisfactory microanalyses obtained: C ±0.40, H ±0.08; exceptions: **1i** (C −1.06), **2g** (C −0.94), **3i** (C −0.64).
[c] Reaction temperature −70 °C.
[d] Reaction with *N*-bromosuccinimide in dichloromethane.

of methanol, and by drying in vacuo, gives pure **1c** as a slight yellow microfine solid; yield: 1.25 g (96%); m.p. 149-152 °C (dec).

C_8H_7AgSO	calc.	C 37.09	H 2.72
(259.1)	found	36.99	2.78

I.R. (Nujol): ν = 1608, 1595, 1570 cm^{-1} (C=O).

3-Chlorobenzoylsulfenyl Bromide (2e); Typical Procedure using Bromine (A):

To a suspension of silver 3-chlorothiobenzoate (**1e**; 0.14 g, 0.5 mmol) in dichloromethane (10 ml), a solution of bromine (0.4 mmol) in the same solvent (4 ml) is added dropwise at 0 °C and the mixture is stirred for 30 min. After removal of solid silver bromide, the solvent is evaporated under reduced pressure below 10 °C. The resulting residue is recrystallized from *n*-hexane to give **2e** as pale yellow needles; yield: 0.063 g (50%); m.p. 78-80 °C (dec.) (Ref.[4b], m.p. 78-79 °C).

I.R. (KBr): ν = 1689 cm^{-1} (C=O) [Ref.[4b], 1685 cm^{-1}].

3-Chlorobenzoylsulfenyl Bromide (2e); Typical Procedure using *N*-Bromosuccinimide (B):

To a suspension of silver 3-chlorothiobenzoate (**1e**; 0.84 g, 3 mmol) in chloroform (20 ml), a solution of *N*-bromosuccinimide (1.068 g, 6 mmol) in the same solvent (10 ml) is added and the mixture is stirred for 30 min at 0 °C. After removal of solids (silver bromide and succinimide), the solvent is evaporated under reduced pressure below 5 °C. Recrystallization of the resulting residue from *n*-hexane gives **2e**; yield: 0.535 g (71%).

4-Methylbenzoylsulfenyl Iodide (3c); Typical Procedure using Iodine:

To a suspension of silver 4-methylthiobenzoate (**1c**; 0.13 g, 0.5 mmol) in dichloromethane/methanol (7:3; 20 ml), iodine (0.4 mmol) in dichloromethane (5 ml) is added and the mixture is stirred for 30 min at room temperature. After removal of the solid silver iodide by filtration, the solvent is evaporated under reduced pressure below 10 °C. Recrystallization of the resulting solid residue from *n*-hexane gives **3c** as pale yellow microfine needles; yield 0.058 g (40%); m.p. 40 °C (dec.) [Ref.[4a], m.p. 40 °C (dec.)].

I.R. (KBr): ν = 1650 cm^{-1} (C=O) [Ref.[4a], ν = 1650 cm^{-1}].

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