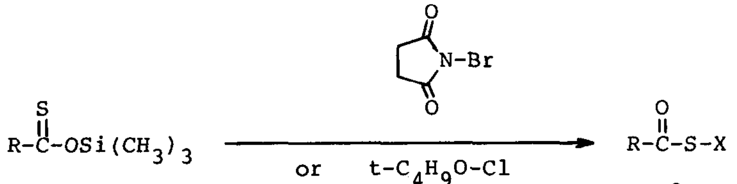
Tetrahedron Letters,Vol.27,No.38,pp 4593-4594,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

THIOPHILIC HALOGENATION OF THIOCARBOXYLIC ACID O-SILYL ESTERS. A FACILE PREPARATION OF ACYLSULFENYL HALIDES

Toshiaki Murai, Shigeru Oida, Shi Min, and Shinzi Kato*
Department of Chemistry, Faculty of Engineering
Gifu University, Yanagido, Gifu 501-11, Japan

Summary: Halogenation of thiocarboxylic acid O-silyl esters gave acylsulfenyl halides in high yields, involving a thiophilic attack of halogen ion on the sulfur atom of thiocarbonyl group. Aliphatic acylsulfenyl bromide was isolated for the first time.

In spite of the easy availability of thiocarboxylic acid O-esters, relatively little attention has been received on these compounds.[1] Our recent efforts to prepare electrophilic thiocarboxylating reagents, acylsulfenyl halides,[2] have led us to utilize these compounds as starting materials. However, it has been reported that halogenation of these compounds occurred with desulfurization.[3] Here we describe the unprecedented thiophilic halogenation of thiocarboxylic acid O-silyl esters (**1**)[4] leading to acylsulfenyl halides (Eq. 1). Moreover, the first isolation of aliphatic acylsulfenyl bromide was achieved by using this method.

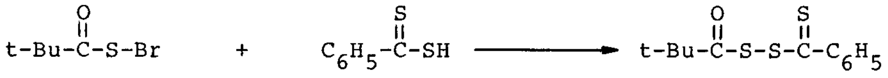

$$R-\overset{S}{\overset{\|}{C}}-OSi(CH_3)_3 \xrightarrow[\text{or}\quad t-C_4H_9O-Cl]{} R-\overset{O}{\overset{\|}{C}}-S-X \quad (1)$$

1

2 X = Br, Cl

Thiopivalic acid O-trimethylsilyl ester (**1a**) (0.39 g, 2 mmol) was added to dichloromethane (5 mL) solution containing methanol (0.16 mL, 4 mmol) and N-bromosuccinimide (0.355 g, 2 mmol) at -23°C under nitrogen. After 30 min., solvent was removed under reduced pressure, and the residue was washed with n-hexane. The white precipitate was separated, and the solvent was removed under reduced pressure. The residue was distilled by bulb to bulb distillation (bp 50°C (oven)/0.5 mmHg) to give **2a** in 70 % yield as a colorless liquid. The present reaction provides an unprecedented thiophilic attack of halogen ion on the sulfur atom of thiocarbonyl group.[5] The isolated product was characterized by spectral data. The mass spectrum shows molecular ions at *m/e* = 196 and 198. The I.R. spectrum of **2a** shows characteristic dual carbonyl bands at 1730 and 1700 cm^{-1} due to rotational isomerism. The product **2a** is stable in the refrigerator within one day. However, it gradually decomposes with liberating free bromine.[6]

In order to substantiate the formation of **2a**, the acyl sulfenyl bromide **2a** isolated was treated with dithiobenzoic acid to lead to the corresponding unsymmetrical disulfides **3** in 60 % isolated yield (Eq. 2).



$$\text{t-Bu-}\overset{O}{\overset{\|}{C}}\text{-S-Br} \quad + \quad C_6H_5\text{-}\overset{S}{\overset{\|}{C}}\text{-SH} \longrightarrow \text{t-Bu-}\overset{O}{\overset{\|}{C}}\text{-S-S-}\overset{S}{\overset{\|}{C}}\text{-}C_6H_5 \qquad (2)$$

2a **3**

When N-bromosuccinimide (NBS) or t-butyl hypochlorite was employed as a halogenating reagent, aromatic thiocarboxylic acid O-silyl esters similarly underwent haloganation to give the corresponding acyl sulfenyl halides in high yields. (Table 1).[7]

Table 1. Acylsulfenyl halides **2** by reaction of the thiocarboxylic acid O-silyl esters **1** with NBS or t-butyl hypochlorite [a]

product			conditions		yield [b]
	R	X	temp.(°C)	time(min.)	%
2a	t-C_4H_9	Br	-23	30	70
2b	C_6H_5	Br	-78	15	71
2c	4-$CH_3C_6H_4$	Br	-78	15	52
2d	3-ClC_6H_4	Br	-78	15	73
2e	4-ClC_6H_4	Br	-78	15	62
2f	4-$CH_3C_6H_4$	Cl	-78	3	78 [c,d]
2g	4-ClC_6H_4	Cl	-78	10	73

a) Substrate (2 mmol), NBS (2 mmol) and methanol (4 mmol) were employed in CH_2Cl_2 (5 mL) unless otherwise noted. b) Isolated yield. c) t-Butyl hypochlorite (2 mmol) was used without methanol. d) n-hexane was used as a solvent.

References and Notes

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6. Unfortunately, elemental analysis of **2a** could not be performed owing to its high volatality and unstability.
7. The products obtained were identified in comparison with previous data.[2]

(Received in Japan 14 June 1986)