Preparation of *S*-Alkyl and *S*-Aryl Thiocarboxylates from Acyl Chlorides and Trimethylsilyl Thioethers

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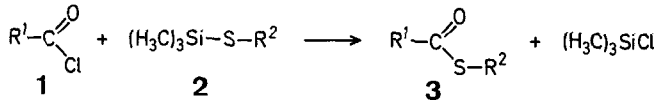
While it is known that certain silyl thioethers react with acid halides to produce thiocarboxylic *S*-esters[1] (thiol esters) the scope of this reaction has not been explored. Interest in thiocarboxylic *S*-esters for organic synthesis has been increasing in recent years[2,3,4], and a number of new methods for preparation of these compounds have been reported[5-11].

We have found that trimethylsilyl thioethers such as octyl and phenyl trimethylsilyl sulfide **(2)** react rapidly and cleanly with acyl chlorides **(1)** to produce thiocarboxylic *S*-esters **(3)**.



1 **2** **3**

S-Phenyl Cyclohexanethiocarboxylate (3, $R^1 = c\text{-}C_6H_{11}$, $R^2 = C_6H_5$); Typical Procedure:

Phenyl trimethylsilyl sulfide (**2**, $R^2 = C_6H_5$; 2.00 g, 11 mmol) is added to a stirred solution of cyclohexanecarbonyl chloride (**1**, $R^1 = c\text{-}C_6H_{11}$; 1.46 g, 10 mmol) in dry chloroform (20 ml) under nitrogen at room temperature. The solution is warmed at 50 °C (bath temperature) for 3 h. Solvent and chlorotrimethylsilane are then removed and the residual product is distilled under reduced pressure; yield: 1.11 g (92%); b.p. torr 116–118 °C; m.p. 38–40 °C (Ref.[13], m.p. 38–39 °C).

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Table. Thiocarboxylic *S*-Esters **(3)**

R^1	R^2	Temperature [°C], Time [h]	Yield[a] [%]	m.p. or b.p. [°C]/torr found	reported
		25°, 8	94	b.p. 163–164°/1.5 m.p. 56–57.5°	m.p. 56°[11]
CH_3		60°, 0.1	95	b.p. 95°/6	b.p. 52–54°/0.16[11]
		50°, 3	92	b.p. 116–118°/0.15 m.p. 39–40°	m.p. 38–39°[13]
		50°, 4	85	m.p. 58–60°	m.p. 61.2–62.1°[14]
Cl_3C–		60°, 3	85	b.p. 115–118°/1.0 m.p. 53–55°	—
		25°, 1[b]	89	m.p. 120–122°	m.p. 125°[15]
CH_3	$n\text{-}C_8H_{17}$	60°, 4	90	b.p. 115–117°/8	b.p. 116–117°/10[16]
	$n\text{-}C_8H_{17}$	80°, 2	92	b.p. 125–130°/0.1	b.p. 130°/0.11[17]
	$n\text{-}C_8H_{17}$	60°, 3	86	b.p. 135–137°/0.45	—[c]

[a] Yield of isolated product. Each ester was pure according to G.L.C. and T.L.C. analyses. In addition, the I.R. and ^{1}H-N.M.R. spectra of esters **3** were identical with those of authentic samples prepared independently[11].

[b] 2 equivalents of **2** were used.

[c] $C_{15}H_{28}OS$ (256.4) calc. C 70.25 H 11.00; found 70.10 10.90

The major advantages of this method are the excellent yields under mild conditions, the ease of isolation of the products, and the ease of preparation of trimethylsilyl thioethers[12]. In general, the reaction is rapid for unhindered trimethylsilyl sulfides. The sterically hindered *t*-butyl trimethylsilyl sulfide reacted only to a small extent, furthermore, decomposition took place at elevated temperatures.

The reaction may be performed in a variety of solvents that do not react with either the acid chloride or thiosilane, or in the absence of solvent. The reaction should be carried out under anhydrous conditions as both reagents **1** and **2** are hydrolyzed in moist air.

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