Synthesis of *S*-Alkyl Thiocarboxylates from Vinylsilanes and Chlorothiocarbonates

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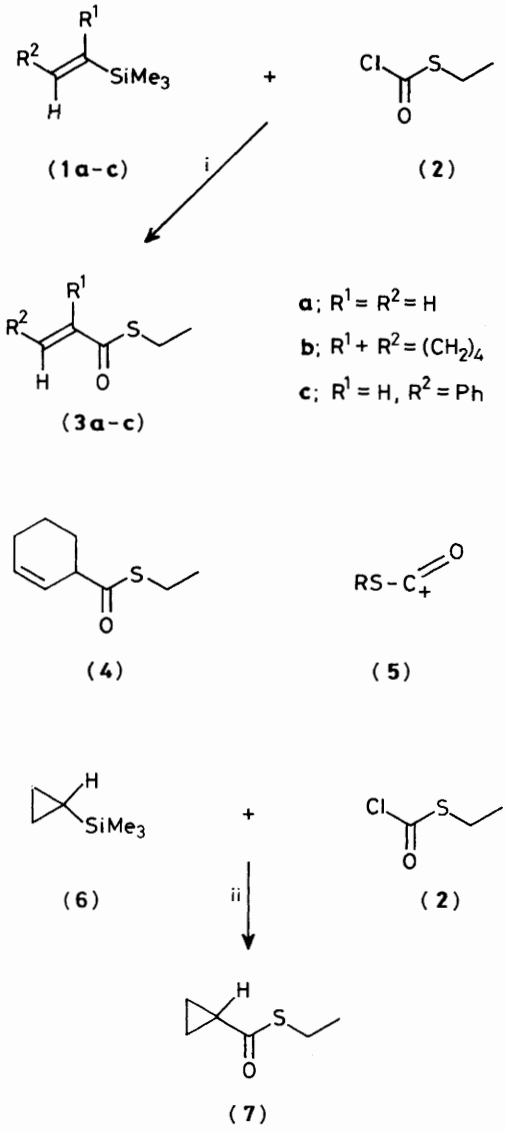
ipso-Substitution of the silyl group in vinylsilanes or cyclopropylsilane by Lewis acid activated *S*-ethyl chlorothiocarbonate gives thiocarboxylates.

Because of their activated carbonyl group, thiocarboxylic *S*-esters are interesting synthetic intermediates.[1] This is particularly true for α,β-unsaturated representatives.[2] Conventionally, these derivatives are prepared by C=C forming reactions or by CO–S bond formation.[3] Based on organosilicon chemistry, we have now developed a synthesis of α,β-unsaturated thiocarboxylates in which the C=C entity is linked to the ester functionality nicely complementing the existing methods.[3]

In the presence of Lewis acids, the reaction of vinylsilanes (**1**) with chlorothiocarbonate[4] (**2**) gives the target molecules (**3**) in good yield (see Scheme and Table). The reaction is particularly clean starting from vinylsilane (**1a**) or (*E*)-1-phenyl-2-trimethylsilylethylene (**1c**) to yield the esters (**3a**)[5] and (**3c**),[6] † respectively.

† ^{1}H N.m.r. (270 MHz, $CDCl_3$) δ 1.30 (t, *J* 7.7 Hz, 3 H, CH_3), 3.00 (q, *J* 7.7 Hz, 2 H, CH_2), 6.68 (d, *J* 16.2 Hz, 1 H, =CH), 7.33—7.50 (m, 5 H, arom.), and 7.58 (d, *J* 16.2 Hz, 1 H, =CH).



Scheme. *Reagents:* i and ii, CH_2Cl_2; Lewis acid and temperature in Table.

Use of 1-(trimethylsilyl)cyclohexene (**1b**) gives a mixture of (**3b**)* and isomer (**4**)† with the C=C bond in a non-conjugated position. This has a parallel in the reaction of acyl halides with vinylsilanes of type (**1b**).[7]

The reactive species formed from the thiocarbonate (**2**) appears to be electrophile (**5**; R = Et), in which the carbonyl entity is stabilized by a favoured hard/hard interaction with the Lewis acid.[8] In line with this, the hard Lewis acid $AlCl_3$ is most efficient in the heterolysis of the CO–Cl bond in (**2**), whereas $TiCl_4$ gives a lower yield and $MgBr_2$ fails to catalyze the reaction (Table). In contrast, even with use of $AlCl_3$ and with the temperature at −78 °C, *S*-t-butyl, -hexyl, or -cyclohexyl thiocarbonates (**2**) give no substitution of silicon in (**1**), since the intermediate cations (**5**) immediately decompose to the corresponding alkyl halides and carbonyl sulphide.[4] Similarly, the reaction of vinylsilanes (**1**) with chlorocarbonates fails to provide α,β-unsaturated esters under our conditions.

Table. Preparation of *S*-ethyl thiocarboxylates (**3**), (**4**), and (**7**) (Scheme)

Silane	Lewis acid	Temp. (°C)	Product(s) (% yield)[a]
(**1a**)	$AlCl_3$	−60	(**3a**) (62)
(**1a**)	$TiCl_4$	−60	(**3a**) (28)
(**1a**)	$MgBr_2$	−30	(**3a**) (0)
(**1b**)	$AlCl_3$	−70	(**3b**) + (**4**) (25%, 1:3.5)
(**1b**)	$AlCl_3$	0	(**3b**) + (**4**) (25%, 1:1.5)
(**1c**)	$AlCl_3$	−30	(**3c**) (66)
(**6**)	$AlCl_3$	42[b]	(**7**) (43)

[a] Isolated yield of pure products. [b] CH_2Cl_2, 2 days reflux.

On the other hand, the approach can be extended to the synthesis of *S*-ethyl cyclopropanethiocarboxylate (**7**) from silylcyclopropane (**6**)‡ and thiocarbonate (**2**). In this case, more vigorous conditions are required (Table), but the reaction proceeds cleanly without opening of the three-membered ring.[9] In comparison with the β-effect of silicon discussed in the reactions above, here edge-co-ordination of the electrophile to the cyclopropane seems to be involved.[10]

Experimental

CAUTION: Thioacrylates and chlorothiocarbonates are strong irritants and should be handled with care.

Typical Procedure using Vinylsilanes.—A suspension of freshly distilled chlorothiocarbonate (**2**) (34 ml, 300 mmol) and $AlCl_3$ (40 g, 300 mmol) in dry CH_2Cl_2 (200 ml) was stirred at −60 °C for 30 min. A solution of vinylsilane (**1a**) (46.3 ml, 300 mmol) in dry CH_2Cl_2 (50 ml) was then added dropwise, and the reaction mixture stirred at −60 °C for 1 h. After completion of the reaction, as indicated by t.l.c. [eluant, hexane–ethyl acetate (9:1), R_F (**3a**) = 0.61, detection u.v. and aq. $KMnO_4$], cold saturated aqueous NH_4Cl (250 ml) was added, and the mixture twirled at room temperature for 1.5 h. The organic layer was separated, washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, brine, and water, dried ($MgSO_4$), and evaporated. The resulting material was distilled *in vacuo* (hydroquinone added) to give (**3a**) as a pale yellow liquid, b.p. 55—58 °C at 35 mmHg (Found: C, 51.7; H, 7.1; S, 27.6. C_5H_8OS requires C, 51.69; H, 6.94; S, 27.62%); $\nu_{max.}$(film) 1 670 and 1 610 cm^{-1}; δ_H(400 MHz, $CDCl_3$) 1.24 (t, *J* 7.2 Hz, 3 H, CH_3), 2.92 (q, *J* 7.2 Hz, 2 H, CH_2), 5.62 (dd, 1 H, AM*X* system), 6.18—6.37 (dq, 2 H, *AM*X system); δ_c (100.6 MHz, $CDCl_3$, DEPT) 14.8 (Me), 23.1 (CH_2), 126.0 (=CH_2), 135.2 (=CH), and 190.2 (C=O).

Synthesis of the Cyclopropanethiocarboxylate (**7**).—A suspension of silylcyclopropane (**6**) (7 ml, 50 mmol), chlorothiocarbonate (**2**) (5.2 ml, 50 mmol), and $AlCl_3$ (6.67 g, 50 mmol) in dry CH_2Cl_2 (50 ml) was stirred under reflux for 2 days. After the reaction was completed [t.l.c., eluant, hexane–ethyl acetate (9:1), R_F (**7**) = 0.52], work-up was carried out as detailed above. The residue was fractionated *in vacuo*, using an effective rotary band column (hydroquinone added), to give (**7**) as pale yellow oil, b.p. 75—79 °C at 35 mmHg; $\nu_{max.}$(film) 3 060 and 1 670 cm^{-1}; δ_H(400 MHz, $CDCl_3$) 0.88 (m, 2 H, cyclopropyl), 1.09 (m, 2 H, cyclopropyl), 1.19 (t, *J* 7.5 Hz, 3 H, CH_3), 1.95 (m, 1 H, AA′BB′*X* system), and 2.82 (q, *J* 7.5 Hz, 2 H, CH_2); δ_C(67.93 MHz, $CDCl_3$, DEPT) δ 10.3 (CH_2), 14.7 (CH_3), 22.4 (CH), 23.0 (CH_2), and 198.8 (C=O).

* ^{1}H N.m.r. (400 MHz, $CDCl_3$) δ 6.92 (m, 1 H, =CH).

† ^{1}H N.m.r. (400 MHz, $CDCl_3$) δ 3.18 (m, 1 H, αCH), 5.70 (dq, 1 H, =CH), and 5.87 (m, 1 H, =CH).

‡ ^{13}C N.m.r. (67.93 MHz, $CDCl_3$, DEPT) δ −4.40 (CH), −2.58 (CH_3), and 1.04 (CH_2).

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