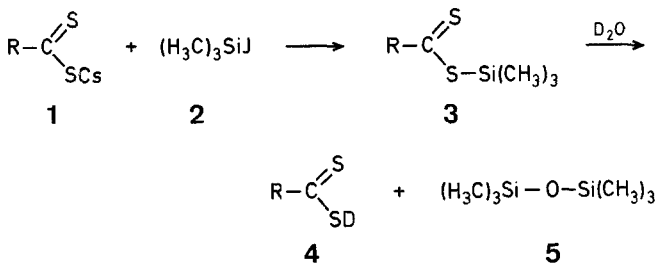

1 2 3

4 5

The effect of both the alkali metals (M) in 4-H_3C—C_6H_4—CS—SM and halogen ions (X) in $(H_3C)_3Si$—X on the rate of this silyl esterification reaction was qualitatively examined. The rates were estimated on the basis of the reaction time, required for the reaction completion: determined by measuring the absorption maximum near 537 nm due to the $n \rightarrow \pi^*$ transitions of **3h**. *As expected, the reaction times decrease with the following order: M = Na > K > Rb > Cs, while X = Cl > Br > J. The beneficial effects of the combination of the caesium salts* **(1)** *and iodotrimethylsilane* **(2)** *for diminishing of the reaction time have been observed.*

An Improved, High-Yield Preparation of Trimethylsilyl Dithiocarboxylates and of *S*-Deuteriodithiocarboxylic Acids via the Silyl Esters

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In our previous papers[1-4], we have reported the preparation of a series of group IV organometal dithiocarboxylates [R^1—CS—$SM(R^2)_3$; M = Si, Ge, Sn, and Pb) by the reaction of the corresponding ammonium salts with group IV organometal chlorides or bromides. These methods have been proven to be very useful for the germanium, tin, and lead esters, but were often found to give unsatisfactory yields for the silyl esters (**3**, R = aryl) of aromatic dithiocarboxylic acids, because of the low reactivity of the starting materials. Very recently, the preparation of the more reactive caesium dithiocarboxylates (**1**) was developed in our laboratory[5]. This result prompted us to improve the preparation of the silyl esters (**3**) of both aliphatic and aromatic dithiocarboxylic acids using the caesium salt and iodotrimethylsilane, and further of the *S*-deuteriodithiocarboxylic acids (**4**) using **3** and deuterium oxide.

The results obtained using caesium dithiocarboxylates (**1**) for the synthesis of compounds **3a-h** are shown in Table 1. The reactions are clean and completed at room temperature within 30 min. The procedures are easy, though careful distillation of the product is required to avoid possible hydrolysis and thermal decomposition.

The results obtained above stimulated us to prepare a series of the previously unknown *S*-deuteriodithiocarboxylic acids (**4**), by deuterolysis of the silyl esters (**3**) (Table 2). To our best knowledge, the preparations of only two *S*-deuteriodithiocarboxylic acids [F_3C—CS—SD[6] and H_3C—CS—SD[7]] have been reported by the deuterium-exchange reaction of dithiocarboxylic acid with large excess deuterium oxide, without, however, giving any spectral data for the S—D bond. However, the very difficult removal of both the water formed as a by-product and the excess D_2O has been observed in our repeated reinvestigations.

The deuterolysis reactions smoothly proceed at room temperature and are complete within 30 min. The procedures are simple and hexamethyldisiloxane (**5**), formed as a by-product, can be easily removed by distillation together with the solvent. The structures of **3** and **4** were confirmed by I.R., U.V.-visible, and ^{1}H-N.M.R. spectral and microanalytical data.

Trimethylsilyl Dithiopropanoate (3b); Typical Procedure for Aliphatic Carboxylates:

To a suspension of caesium dithiopropanoate[5] (1.43 g, 6 mmol) in anhydrous ether (20 ml), iodotrimethylsilane (2.4 g, 12 mmol) is added at 0 °C and the mixture is stirred for 2 h at this temperature. After removal of caesium iodide by filtration, the solvent is evaporated off under reduced pressure. Distillation of the resulting residue in vacuo gives pure **3b**; yield: 0.77 g (78%); b.p. 65–70 °C/23 torr.

$C_6H_{14}S_2Si$	calc.	C 40.40	H 7.91	S 35.94
(178.4)	found	40.64	8.02	35.71

M.S.: $m/e = 178$ (M^+).

I.R. (neat): $\nu = 1250$ (δ_{Si-C}); 1170 (ν_{CS_2}); 842 cm^{-1} (ρ_{Si-C}).

U.V. (n-C_6H_{14}): $\lambda_{max} = 299$, 487 nm.

^{1}H-N.M.R. (CCl_4): $\delta = 0.47$ (s, 9 H); 1.35 (t, 3 H); 3.05 ppm (q, CH_2).

Trimethylsilyl Dithiobenzoate (3g); Typical Procedure for Aromatic Carboxylates:

To a suspension of caesium dithiobenzoate[5] (0.28 g, 1 mmol) in *n*-hexane (10 ml), iodotrimethylsilane (0.4 g, 2 mmol) is added at 0 °C and the mixture is stirred for 2 h at 0–5 °C. After removal of caesium iodide by filtration, vacuum evaporation of the solvent and the excess iodotrimethylsilane from the filtrate gives **3g** as a reddish purple oil; yield: 0.20 g (94%); spectral data identical with that in Ref.[1].

M.S.: $m/e = 226$ (M^+).

I.R. (neat): $\nu = 1250$ (δ_{Si-C}); 1220 (ν_{CS_2}); 836 cm^{-1} (ρ_{Si-C}).

U.V. (n-C_6H_{14}): $\lambda_{max} = 296$, 535 nm.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 0.52$ (s, 9 H); 7.3–8.2 ppm (m, 5 H).

0039-7881/82/0632-0457 $ 03.00

Table 1. Trimethylsilyl Dithiocarboxylate **3**

Product No.	R	Yield [%][a]	b.p. [°C]/torr	Molecular Formula[b]	I.R. (neat) [cm^{-1}] δ_{Si-C}	ν_{CS_2}	ρ_{Si-C}	U.V. (n-C_6H_{14}) λ_{max} [nm]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
3a	CH_3	58 (30)	65–70°/25	66–67°C/ 17 torr[1]	1251	1194, 1178	842	295, 484	0.47 (s, 9H); 2.97 (s, 3H)[c]
3b	C_2H_5	78 (40)	65–70°/23	see experimental				—	—
3c	n-C_3H_7	81 (37)	80–86°/3	$C_7H_{16}S_2Si$ (192.4)	1250	1170	842	302, 486	0.47 (s, 9H); 0.96 (t, 3H); 1.8 (m, 2H); 3.03 (t, 2H)
3d	i-C_3H_7	78 (30)	50–51°/0.5	37–37.5°C/ 0.05 torr[3]	1250	1202	848	304, 487	0.47 (s, 9H); 1.24 (d, 6H); 3.4 (m, 1H)
3e	n-C_4H_9	60	60–65°/3	—	1250	1170	843	302, 386	0.48 (s, 9H); 0.7–2.1 (m, 7H); 3.05 (t, 2H)
3f	c-C_6H_{11}	51	115–125°/25	$C_{10}H_{20}S_2Si$ (232.5)	1250	1170	843	305, 486	0.47 (s, 9H); 1.1–3.5 (m, 11H)
3g	C_6H_5	94	oil	see Ref.[1] and experimental				—	—
3h	4-H_3C—C_6H_4	95 (45)	oil	—	1250	1228	841	307, 537	0.51 (s, 9H); 2.32 (s, 3H); 7.1–8.1 (m, 4H)
3i	4-H_3CO—C_6H_4	93 (53)	oil	$C_{11}H_{16}OS_2Si$ (256.5)	1250	1239	831	328, 529	0.55 (s, 9H); 3.88 (s, 3H); 6.9–8.3 (m, 4H)
3j	4-Cl-C_6H_4	94	oil	$C_{10}H_{13}ClS_2Si$ (260.6)	1251	1212	826	309, 534	0.54 (s, 9H); 7.3–8.1 (m, 4H)

[a] Yield of isolated product; value in brackets obtained using the sodium salt.
[b] Satisfactory microanalyses obtained: C ±0.24, H ±0.24, S ±0.25.
[c] CCl_4 solution.

Table 2. *S*-Deuteriodithiocarboxylic Acids **4**

Product No.	R	Yield [%]	b.p. [°C]/ torr	Molecular Formula[a]	I.R. (neat) [cm^{-1}] ν_{S-D}	ν_{CS_2}	U.V. (n-C_6H_{14}) λ_{max} [nm]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
4a	CH_3	50	35–40°/23	$C_2H_3DS_2$ (93.2)	1811	1200, 870	292, 484	2.85 (s, 3H)
4b	C_2H_5	54	see experimental					
4c	n-C_3H_7	68	85–90°/26	$C_4H_7DS_2$ (121.2)	1810	1182, 950	294, 486	0.91 (t, 3H); 1.9 (m, 2H); 3.05 (t, 2H)
4d	i-C_3H_7	68	85–90°/26	$C_4H_7DS_2$ (121.2)	1815	1155, 940	292, 485	1.30 (d, 6H); 3.4 (m, 1H)
4e	n-C_4H_9	72	75–80°/22	$C_5H_9DS_2$ (135.3)	1813	1180, 970	294, 484	2.95 (t, 2H); 0.7–2.9 (m, 7H)
4f	c-C_6H_{11}	55	67–70°/0.3	$C_7H_{11}DS_2$ (161.4)	1810	1190, 950	295, 485	1.1–2.1 (m, 10H); 3.1 (m, 1H)
4g	C_6H_5	94	oil	$C_7H_5DS_2$ (155.3)	1905[b,c]	1240	297, 534	7.3–8.1 (m, 5H)
4h	4-H_3C—C_6H_4	93	oil	$C_8H_7DS_2$ (169.3)	1915 (b)[b]	1240	307, 536	2.39 (s, 3H); 7.1–8.1 (m, 4H)[d]
4i	4-H_3CO—C_6H_4	92	oil	$C_8H_7DOS_2$ (185.3)	1900[b,c]	1240	328, 522	3.95 (s, 3H); 6.6–8.0 (m, 4H)[d]
4j	4-Cl-C_6H_4	93	oil	$C_7H_4DClS_2$ (189.7)	1900 (b)[b]	1250	306, 538	7.3–8.1 (m, 4H)

[a] Satisfactory microanalyses obtained: C ±0.34, H+D ±0.25, S ±0.31.
[b] Solvent CCl_4.
[c] Assignment not certain.
[d] Solvent 2.8 $CDCl_3/CCl_4$.

Received: July 14, 1981
(Revised form: November 16, 1981)

***S*-Deuteriothiopropanoic Acid (4b):**

Three drops (~0.2 ml, ~10 mmol) of deuterium oxide are added with a syringe to trimethylsilyl dithiopropanoate (1.80 g, 10 mmol) in anhydrous ether (5 ml) at 0°C and the mixture is stirred for 30 min at room temperature. After evaporation of the resulting residue, distillation under reduced pressure affords the product; yield: 0.58 g (54%); b.p. 50–55°C/22 torr.

$C_3H_5DS_2$ (107.2)	calc.	C 33.61	H + D 6.58
	found	33.39	6.72

I.R. (neat): ν = 1809 (S—D); 1185, 900 cm^{-1} (CS_2).

U.V.-visible (n-C_6H_{14}): λ_{max} = 294, 484 nm.

^{1}H-N.M.R. ($CDCl_3$): δ = 1.30 (t, 3H, CH_3); 2.99 ppm (q, 2H, CH_2).

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