Evidence for the 1,3-Silyl Shift Equilibrium between the C=O- and C=Te-Bonded Isomers of a Stable Trimethylsilyl Tellurocarboxylate

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The reaction of bis(trimethylsilyl) telluride with equimolar amounts of pivaloyl chloride affords $Bu^tCOTeSiMe_3$, which exists as a mixture of C=O- and C=Te-bonded isomers related by a 1,3-silyl shift equilibrium (multinuclear n.m.r. spectroscopic evidence).

Owing to the strong affinity of silicon for oxygen, thio- and seleno-carboxylic silyl esters appear to exist exclusively in the 'thiono' or 'selenono' form (**b**) with C=S or C=Se double bonds.[1] Tellurocarboxylic silyl esters have not previously been isolated. Telluroanhydrides[2] and phenyl telluro esters[3] have recently been prepared by Te–Si bond cleavage of bis(trimethylsilyl) telluride and phenyl trimethylsilyl telluride with acyl halides under mild conditions. Thus diacetyl telluride is available from bis(trimethylsilyl) telluride with two equivalents of acetyl chloride, but the reaction of the same silyl telluride with only one equivalent of acetyl chloride led, surprisingly, to an acyloin-like coupling.[2] The key intermediate in the latter reaction is *O*-trimethylsilyl telluroacetate, MeC(=Te)OSiMe$_3$, which decomposes at room temperature by spontaneous detelluration to give the (*E*)- and (*Z*)-isomers of the corresponding disilyl enediol ether.[2] In order to obtain more detailed information about the properties of silyl tellurocarboxylates, we attempted to isolate a thermally stable compound of this type for the first time.

The reaction of pure pivaloyl chloride with an equimolar amount of bis(trimethylsilyl) telluride (**1**) (without solvent) leads to a blue liquid containing trimethylsilyl telluropivalate (**2**) and chlorotrimethylsilane. (Scheme 1) Removal of the latter (10 mbar, 1 mbar = 10^2 Pa; 3 h) provides a high yield of pure (**2**) as a blue liquid,† which is very sensitive to air and moisture, but is thermally stable at room temperature. In contrast to trimethylsilyl thiopivalate, which exists exclusively as the C=S-bonded (type **b**, 'thiono') isomer,[4] the telluroester (**2**) (as the pure liquid or in C_6D_6 solution) contains both C=O-

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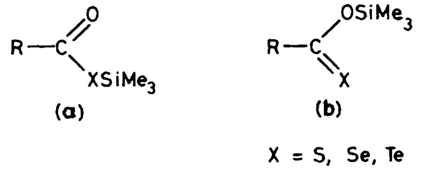
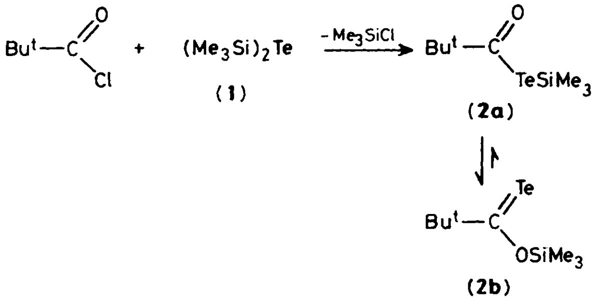
† Compound (**2**) gave satisfactory analytical and spectral data: *m/z* (70 °C, 70 eV) 288 (20%, M^+), 273 (10%, M^+ −Me), 161 (50%), 160 (100%), 159 [100%, $(Me_3SiO–CHBu^t)^+$; b.p. 25—30 °C at 1 mbar.

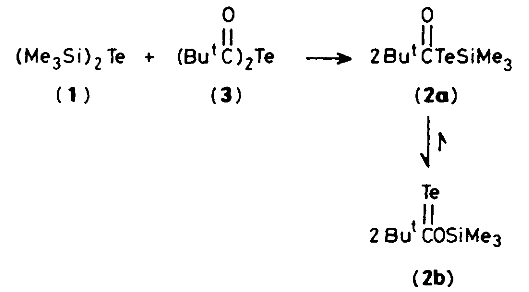
Table 1. N.m.r. data for (**2a**) and (**2b**).[a,b]

	δ(^{1}H)		δ(^{13}C)				δ(^{29}Si)/p.p.m.	δ(^{125}Te)/p.p.m.
	CH_3–Si	CH_3–C	CH_3–Si	CH_3–C	CH_3–C	C=X		
(**2a**)	0.55	0.95	2.6	26.9	53.9	207.5	3.8	229
(**2b**)	0.41	1.23	0.67	29.3[c]	60.9	251.2[d]	28.9	1418

[a] ^{1}H, ^{13}C, and ^{29}Si n.m.r.: Me_4Si standard. [b] ^{125}Te N.m.r.: Me_2Te standard; shifts were determined relative to di-*p*-tolyl ditelluride (Tol_2Te_2) and related to Me_2Te with δ (Tol_2Te_2) = 430 p.p.m. relative to Me_2Te. Measurements conducted on Bruker WP 80 and AM 270 spectrometers; 15.89 (^{29}Si), 25.27 (^{125}Te), and 67.92 MHz (^{13}C). [c] $^3J(^{125}Te,^{13}C)$ 35.4 Hz. [d] $^3J(^{13}C,^1H)$ 5 Hz.







and C=Te-bonded isomers [65% (**2b**), 35% (**2a**)], as shown by multinuclear n.m.r. spectroscopy (Table 1). ^{1}H N.m.r. spectra indicate that two different species with trimethylsilyl and t-butyl groups are present in pure (**2**), but the most convincing evidence comes from ^{13}C and ^{125}Te n.m.r. spectra of the tellurocarbonyl function. The ^{13}C n.m.r. spectrum shows two resonances in the carbonyl region; the signal at δ 207.5 was assigned to the *Te*-silyl ester (**2a**), the ^{13}C nucleus of the C=Te function being far more deshielded [δ 251.2, *cf.* 229.38 for $Bu^tC(=Te)OCH_2Bu^t$.[5] The ^{125}Te n.m.r. signal of the C=Te group in (**2b**) (δ 1 419 p.p.m.) appears more than 1 100 p.p.m. to low field of that of (**2a**), whose resonance is close to the average shift of the 'symmetrically substituted' compounds $(Me_3Si)_2Te$ (**1**), δ (^{125}Te) – 858 p.p.m.,[6] and $(Bu^tCO)_2Te$ (**3**), δ (^{125}Te) 936 p.p.m. As for compounds with C=Se double bonds,[7] the low field ^{13}C and ^{125}Te resonances of (**2b**) coincide with a rather small average excitation energy [(**2b**): $\lambda_{max.}$ 624 nm[2]].

The blue liquid (**2**) consisting of isomers (**2a**) and (**2b**) in a 1 : 2 ratio is also obtained by mixing equimolar amounts of the symmetrically substituted compounds (**1**) and (**3**). A slight excess of (**1**) or (**3**) leads to separate n.m.r. signals for (**1**) or (**3**) and (**2a**)–(**2b**) at room temperature, *i.e.* the [1,3] sigmatropic rearrangement (**2a**) $\rightleftarrows$ (**2b**) is slow on the n.m.r. time scales and there is no fast scrambling at the two-co-ordinate tellurium of (**1**) or (**3**) and (**2a**). Measurements at elevated temperatures led to decomposition of (**2**).[2]

The reactions of (**2**) that we carried out, at room temperature, always proceeded with consumption of both isomers. With pivaloyl chloride, (**3**) and chlorotrimethylsilane are formed quantitatively; [2 + 4]cycloaddition reactions of the C=Te double bond[8] of (**2b**) with cyclopentadiene or 2,3-dimethylbutadiene lead to new cyclic telluroacetals.‡

The existence of a 1 : 2 equilibrium mixture of (**2a**) and (**2b**) which are related by a 1,3-trimethylsilyl shift indicates that the strong affinity of silicon for oxygen, which favours C=S and C=Se bonds in thio- or seleno-carboxylic silyl esters,[1,4] is not sufficient to provide the rather high energy that would be needed for the *quantitative* formation of a C=Te double bond.

Added in proof: A spin saturation transfer experiment has meanwhile confirmed the dynamic equilibrium (**2a**) $\rightleftharpoons$ (**2b**). The experiment was carried out on a Bruker AM270 spectrometer using an Aspect 3000 microprogram for nuclear Overhauser enhancement difference spectroscopy. Continuous wave irradiation at the frequency of the Bu^t or Me_3Si protons of (**2b**) leads to enhanced signal intensity for the Bu^t or Me_3Si protons of (**2a**) (R. Zeisberg and J. Jakupovic, Technische Universität Berlin, personal communication).

We thank Professor H. Schumann and Dr. M. Gallagher (Technical University of Berlin) for the ^{13}C n.m.r. spectra.

Received, 10th November 1986; Com. 1597

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‡ Reaction of (**2**) with 2,3-dimethylbutadiene gave a yellowish liquid: *m/z* (28 eV, 70 °C) 370 [20%, M^+, $(C_{14}H_{28}OSi^{130}Te)^+$], 355 ($M^+$ –Me), 314 (M^+ $-C_4H_8$), 299 (M^+ –Me, $-C_4H_8$), 288 (M^+ $-C_6H_{10}$), 273 (M^+ $-C_6H_{10}$, –Me), 240 (100%, M^+ –Te), 183 (100%, M^+ –Te, $-C_4H_9$), 160 [60%, $(Me_3Si\text{-}OCH_2CMe_3)^+$]; (**2**) with cyclopentadiene gave a product with *m/z* (70 °C, 70 eV) 354 [M^+, $(C_{13}H_{24}OSi^{130}Te)^+$, correct isotopic distribution].