Stereospecific Synthesis of (*Z*)-β-Trifluoroacetylvinyltellurides; X-Ray Crystal Structure of (*Z*)-β-Trifluoroacetylvinyl-2-(ethoxycarbonyl)ethyltelluride

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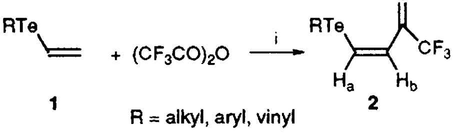
Vinyltellurides **1** react with trifluoroacetic anhydride (TFAA) under heating in the presence of *N,N,N,N*-tetramethylethylenediamine (tmeda) in THF to give stereospecific (*Z*)-β-trifluoroacetylvinyltellurides **2** in good yields (50–84%); the X-ray crystal structure of (*Z*)-β-trifluoroacetylvinyl-2-(ethoxycarbonyl)ethyltelluride **2c** shows that an intramolecular coordination bond O→Te exists.

The trifluoroacetylation of heteroatom-substituted olefins occurs easily. Ketene dithioacetals,[1,2] vinyl sulfides,[1,2] vinyl ethers,[3] *N*-vinyl amides,[2,3] *N*-vinyl carbazole,[2] 1,1-bisalkylthiobuta-1,3-diene[4] and *trans*-*N*-acetyl-*N*-isopropyl-1-aminobuta-1,3-diene[4] all react with trifluoroacetic anhydride at room temperature or under heating to furnish the corresponding β-trifluoroacetylated compounds in high yields. In recent years there has been great interest in the preparation of organotellurium compounds and their utilization for organic synthesis.[5] To our knowledge, no report on the trifluoroacetylation of vinyltellurides has appeared in the literature. We report here that vinyltellurides react with trifluoroacetic anhydride (TFAA) to afford stereospecific (*Z*)-β-trifluoroacetylated products in good yields (Scheme 1) and the X-ray crystal structure of (*Z*)-β-trifluoroacetylvinyl-2-(ethoxycarbonyl)ethyltelluride **2c**, which shows the existence of the intramolecular coordination bond O→Te.

Table 1 Effects of reaction conditions on the trifluoroacetylation of *n*-butylvinyltelluride **1a**[a]

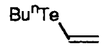
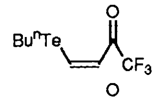
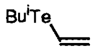
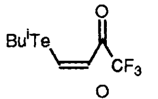
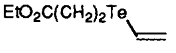
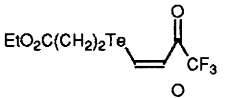
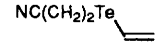
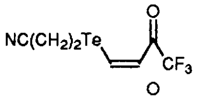
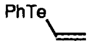
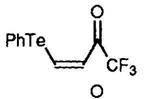
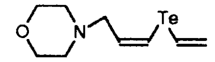
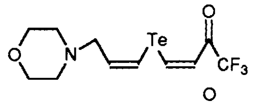
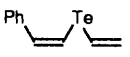
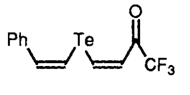
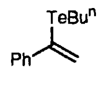
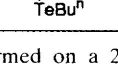
Entry	Solvent	Base (equiv.)	*T*/°C	*t*/h	Yield (%)[b]
1	CH_2Cl_2	Pyridine (0.3)	r.t[c]–reflux	24	Trace[d]
2	$CHCl_3$	Pyridine (0.3)	r.t–reflux	24	Trace[d]
3	$CHCl_3$	Pyridine (1.0)	r.t–reflux	24	Trace[d]
4	$CHCl_3$	Pyridine (2.0)	r.t–reflux	24	Trace[d]
5	THF	Pyridine (2.0)	r.t–reflux	24	Trace[d]
6	THF	Et_3N (1.5)	r.t–reflux	46	42[e]
7	THF	$Bu^n{}_3N$ (1.5)	r.t–reflux	33	72
8	THF	TMEDA (0.75)	r.t–50	18	81
9	THF	TMEDA (0.15)	50	22	65

[a] The reaction was performed on a 2 mmol scale; Bu^n-$TeCH{=}CH_2 : (CF_3CO)_2O$ = 1 : 1.5. [b] Isolated yields based on Bu^n-$TeCH{=}CH_2$. [c] r.t. = room temp. [d] *ca.* 90% of vinyltelluride was recovered. [e] 30% of vinyltelluride was recovered.



Scheme 1 *Reagents and conditions*: i, tmeda, THF, 50 °C or reflux

Table 2 Trifluoroacetylation of vinyltellurides[a]

Entry	Vinyltelluride	*T*/°C	*t*/h	Product[b]	Yield (%)[c]
1	 **1a**	50	18	 **2a**	81[d]
2	 **1b**	50	18	 **2b**	84
3	 **1c**	50	20	 **2c**	75[e]
4	 **1d**	50	25	 **2d**	70
5	 **1e**	Reflux	50	 **2e**	69
6	 **1f**	50	40	 **2f**	55
7	 **1g**	Reflux	40	 **2g**	50
8	 **1h**	Reflux	50	—	0[f]
9	 **1i**	Reflux	50	—	Trace[f]

[a] The reaction was performed on a 2 mmol scale; $RTeCH{=}CH_2$: $(CF_3CO)_2$:TMEDA = 1.0:1.5:0.75. All products gave satisfactory elemental analyses, ^1H NMR, MS and IR spectra‡ [b] Determined by 300 MHz ^1H and/or ^1H–^1H NOESY NMR analysis. [c] Isolated yields based on $RTeCH{=}CH_2$. [d] This yield was obtained even at a reaction scale of 200 mmol of vinyltelluride. [e] X-ray crystal structure was determined. [f] *ca.* 90% of the starting material was recovered.

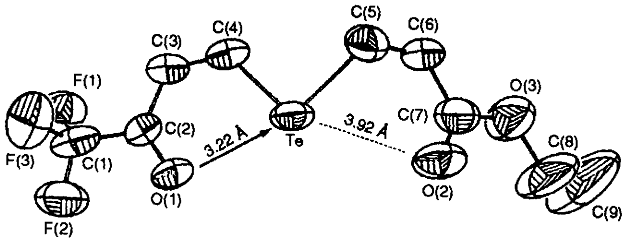


Fig. 1 X-ray crystal structure of **2c**. Selected bond lengths (Å) and angles (°): Te–C(4) 2.06(1), Te–C(5) 2.14(1), O(1)–C(2) 1.24(1), O(2)–C(7) 1.19(2), C(1)–C(2) 1.48(2), C(2)–C(3) 1.42(2), C(3)–C(4) 1.34(2), F(1)–C(1) 1.35(2), F(2)–C(1) 1.33(2), F(3)–C(1) 1.33(2), C(4)–Te–C(5) 94.1(5), Te–C(4)–C(3) 126(1), Te–C(5)–C(6) 115(1), C(2)–C(3)–C(4) 112(1), O(1)–C(2)–C(3) 124(1), C(1)–C(2)–C(3) 118(1), O(1)–C(2)–C(1) 117(1), C(5)–C(6)–C(7) 113(1), C(6)–C(7)–O(2) 127(1).

Under the reaction conditions described by Hojo and *et al.*[1–4] the trifluoroacetylation of *n*-butylvinyltelluride **1a** was unsuccessful even at elevated temperature (Table 1, entries 1–5). Triethylamine promoted the trifluoroacetylation, which gave the β-acylated compound **2a** in 42% yield with the recovery of *ca.* 30% of **1a** (reaction incomplete even after 46 h) (entry 6). In the presence of tri(*n*-butyl)amine, the reaction occurred easily to afford **2a** in 72% yield (entry 7). However, tmeda (0.75 equiv.) was the most effective for forming **2a**, with an 81% yield (entry 8). In the presence of a small amount of tmeda (0.15 equiv.), the telluride **1a** also reacted with TFAA to furnish **2a** in 65% yield (entry 9). As shown in Table 1, tmeda (0.75 equiv.) was the most effective base for the reaction (entry 8). Under these reaction conditions, the trifluoroacetylation of other vinyltellurides **1** was exploited, and the results are summarized in Table 2. The electrophilic substitution reactions of vinyltellurides **1** with TFAA were performed by stirring the mixture at 50 °C or under reflux in the presence of tmeda (0.75 equiv.) in THF to give the corresponding β-trifluoroacetylvinyltellurides **2** in good yields.[†] Alkyl-, aryl- and vinyl-vinyltellurides reacted with TFAA easily under more extreme reaction conditions than those of other heteroatom-substituted olefins.[1–4] The yields of alkylvinyltellurides were better than those of aryl- and vinyl-vinyltellurides. 1,1-Disubstituted vinyltelluride **1h** was not trifluoroacetylated, although the equivalent sulfide reacted quite readily,[1,2] nor was conjugated dienyltelluride **1i**. In all cases, the products **2a–2g** had only (*Z*)-stereochemistry. The stereospecific result is noteworthy since the trifluoroacetylation of other heteroatom-substituted olefins leads to mixtures of (*Z*) and (*E*) products or (*E*) products.[1–4] It is interesting and unusual that the chemical shifts of H_a in products **2a–2g** ranged between δ 9.50 and 9.90 which is a long way downfield in ^1H NMR for olefinic hydrogens. This may be due to the effect of the intramolecular coordination bond O→Te.[6]

The molecular structure of **2c**[§] has been determined by a single-crystal X-ray diffraction study and is shown in Fig. 1. It further confirmed the (*Z*)-configuration of the product and showed that there was an interaction between the carbonyl oxygen of the ketone group and the tellurium atom. The presence of the intramolecular coordination bond O→Te whose length (3.22 Å) was less than the sum of the van der Waals radii of Te and O, which amounts to 3.60 Å,[7] led to an unusual result, which was the formation, upon trifluoroacetylation, (an electrophilic substitution reaction) of the thermodynamically less stable product **2c**. The structure of tellurium(II) derivatives that contain a carbonyl group in the *ortho*-position relative to the tellurium atom has been examined by several authors.[6] For these compounds in the crystalline form, the *S-cis* conformation is realized with the secondary O→Te bond, which in some cases are similar in their characteristics to the respective single covalent bonds. In compound **2c**, the intramolecular interaction is weak, and may be accounted for by a decrease in the electron density of the carbonyl oxygen owing to the effect of trifluoromethyl group, a strong electron-withdrawing substituent, and an increase in the electron density of the tellurium atom owing to the influence of the 2-(ethoxycarbonyl)ethyl group, an electron-donating group.

In summary, the electrophilic substitution reactions of vinyltellurides with TFAA leads to the pure, thermodynamically less stable (*Z*)-products, (*Z*)-β-trifluoroacetylvinyltellurides **2**, in good yields, owing to intramolecular interactions. Work on their utilization for organic synthesis is now in progress in our laboratory.

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Footnotes

[†] *General procedure*: a solution of $(CF_3CO)_2O$ (3.0 mml) in THF (3 ml) was added dropwise to the solution of tmeda (1.5 mmol) in THF (2 ml) at −20 °C under an N_2 atmosphere. The mixture was warmed slowly at room temp. and then vinyltelluride **1** (2.0 mmol) in THF (3 ml) was added. The reaction mixture was then stirred at 50 °C or under reflux. After the reaction was completed (monitored by TLC), standard workup and flask chromatography gave the pure product **2**.

[‡] *Typical spectral data* for (*Z*)-β-trifluoroacetylvinyl-2-(ethoxycarbonyl)ethyltelluride **2c**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, J = 7.10 Hz, 3H), 2.85 (t, J = 7.10 Hz, 2H), 3.05 (t, J = 7.10 Hz, 2H), 4.18 (q, J = 7.10 Hz, 2H), 7.85 (d, J = 9.30 Hz, 1H), 9.88 (d, J = 9.30 Hz, 1H); MS *m/z* (rel. intensity) 353 ($M^+ - 1$, ^{130}Te, 61), 351 ($M^+ - 1$, ^{128}Te, 57), 351 ($M^+ - 1$, ^{126}Te, 41), 252 (100), 251 (94), 248 (90); IR (KBr), ν/cm^{-1} 1725s, 1640m, 1500s, 1380m, 1300m, 1200s, 1130s, 1080s and 870m; Anal. Calc. for $C_9H_{11}F_3O_3Te$: C, 30.73; H, 3.15. Found: C, 30.30; H, 3.16%.

[§] *Crystal data* for **2c** $C_9H_{11}F_3O_3Te$: M = 351.8, monoclinic, space group $P2_1/c$, $a = 14.21(2)$, $b = 10.98(1)$, $c = 8.02(1)$ Å, $\beta = 89.85(8)°$, V = 1251 Å^3, $F(000) = 672$, $Z = 4$, D_c = 1.868 g cm^{-3}, μ = 2.408 mm^{-1}, specimen 0.15 × 0.40 × 0.50 mm; data were collected on a Siemens R3m/V (Mo-Kα 0.71703 Å) diffractometer at 273 K ($3 < 2\theta < 45°$). The structure was solved by direct methods and refined by full-matrix least-squares analysis using SHELXTL plus (VMS) system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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