Synthesis of *Te*-Butyl Tellurocarboxylates by the Reaction of Esters with $^{i}Bu_2AlTe^{n}Bu$

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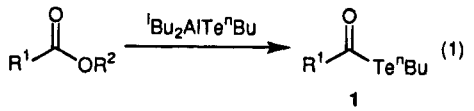
A variety of esters were converted to corresponding tellurol esters in moderate to good yields by the reaction with $^{i}Bu_2AlTe^{n}Bu$. This transesterification proceeds smoothly in nonpolar solvents. Aryl esters reacted efficiently in comparison with alkyl esters. Addition of a catalytic amount of PPh_3 or $ZnCl_2$ accelerated the reaction and improved the yields. Substituents on the oxygen of esters exert significant steric effects on this transesterification, but the reaction is insensitive to the steric bulkiness of substituents on the carbonyl carbon. Competitive reactions of substituted ethyl benzoates showed a small positive ρ value of 0.43 against σ^+.

Introduction

With recent progress of organotellurium chemistry in organic synthesis,[1] tellurol esters **1** attract a special attention, in particular, as acylation reagents, which transfer acyl moieties in various electronic forms, e.g., acyl cations,[2] anions,[3] and radicals,[4] to organic molecules. They are also useful as protecting groups of carboxylic acids.[5] In contrast to their growing utility in organic synthesis, their preparative methods are limited to only a few methodologies. They have usually been prepared by conventional methods based on the reactions of tellurolate anions with acid halides or acid anhydride.[2,6] Only one exception had been $Co_2(CO)_8$-mediated carbonylation of ditellurides.[7] Very recently, we have revealed that tellurol esters can be prepared from aldehydes by Tischenko-type reactions with $^{i}Bu_2AlTe^{n}Bu$.[8] Here we report that esters undergo transesterification by the reaction with $^{i}Bu_2AlTe^{n}Bu$ as shown by eq 1. This paper also describes the steric and



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electronic effects of the substituents of esters, R^1 and R^2, on this transesterification. Although similar transformations to give thiol and selenol esters have been reported,[9] little attention has been paid to the substituent effects or the reaction pathways (vide infra).

Results and Discussion

Transesterification was examined using ethyl benzoate and $^{i}Bu_2AlTe^{n}Bu$, prepared in situ by Ogura's method from $^{n}BuTeTe^{n}Bu$ and 2 mol equiv of $^{i}Bu_2AlH$ (1 N in toluene or hexane),[10] and the results are summarized in Table 1. A reaction of ethyl benzoate with 1.3 equiv of $^{i}Bu_2AlTe^{n}Bu$ at 25 °C in toluene for 2 h afforded *Te*-butyl tellurobenzoate (**1a**) in 33% yield (entry 1). Prolonged reaction time improved the yield of **1a**. When the reaction was conducted for 40 h, most of the substrate used was consumed and **1a** was obtained in 71% yield along with 14% of benzyl alcohol (entry 3). A control reaction of **1a** with an equimolar amount of $^{i}Bu_2AlTe^{n}Bu$ at 25 °C for 5 h afforded benzyl alcohol in 30% yield and a trace amount of benzaldehyde with recovery of unreacted **1a**. This may suggest that benzyl alcohol formed as byproduct arises from reduction of **1a** with remaining $^{i}Bu_2AlTe^{n}Bu$ and/or $^{i}Bu_2AlOEt$ generated in situ by transesterification. Addition of a catalytic amount of PPh_3 or $ZnCl_2$ improved the yield of **1a**, and the former was more effective (entries 4, 5). When the reaction was conducted at 50 °C,

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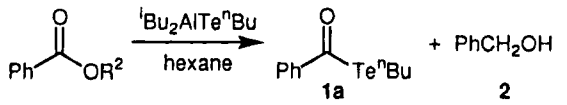
Table 1. Reaction of $^{i}Bu_2AlTe^{n}Bu$ with Ethyl Benzoate[a]

entry	solvent	time (h)	additive	yield of **1a**,[b] (%)
1	toluene	2		33
2		20		61
3		40		71
4		20	$ZnCl_2$	69
5			PPh_3	82
6[c]				49
7	CH_2Cl_2/toluene[d]			21
8	hexane	0.2		50
9		0.5		62
10		3		77
11		20		90 (83)
12		40		84
13		20	PPh_3	94

[a] Conditions: $^{i}Bu_2AlTe^{n}Bu$ (1.3 mmol, prepared by the reaction of 0.65 mmol of $^{n}BuTeTe^{n}Bu$ with 1.3 mL of 1 N $^{i}Bu_2AlH$ in toluene or hexane), ethyl benzoate (1.0 mmol), additive (0.05 mmol when used), 25 °C. [b] NMR yield (isolated yield). [c] Reaction was conducted at 50 °C. [d] CH_2Cl_2 (5 mL) was added to the toluene solution of $^{i}Bu_2AlTe^{n}Bu$ before injection of ethyl benzoate.

Table 2. Reaction of $^{i}Bu_2AlTe^{n}Bu$ with Various Benzoates[a]



entry	R^2	recovery of ester (%)[b]	yield of **1a** (%)[b]	yield of **2** (%)[b]
1	Me	12[c]	65	14
2	Et	15	80	5
3	^{n}Bu	29	62	8
4	^{i}Pr	35	3	23
5	^{t}Bu	96	0	0
6	Ph	10	62	28

[a] Conditions: benzoate (1 mmol), $^{i}Bu_2AlTe^{n}Bu$ (1.3 mmol), 25 °C, 12 h. [b] Determined by NMR. [c] GLC yield.

formation of **1a** decreased and ethyl benzoate was recovered in 32% yield (entry 6).[11]

We then examined the effect of solvents. A similar reaction in hexane afforded **1a** in a very good yield (entry 11), but addition of CH_2Cl_2 as a cosolvent decreased the yield of **1a** and resulted in the recovery of 58% of ethyl benzoate (entry 7). This transesterification is fast in hexane. For example, **1a** was formed in 50% yield within the first 12 min followed by a gradual increase up to 90% yield during the next ca. 20 h (entries 8–11). However, further prolonged reaction time decreased the yield, probably due to the formation of benzyl alcohol (entry 12). When $^{i}Bu_2AlTePh$ was used, *Te*-phenyl tellurobenzoate was not obtained at all under the same conditions as in entry 1 and 69% of ethyl benzoate was recovered.

Table 2 shows the results obtained using several different benzoates. The bulkier the substituent on the oxygen, the lower the yield, except for the case of methyl benzoate where benzyl alcohol was formed in an appreciable amount. *tert*-Butyl benzoate did not react under these conditions. Isopropyl benzoate predominantly afforded benzyl alcohol (entry 4). A possible explanation of this result is that further reduction of **1a** with $^{i}Bu_2AlTe^{n}Bu$ and/or $^{i}Bu_2AlO^{i}Pr$ is faster than its formation from isopropyl benzoate. Phenyl benzoate also reacted, but the product selectivity was poor (entry 6). This may be because that an alternative reduction pathway from phenyl benzoate to **2** without formation of **1a** may operate or that concomitantly formed $^{i}Bu_2AlOPh$ reduces **1a** to **2** more readily than $^{i}Bu_2AlOR^2$ (R^2 = Et or ^{n}Bu) does, which is generated in the reaction of entry 2 or 3.

Table 3. Transesterification of Esters with $^{i}Bu_2AlTe^{n}Bu$[a]

entry	R^1	R^2	time (h)	isolated yield (%)
1	Ph	Et	20	**1a**, 83
2	4-Me-C_6H_4	Et	3	**1b**, 60
3	4-Me-C_6H_4	Et	12	**1b**, 71
4	3-Me-C_6H_4	Et	12	**1c**, 71[b]
5	3-Me-C_6H_4	Et	20	**1c**, 67
6	4-Cl-C_6H_4	Et	0.5	**1d**, 58[b]
7	4-Cl-C_6H_4	Et	3	**1d**, 81[b]
8	4-Cl-C_6H_4	Et	20	**1d**, 92
9	3-Cl-C_6H_4	Et	20	**1e**, 77
10[c]	4-MeO-C_6H_4	Me	20	**1f**, 52
11	$^{n}C_7H_{15}$	Et	20	**1g**, 35[b]
12	$^{n}C_7H_{15}$	Et	48	**1g**, 48[b]
13[d]	$^{n}C_7H_{15}$	Et	24	**1g**, 61
14[d]	^{i}Pr	Et	20	**1h**, 58
15	cyclo-C_6H_{11}	Et	40	**1i**, 51[b]
16[d]	cyclo-C_6H_{11}	Et	20	**1i**, 73, 82[b]
17[d]	^{t}Bu	Et	20	**1j**, 57

[a] Conditions: $^{i}Bu_2AlTe^{n}Bu$ (1.3 mmol, prepared by the reaction of 0.65 mmol of $^{n}BuTeTe^{n}Bu$ with 1.3 mL of 1 N $^{i}Bu_2AlH$ in hexane), ester (1.0 mmol), 25 °C. [b] NMR yield. [c] THF (2 mL) was added to dissolve the ester used. [d] PPh_3 (0.10 mmol) was added.

In Table 3 are summarized the results of similar reactions of various ethyl or methyl esters with $^{i}Bu_2AlTe^{n}Bu$. Aryl esters generally afforded corresponding tellurol esters in better yields in comparison with alkyl esters. *p*-Methoxybenzoate gave **1f** in a moderate yield, and 37% of the starting ester was recovered (entry 10). In cases of alkyl esters, transesterification was apparently accelerated by the addition of PPh_3 and better yields of products were obtained in a shorter reaction time (entries 11–13, 15, 16), although its role is still unclear. Noteworthy is that the reaction was not affected by the steric bulkiness of R^1 attached to the carbonyl carbon, whereas the substituent R^2 on oxygen apparently exerted a crucial steric effect as described above (see Table 2). Kochetkov et al. have also reported that reactivity of alkyl esters toward $Me_2AlSeMe$ in a similar transesterification was largely affected by the alkoxy group but less efficiently by its acyl group.[9g]

We then examined electronic effects of substituents by competitive reactions. To a hexane solution of $^{i}Bu_2AlTe^{n}Bu$ (1 mmol) was added a mixture of ethyl benzoate and one of its derivatives (2 mmol each) at once at 25 °C. After 10 min, the reaction was quenched with aqueous NH_4Cl and the solution analyzed by ^1H NMR and/or GLC. From the results shown in the Experimental Section, a small positive ϱ value of 0.43 against σ^+ (r = 0.96)[12] was obtained, indicating that electron-withdrawing groups accelerate the reaction but not dramatically.

In order to provide evidence for the reaction mechanism, a mixture of $^{i}Bu_2AlTe^{n}Bu$ and *tert*-butyl benzoate in toluene-d_8 was subjected to NMR analysis. The ^{13}C NMR spectrum of the resulting mixture showed two signals at δ 165.3 and 173.4 which could be assigned to ester carbonyl carbons. The former is the same as the

(11) The reaction mixture, initially pale yellow, gradually turned to red due to the formation of $^{n}BuTeTe^{n}Bu$ arising probably from thermal decomposition of $^{i}Bu_2AlTe^{n}Bu$.

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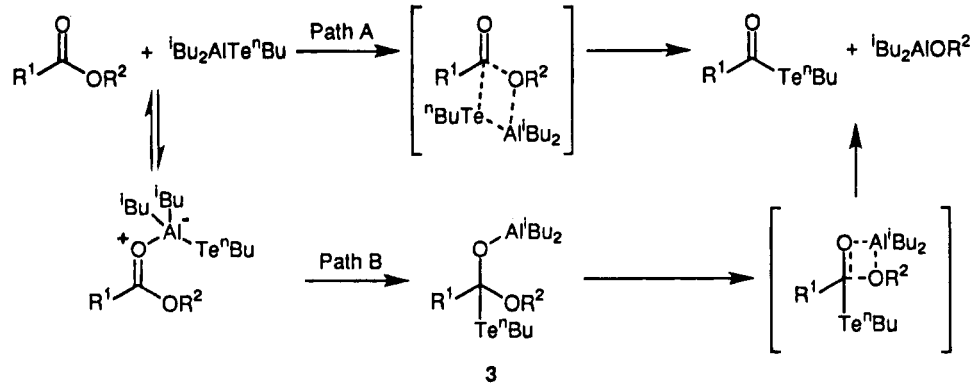
Scheme 1. Plausible Reaction Pathways



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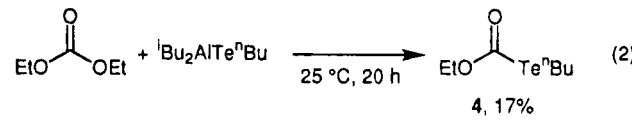
chemical shift of free *tert*-butyl benzoate, and the latter may be that of a carbonyl group coordinated by an aluminum.[13] When D_2O was added to the mixture, the peak at δ 173.4 disappeared and *tert*-butyl benzoate was recovered quantitatively without formation of **1a**. These results indicate that coordination of aluminum to the carbonyl oxygen is fast and reversible but may not play an important role for transesterification. A similar NMR experiment using ethyl benzoate showed two carbonyl carbons at δ 165.9 and 194.7 which correspond to those of free ethyl benzoate and **1a**, respectively, and any unique peak assignable to the central carbon of **3** was not observed.

With these evidences obtained by the NMR study together with the fact mentioned above that the rate of the transesterification depends largely on the alkoxy group but is less affected by substituents on the carbonyl carbon, either sterically or electronically, a concerted pathway (path A) as shown in Scheme 1 seems to be probable. An alternative stepwise pathway (path B) via an addition intermediate **3** can not be ruled out yet but might not be likely due to the following reasons. If addition of $^{i}Bu_2AlTe^{n}Bu$ to esters is a rate-determining step, R^1 should exert more crucial steric effects than R^2 does. Secondly, if elimination of $^{i}Bu_2AlOR^2$ from **3** is rate determining, **3** could be observed by NMR in the reaction of $^{i}Bu_2AlTe^{n}Bu$ with *tert*-butyl benzoate which does not undergo transesterification. This is in large contrast with the reaction of $^{i}Bu_2AlTe^{n}Bu$ with aldehydes where addition products were formed quickly.[8]

Under similar conditions, benzamides, γ- and δ-lactones, and diisobutylaluminum benzoate, generated in situ by the reaction of benzoic acid with $^{i}Bu_2AlH$, did not afford tellurol esters. On the other hand, the reaction of diethyl carbonate gave a corresponding tellurocarbonate, **4**, although the yield is not satisfactory



4, 17% (2)

yet.[18]

Conclusion

In conclusion, a new convenient synthetic method of tellurol esters from various esters has been developed by the use of $^{i}Bu_2AlTe^{n}Bu$ prepared in situ. Small steric and electronic effects of the acyl and aroyl groups and a large steric effect of the alkoxy group on this transesterification along with results of NMR studies may suggest that the reaction proceeds via direct substitution at the carbonyl carbon with coordination of aluminum on the oxygen atom of the leaving alkoxy or phenoxy group.

Experimental Section

General Procedures. $^{i}Bu_2AlH$ (1 N in hexane or toluene) was purchased from Kanto Chemical Co., Inc. Dibutyl ditelluride was synthesized by air oxidation of $^{n}BuTeLi$, prepared by the reaction of $^{n}BuLi$ with an equimolar amount of metallic tellurium.[19] Esters which were not commercially available were prepared by the reaction of acid halides with lithium alkoxides generated from corresponding alcohols and $^{n}BuLi$. CH_2Cl_2 was distilled from CaH_2. Products were purified by medium pressure liquid chromatography (MPLC) using Merck 25–40 μm mesh silica gel. ^1H and ^{13}C NMR spectra were recorded using $CDCl_3$ as solvent with Me_4Si as an internal standard.

A Typical Experiment. Reaction of Ethyl Benzoate with $^{i}Bu_2AlTe^{n}Bu$. Into a flame-dried flask equipped with an Ar inlet and a rubber septum were placed $^{n}BuTeTe^{n}Bu$ (240 mg, 0.65 mmol) and $^{i}Bu_2AlH$ (1 N in hexane, 1.3 mL) under Ar. The solution was stirred at 25 °C for 1 h, and 1 mmol of ethyl benzoate (150 mg) was injected. The resulting mixture was stirred for another 20 h and poured into a saturated NH_4Cl solution. Products were extracted with Et_2O (30 mL × 3), dried over $MgSO_4$, and concentrated in vacuo. MPLC of the residue gave pure *Te*-butyl tellurobenzoate (**1a**) in 83% yield (241 mg) in a hexane/Et_2O (400/1) fraction: ^1H NMR (270

(13) A similar downfield shift of a carbonyl carbon has been observed in the reaction of an organoaluminum compound with fumalate and is ascribed to the coordination of the aluminum on its carbonyl oxygen. See: Maruoka, K.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1992**, *114*, 1089.

(14) By calculation using chemical shifts of the following compounds, the central carbon of **3** is expected to appear near δ 83 ppm: $PhCH_2Me$ (δ 28.9 in $CDCl_3$),[15] $PhCHMeTe^{n}Bu$ (δ 18.1 in $CDCl_3$),[16] $PhCH(OMe)_2$ (δ 103.1 in $CDCl_3$),[15] $PhCH_2OMe$ (δ 75.8 in $CDCl_3$),[17] and $PhCH_2OAl^{i}Bu_2$ (δ 66.4 in toluene-d_8) formed by the reaction of $PhCH_2OH$ with $^{i}Bu_2AlH$ and measured in this study. No peak assignable to that carbon was observed in the region from δ 60 to 120.

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MHz, $CDCl_3$) δ 0.94 (t, J = 7.45 Hz, 3 H), 1.43 (sextet, J = 7.45 Hz, 2 H), 1.84 (quint, J = 7.45 Hz, 2 H), 3.06 (t, J = 7.45 Hz, 2 H), 7.40 (t, J = 7.57 Hz, 2 H), 7.55 (t, J = 7.57 Hz, 1 H), 7.75 (d, J = 7.57 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.4 ($J_{C\text{-}Te}$ = 76.30 Hz), 13.5, 25.4, 34.0, 126.9, 128.8, 133.6, 143.1, 196.2; IR (neat) 2956, 1662, 1446, 1200, 1168, 863, 762, 685, 665 cm^{-1}; MS m/z (rel intensity) 292 (M^+, 1.6), 105 (100), 77 (55), 57 (5). Anal. Calcd for $C_{11}H_{14}OTe$: C, 45.57; H, 4.87. Found: C, 45.79; H, 4.77.

***Te*-Butyl *p*-methyltellurobenzoate (1b):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J = 7.45 Hz, 3 H), 1.43 (sextet, J = 7.45 Hz, 2 H), 1.84 (quint, J = 7.45 Hz, 2 H), 2.35 (s, 3 H), 3.05 (t, J = 7.45 Hz, 2 H), 7.21 (d, J = 7.82 Hz, 2 H), 7.64 (d, J = 7.82 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.1 ($J_{C\text{-}Te}$ = 75.70 Hz), 13.4, 21.7, 25.4, 34.1, 127.0, 129.5, 140.7, 144.6, 195.4; IR (neat) 2956, 2927, 1673, 1643, 1601, 1201, 1167, 869 cm^{-1}; MS m/z (rel intensity) 306 (M^+, 1.0), 119 (100), 91 (35). Anal. Calcd for $C_{12}H_{16}OTe$: C, 47.43; H, 5.31. Found: C, 46.96; H, 5.33.

***Te*-Butyl *m*-methyltellurobenzoate (1c):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.45 Hz, 3 H), 1.42 (sextet, J = 7.45 Hz, 2 H), 1.83 (quint, J = 7.45 Hz, 2 H), 2.38 (s, 3 H), 3.04 (t, J = 7.45 Hz, 2 H), 7.27 (t, J = 7.81 Hz, 1 H), 7.36 (d, J = 7.81 Hz, 1 H), 7.52 (s, 1 H), 7.53 (d, J = 7.81 Hz, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.2 ($J_{C\text{-}Te}$ = 76.30 Hz), 13.5, 21.2, 25.3, 34.1, 124.3, 127.2, 128.7, 134.4, 138.7, 143.1, 196.2; IR (neat) 2956, 2927, 1666, 1240, 1141, 802, 764, 665 cm^{-1}; MS m/z (rel intensity) 306 (M^+, 0.7), 119 (100), 91 (41), 65 (11). Anal. Calcd for $C_{12}H_{16}OTe$: C, 47.43; H, 5.31. Found: C, 47.76; H, 5.27.

***Te*-Butyl *p*-chlorotellurobenzoate (1d):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.32 Hz, 3 H), 1.42 (sextet, J = 7.32 Hz, 2 H), 1.86 (quint, J = 7.32 Hz, 2 H), 3.08 (t, J = 7.32 Hz, 2 H), 7.39 (d, J = 8.79 Hz, 2 H), 7.67 (d, J = 8.79 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.8 ($J_{C\text{-}Te}$ = 75.69 Hz), 13.5, 25.4, 34.0, 128.1, 129.1, 134.0, 141.5, 194.7; IR (neat) 2957, 2927, 1663, 1196, 1165, 866 cm^{-1}; MS m/z (rel intensity) 326 (M^+, 1), 141 (37), 139 (100), 111 (28). Anal. Calcd for $C_{11}H_{13}ClOTe$: C, 40.74; H, 4.04. Found: C, 40.70; H, 4.15.

***Te*-Butyl *m*-chlorotellurobenzoate (1e):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.45 Hz, 3 H), 1.46 (sextet, J = 7.45 Hz, 2 H), 1.86 (quint, J = 7.45 Hz, 2 H), 3.08 (t, J = 7.45 Hz, 2 H), 7.37 (t, J = 7.81 Hz, 1 H), 7.55 (d, J = 7.81 Hz, 1 H), 7.62 (d, J = 7.81 Hz, 1 H), 7.71 (s, 1 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.9 ($J_{C\text{-}Te}$ = 75.80 Hz), 13.4, 25.3, 33.9, 125.1, 126.3, 130.1, 133.3, 135.2, 144.7, 195.0; IR (neat) 2957, 2928, 1668, 1183 cm^{-1}; MS m/z (rel intensity) 326 (M^+, 2), 141 (67), 139 (100), 111 (74), 57 (14). Anal. Calcd for $C_{11}H_{13}ClOTe$: C, 40.74; H, 4.04. Found: C, 40.40; H, 4.23.

***Te*-Butyl *p*-methoxytellurobenzoate (1f):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.32 Hz, 3 H), 1.43 (sextet, J = 7.32 Hz, 2 H), 1.85 (quint, J = 7.32 Hz, 2 H), 3.05 (t, J = 7.32 Hz, 2 H), 3.85 (s, 3 H), 6.90 (d, J = 8.85 Hz, 2 H), 7.72 (d, J = 8.85 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.0 ($J_{C\text{-}Te}$ = 76.23 Hz), 13.4, 25.3, 34.1, 55.5, 113.9, 129.2, 136.1, 164.0, 193.4; IR (neat) 2957, 2929, 1668, 1597, 1263, 1160, 870 cm^{-1}; MS (CI) m/z (rel intensity) 323 (M^+ + 1, 56), 321 (52), 153 (25), 135 (100). Anal. Calcd for $C_{12}H_{16}O_2Te$: C, 45.06; H, 5.04. Found: C, 45.15; H, 5.19.

***Te*-Butyl heptanecarbotelluroate (1g):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 7.33 Hz, 3 H), 0.92 (t, J = 7.33 Hz, 3 H), 1.20–1.45 (m, 10 H), 1.63 (quint, J = 7.33 Hz, 2 H), 1.79 (quint, J = 7.33 Hz, 2 H), 2.61 (t, J = 7.33 Hz, 2 H), 2.88 (t, J = 7.33 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.8 ($J_{C\text{-}Te}$ = 75.68 Hz), 13.5, 14.1, 22.6, 25.2, 25.4, 28.6, 29.0, 31.6, 34.2, 56.1, 202.7; IR (neat) 2956, 2924, 2854, 1700, 1458, 970 cm^{-1}; MS m/z (rel intensity) 314 (M^+, 3.5), 127 (100), 57 (14). Anal. Calcd for $C_{12}H_{24}OTe$: C, 46.21; H, 7.76. Found: C, 46.51; H, 7.86.

***Te*-Butyl 1-methylethanecarbotelluroate (1h):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.33 Hz, 3 H), 1.14 (d, J = 6.84 Hz, 6 H), 1.38 (sextet, J = 7.33 Hz, 2 H), 1.77 (quint, J = 7.33 Hz, 2 H), 2.63 (septet, J = 6.84 Hz, 1 H), 2.86 (t, J = 7.33 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.1 ($J_{C\text{-}Te}$ = 75.8 Hz), 13.4, 18.4, 25.3, 34.1, 52.8, 209.0; IR (neat) 2961, 2929, 1702, 934 cm^{-1}; MS m/z (rel intensity) 258 (M^+, 5), 71 (100), 57 (41). Anal. Calcd for $C_8H_{16}OTe$: C, 37.12; H, 6.23. Found: C, 37.50; H, 6.16.

***Te*-Butyl cyclohexanecarbotelluroate (1i):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (t, J = 7.32 Hz, 3 H), 1.26–1.41 (m, 7 H), 1.61–1.66 (m, 1 H), 1.74–1.79 (m, 4 H), 1.91–1.98 (m, 2 H), 2.39 (tt, J = 10.74, 3.42 Hz, 1 H), 2.85 (t, J = 7.32 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.0 ($J_{C\text{-}Te}$ = 76.8 Hz), 13.4, 25.1, 25.3, 25.8, 28.9, 34.2, 62.0, 208.1; IR (neat) 2928, 2854, 1704, 1449, 951 cm^{-1}; MS m/z (rel intensity) 298 (M^+, 7), 111 (50), 83 (100), 55 (35), 41 (14). Anal. Calcd for $C_{11}H_{20}OTe$: C, 44.65; H, 6.81. Found: C, 44.63; H, 6.82.

***Te*-Butyl 1,1-dimethylethanecarbotelluroate (1j):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (t, J = 7.33 Hz, 3 H), 1.14 (s, 9 H), 1.38 (sextet, J = 7.33 Hz, 2 H), 1.75 (quint, J = 7.33 Hz, 2 H), 2.83 (t, J = 7.33 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 9.9 ($J_{C\text{-}Te}$ = 76.9 Hz), 13.5, 25.4, 26.4, 34.2, 52.9, 212.8; IR (neat) 2959, 2728, 1702, 1674, 1461, 898, 789 cm^{-1}; MS m/z (rel intensity) 272 (M^+, 3.7), 85 (48), 57 (100). Anal. Calcd for $C_9H_{18}OTe$: C, 40.06; H, 6.72. Found: C, 40.15; H, 6.90.

A Typical Procedure of Competitive Experiments. Into a hexane solution of 1 mmol of $^iBu_2AlTe^nBu$, prepared by $^iBu_2AlH$ (1 mL, 1 N hexane solution) and $^nBuTeTe^nBu$ (0.5 mmol, 185 mg), was added a mixture of ethyl benzoate and ethyl *p*-methylbenzoate (2 mmol each) at once at 25 °C under Ar with stirring. After the solution had stirred for 10 min, the reaction was quenched by aqueous NH_4Cl and the products were extracted with Et_2O (30 mL × 3), dried over $MgSO_4$, and concentrated. MPLC of the residue (hexane/Et_2O = 400/1) afforded a mixture of two tellurol esters, the yields of which were determined by ^1H NMR: **1a**, 29%; **1b**, 25% based on $^iBu_2AlTe^nBu$. Similar competitive reactions were carried out under identical conditions using *m*-Me, *p*-Cl, and *m*-Cl derivatives. Relative product ratios obtained were **1b**/**1a** = 0.86, **1c**/**1a** = 1.13, **1d**/**1a** = 1.14, and **1e**/**1a** = 1.74.

***O*-Ethyl *Te*-butyl carbonotelluroate (4):** ^1H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 7.33 Hz, 3 H), 1.30 (t, J = 6.84 Hz, 3 H), 1.40 (sextet, J = 7.33 Hz, 2 H), 1.86 (quint, J = 7.33 Hz, 2 H), 2.90 (t, J = 7.33 Hz, 2 H), 4.32 (t, J = 6.84 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.2 ($J_{C\text{-}Te}$ = 72.3 Hz), 13.4, 14.5, 25.1, 34.1, 63.3, 155.2; IR (neat) 2958, 2930, 1704, 1102 cm^{-1}; MS m/z (rel intensity) 260 (M^+, 50), 258 (48), 57 (100), 55 (40). Anal. Calcd for $C_7H_{14}O_2Te$: C, 32.61; H, 5.47. Found: C, 32.99; H, 5.47.

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