HETEROCYCLES, Vol. 76, No. 2, 2008, pp. 1577 - 1584. © The Japan Institute of Heterocyclic Chemistry
Received, 17th May, 2008, Accepted, 12th June, 2008, Published online, 19th June, 2008. COM-08-S(N)124

FREE RADICAL TANDEM ADDITION-CYCLIZATION OF *Te*-PHENYL *N*,*N*-DIMETHYLCARBAMOTELLUROATE TO 1,6-ENYNES†

**Shin-ichi Fujiwara,[a,*] Yoshihiko Shimizu,[b] Yoshimasa Makita,[a]
Tsutomu Shin-ike,[a] and Nobuaki Kambe[b,*]**

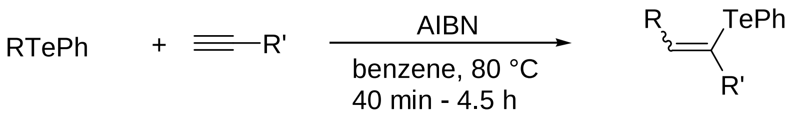
a) Department of Chemistry, Osaka Dental University, Hirakata, Osaka 573-1121, Japan; b) Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
E-mail: fujiwara@cc.osaka-dent.ac.jp; kambe@chem.eng.osaka-u.ac.jp

† This paper is dedicated to Professor Dr. Ryoji Noyori on the occasion of his 70th birthday.

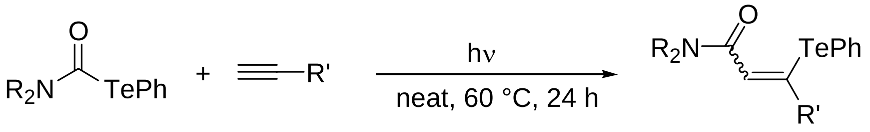
Abstract – Free radical tandem addition of *Te*-phenyl *N*,*N*-dimethylcarbamotelluroate (**1**) to alkenes and alkynes was examined. Simple addition of carbamotelluroate **1** to alkenes such as styrene and methyl acrylate did not take place under irradiation of visible light. However, when alkynes were added to this system, photo-induced three-component radical coupling proceeded to give alkenyl tellurides **6** in moderate yields. This reaction could be applied to heterocycles synthesis by use of 1,6-dienes **7**. Carbamotelluroate **1** added to allyl propargyl ethers or an amine **7** under light giving rise to tetrahydrofuran or pyrrolidine **8** by tandem radical addition/cyclization reaction.

INTRODUCTION

Addition of organotellurium functionality to carbon-carbon unsaturated bonds is of importance since the products, alkyl and alkenyl tellurides, can successfully be subjected to further manipulation.[1,2] During the course of our study on free radical addition of organotellurium compounds to alkynes, we disclosed that dialkyl tellurides[3] and carbamotelluroates[4] added to alkynes efficiently in the presence of radical initiator or under irradiation with visible light giving rise to the corresponding alkenyl tellurides in high yields (eqs 1-2). The latter reaction is triggered by photo-induced homolytic cleavage of carbon-tellurium bond generating the corresponding radicals.



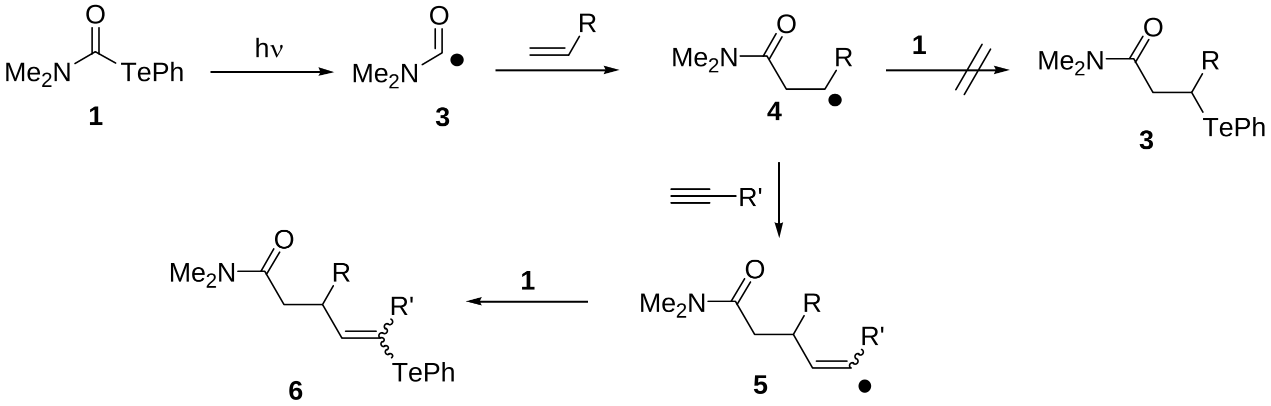
(1)



(2)

These successful results led us to examine the addition of carbamotelluroate **1** to alkenes. However, the reaction of carbamotelluroate **1** with alkenes such as styrene and methyl acrylate under irradiation of visible light at 60 °C did not take place. Since carbamoyl radicals like **3** are known to be nucleophilic [5] and add to electron deficient alkenes,[6] alkyl radical **4** can be expected to be formed under these conditions as shown in Scheme 1. Therefore, the failure can be ascribed to insufficient reactivity of alkyl radical **4** to abstract PhTe group from **1**. To overcome this problem by way of transforming the alkyl radical **4** to the more reactive alkenyl radical **5**, we performed the reaction of **1** with electron deficient alkenes in the presence of electron rich alkynes and found that three-component radical coupling took place to give alkenyl tellurides **6** (Scheme 1).

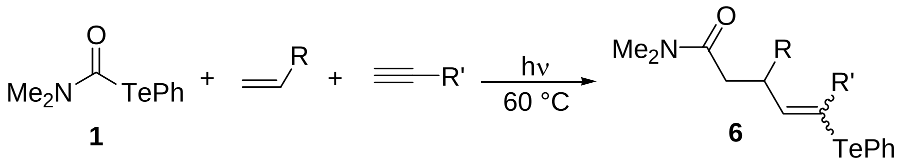
Scheme 1

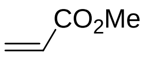
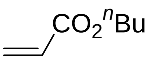
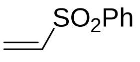


RESULTS AND DISCUSSION

A mixture of **1** with one equiv of methyl acrylate and 10 equiv of 1-octyne was irradiated with visible light at 60 °C for 18 h. Three-component radical coupling reaction took place to form alkenyl telluride **6a** in 33% yield (*E*/*Z* = 60/40). The main by-product was the 1:1 addition product of **1** to 1-octyne (27%). Thus, the amount of 1-octyne was reduced; however, the yield of **6a** was diminished (entry 2). When AIBN was employed as a radical initiator in place of visible light, **6a** was also formed (entry 3). By using *n*-butyl acrylate or phenyl vinyl sulfone as an alkene together with 1-hexyne as an alkyne, 3-component coupling products were obtained in similar yields (entries 4-6).

Table 1. 3-Component coupling of carbamotelluroate **1** with alkenes and alkynes



entry	alkene	alkyne	yield[a]	*E*/*Z*
1		≡—^{n}Hex	**6a**, 33%(35%)	40/60
2		(2 eq)	**6a**, (14%)	
3[b]			**6a**, (34%)	
4			**6b**, 24%(32%)	42/58
5			**6c**, 38%(45%)	60/40
6		≡—^{n}Bu	**6d**, 42%(52%)	53/47

Conditions: **1** (1 mmol), alkene (1 mmol), alkyne (10 mmol), 60 °C, 18-24 h.
a) Isolated yield (NMR yield). b) AIBN (10 mol%) was used in place of visible light as an initiator.

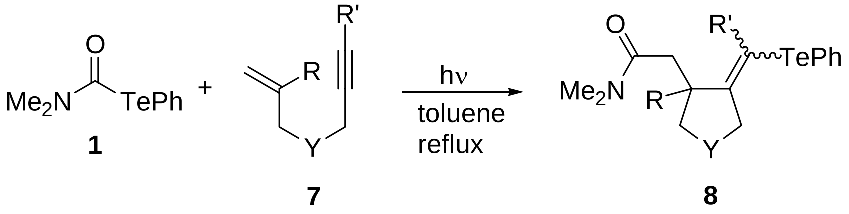
We then examined intramolecular tandem radical addition/cyclization by the use of 1,6-enynes having a heteroatom in the chain aiming at the construction of heterocycles (Table 2). Treatment of **1** with 1,6-enyne **7a** (R = CO_2Et, R' = H, Y = O) under irradiation of visible light in refluxing toluene resulted in the formation of β-alkylidenetetrahydrofuran **8a** in 42% yield (entry 1).

This reaction would proceed via similar reaction pathways shown in Scheme 1. The first step is generation of carbamoyl radical **3** which adds to C-C double bond of 1,6-enyne **7** to afford alkyl radical. Subsequent intramolecular addition to the internal C-C triple bond yields vinylic radical, which abstracts PhTe group from **1** to form product **8**. The ester group in **7a** seems to be essential to promote this cyclization because a reaction of **1** with an enyne **7b** (R = H, R' = Ph, Y = O) did not afford **8b** at all (entry 2). **7c** having a nitrogen tether unit afforded a β-alkylidene pyrrolidine (entry 3). When methyl group was introduced at the acetylenic terminus as in **7d**, the expected product was formed in 71% yield (entry 4).

CONCLUSION

Three-component radical coupling of carbamotelluroate with alkenes and alkynes was attained by using excess amounts of alkynes to give alkenyl tellurides. When 1,6-enynes having oxygen or nitrogen atom in

Table 2. Tandem addition/cyclization of carbamotelluroate **1** onto 1,6-enynes **7**[a]



entry	7	R	R'	Y	product	yield[b] (E/Z ratio)
1	**7a**	CO_2Et	H	O	**8a**	42% (20/80)
2	**7b**	H	Ph	O	**8b**	0%
3	**7c**	CO_2Et	H	NTs	**8c**	43% (18/82)
4[b]	**7d**	CO_2Et	Me	O	**8d**	71% (16/84)

Conditions: **1** (1 mmol), **7** (1 mmol), toluene (0.5 mL), reflux, 19-22 h.
a) Carbamotelluroate **1** was completely consumed in each entry.
b) Isolated yield. c) 5 h.

the chain were employed in place of alkenes and alkynes, β-alkylidene tetrahydrofuran and pyrrolidine rings were constructed.

EXPERIMENTAL

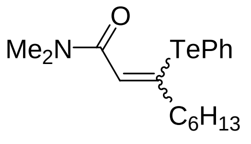
Carbamotelluroate **1** was prepared according to the procedure we reported.[4] 1,6-Enynes **7** were synthesized by modified procedure for 3-prop-2-ynyloxyypropene.[7] Alkenes and alkynes are commercially available and were used after distillation.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ALICE-400 (400 MHz and 100 MHz, respectively) spectrometer using Me_4Si as an internal standard. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer. HPLC separation was performed on recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent. Mass spectra (EI) were taken on a SHIMADZU GCMC-QP2000 operating in the electron impact mode (70 eV) equipped with CBP1-M25-025 column. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Elemental analyses were performed on Perkin Elmer 240C apparatus.

General Procedure for the 3-Component Coupling of Carbamotelluroate 1 with Alkene and Alkyne: Into a 3 mL Pyrex flask were placed carbamotelluroate **1** (1 mmol), alkyne (10 mmol), and alkene (1 mmol) under Ar. The mixture was then irradiated in a water bath kept at 60 °C using a 500W tungsten lamp with a distance of 10 cm for 18-24 h. After cooling to rt, excess alkyne was removed *in vacuo* and the residue was purified by silica gel column chromatography and further by preparative recycling HPLC to provide the expected product **6**. Although the *E*/*Z* ratio was determined by ^{1}H NMR, attempts for isolation of *E*/*Z* isomers failed, so the following spectra and analytical data were obtained from the *E*/*Z* mixture.

6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.3 Hz, 3 H, *Z*), 0.85 (t, *J* = 7.3 Hz, 3 H, *E*), 1.14-1.45 (m, 8 H, *E* and *Z*), 2.23 (t, J = 7.3 Hz, 2H, *Z* ($C\underline{H_2}$-C_5H_{13}), 2.33-2.50 (m , 2 H, *E* and *Z* ($C\underline{H_2}C(O)$ and *E* ($C\underline{H_2}$-C_5H_{13})), 2.83-2.98 (m , *E* and *Z* ($N\underline{Me_2}$) and *E* (methine)), 3.689 (s, 3 H, *Z*), 3.694 (s, 3 H, *E*), 3.91-3.99 (m, 1 H, *Z* (methine)), 5.72 (d, *J* = 9.3 Hz, 1 H, *Z* (vinyl)), 5.96 (d, *J* = 10.3 Hz, 1 H, *E* (vinyl)), 7.17-7.28 (m, 4 H, *E* and *Z*), 7.69 (d, *J* = 7.8 Hz, *E*), 7.73 (d, *J* = 7.9 Hz, *Z*); NOE experiment: irradiation at methylene triplet at δ 2.23 resulted in a 12.5% enhancement of the signal at δ 5.72; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 22.5, 22.6, 28.1, 28.7, 29.6, 29.7, 31.5, 31.6, 35.3, 35.5, 35.6, 36.1, 37.0, 41.8, 42.9, 49.0, 51.97, 52.00, 113.0, 113.6, 125.5, 127.5, 128.8, 129.0, 129.1, 133.3, 137.0, 138.1, 138.8, 169.7, 173.1, 173.5; IR (NaCl) 2926, 2855, 1738, 1732, 1659, 1651, 1644, 1634 cm^{-1}; MS(EI), m/z (relative intensity, %) 475 (M+,7), 292 (5), 268 (100), 236 (47), 226 (25), 72 (61). HRMS calcd for $C_{21}H_{31}NO_3Te$: 475.1366, found 475.1356.

Addition Product of 1 to 1-Octyne (By-product of 6a): Obtained as a mixture of stereoisomers



(major/minor = 52/48); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, *J* = 7.2 Hz, 3 H), 0.87 (t, *J* = 7.3 Hz, 3 H), 0.94-1.04 (m, 2 H), 1.11-1.19 (m, 2 H), 1.24-1.32 (m, 4 H), 1.51-1.57 (m, 2 H), 2.31 (t, *J* = 7.8 Hz, 2 H), 2.66 (t, *J* = 7.6 Hz, 2 H), 2.80 (s, 3 H), 2.90 (s, 3 H), 3.04 (s, 3 H), 3.08 (s, 3 H), 6.10 (s, 1 H), 6.95 (s, 1 H), 7.20-7.39 (m , 6 H), 7.84 (d, *J* = 7.8 Hz, 2 H), 7.92 (d, *J* = 7.8 Hz, 2 H); NOE experiment: irradiation at vinyl singlet at δ 6.95 resulted in a 5.2% enhancement of the signal at δ 2.31; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2, 22.5, 22.6, 28.8, 30.3, 31.1, 31.4, 31.6, 34.8, 35.9, 37.1, 37.5, 39.8, 112.9, 116.4, 119.6, 127.7, 128.5, 128.6, 129.4, 139.3, 140.5, 141.2, 154.7, 166.2, 167.6; IR (NaCl) 2926, 2855, 1735, 1737, 1612 cm^{-1}; MS (EI), m/z (relative intensity, %) 389 (M^+, 26), 312 (27), 182 (100), 72 (94). Anal. Calcd for $C_{17}H_{25}NOTe$: C, 52.76; H, 6.51; N, 3.62. Found: C, 53.05; H, 6.50; N, 3.70.

6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.1 Hz, 3 H), 0.86 (t, *J* = 7.1 Hz, 3 H), 0.92 (t, *J* = 7.6 Hz, 3 H), 0.93 (t, *J* = 7.3 Hz, 3 H), 1.05-1.66 (m, 28 H), 2.22 (t, *J* = 7.3 Hz, 2 H), 2.35 (dd, *J* = 4.6, 13.8 Hz, 2 H), 2.49 (dd, *J* = 4.4, 13.4 Hz, 2 H), 2.90-3.00 (m, 7 H), 3.89-4.02 (m, 1 H), 4.03-4.16 (m, 4 H), 5.71 (d, *J* = 9.3 Hz, 1 H), 5.96 (d, *J* = 10.2 Hz, 1 H), 7.15-7.29 (m , 6 H), 7.69 (d, *J* = 7.8 Hz, 2 H), 7.74 (d, *J* = 7.8 Hz, 2 H); NOE experiment: irradiation at methylene triplet at δ 2.22 resulted in a 11.4% enhancement of the signal at δ 5.71; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.69, 13.70, 14.00, 14.02, 19.0, 19.1, 22.48, 22.51, 28.0, 28.7, 29.65, 29.74, 30.5, 30.6, 31.5, 31.6, 35.3, 35.4, 36.1, 37.0, 41.6, 43.0, 49.1, 64.60, 64.63, 113.1, 113.6, 125.3, 127.46, 127.48, 128.8, 129.0, 129.3, 133.3, 137.4, 138.0, 138.8, 169.77, 169.83, 172.6, 173.0; IR (NaCl) 2930, 2856, 1738, 1732, 1659, 1651, 1644, 1169, 1147, 734 cm^{-1}; MS (EI), m/z (relative intensity, %) 517 (M$^+$, 5), 410 (8), 310 (100), 72 (60). HRMS calcd for $C_{24}H_{37}NO_3Te$: 517.1836, found 517.1850.

6c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77-0.87 (m, 6 H), 1.00-1.37 (m, 16 H), 1.88-2.10 (m, 4 H), 2.54-2.68 (m, 2 H), 2.80-3.30 (m, 12 H), 4.56-4.65 (m, 1 H), 4.82-4.90 (m, 1 H), 5.56 (d, *J* = 10.0 Hz, 1 H), 5.75 (d, *J* = 10.5 Hz, 1 H), 7.04-7.95 (m, 20 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 22.37, 22.43, 27.9, 28.6, 29.2, 29.4, 30.8, 31.2, 31.3, 31.4, 35.6, 37.2, 41.1, 62.1, 68.2, 113.0, 113.5, 127.4, 128.0, 128.5, 128.6, 128.8, 128.9, 129.0, 129.7, 132.4, 133.4, 137.2, 137.5, 138.8, 139.3, 167.7, 167.8; IR (NaCl) 2926, 2856, 1659, 1652, 1644, 1634, 1614, 1446, 1398, 1305, 1149, 736, 691 cm^{-1}; MS (EI), m/z (relative intensity, %) 557 (M$^+$, 3), 416 (11), 389 (10), 350 (13), 312 (12), 208 (62), 182 (56), 72 (100). HRMS calcd for $C_{25}H_{33}NO_3Te$: 557.1243, found 557.1246.

6d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67-0.78 (m, 6 H), 1.00-1.07 (m, 4 H), 1.26-1.35 (m, 4 H), 1.92-2.09 (m, 4 H), 2.55-2.64 (m, 4 H), 2.899 (s, 3 H), 2.903 (s, 3 H), 2.93-2.96 (m, 6 H), 2.99-3.03 (m, 3 H), 3.13 (d, *J* = 15.9 Hz, 1 H), 3.23 (d, *J* = 15.6 Hz, 1 H), 4.61 (t, *J* = 9.7 Hz, 1 H), 4.86 (t, *J* = 10.0 Hz, 1 H), 5.56 (d, *J* = 9.7 Hz, 1 H), 5.75 (d, *J* = 10.5 Hz, 1 H), 7.04-7.95 (m, 20 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 13.8, 21.4, 22.1, 30.8, 31.3, 31.7, 35.4, 35.6, 35.7, 37.23, 37.25, 40.9, 62.1, 68.3, 113.0, 113.5, 127.45, 127.49, 128.0, 128.6, 128.7, 128.8, 128.9, 129.1, 129.9, 132.3, 133.4, 137.2, 137.4, 137.5, 138.8, 139.3, 167.8, 167.8; IR (NaCl) 3064, 2929, 2871, 1659, 1652, 1644, 1634, 1304, 737 /cm^{-1}; MS (EI), m/z (relative intensity, %) 529 (M$^+$, 4), 388 (20), 322 (21), 180 (100), 72 (89). HRMS calcd for $C_{23}H_{29}NO_3STe$: 529.0930, found 529.0939.

General Procedure for the Synthesis of 1,6-Enynes 7

Sodium hydride (20 mmol, ~60% in mineral oil) was washed with THF under Ar. A mixture of Et_2O (3 mL) and THF (3 mL) was added and the heterogeneous mixture was stirred at 0 °C. Propargylic alcohol (10 mmol) was added dropwise via syringe and left to stir for 45 min. Allylic bromide (12 mmol) was then added and the mixture was left to stir overnight at rt. The reaction mixture was then cooled to 0 °C and quenched with H_2O (5 mL). The mixture was extracted with Et_2O (20 mL), and the organic layer was washed with brine (20 mL) and then dried over Na_2SO_4. After removal of the drying agent and solvent, 1,6-enyne was obtained as a colorless oil by Kugelrohr distillation or preparative HPLC.

7a: Purification by Kugelrohr distillation (120-130°C/5 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28-1.34 (m, 3 H), 2.49 (t, *J* = 2.5 Hz, 1 H), 4.19-4.28 (m, 2 H), 4.29 (t, *J* = 1.5 Hz, 2 H), 5.89 (t, *J* = 1.5 Hz, 1 H), 6.32 (d, *J* = 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 57.7, 60.6, 67.2, 74.6, 79.2, 125.8, 136.4, 165.2; IR (NaCl) 3292, 2983, 2906, 1716, 1310, 1178, 1099 cm^{-1}; MS (EI), m/z (relative intensity, %)

129 (M^+, 67), 101 (69), 83 (100). HRMS calcd for $C_9H_{13}O_3$: 169.0865, found 169.0872.

7b[8]**:** Purification by Kugelrohr distillation (120-130°C/40 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (dt, J = 5.9, 1.3 Hz, 1 H), 4.35 (s, 2 H), 5.30 (d, J = 1.7 Hz, 1 H), 5.35 (d, J = 1.7 Hz, 1 H), 7.26-7.29 (m, 3 H), 7.41- 7.46 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.8, 70.5, 84.9, 86.0, 117.4, 122.4, 127.9, 128.1, 131.4, 133.8.

7c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J = 7.1 Hz, 3 H, major), 1.30 (t, J = 7.1 Hz, 3 H, minor), 2.02 (t, J = 2.5 Hz, 1 H), 2.415 (s, 3 H, major), 2.423 (s, 3 H, minor), 4.05-4.14 (brs, 4 H, major and minor), 4.20 (q, J = 7.1 Hz, 2 H, major), 4.21 (q, J = 7.1 Hz, 2 H, minor), 5.92 (m, 1 H), 6.38 (m, 1 H), 7.25-7.34 (m, 2 H), 7.72-7.77 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 21.6, 37.0, 46.8, 61.0, 74.0, 127.3, 127.6, 128.2, 129.3, 134.8, 135.7, 143.5, 165.4; IR (NaCl) 3275, 2983, 2928, 1716, 1377, 1351, 1301, 1161, 1095, 663 cm^{-1}; MS (CI), m/z (relative intensity, %) 322 (M^++H, 100), 276 (3). HRMS calcd for $C_{16}H_{20}NO_4S$: 322.1113, found 322.1111.

7d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28-1.34 (m, 3 H), 1.84-1.88 (m, 3 H), 4.14-4.18 (m, 2 H), 4.20-4.27 (m, 4 H), 5.87-5.90 (m, 1 H), 6.29-6.32 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 57.7, 60.6, 67.2, 74.6, 79.2, 125.8, 136.4, 165.2. δ 3.4, 14.1, 58.2, 60.4, 67.4, 74.6, 82.4, 125.3, 136.6, 165.2; MS (EI), m/z (relative intensity, %) 129 (M^+, 77), 124 (54), 114 (64), 107 (64), 83 (84), 53 (100). HRMS calcd for $C_{10}H_{15}O_3$: 183.1022, found 183.1031.

General Procedure for the Tandem Addition/Cyclization of Carbamoselenoate onto 1,6-Enynes

Into a 3 mL Pyrex flask were placed carbamotelluroate **1** (1 mmol), 1,6-enyne **7** (1 mmol), and toluene (0.5 mL) under Ar. The mixture was refluxed with irradiation by a 500W tungsten lamp with a distance of 10 cm for 19-22 h. After cooling to rt, the solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography and further by preparative recycling HPLC to provide the expected product **8**. Although the *E*/*Z* ratio was determined by ^{1}H NMR, attempts for isolation of E/Z isomers failed, so the following spectra and analytical data were obtained from the *E*/*Z* mixture.

8a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1 Hz, 3 H), 1.31 (t, J = 7.1 Hz, 3 H), 2.38 (d, J = 16.9 Hz, 1 H), 2.62 (d, J = 16.6 Hz, 1 H), 2.90 (s, 3 H), 2.92 (s, 3 H), 2.98 (s, 3 H), 3.05 (s, 3 H), 3.14 (d, J = 16.6 Hz, 1 H), 3.97 (d, J = 10.0 Hz, 1 H), 4.01 (d, J = 9.7 Hz, 1 H), 4.15-4.33 (m, 4 H), 4.74 (d, J = 9.5 Hz, 1 H), 4.83 (d, J = 9.8 Hz, 1 H), 6.72 (s, 1 H), 6.94 (d, J = 2.2 Hz, 1 H), 7.19-7.32 (m, 3 H), 7.61-7.76 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.3, 35.3, 35.4, 37.0, 37.2, 41.2, 54.9, 56.6, 61.2, 61.6, 74.0, 75.0, 77.9, 93.9, 97.5, 113.3, 116.8, 127.8, 129.1, 129.3, 137.0, 137.6, 146.1, 151.3, 169.5, 169.7, 171.1, 171.2; IR (NaCl) 2979, 2932, 1732, 1652 cm^{-1}; MS (EI), m/z (relative intensity, %) 447 (M^+, 9), 240 (100). HRMS calcd for $C_{28}H_{23}NO_4Te$: 447.0689, found 447.0692.

8c: ^{1}H NMR (400 MHz, $CDCl_3$) [*Z* isomer] δ 1.08 (t, J = 7.1 Hz, 3 H), 2.43 (s, 6 H), 2.65 (d, J = 16.6 Hz, 1 H), 2.88 (s, 3 H), 2.93 (s, 3 H), 3.03 (d, *J* = 16.9 Hz, 1 H), 3.45 (dd, *J* = 2.4, 12.9 Hz, 1 H), 3.65 (d, *J* = 10.7 Hz, 1 H), 3.91 (d, *J* = 10.5 Hz, 1 H), 4.02 (d, *J* = 14.1 H, 1 Hz), 4.06 (q, *J* = 7.2 Hz, 2 H), 6.97 (t, *J* = 2.0 Hz, 1 H), 7.18-7.38 (m, 4 H), 7.58-7.74 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) [*E*/*Z* mixture] δ 13.8, 13.9, 21.5, 21.6, 35.2, 35.3, 35.4, 36.9, 37.0, 41.4, 53.9, 55.0, 55.7, 56.0, 56.3, 57.0, 61.1, 61.6, 98.5, 101.3, 113.0, 116.9, 127.5, 127.67, 127.74, 127.82, 127.84, 128.1, 129.1, 129.3, 129.4, 129.46, 129.57, 129.63, 129.9, 131.4, 131.7, 131.8, 132.8, 133.0, 137.2, 137.4, 137.52, 137.55, 140.8, 143.4, 143.5, 143.6, 145.9, 169.0, 169.2, 170.1, 170.3; IR (NaCl) 2981, 2931, 1738, 1732, 1716, 1658, 1651, 1644, 1634 cm^{-1}; MS (EI), m/*z* (relative intensity, %) 600 (M$^+$, 8), 445 (24), 393 (100), 72 (29). HRMS calcd for $C_{25}H_{30}N_2O_5STe$: 600.0938, found 600.0940.

8d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.1 Hz, 3 H, *Z*), 1.30 (t, *J* = 7.1 Hz, 3 H, *E*), 1.98 (s, 3 H, *E*), 2.26 (s, 3 H, *Z*), 2.52 (d, *J* = 16.6 Hz, 1 H, *Z*), 2.92 (s, 3 H, *Z*), 3.02 (s, 3 H, *Z* and *E*), 3.06 (s, 3 H, *E*), 3.34 (d, *J* = 16.3 Hz, 1 H, *Z*), 4.06-4.62 (m , 5 H, Z including 6 H (*E*)), 4.73 (d, *J* = 9.5 Hz, 1 H, *Z*), 7.22-7.34 (m, 3 H, *E* and *Z*), 7.71 (d, *J* = 6.9 Hz, 2 H, *Z*), 7.76 (d, *J* = 7.1 Hz, 2 H, *E*); ^{13}C NMR (100 MHz, $CDCl_3$) δ [*E* isomer] 14.1, 27.1, 35.3, 35.5, 37.3, 55.8, 61.4, 72.6, 78.3, 105.6, 114.6, 127.8, 128.9, 139.5, 144.5, 169.7, 172.2; [*Z* isomer] 14.1, 24.9, 35.3, 37.1, 37.2, 55.2, 61.1, 77.5, 79.5, 107.7, 113.0, 127.8, 129.1, 138.5, 145.7, 169.4, 172.0; IR (NaCl) 2980, 2934, 1732, 1716, 1659, 1651, 1644, 1634 cm^{-1}; MS (EI), m/*z* (relative intensity, %) 461 (12, M$^+$), 254 (100). HRMS calcd for $C_{19}H_{25}NO_4Te$ 461.0846, found 461.0842.

REFERENCES

1. N. Petragnani, ‘Tellurium in Organic Synthesis,’ Academic Press, London, 1994.
2. For recent reviews: J. V. Comasseto, L. W. Ling, N. Petragnani, and H. A. Stefani, *Synthesis*, 1997, 373; J. V. Comasseto and R. E. Barrentos-Asigarraga, *Aldrichimica Acta*, 2000, **33**, 66; N. Petragnani and H. A. Stefani, *Tetrahedron*, 2005, **61**, 1613; G. Zeni, D. S. Lüdtke, R. B. Panatieri, and A. L. Braga, *Chem. Rev.*, 2006, **106**, 1032.
3. L.-B. Han, K. Ishihara, N. Kambe, I. Ryu, A. Ogawa, and N. Sonoda, *J. Am. Chem. Soc.*, 1992, **114**, 7591; L.-B. Han, K. Ishihara, N. Kambe, A. Ogawa, and N. Sonoda, *Phosphorus Sulfur Silicon,* 1992, **67**, 243.
4. S. Fujiwara, Y. Shimizu, T. Shin-ike, and N. Kambe, *Org. Lett.*, 2001, **3**, 2085.
5. F. Minisci and A. Citterio, *Adv. Free-Radical Chem.*, 1980, **6**, 65.
6. G. B. Gill, G. Pattenden, and S. J. Reynolds, *J. Chem. Soc., Perkin Trans. 1*, 1994, 369.
7. D. Daniel, R. Middleton, H. L. Henry, and W. H. Okamura, *J. Org. Chem.*, 1996, **61**, 5617.
8. A. J. Bartlett, T. Laird, and W. D. Ollis, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1315.