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Photoinduced Group Transfer Radical Addition of Carbamotelluroates to Acetylenes

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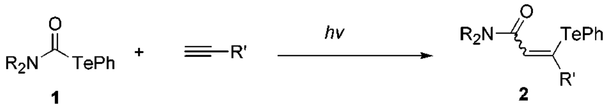
ABSTRACT



Te-Phenyl carbamotelluroates 1 add to acetylenes under irradiation of visible light to yield β-telluroacrylamides 2 regioselectively. This reaction would be initiated by homolytic cleavage of the carbamoyl carbon–tellurium bond, producing carbamoyl and PhTe radicals. The addition reaction proceeds via a radical chain mechanism comprising two processes: (i) addition of carbamoyl radicals at the terminal carbon of the triple bond, giving vinylic radicals, and (ii) S_H2 reaction on the Te atom caused by the attack of the vinyl radicals to 1.

Carbamoyl radicals have promising synthetic potential as a useful source for introduction of amide units into organic molecules, but their synthetic application has been much less explored than that of acyl radicals.[1] It has long been known that carbamoyl radicals can be generated from formamides by hydrogen abstraction with a *tert*-butoxy radical[2] or by photochemically induced C−H bond cleavage.[3−5] Recently, several new methods have been developed for their generation, i.e., abstraction of PhS, PhSe, or cobalt salophen groups from carbamothioates,[6] carbamoselenoates,[7] or carbamoylcobalt(III) salophens,[8] respectively, by oxidative decarboxylation of monoamides of oxalic acid,[9] and by radical-induced degradation of 1-carbamoyl-1-methylcyclohexa-2,5-dienes.[10] The synthetic usefulness of carbamoyl radicals has been well demonstrated by the successful formation of β-, γ-, δ-lactams[7a,8,10] and oxazolidine-2,4-diones[6] where carbamoyl radicals add intramolecularly to C−C and C−O double bonds. As for the intermolecular reaction of carbamoyl radicals, addition on aromatic rings[2c−e,9] and on olefinic carbons[7b] has been reported. It is also known that *N*-

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(1) For a recent overview, see: Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991−2069.

(2) (a) Friedman, L.; Shechter, H. *Tetrahedron Lett.* **1961**, 238−242. (b) Rieche, A.; Schmitz, E.; Gründemann, E. *Angew. Chem.* **1961**, *73*, 621. (c) Gardini, G. P.; Minisci, F.; Palla, G.; Arnone, A.; Galli, R. *Tetrahedron Lett.* **1971**, 59−62. (d) Leardini, R.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3164−3167. (e) Minisci, F.; Citterio, A.; Vismara, E. *Tetrahedron* **1985**, *41*, 4157−4170.

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(4) ESR studies of carbamoyl radicals: (a) Bosco, S. R.; Cirillo, A.; Timmons, R. B. *J. Am. Chem. Soc.* **1969**, *91*, 3140−3143. (b) Yonezawa, T.; Noda, I.; Kawamura, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 650−657. (c) Hefter, H.; Fischer, H. *Chem. Ber.* **1970**, *74*, 493−500. (d) Sutcliffe, R.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 7686−7687. (e) Grossi, L. *J. Chem. Soc., Chem. Commun.* **1989**, 1248−1250.

(5) Photogeneration of carbamoyl radicals from acetamides is quite an inefficient process: Mazzocchi, P. H.; Bowen, M. *J. Org. Chem.* **1976**, *41*, 1279−1282.

(6) Sakamoto, M.; Takahashi, M.; Fujita, T.; Nishio, T.; Iida, I.; Watanabe, S. *J. Org. Chem.* **1995**, *60*, 4682−4683.

(7) (a) Rigby, J. H.; Danca, D. M.; Horner, J. H. *Tetrahedron Lett.* **1998**, *39*, 8413−8416. (b) Keck, G. E.; Grier, M. C. *Synlett* **1999**, 1657−1659.

(8) (a) Gill, G. B.; Pattenden, G.; Reynolds, S. J. *Tetrahedron Lett.* **1989**, *30*, 3229−3232. (b) Gill, G. B.; Pattenden, G.; Reynolds, S. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 369−378.

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(10) Jackson, L. V.; Walton, J. C. *Chem. Commun.* **2000**, 2327−2328.

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monosubstituted carbamoyl radicals (RNHĊ(O)) are oxidized to isocyanates in the presence of Ag and Cu salts.[9]

We have developed a carbotelluration reaction of acetylenes with diorganyl tellurides in the presence of a radical initiator[11] or under light[11b] to form alkenyl tellurides. We have also disclosed convenient preparative methods of carbamotelluroates.[12] These findings and recent studies of other groups[13,14] for efficient generation of acyl radicals from tellurol esters and their trapping prompted us to examine the generation of carbamoyl radicals from carbamotelluroates and their addition to acetylenes aiming at the synthesis of β-telluroacrylamides.

Since *Te*-phenyl *N*,*N*-dimethylcarbamotelluroate (**1a**) exhibits its absorption in near UV−vis regions (λ_{max} = 311 nm (ϵ_{max} = 617)) (Figure 1), we irradiated a mixture of **1a** (1 mmol) and phenylacetylene (2 mmol) in a Pyrex flask with a tungsten lamp[15] at 60 °C for 24 h. Usual workup of the resulting mixture using preparative HPLC gave the corresponding β-telluroacrylamide **2a** in 72% yield (E/Z = 42/58) in pure form (Scheme 1).[16]

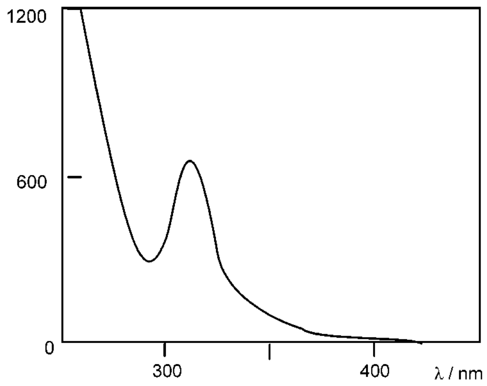
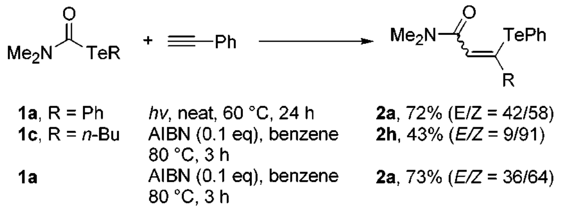


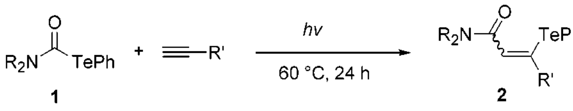
Figure 1. UV−vis spectra of carbamotelluroate **1a**.

Scheme 1



When the reaction was conducted in the dark at 60 °C or with light at 20 °C, **2a** was obtained only in <1% and <7% yields, respectively. These results indicate that irradiation and heating are both essential to promote the present reaction. Table 1 shows representative examples of addition to terminal acetylenes. These results suggest that reactions proceed efficiently when electron-deficient acetylenes are used. A reaction of **1a** with 1-octyne did not give the expected product under similar conditions. These results coincide with the nucleophilic nature of carbamoyl radicals.[17]

Table 1. Photoinduced Addition of Carbamotelluroates to Terminal Acetylenes[a]



run	R	R′	prod.	yield, %	E/Z[b]
1	Me	p-BrC$_6$H$_4$	**2b**	84	35/65
2	Me	p-CH$_3$OC$_6$H$_4$	**2c**	18	44/56
3	Me	2,4,6-(CH$_3$)$_3$C$_6$H$_2$	**2d**	31[c]	7/93
4	Me	CH$_3$OC(O)	**2e**	57	24/76
5	Me	(CH$_3$)$_3$Si	**2f**	35	61/39
6	Et	C$_6$H$_5$	**2g**	72	37/63

[a] Conditions: **1** (1 mmol), acetylene (2 mmol), 60 °C, irradiation with a tungsten lamp, 24 h. [b] E/Z ratio was determined by ^{1}H NMR. [c] 47 h.

Te-Phenyl carbamotelluroate **1b** (R = Et) added to phenylacetylene in 72% yield (run 6); however, *Te*-butyl

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(11) (a) Han, L.-B.; Ishihara, K.-I.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 7591−7592. (b) Han, L.-B.; Ishihara, K.-I.; Kambe, N.; Ogawa, A.; Sonoda, N. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *67*, 243−246. (c) Terao, J.; Kambe, N.; Sonoda, N. *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *136−138*, 637−638.

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(14) Imidoyl radicals, which have an isoelectronic structure of acyl radicals, were also generated from telluroimidates: (a) Ueda, Y.; Watanabe, H.; Uemura, J.; Uneyama, K. *Tetrahedron Lett.* **1993**, *34*, 7933−7934. (b) Yamago, S.; Miyazoe, H.; Goto, R.; Yoshida, J. *Tetrahedron Lett.* **1999**, *40*, 2347−2350.

(15) Photoinduced addition of tellurides to acetylenes reported by other groups: (a) Reference 14a. (b) Yamago, S.; Miyazoe, H.; Yoshida, J. *Tetrahedron Lett.* **1999**, *40*, 2343−2346.

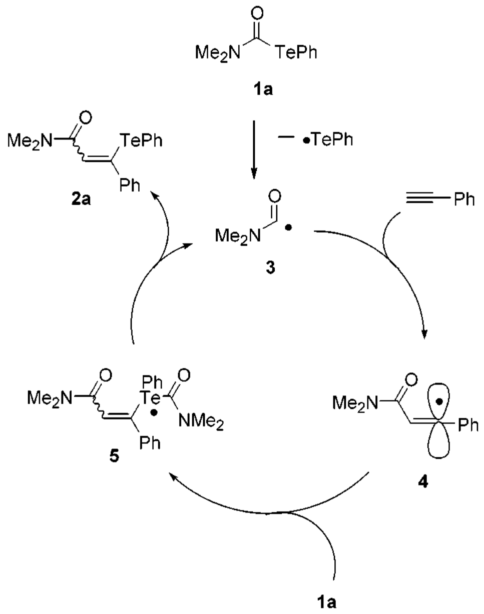
(16) **Typical experimental procedure**: Into a 3-mL Pyrex flask were placed carbamotelluroate **1a** (1 mmol) and phenylacetylene (2 mmol) under Ar. The mixture was irradiated in a water bath kept at 60 °C using a 500 W tungsten lamp with a distance of 10 cm for 24 h. After cooling to room temperature, excess phenylacetylene was removed in vacuo and the residue was purified by preparative recycling HPLC to provide *N*,*N*-dimethyl-3-phenyl-3-phenyltelluroacrylamide (**2a**) in 72% yield. The E/Z ratio was determined by ^{1}H NMR (E/Z = 42/58). The mixture was then treated with preparative TLC (silica gel) using n-hexane/Et$_2$O (5/1) as eluent to give pure (Z)-**2a** as a yellow solid. (Z)-**2a**: mp 76−77 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.10 (s, 6 H), 6.86−7.02 (m, 9 H), 7.39 (d, J = 7.8 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 36.1, 37.2, 119.37, 119.40, 121.2, 126.9, 127.0, 127.8, 128.0, 140.0, 141.5, 152.9, 167.0; IR (NaCl) 1614 (C═O) cm^{-1}. Anal. Calcd for C$_{17}$H$_{17}$NOTe: C, 53.88; H, 4.52; N, 3.70. Found: C, 54.15; H, 4.41; N, 3.59. An attempt for isolation of (E)-**2a** by PTLC failed, so the following spectra data were obtained from the E/Z mixture. (E)-**2a**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.62 (s, 3 H), 2.71 (s, 3 H), 6.07 (s, 1 H), 7.22−7.40 (m, 8 H), 7.83−7.86 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 34.5, 37.7, 114.3, 127.5, 128.1, 128.2, 128.5, 128.6, 128.8, 129.6, 130.0, 140.3, 167.5; IR (NaCl) 1628 (C═O) cm^{-1}.

(17) Minisci, F.; Citterio, A. *Adv. Free-Radical Chem.* **1980**, *6*, 65−153. Acyl radicals, an analogous structure of carbamoyl radicals, also possess a nucleophilic nature, see ref 1.

carbamotelluroate (**1c**) (R = Me) gave the product only in 6% yield, resulting in the recovery of most of **1c**. This might be due to the fact that **1c** has no absorption in the visible region. Therefore, we used a radical initiator in place of light to trigger the reaction. Thus, the reaction of **1c** with phenylacetylene was conducted in the presence of 0.1 equiv of AIBN at 80 °C for 3 h, affording **2h** in 43% yield (Scheme 1). Similar reaction of **1a** with phenylacetylene afforded **2a** in 73% yield. One practical drawback of this procedure is the difficulty in purification of products contaminated with byproducts **6** arising from direct addition of a 1-cyano-1-methylethyl group to phenylacetylene.

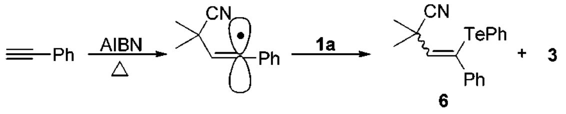
The present reaction may proceed via a radical chain mechanism initiated by photoinduced homolytic dissociation of **1** to carbamoyl radical **3** and PhTe radical (Scheme 2).

Scheme 2. A Plausible Reaction Patrhway



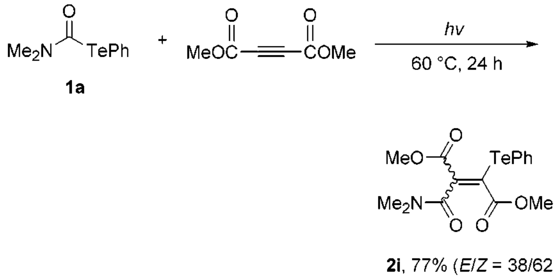
The initiation step of the reaction using AIBN is shown in Scheme 3. Since carbamoyl radicals added to the triple bond at the terminal carbon exclusively, this reaction affords only one regioisomer. The stereochemistry of the products was determined by NOE experiments, by chemical shifts of vinylic hydrogens, by frequencies of CO stretching vibration,[18] and/or by X-ray analysis ((*Z*)-**2b**[19]). Except in the case of run 5, *syn* addition predominated. The evidence that the *E*/*Z* ratio of products stays constant throughout the reaction period might imply that the stereochemistry of the addition is kinetically controlled. Since vinyl radicals **4** have either a π radical structure or a σ radical structure with rapid cis−trans isomerization,[20] the stereoselectivity would be determined by the relative stabilities of the transition states of the S_H2 reactions on tellurium (**5** or its analogous structure).

Scheme 3. Initiation Step Using AIBN



When dimethyl acetylenedicarboxylate was employed as a disubstituted acetylene, the addition also proceeded efficiently, affording the corresponding product **2i** in 77% yield (*E*/*Z* = 38/62) (Scheme 4).

Scheme 4



In summary, we have disclosed here a facile method for generation of carbamoyl radicals from carbamotelluroates. This is the first example of addition of carbamoyl radicals to the triple bond. The present reaction would be of great synthetic importance since alkenyl tellurides can successfully

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[18] Probably due to an intramolecular interaction between carbonyl oxygen and tellurium atoms, absorption of the carbonyl group of the *Z* isomers appears at lower frequency area than that of *E* isomers, see: (a) Ogawa, A.; Yokoyama, H.; Obayashi, R.; Kambe, N.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1748−1750. (b) Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N.; Sonoda, N. *Tetrahedron* **1993**, *49*, 1177−1188.

[19] Single crystals of (*Z*)-**2b** were obtained from *n*-hexane−$CHCl_3$ (1:1): monoclinic, $a = 13.946(1)$ Å, $b = 8.6562(7)$ Å, $c = 15.373(1)$ Å, $V = 1754.4$ Å^3, space group $P2_1/c$ (No. 14), $Z = 4$, $D_m = 1.733$ g cm^{-3}, μ(Mo Kα) = 39.78 cm^{-1}, $T = 296$ K. $R = 0.055$, $R_w = 0.097$ for 3984 observed intensities ($I > 2\sigma(I)$). The distance between the carbonyl oxygen and tellurium atoms is 2.67 Å which is much shorter than the sum of van der Waals radii (3.60 Å).

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[21] For recent reviews, see: (a) Petragnani, N. *Tellurium in Organic Synthesis*; Best Synthetic Methods; Academic Press: London, 1994. (b) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373−403. (c) Comasseto, J. V.; Barrentos-Asigarraga, R. E. *Aldrichimica Acta* **2000**, *33*, 66−78.

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be subjected to further manipulation, leading to useful organic compounds with retention of configuration,[21] e.g., the tellurium/metal exchange reactions such as Te/Li,[22] Te/Cu,[23] Te/Zn,[24] Te/Mg,[25] Te/Ca,[25] and Te/Na[25] and cross-coupling reactions.[26]

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Supporting Information Available: Full compound characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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