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Facile Synthesis of β-Organotellurobutenolides via Electrophilic Tellurolactonization of α-Allenoic Acids

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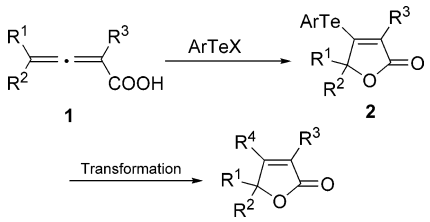
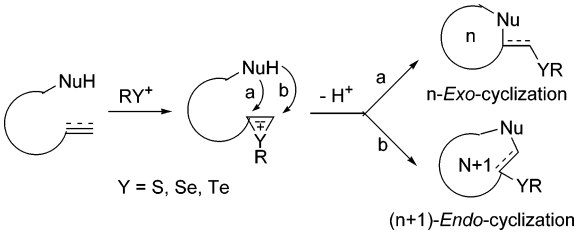


We report a convenient and highly efficient method for the synthesis of β-organotellurobutenolides by the aryltellurenyl halides-induced electrophilic tellurolactonization of α-allenoic acids under mild conditions. The resulting β-organotellurobutenolides can be utilized as precursors for versatile butenolide derivatives through a substitution reaction with organocuprate reagent or Pd/Cu(I)-catalyzed cross-coupling with terminal alkyne.

Ring structures abound in naturally occurring and biologically active molecules, and developing methods to construct those ring systems has been of substantial interest to synthetic organic chemists. Among the cyclization methods reported to date, electrophilic cyclization of alkenes or alkynes with a suitably positioned intramolecular nucleophile represents one of the most efficient and powerful means to construct ring systems because various functional auxiliaries can be easily introduced into the molecule, which allows further transformations for complex natural product synthesis.[1,2]

SCHEME 1



Recently, organotellurides,[3] especially the vinyltellurides,[4] have been regarded as an important intermediate in organic synthesis for their facile transformations to regio- and stereocontrolled substituted alkenes by reactions with organometallic reagents.[5] On the other hand, tellurium reagents-induced tellurocyclofunctionalization of unsaturated compounds, which may lead to heterocycles, has not been studied in detail (Scheme 1, Y = Te).[3b,6] Unlike similar seleno- and thiocyclofunctionalizations that have been extensively studied and applied in heterocycle synthesis (Scheme 1, Y = S, Se),[2,7] tellurocyclofunctionalization was reported only occasionally

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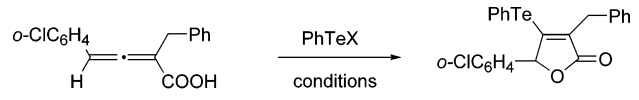
TABLE 1. Electrophilic Tellurolactonization of α-Allenoic Acid 1a with PhTeX



1a **2a**

entry	X (equiv)	base	solvent	temp, °C	time	yield,[a] %
1	I (1.2)	Et_3N	THF	0	24 h	trace
2	I (2.0)	Et_3N	MeCN	0	24 h	32
3	I (2.0)		MeCN	0	24 h	45
4	Br (1.2)	Et_3N	THF	0	24 h	38
5	Br (1.2)		THF	0	24 h	44
6	Br (2.0)		THF	0	23 h	92[b]
7	Br (2.0)		MeCN	0	9 h	93[b]
8	Br (2.0)		MeCN	rt	24 h	76
9	Cl (2.0)		MeCN	0	25 min	93[b]
10	Cl (2.0)		MeCN	rt	5 min	94[b]
11	Cl (1.1)		MeCN	rt	5 min	93[b]

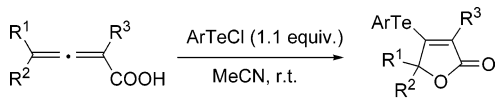
[a] Isolated yields based on **1a**. [b] Complete conversion of **1a** was observed by TLC analysis.

since its first example for tellurolactone synthesis in 1960.[8] In addition, the most frequently employed tellurium reagents are aryltellurium trihalides,[6a−d,8] tellurium tetrachloride,[6h,8b] or their equivalents,[6e−g] which usually requires the reduction of the cyclization products to tellurides prior to further transformations. Furthermore, only a few utilities of the resulting tellurides have been developed and are mainly confined to detelluration by tributyltin hydride.[6c−e]

In our ongoing efforts to develop organotellurides[9] and heterocycle compounds,[10] recently we achieved an efficient method for the preparation of β-iodovinyltellurides through the addition of aryltellurenyl iodide to alkynes.[9a] In this regard we deduced that the simple aryltellurenyl halides could also serve as the tellurenylating reagents in tellurocyclofunctionalization. Besides, it is well-known that allenes are interesting compounds with particular properties due to the presence of the unique cumulated diene structural unit.[11] Therefore, incorporating the allenyl structure with a readily available nucleophile, we commenced our study on the reaction of α-allenoic acids **1**[12] and aryltellurenyl halides. Herein reported are our preliminary findings on the ArTeX-induced electrophilic tellurolactonization of α-allenoic acids (Table 1).

When the reaction of α-allenoic acid **1a** ($R^1 = o\text{-}ClC_6H_4$, $R^2 = H$, $R^3 = PhCH_2$) and PhTeI[9a] as the tellurenylating reagent (1.2 equiv) was carried out in the presence of triethylamine (1 equiv) in THF, only a trace amount of a new product was observed, which was proved to be the cyclization product **2a** by spectra analysis (entry 1). While better yields were obtained by using 2 equiv of PhTeI and/or performing the reaction in the absence of an external base in acetonitrile (entries 2 and 3), it was still far from complete. It was observed that the reactions with PhTeBr as the tellurenylating reagent allowed higher conversion compared with those of PhTeI under similar conditions (entries 4 and 5). A complete conversion was achieved with 2 equiv of PhTeBr in THF at 0 °C in 23 h to give **2a** in 93% isolated yield (entry 6), and a similar yield could be obtained in a shortened reaction time of 9 h when acetonitrile was used as the solvent instead of THF (entry 7). However, attempts to shorten the reaction time by executing the reaction at elevated temperature failed even in prolonged reaction time affording lower product yield than at 0 °C may be due to the limited thermal stability of PhTeBr at room temperature (entry 8). On the other hand, we were pleased to find that PhTeCl[13] showed much higher reactivity than its bromide and iodide analogues. With 2 equiv of PhTeCl as the tellurenylating reagent, the reaction was complete in 25 min in acetonitrile at 0 °C (entry 9). Unlike PhTeBr that is unstable above 0 °C, PhTeCl is thermally stable and the reaction could be carried out at room temperature to afford the product in high yield with complete conversion in only 5 min (entry 10). Furthermore, the amount of PhTeCl could be reduced to 1.1 equiv without any decrease in reactivity (entry 11).

TABLE 2. Synthesis of Substituted β-Organotellurobutenolides 2



1 **2**

entry	**1**: R^1, R^2, R^3	Ar	time	product	yield,[a] %
1	**1a**: $o\text{-}ClC_6H_4$, H, $PhCH_2$	Ph	5 min	**2a**	93
2	**1b**: H, H, $PhCH_2$	Ph	30 min	**2b**	79
3	**1c**: $n\text{-}C_4H_9$, H, H	Ph	10 min	**2c**	84
4	**1c**: $n\text{-}C_4H_9$, H, H	α-naphthyl	30 min	**2d**	81
5	**1d**: $n\text{-}C_4H_9$, H, $PhCH_2$	Ph	10 min	**2e**	92
6	**1e**: $n\text{-}C_8H_{17}$, H, H	Ph	10 min	**2f**	85
7	**1f**: Ph, H, Allyl	Ph	5 min	**2g**	94
8	**1g**: Ph, H, $PhCH_2$	Ph	5 min	**2h**	94
9	**1h**: $o\text{-}ClC_6H_4$, H, H	Ph	5 min	**2i**	91
10	**1i**: H, H, H	Ph	24 h		—[b]
11	**1j**: H, H, Allyl	Ph	24 h		trace[b]

[a] Isolated yields based on **1**. [b] 2.0 equiv of PhTeCl was added at room temperature. Complex reaction occurred and a mixture of multiple unidentified products was obtained.

Once the reaction condition was optimized with PhTeCl as an effective tellurenylating reagent, we applied this protocol for the tellurolactonization of α-allenoic acid. As summarized in Table 2, various di- and trisubstituted α-allenoic acids can be utilized as substrates to afford corresponding substituted β-organotellurobutenolides in good to high yield within 30 min. A bulky tellurenylating

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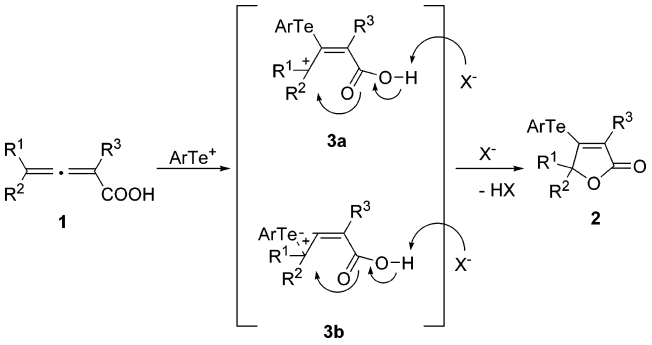
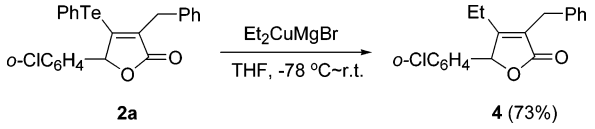
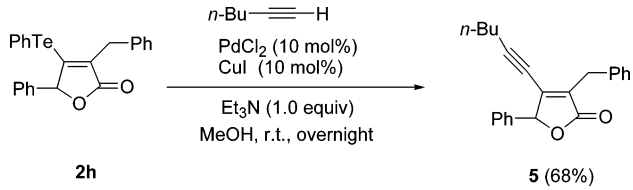
SCHEME 2



SCHEME 3



SCHEME 4



reagent bearing the naphthyl group also gave cyclization product in good yield (entry 4). In the case of 2-allyl α-allenoic acid **1f**, the allyl group remained unreacted indicating that the allenyl moiety is more reactive than the individual carbon−carbon double bond (entry 7). However, with the reaction of nonsubstituted 2,3-butadienoic acid **1i** no cyclization product was observed by NMR analysis of the reaction mixture (entry 10). When monosubstituted 2-ally-2,3-butadienoic acid **1j** was used as the substrate, the reaction was sluggish, giving only a trace amount of the desired product, as was observed by NMR analysis (entry 11).

The tellurolactonization of α-allenoic acids probably proceeds through the electrophilic attack of the aryltelluro cation on the central carbon atom of the allenyl moiety to afford the intermediate, the allyl cation **3a** and/or the onium cation **3b**,[3j] which is stabilized by neighboring group participation (Scheme 2).[14] Further cyclization of the intermediate affords the final product. Because the stabilization of the cationic intermediate by substituents is important for the generation of **3a** or **3b**, the lack of neighboring group participation will result in sluggish tellurolactonization of the α-allenoic acids. Therefore, in the case of nonsubstituted **1i** and monosubstituted **1j**, no or only a trace amount of the cyclization product was observed, respectively (entries 10 and 11).

Butenolides are a class of compounds commonly observed in natural products,[15] and are also important intermediates in organic synthesis.[16] Bearing a versatile vinyltelluro moiety, the obtained β-organotellurobutenolides can be considered as potential precursors for useful substituted butenolides, which was confirmed by the following preliminary synthetic transformation studies. Substitution reaction of **2a** with diethyl cuprate reagent at −78 °C gave a good yield of target product **4** (Scheme 3). Furthermore, in the presence of a catalytic amount of Pd/Cu(I) and 1 equiv of Et_3N, the mixture of **2h** and 1-hexyne in methanol afforded the cross-coupling product **5** in a moderate yield after overnight stirring at room temperature (Scheme 4).

In conclusion, we developed a convenient and highly efficient method for the preparation of β-organotellurobutenolides via ArTeCl-induced electrophilic tellurolactonization of α-allenoic acids. Preliminary transformation studies suggest that the obtained tellurobutenolides are practical precursors for useful substituted butenolides. Extensive studies of the reaction in heterocycle synthesis as well as detailed mechanistic studies are still in progress and will be reported in due course.

Experimental Section

General Procedure for Electrophilic Tellurolactonization of α-Allenoic Acids. To a solution of diaryl ditelluride (0.50 mmol) in dry MeCN (2 mL) under N_2 was added dropwise SO_2Cl_2 (0.081 g, 0.60 mmol) and the mixture was stirred at room temperature for 1 h. α-Allenoic acid (0.50 mmol) in dry MeCN (2 mL) was then added to above ArTeCl solution with stirring. After the reaction was complete, the mixture was concentrated and the residue purified by flash chromatography or preparative TLC to afford β-organotellurobutenolides **2**. Reactions carried out under different conditions were conducted in a similar manner.

3-Benzyl-4-phenyltelluro-5-(*o*-chloro)phenyl-2(5*H*)-butenolide (2a): 93%, pale yellow crystal, mp 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.25 (m, 8H), 7.20−7.12 (m, 3H), 7.06−7.02 (m, 2H), 6.97−6.96 (d, J = 5.6 Hz, 1H), 6.03 (s, 1H), 3.91−3.87 (d, J = 15.3 Hz, 1H), 3.71−3.67 (d, J = 15.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 144.7, 141.0, 137.1, 136.2, 135.4, 132.3, 130.5, 129.7, 129.60, 129.5, 129.3, 128.9, 127.2, 127.0, 109.0, 33.4. MS (*m/z*) 490 (13, M^+), 455 (5), 282 (7), 265 (13), 239 (8), 207 (6), 139 (53), 115 (43), 91 (35), 77 (100). IR (KBr) ν 1739, 1602, 1473, 1435, 1300, 1171, 1065 cm^{-1}. Anal. Calcd for $C_{23}H_{17}ClO_2Te$: C, 56.56; H, 3.51. Found: C, 56.32; H, 3.54.

Substitution Reaction of Organotellurobutenolide 2a with Diethyl Cuprate Reagent. Ethylmagnesium bromide (1.50 mmol) in dry THF was added at 0 °C to the THF suspension of CuI (0.75 mmol) in a tube reactor under nitrogen to form the diethyl cuprate reagent. The mixture was then cooled to −78 °C and tellurobutenolide **2a** (0.50 mmol) in dry THF was added dropwise. After the temperature was gradually returned to room temperature, the mixture was washed with saturated aqueous NH_4Cl and NaCl, extracted with EtOAc, and dried over $MgSO_4$. The solvent was evaporated and the residue purified by TLC to afford substitution product **4**.

3-Benzyl-4-ethyl-5-(*o*-chloro)phenyl-2(5*H*)-butenolide (4): 73%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.39 (dd, J = 7.8, 1.4 Hz, 1H), 7.30−7.20 (m, 7H), 7.01−6.99 (dd, J = 7.2, 1.6 Hz, 1H), 6.35 (s, 1H), 3.74−3.64 (m, 2H), 2.53−2.43 (m,

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1H), 2.10−2.01 (1H), 0.96−0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 165.6, 138.1, 133.8, 132.5, 130.4, 130.0, 128.7, 128.5, 127.9, 127.5, 126.6, 126.4, 79.7, 29.6, 20.1, 12.2. MS (*m/z*) 312 (2, M^+), 84 (100). IR (film) ν 3029, 1760, 1669, 1602, 1495, 1454, 1299, 1164, 1107, 1044, 1015 cm^{-1}. Anal. Calcd for $C_{19}H_{17}ClO_2$: C, 72.96; H, 5.48. Found: C, 72.65; H, 5.51.

Cross-Coupling Reaction of Organotellurobutenolide 2h with 1-Hexyne. The mixture of **2h** (0.50 mmol), 1-hexyne (1.0 mmol), $PdCl_2$ (10 mol %), CuI (10 mol %), and triethylamine (0.50 mmol) in MeOH (5 mL) was stirred overnight under nitrogen. Conventional workup and preparative TLC purification afforded **5**.

3-Benzyl-4-(1-hexynyl)-5-phenyl-2(5*H*)-butenolide (5): 68%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.22 (m, 10H), 5.71 (s, 1H), 3.79−3.71 (m, 2H), 2.38−2.35 (t, J = 7.0 Hz, 2H), 1.48−1.42 (m, 2H), 1.33−1.28 (m, 2H), 0.88−0.84 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 115.0, 137.6, 134.7, 133.0, 129.2, 128.9, 128.7, 128.6, 126.7, 110.0, 83.7, 72.1, 31.1, 30.1, 21.8, 19.7, 13.5. MS (*m/z*) 330 (2, M^+). IR (film) ν 3031, 2958, 2872, 2221, 1761, 1640, 1495, 1455, 1356, 1163, 1084, 1021 cm^{-1}. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.34; H, 6.75.

Characterization data of other products are shown in the Supporting Information.

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Supporting Information Available: Experimental procedures, characterization data, and copies of ^{1}H NMR and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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