

Telluroacylative Addition of Telluroesters to Terminal Alkynes Catalyzed by Cuprous Iodide

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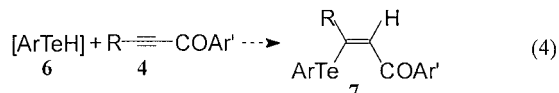
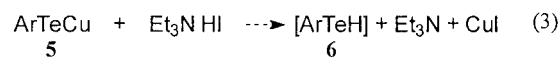
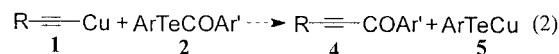
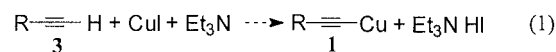
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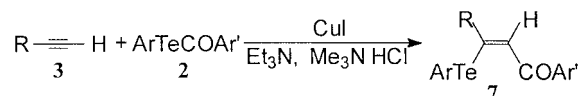
Research on vinyl selenides and tellurides has attracted considerable attention in recent years due to the varied reactivity of their selenium and tellurium atoms. These compounds can normally be prepared from the addition reactions of selenium and tellurium reagents with alkynes or from the elimination reactions of saturated (haloalkyl)selenides and tellurides.¹ The bifunctional addition reactions involving selenium and tellurium atoms have recently been developed as useful methods for preparation of vinyl selenides and tellurides with various functional groups.² Among them, the addition reactions involving the simultaneous introduction of carbon-centering functional groups have special importance for organic synthesis.³ Han et al. have reported the radical addition of diorganyl tellurides to alkynes to afford (β -alkylvinyl)tellurides.⁴ Now we have developed a practical method for the preparation of (*Z*)- β -(aryltelluro)- α,β -unsaturated ketones via Cu(I)-catalyzed telluroacylative addition of telluroesters to terminal alkynes, with which the aryl tellurenyl and acyl groups were simultaneously introduced to the organic molecules.

It has been reported that cuprous alkynylides could be acylated with acyl chlorides to produce α,β -alkynones.⁵ Considering that the C–Te bond of telluroesters is weak and very easy to be broken,^{3a} we assumed that telluroesters **2** would have the reactivity toward cuprous alkynylides similar to that of acyl chlorides. Cuprous alkynylides **1**, formed from alkynes **3** and cuprous halide in the presence of organic base,⁶ were expected to be directly acylated by telluroesters **2** in a similar manner to afford α,β -alkynones **4** and cuprous tellurides **5**. It was expected that the cuprous aryl tellurides **5** be converted to arenetellurols **6** by triethylamine hydro-

Scheme 1



Scheme 2



halide that was produced during the formation of cuprous alkynylides **1**. Arenetellurols **6** would add to α,β -alkynones **4** nucleophilically to form the adducts **7**. The above assumption is shown in Scheme 1.

Telluroesters **2** were prepared by the reaction of arylmagnesium bromides with powder tellurium, followed by the acylation with acyl chlorides.⁷ The experimental results indicated that when the mixture of telluroesters **2** and terminal alkynes **3** was heated in anhydrous dimethylformamide in the presence of cuprous iodide and triethylamine for 1 h and then was exposed to the air, α,β -alkynones **4** and diaryl ditellurides **8** were isolated in 86–89% and 91–94% yields, respectively. In addition, a trace amount of yellowish solids was isolated and characterized by IR, ¹H NMR, and MS as (*Z*)- β -aryltelluro- α,β -unsaturated ketones **7**.

The isolation of diaryl ditellurides **8** implied that the anions of tellurides, which are readily oxidized by oxygen to give **8**, may be formed. Phenylethyne reacted with telluroesters to afford mainly α,β -alkynones **4** and diaryl ditellurides **8**, while the additive products were isolated in less than 10% yields. We assumed that the acidification and addition of cuprous aryl tellurides to α,β -alkynones **4** (eqs 3 and 4 in Scheme 1) would be the rate-determining steps of the reaction. Thus, after the telluroesters disappeared in the above reaction, trimethylamine hydrochloride was added to ensure that cuprous aryl tellurides **5** be converted to arenetellurols **6**, which then add to **4** as quickly as possible. In this case, the addition reaction of telluroesters with alkynes was completed within 8 h when heated at 60–70 °C, producing the adducts **7** with high stereoselectivity in high yields⁸ (Scheme 2 and Table 1).

Through the above procedure only (*Z*)-adducts were isolated, whose configuration was confirmed based on the study of ¹H NMR. In a difference NOE experiment of **7e**, irradiation of the peak of phenyl at δ 6.99 responded to the vinylic protons (δ 8.04) with 7% enhancement. The ortho-protons of carbonyl in *p*-chlorobenzoyl (δ 8.00) showed 4%

(1) For recent reviews about vinyl selenides and tellurides see: (a) Comassetto, J. V.; Ling, L. W.; Petraghani, N.; Stefani, H. A. *Synthesis* **1997**, 373. (b) Comassetto, J. V. *J. Organomet. Chem.* **1983**, 253, 134.

(2) For bifunctional addition of X–Y bonds (X = Se, Te; Y = P, S, Si, etc.) to alkynes, see the following: (a) Han, L.-B.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, 118, 7000. (b) Kanda, T.; Koike, T.; Kagohashi, S.; Mizoguchi, K.; Murai, T.; Kato, S. *Organometallics* **1995**, 14, 4975. (c) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, 48, 3077. (d) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, 46, 3249. (e) Ogawa, A.; Obayashi, R.; Ine, H.; Tsuboi, Y.; Sonoda, N.; Hira, T. *J. Org. Chem.* **1998**, 63, 881. (f) Murai, T.; Nonomura, K.; Kato, S. *Organometallics* **1991**, 10, 1095. (g) Ogawa, A.; Sonoda, N. *J. Synth. Org. Chem. Jpn.* **1993**, 51, 815.

(3) (a) Crich, D.; Chen, C.; Hwang, J.; Yuan, H.; Papadatos, A.; Walter, R. I. *J. Am. Chem. Soc.* **1994**, 116, 8937. (b) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.-I.; Rau, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, 113, 9796.

(4) (a) Han, L.-B.; Ishihara, K. I.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, 114, 7591. (b) Han, L.-B.; Ishihara, K. I.; Kambe, N.; Ogawa, A.; Sonoda, N. *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, 67, 243.

(5) Normant, J. F.; Bourgain, M. *Tetrahedron Lett.* **1970**, 2659.

(6) Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Chem. Lett.* **1982**, 253. We found that cuprous alkynylides could be prepared from cuprous iodide and terminal alkynes in the presence of triethylamine. The typical procedure is as follows: Terminal alkyne (2 mmol) was added dropwise to a solution of cuprous iodide (0.38 g, 2 mmol) and triethylamine (0.42 mL, 3 mmol) in 10 mL of dimethylformamide with stirring at room temperature. The resulting mixture was stirred for 30 min. Water (20 mL) was added, and the solid was filtered, washed with water, ethanol, and ether, respectively, affording a yellow solid of cuprous alkynylide, with 80–93% yields for different alkynes.

(7) Zhao, C. Q.; Huang, X. *Synth. Commun.* **1997**, 27, 249.

(8) Typical procedure for telluroacylation: Under N₂, telluroester (1 mmol), phenylethyne (0.11 g, 1 mmol), cuprous iodide (0.09 g, 0.5 mmol), and triethylamine (0.14 mL, 1 mmol) in 5 mL of anhydrous DMF were heated at 50–60 °C for 1 h. Trimethylamine hydrochloride was then added after cooling, and the mixture was heated at 60–70 °C for another 8 h. The saturated solution of NH₄Cl (20 mL) was added after cooling. The precipitate was filtered away and washed with ether. The filtrate was extracted with ether three times. The combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the residue was recrystallized from ether.

Table 1. Tellurocarbonylative Addition of Telluroesters to Alkynes

Entry	Alkynes	Telluroesters	Products	Yields (%) ^a
1		PhTeCOPh 2a		81
2	3a			86
3	3a			88
4	3a			75
5	3a			91
6	3a			79
7		2f		64

^a Isolated yields.

enhancement when irradiated at the peak of protons in (*p*-chlorophenyl)tellurenyl (δ 6.90). It was confirmed that the phenyl and vinylic proton were in the *cis*-position and the products **7** were in the (*Z*)-configuration.

We suggested that the mechanism of this reaction may involve nucleophilic addition of arenetellurolys to alkynes.⁹ It has been reported that the heavy metallic ions^{6,10} such as copper and mercury can promote the cleavage of C–Se or C–Te bonds. As a soft acid, cuprous ion has a strong affinity for the aryl telluride anions, which are soft bases. In the presence of cuprous ion, selenoesters and telluroesters are easily attacked at the carbonyl carbon atom by a variety of nucleophilic reagents, such as water, alcohol, and stable carboanion, to afford carboxylic acids, esters, and other acylated products, respectively.¹⁰ In the titled reaction, the anions of alkynes attacked at telluroesters as nucleophilic reagents by analogy, producing alkynes readily. The subsequent addition to afford (*Z*)-adducts was similar to the reported case.^{9,11}

In conclusion, herein we have revealed telluroacylation addition of telluroesters to terminal alkynes, with which (*Z*)- β -(aryltelluro)- α,β -unsaturated ketones were generated by one step. To the best of our knowledge, the bifunctional addition involving the introduction of tellurenyl and acyl groups to alkynes has scarcely been reported. This reaction provided a new way for formation of C–C bonds and expanded the methodological application of tellurium reagents to organic synthesis.

Probably due to the heat-sensitivity, the attempted isolation of aliphatic derivatives of β -telluro- α,β -unsaturated ketones was unsuccessful in most cases. It seems that this reaction is limited to only aromatic telluroesters. The examination of aliphatic substrates and the synthetic application of the adducts **7** are now in progress.

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Supporting Information Available: Experimental procedures and compound characterization data (2 pages).

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(10) (a) For the reactions involving selenium and tellurium reagents promoted by heavy metallic ions, see ref 6 and references therein. (b) Dabdoub, M. J.; Viana, L. H. *Synth. Commun.* **1992**, *22*, 1619.

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