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# Cesium Hydroxide-Catalyzed Reaction of Terminal Alkynes with Diarylditellurides to Synthesize Alkynyl Tellurides

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### Cesium Hydroxide–Catalyzed Reaction of Terminal Alkynes with Diarylditellurides to Synthesize Alkynyl Tellurides

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**Abstract:** In the presence of a catalytic amount of cesium hydroxide under an air atmosphere, the reaction of diarylditellurides (1.0 mmol) with terminal alkynes (2.2 mmol) at room temperature exclusively give alkynyl tellurides in good yields.

Keywords: Alkynyl telluride; Cesium hydroxide; Diarylditelluride; Terminal alkyne

Cesium base has received increasing interest in the past few years, and many articles have reported its powerful basicity, offering a new reagent for the formation of a variety of carbon–heteroatom and carbon–carbon bonds. Because of its strong basicity, it can efficiently promote many reactions such as areneselenylation of aryl bromides and iodides;<sup>[1]</sup> three-component coupling of aliphatic alcohols, CO<sub>2</sub>, and alkyl halides;<sup>[2]</sup> cross-coupling reaction of arylsilanols with substituted aryl halide;<sup>[3]</sup> a one-pot, two-step synthesis of tetrahydro asterriquinone E;<sup>[4]</sup> palladium-catalyzed amination of aryl iodide;<sup>[5]</sup> *O*-alkylation of alcohols for the efficient ether synthesis and mixed alkyl carbonates;<sup>[6,7]</sup> *Se*-alkylation of benzeneselenol and benzeneselenenyl bromide for the highly efficient synthetic unsymmetrical organoselenides;<sup>[8]</sup> *N*-alkylation of primary amines for the efficient preparation of secondary amines;<sup>[9]</sup> and so on. Cesium base can react with terminal alkynes to give a nucleophilic alkynide

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Entry	R	Ar	Mp (°C)	Yield (%)
3a	CH <sub>3</sub> OCH <sub>2</sub>	$C_6H_5$	Oil	89
3b	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub>	$C_6H_5$	Oil	83
3c	HOCH <sub>2</sub>	$C_6H_5$	Oil	78
3d	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	$C_6H_5$	Oil	86
3e	$C_6H_5$	$C_6H_5$	Oil	86
3f	$C_6H_5$	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	70–71 <sup>[12]</sup>	88
3g	$C_6H_5$	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	69–70 <sup>[20]</sup>	90

Table 1. Synthesis of alkynyl tellurides 3a-g

anion. Literature reports show that cesium hydroxide catalyzed alkynylation of aldehyde, ketones, and nitrills<sup>[10]</sup> and promoted the reaction of terminal alkynee with benzeneselenenyl bromide.<sup>[8]</sup> Our group reported the cesium hydroxide catalyzed a reaction of terminal alkynes with diaryldiselenides, and the results showed that under an air atmosphere and at room temperature, it gave a mixture of (Z)-1,2-bis-(aryseleno)-1-alkenes and alkynyl selenides. Under an N<sub>2</sub> atmosphere and at room temperature, the reaction gave exclusively (Z)-1,2-bis-(aryseleno)-1-alkenes.<sup>[11]</sup> Diarylditelluride is similar to diaryldiselenide in properties, and this promoted us to investigate the reaction of terminal alkynes with diarylditellurides in the presence of a catalytic amount of cesium hydroxide. In this article we report the results.

The experiments showed that in the presence of a catalytic amount of cesium hydroxide (0.2 mmol), using tetrahydrofuran (THF) as solvent, at room temperature and under an air atmosphere, terminal alkynes (2.2 mmol) reacted with diarylditellurides (1.0 mmol) to give exclusively alkynyl tellurides in good yields (Scheme 1). The results are summarized in Table 1.

The mechanism of the cesium hydroxide-catalyzed reaction is described in Scheme 2.

The terminal alkynes reacted with cesium hydroxide to give water and acetylide ion, which reacted with diarylditellurides to give alkynyl tellurides and cesium aryltelluride. The latter was oxidized by oxygen in the presence of water and was converted into the starting diarylditelluride. Thus, to make ArTeTeAr react completely, air is necessary. In the absence of oxygen, the highest yields of alkynyl tellurides are 50% based on telluride atom.

We investigated the case under an  $N_2$  atmosphere, and the result showed it gave only alkynyl telluride. About 50% diarylditelluride was

$$RC \equiv CH + 0.5 \text{ ArTeTeAr} \xrightarrow{\text{CsOH (cat.), Air}} RC \equiv CTeAr$$

$$1 \qquad 2 \qquad 3a\sim g$$

Scheme 1. Cesium hydroxide catalyzed alkynyl tellurides synthesis.

$$RC \equiv CH + CsOH \longrightarrow RC \equiv CCs + H_2O$$
  

$$RC \equiv CCs + ArTeTeAr \longrightarrow RC \equiv CTeAr + ArTeCs$$
  

$$ArTeCs + H_2O + O_2 \longrightarrow 0.5 ArTeTeAr + CsOH$$

Scheme 2. The possible mechanism of the reaction.

recovered, and no 1,2-bis(arytelluro)-1-alkene was obtained. This result indicated that in room temperature and in THF, the ArTeCs cannot undergo the nucelophilic addition to alkynyl tellurides. Under the same conditions, ArSeCs could efficiently carry out addition to alkynyl selenides.<sup>[11]</sup> It is well known that ArTeM is a stronger nucleophile than ArSeM in the usual nucleophilic substitution reaction. Thus, the difference in the reaction is because arylselenovinylic anions have higher stability than the corresponding aryltellurovinylic anions.

The alkynyl tellurides is an important synthetic intermediate. Some methods to prepare alkynyl tellurides were developed, such as the reaction of the lithium alkynides with elemental tellurium, followed by trapping the intermediates lithium tellurolates with alkyl halides or by the reaction of the corresponding lithium alkynylides with aryltellurium bromides,<sup>[12,13]</sup> treatment of haloacetylenes with lithium organotellurolates,<sup>[14]</sup> reaction of appropriate terminal alkynes with phenvltellurium bromide in the presence of cuprious iodide.<sup>[15]</sup> reaction of terminal alkynes with diarylditellurides in DMSO in the presence of cuprious iodide, treatment of alkynylphenyliodonium tosylates with arenetellurolates,<sup>[16]</sup> treatment of arenetellurenyl halides sodium with Grignard reagents,<sup>[17]</sup> and the reaction of arenetellurenamides with terminal alkynes.<sup>[18]</sup> However, these methods are deficient in some respects; they are expensive or toxic, use not readily available reagents, have strict reaction conditions or difficulties with isolation of the products, or have limited scope.

The present method has its own advantages: atom economy based on tellurium, readily available starting materials, undried and nontoxic solvent, no inert atmosphere, mild conditions, and simple reaction and workup procedures. It provides a simple and practical path for the preparation of alkynyl tellurides.

#### **EXPERIMENTAL**

<sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on an Inova-400 spectrometer using CDCl<sub>3</sub> as the solvent with TMS as an internal standard. MS spectra were determined on an HP5989A spectrometer.

#### General Procedure for the Preparation of Alkynyl Tellurides

Diaryl ditelluride (1.0 mmol) and cesium hydroxide (30 mg, 0.2 mmol) were added to a solution of alkynes (2.2 mmol) in THF (10.0 mL). The reaction mixture was stirred at room temperature for 48 h under an air atmosphere and monitored by thin-layer chromatography (TLC) until the diarylditelluride was fully reacted. After removal of THF under vacuum, 10 mL of water were added to the residue and extracted with petroleum ether ( $3 \times 30$  ml). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by flash chromatography and eluted with petroleum ether/ethyl ethyl ether (30:1) to give 3a–g.

#### Data

Compound 3a: IR (film)  $\nu/\text{cm}^{-1}$ : 2150; <sup>1</sup>H NMR 3.42 (s, 3H), 4.39 (s, 2H), 7.26–7.28 (m, 3H), 7.69–7.71 (m, 2H); <sup>13</sup>C NMR 135.4, 129.7, 128.0, 112.4, 111.0, 61.0, 57.6, 44.8; MS (m/z): 276 (M<sup>+</sup>).

Compound 3b: IR (film)  $\nu/\text{cm}^{-1}$ : 2145; <sup>1</sup>H NMR 4.93 (s, 2H), 6.96– 6.98 (m, 4H), 7.22–7.31 (m, 4H), 7.62–7.64 (m, 2H), <sup>13</sup>C NMR 157.6, 135.5. 129.7, 129.4, 128.0, 121.4, 115.0, 112.3, 109.9, 57.1, 29.7; MS (m/z): 333 (M<sup>+</sup>).

Compound 3c: IR (film)  $\nu/cm^{-1}$ : 2140; <sup>1</sup>H NMR 2.02 (s, 1H), 4.53 (s, 2H), 7.27–7.28 (m, 3H), 7.70–7.72 (m, 2H); MS (m/z): 262 (M<sup>+</sup>).

Compound  $3d^{[19]}$ : IR (film)  $\nu/cm^{-1}$ : 2140; <sup>1</sup>H NMR 0.87 (t, 3H), 1.07–1.74 (m, 8H), 2.58 (t, J = 6.9 Hz, 2H), 7.10–7.26 (m, 3H), 7.53–7.74 (m, 2H); MS (m/z): 316 (M<sup>+</sup>).

Compound 3e: IR (film)  $\nu/cm^{-1}$ : 2135; <sup>1</sup>H NMR 7.26–7.30 (m, 1H), 7.33–7.36 (m, 5H), 7.51–7.53 (m, 2H), 7.59–7.62 (m, 2H); MS (m/z): 308 (M<sup>+</sup>).

Compound 3f: IR (KBr)  $\nu/\text{cm}^{-1}$ : 2140; <sup>1</sup>H NMR 3.70 (s, 3H), 6.79 (d, J = 9.0 Hz, 2H), 7.30 (m, 5H), 7.71 (d, J = 9.0 Hz, 2H); MS (m/z): 338 (M<sup>+</sup>).

Compound 3g: IR (KBr)  $\nu/cm^{-1}$ : 2140; <sup>1</sup>H NMR 2.34 (s, 3H), 7.14 (d, 2H, J = 8.0 Hz), 7.31–7.33 (m, 3H), 7.47–7.49 (m, 4H); MS (m/z): 322 (M<sup>+</sup>).

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