



## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

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Accepted author version posted online: 16 Apr 2014. Published online: 09 Jun 2014.

To cite this article: Ling Xiao Wang, Liu Su, Jian Hua Li, Ning Bo Li, Zhi Hong Peng, Yuan Yuan Li & Xin Hua Xu (2014) Simple and Convenient Method for the Synthesis of Aryltelluorophosphates Catalyzed by Cesium Hydroxide, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 44:14, 2088-2093, DOI: [10.1080/00397911.2013.879897](https://doi.org/10.1080/00397911.2013.879897)

To link to this article: <http://dx.doi.org/10.1080/00397911.2013.879897>

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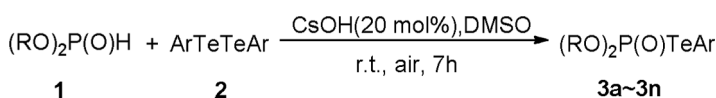


## SIMPLE AND CONVENIENT METHOD FOR THE SYNTHESIS OF ARYLTELLUROPHOSPHATES CATALYZED BY CESIUM HYDROXIDE

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### GRAPHICAL ABSTRACT



**Abstract** In the presence of a catalytic amount cesium hydroxide, the corresponding aryltellurophosphates can be obtained by the reactions of dialkyl phosphites with diaryl ditellurides in excellent yield at room temperature, using dimethylsulfoxide as solvent. The possible reaction mechanism was discussed. The method could provide a new and expedient path for the preparation of aryltellurophosphates.

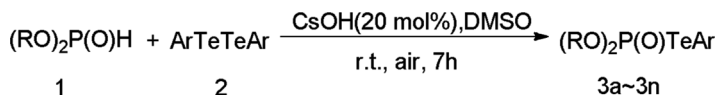
**Keywords** Aryltellurophosphates; cesium hydroxide; diaryl ditellurides

## INTRODUCTION

*S*-, *Se*-, and *Te*-aryl phosphorochalcogenoates (chalcogenophosphates) are very useful synthetic intermediates for synthetic and biological studies.<sup>[1–10]</sup> General methods for the preparation of phosphorochalcogenoates esters bearing thio and/or seleno substituents have been well documented.<sup>[11–15]</sup> However, as congener element, there are a few reports for the preparation of *Te*-aryl phosphorotelluroates; therefore only little was known about their reactivities, although the phosphorotellurate esters should provide a great interest on account of their reactivities. To our knowledge, Huang reported the aryltellurophosphates were prepared by the free radical reaction initiated by azobisisobutyronitrile (AIBN) or sodium azide (NaN<sub>3</sub>).<sup>[16–18]</sup> An alternative preparation of *Te*-aryl phosphorotelluroates in good yields that used 4-methoxyphenyltellurium trichloride and dialkyl or trialkyl phosphites was reported by Hayashi et al.<sup>[19]</sup> The first method was in poor yield because the aryltellurophosphates are instable compounds<sup>[20]</sup> and may decompose under such conditions,

Received October 19, 2013.

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Scheme 1. Synthesis of aryltellurophosphates.

whereas the second method needed extremely labile reagents  $\text{ArTeCl}_3$  and thus needed to be performed under strict reaction conditions. Recently, Gao and coworkers reported the reaction of diaryl ditellurides with dialkyl phosphites  $[(\text{RO})_2\text{P}(\text{O})\text{H}]$  catalyzed by  $\text{CuI}$  in the presence of organic base.<sup>[3]</sup> Though this method is an atom-economical reaction and has excellent yields, it needs a stoichiometric amount of organic base. Considering the growing utility of organotellurium compounds in organic synthesis, the development of a general, efficient, and economical method for the preparation of aryltellurophosphates is still highly desirable.

Cesium hydroxide, which performs as a super inorganic base, can react with weakly acid substances to give a strongly nucleophilic anion.<sup>[21–23]</sup> The diaryl ditellurides are not only nucleophiles but also electrophiles. The P–H bond in dialkyl phosphites  $[(\text{RO})_2\text{P}(\text{O})\text{H}]$  is a polar bond. It exhibits weak acid, which should react with cesium hydroxide to form strongly nucleophilic  $(\text{RO})_2\text{P}^-(\text{O})\text{Cs}^+$ . Therefore, we assume that cesium hydroxide could catalyze the reaction of diaryl ditellurides with dialkyl phosphates. In this article, we report the results (Scheme 1).

## RESULTS AND DISCUSSION

We first tested the reaction of diethyl phosphite (DEP) and diphenyl ditelluride, and the experiment showed that the yield was only 58% using commercial tetrahydrofuran (THF) as solvent in the presence of 20 mol% cesium hydroxide at room temperature under an air atmosphere for 7 h. To determine the best experimental conditions, we studied the effect of other solvents on the reaction. The results are summarized in Table 1, and it can be seen that the reactions can hardly occur in dichloromethane or toluene even when extending the reaction time (Table 1, entries 1–6). When dimethylformamide (DMF) was used as solvent, the reactions afforded compound **3b** in the yield of 76% for 7 h (Table 1, entry 10). The greatest yield was obtained in dimethylsulfoxide (DMSO; Table 1, entry 12, 92%). This surprising result together with the lack of reactivity in other solvents suggests that DMSO might act not only as the solvent but also as an oxidant in the reaction.<sup>[24,25]</sup> Also, we investigated the loading of catalyst and found that the optimal dosage of cesium hydroxide was 20 mol% (Table 1, entries 12–14).

To assess the catalytic ability of cesium hydroxide to catalyze Te–P bond formation, we evaluated several alkali metal hydroxides including lithium hydroxide, sodium hydroxide, potassium hydroxide, and rubidium hydroxide (Table 2). The results showed that cesium hydroxide had enough ability to catalyze Te–P bond formation in the same conditions.

With the optimal condition in hand, the reactions of various diaryl ditellurides and dialkyl phosphites were investigated, and the results are given in Table 3. The reactions worked well for a variety of diaryl ditellurides and dialkyl phosphites. Different dialkyl phosphites (such as dimethyl, diethyl, di-*i*-Pr, di-*n*-Bu) showed

**Table 1.** Preparation of compound **3b** under various conditions<sup>a</sup>

Entry	Solvent	Catalyst (mol%)	Time (h)	Yield (%)
1	CH <sub>2</sub> Cl <sub>2</sub>	20	3	Trace
2	CH <sub>2</sub> Cl <sub>2</sub>	20	7	10
3	Toluene	20	3	Trace
4	Toluene	20	7	16
5	EtOH	20	3	21
6	EtOH	20	7	44
7	THF	20	3	39
8	THF	20	7	58
9	DMF	20	3	43
10	DMF	20	7	76
11	DMSO	20	3	62
12	DMSO	20	7	92
13	DMSO	15	7	76
14	DMSO	25	7	93

<sup>a</sup>Diethylphosphite: 2.0 mmol; diphenylditelluride: 1.0 mmol; CsOH: 0.2 mmol; temp: rt.**Table 2.** Influence of various bases on the reaction for diethyl phosphite with diphenylditelluride<sup>a</sup>

Entry	1	2	3	4	5
Base	LiOH	NaOH	KOH	RbOH	CsOH
Yield(%)	0	22	29	69	92

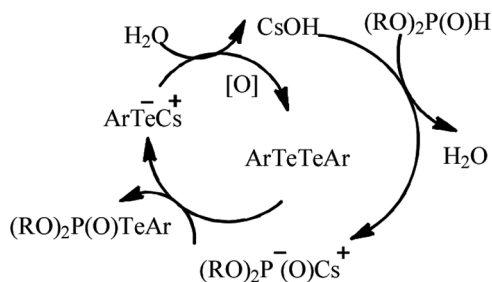
<sup>a</sup>Diethylphosphite: 2.0 mmol; diphenylditelluride: 1.0 mmol; solvent: DMSO; temp: rt; time: 7 h; alkali metal hydroxide: 0.2 mmol.

good reactivity with diphenyl ditelluride in high yields (Table 3, entries 1–4). Diaryl ditellurides with electron-donating (methyl, methoxyl) and electron-withdrawing (chloride) groups were also employed (Table 3, entries 5–14). Despite variation of

**Table 3.** Preparation of *Te*-aryl phosphorotelluroates<sup>a</sup>

Entry	R	Ar	Product <sup>b</sup>	Yield (%)
1	Me	C <sub>6</sub> H <sub>5</sub>	<b>3a</b> <sup>[16]</sup>	91
2	Et	C <sub>6</sub> H <sub>5</sub>	<b>3b</b> <sup>[16]</sup>	92
3	<i>i</i> -Pr	C <sub>6</sub> H <sub>5</sub>	<b>3c</b> <sup>[3]</sup>	91
4	<i>n</i> -Bu	C <sub>6</sub> H <sub>5</sub>	<b>3d</b> <sup>[17]</sup>	90
5	Me	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>3e</b> <sup>[17]</sup>	88
6	Et	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>3f</b> <sup>[17]</sup>	87
7	<i>n</i> -Bu	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>3g</b> <sup>[17]</sup>	84
8	Me	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3h</b> <sup>[16]</sup>	90
9	Et	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3i</b> <sup>[3]</sup>	91
10	<i>n</i> -Bu	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3j</b> <sup>[3]</sup>	89
11	Me	<i>o</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3k</b>	91
12	Et	<i>o</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3l</b>	93
13	<i>i</i> -Pr	<i>o</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3m</b>	89
14	<i>n</i> -Bu	<i>o</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>3n</b>	90

<sup>a</sup>Dialkyl phosphates: 2.0 mmol; diarylditellurides: 1.0 mmol; solvent: DMSO; temp: rt; time: 7 h; CsOH: 0.2 mmol.<sup>b</sup>**3a–3j** are known compounds from the literature and **3k–3n** are new compounds.



**Scheme 2.** Possible reaction mechanism for the synthesis of aryltellurophosphates.

reaction rate, the yields were good and the functional groups present in the phenyl group of diaryl ditellurides did not affect the yields obviously. Thus, this method could be widely used in the synthesis of a variety of aryltellurophosphates.

A possible reaction mechanism for the reaction of diaryl ditellurides and dialkyl phosphites to aryltellurophosphates in the presence of cesium hydroxide is depicted in Scheme 2. Dialkyl phosphites reacted with cesium hydroxide to give  $(\text{RO})_2\text{P}^-(\text{O})\text{Cs}^+$ , which underwent nucleophilic attack on  $\text{ArTeTeAr}$  to give aryltellurophosphates and  $\text{ArTe}^-\text{Cs}^+$ . The latter was oxidized in the presence of water to form diaryl ditellurides and catalyst cesium hydroxide.<sup>[25]</sup>

In summary, we have developed a highly efficient and simple method for the preparation of *Te*-aryl phosphorotelluroates. It has many merits such as mild reaction condition, convenient manipulation, solvents without need to remove water, a catalytic amount of cesium hydroxide, and good yields.

## EXPERIMENTAL

In a round-bottomed flask, cesium hydroxide (0.2 mmol) was added to a solution of dialkyl phosphites (2.0 mmol) and diaryl ditellurides (1.0 mmol) in DMSO (5.0 mL). The reaction mixture was stirred at room temperature under an air atmosphere for 7 h. The reaction was monitored by thin-layer chromatography (TLC) analysis. Then water (15 mL) was added and the mixture was extracted with ethyl acetate (15 mL  $\times$  3). The combined organic phase was washed with water (20 mL  $\times$  2), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether–ethyl acetate = 5:1). Compound **3b**:<sup>[16]</sup> yellow oil,  $^{31}\text{P}$  NMR (162 Hz,  $\text{CDCl}_3$ )  $\delta$  (ppm)  $-0.88$ ;  $^1\text{H}$  NMR (400 Hz,  $\text{CDCl}_3$ )  $\delta$  (ppm)  $7.82\text{--}7.78$  (m, 2H, Ph),  $7.36\text{--}7.29$  (m, 1H, Ph),  $7.25\text{--}7.20$  (m, 2H, Ph),  $4.18\text{--}4.04$  (m, 4H,  $\text{CH}_2$ ),  $1.31\text{--}1.26$  (m, 6H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ )  $\delta$  (ppm)  $139.3$ ,  $129.9$ ,  $129.1$ ,  $108.7$ ,  $64.1$ ,  $16.6$ ; MS (EI):  $m/z = 344$  ( $M + 2$ ) $^+$ .

## FUNDING

The authors thank the National Natural Science Foundation of China (Nos. 21172061, 21273068) and the NSF of Hunan Province (11JJ5009).

## SUPPLEMENTAL MATERIAL

Compounds **3a–3j** are known from the literature and **3k–3n** are new compounds. Full experimental detail,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR, and mass spectral (MS) data, and the copies of representative compounds **3c** and new compounds **3k–3n** spectra ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR, IR, MS) can be accessed on the publisher's website.

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