



Fast and transition metal-free general method for the preparation of chalcogenophosphates

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ABSTRACT

In the presence of Cs_2CO_3 and I_2 , the coupling reaction of dialkyl phosphites with dichalcogenides (S, Se and Te) proceeds efficiently and completes in several minutes under mild conditions, affording the corresponding chalcogenophosphates in moderate to good yields. This fast and transition metal-free procedure provides a general method for the preparation of chalcogenophosphates.

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1. Introduction

S-, Se-, and Te-Aryl chalcogenophosphates, due to the chalcogenophosphate moieties having both chalcogen and phosphorus atoms, are frequently used as synthetic intermediates in organic chemistry, they are also widely applied in pharmaceuticals and medicinal biology [1]. Much progress has been made in the synthesis of these compounds, mainly in the formation of S-aryl thiophosphates. Traditional methods for obtaining S-aryl thiophosphates involve the nucleophilic reaction of trialkyl phosphites with sulfonyl chlorides or the condensation reaction between phosphorylation reagents with thiols [2]. The direct coupling reaction of readily available dialkyl phosphites with diaryl disulfides catalyzed by CuI or $Cs(OH)_2$ is another method [3]. Recently, using sulfur powder instead of organosulfur sources, the copper-catalyzed coupling reaction of dialkyl phosphites with sulfur powder and aryl boronic acids or diaryliodonium/arenediazonium salts provides a facile access to S-aryl thiophosphates [4]. Similarly, there are some methods for the synthesis of Se-aryl selenophosphates. Using dialkyl phosphites and diaryl diselenides as starting materials, Se-aryl selenophosphates can be prepared by promotion of radical initiators (AIBN or $NaN_3/PhI(OAc)_2$) [5]. They are also

obtained by the coupling reaction of dialkyl phosphites with diaryl diselenides catalyzed by CuI, $Cs(OH)_2$ or KOH/calix [4] arene [3a,6]. In 2014, Hajra's group reported an environmentally benign zinc mediated synthesis of Se-aryl selenophosphates within a short reaction time [7]. However, compared with S-aryl thiophosphates and Se-aryl selenophosphates, only a few approaches are reported in literature for the preparation of Te-aryl tellurophosphates because they are usually unstable compounds [5a,8] and consequently, the general methods for the preparation of S-, Se-, and Te-Aryl chalcogenophosphates are much limited. Although Xu's group described an efficient copper iodide catalyzed method for the synthesis of chalcogenophosphates [3a], the development of general and practical methods, especially in fast and metal catalyst-free methods for access to chalcogenophosphates is highly desired.

Over the past few years, iodine-catalyzed or iodine-mediated reactions have been increasingly explored because iodine is cheap, readily available and eco-friendly, especially it has the metal-like behavior [9]. We have been interested in oxidation and functionalization of organic compounds using hypervalent iodine reagents because they can promote the oxidative cleavage of Se-Se bond of diselenides, resulting in the reactive electrophilic selenium species [10]. In our recent research, we have found that molecular iodine can replace hypervalent iodine reagents to promote some similar reactions, and a novel aminoselenation of alkenes using benzotriazoles as amino sources was just reported [11]. On this base, we have investigated a general method for the preparation of

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chalcogenophosphates mediated by I_2 . To the best of our knowledge, this fast and transition metal-free method has not been reported before.

2. Discussion and results

At the outset of this work, both readily available O,O-diethyl phosphonate **1a** with diphenyl diselenide **2a** were chosen as the model substrates to attempt their coupling reaction. When 1.2 equiv of **1a** with 1.0 equiv of **2a** was stirred in MeOH for 24 h at room temperature, it was found that the coupling reaction was difficult to effect and the desired coupling product, O,O-diethyl Se-phenyl phosphoroselenoate **3a** was not determined. We then added 0.5 equiv of CS_2CO_3 to the mixture, and after 24 h **3a** was obtained but in a poor yield. To improve the reaction, I_2 was used to promote the cleavage of Se-Se bond of diphenyl diselenide. Fortunately, in the presence of CS_2CO_3 and I_2 , a moderate yield was reached for the reaction. Prompted by this result, a series of experiments were performed on the coupling reaction to determine the optimal reaction conditions. As shown from the experiment results, a mixed solvent MeOH/THF (v/v, 1/3) was determined as the suitable solvent for the reaction and CS_2CO_3 was chosen as the best effective base compared with several other bases. When the optimal amount of CS_2CO_3 was investigated, an exciting result was found that when 3.0 equiv of CS_2CO_3 was used, the reaction carried out quickly and completed in only several minutes (monitored by TLC). Therefore, a fast and transition metal-free procedure was developed for the preparation of chalcogenophosphates. Finally, the suitable amount of I_2 was screened at the optimal conditions (Table 1). It became apparent from Table 1 that when 2.0 equiv of I_2 was added to the mixture of 1.2 equiv of **1a**, 1.0 equiv of **2a** and 3.0 equiv of CS_2CO_3 , and the mixture was stirred for only one minute, the reaction was completed and provided product **3a** in 87% yield (Table 1, entry 5). However, if I_2 was absent, a parallel experiment gave only 15% yield of **3a** (entry 1). To explore the reaction mechanism, a stoichiometric radical scavenger, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), was added in the reaction of **1a** with **2a**, CS_2CO_3 and I_2 under the optimized conditions. It was found that the coupling reaction was still carried out well, affording the product **3a** in 85% yield (entry 8), which suggests that the reaction may not undergo a radical pathway.

Based on the extensive screening process, we arrived at the optimal reaction conditions. Next, the coupling reaction of 1.2 equiv of dialkyl phosphites **1** with 1.0 equiv of dichalcogenides **2** (S, Se and Te) and 3.0 equiv of CS_2CO_3 in the presence of 2.0 equiv of I_2 in MeOH/THF (1:3) at room temperature for several minutes was investigated, and as a result, a series of corresponding

chalcogenophosphates **3** were obtained. The results are summarized in Table 2.

As shown in Table 2, the coupling reaction of dialkyl phosphites **1** was compatible with **2a**, affording the corresponding Se-phenyl selenophosphates **3a–3e** in good to excellent yields (entries 1–5). Compared with **2a**, dibenzyl diselenide **2b**, an aliphatic diselenide also reacted easily with most of dialkyl phosphites **1** except O,O-(*n*-butyl) phosphonate **1c** in five minutes, resulting in Se-benzyl selenophosphates **3f, 3g, 3i** and **3j** in the slightly dropped down yields (entries 6–7, 9–10). Taking advantage of above results, we further investigated the reaction of **1** with diphenyl disulfide **2c** and diphenyl ditelluride **2d**. Under the same reaction conditions, the reaction led to several S-phenyl thiophosphates **3k–3n** in moderate to good yields in short time (entries 11–14). Similarly, three Te-phenyl tellurophosphate representatives **3o–3q** were also prepared in three minutes in moderate yields due to their instability (entries 15–17).

A plausible reaction pathway is suggested in Scheme 1: I_2 first reacts with dichalcogenide **2** smoothly to promote a rapid cleavage of Y–Y bond of dichalcogenide (S, Se, Te). Then, the *in situ* generated active R^2YI is attacked by a nucleophilic reagent from dialkyl phosphite **1**, affording the corresponding chalcogenophosphate **3** in short time.

3. Conclusions

We have developed a novel and general procedure for the synthesis of chalcogenophosphates by coupling reaction of readily available dialkyl phosphites with dichalcogenides in the presence of CS_2CO_3 and I_2 at room temperature. This I_2 mediated transition metal-free method has some advantages such as mild reaction conditions and simple procedure, which provided a series of chalcogenophosphates in moderate to good yields in short time. Furthermore, this reaction will extend the application scope of molecular iodine in organic synthesis.

4. Experimental

IR spectra were recorded on a Thermo-Nicolet 6700 instrument. 1H NMR and ^{13}C NMR spectra were measured on a Bruker-AVANCE III (500 MHz) spectrometer. Mass spectra were determined on Thermo-ITQ 1100 mass spectrometer. Dialkyl phosphites, dichalcogenides, I_2 , CS_2CO_3 and solvents were commercially available.

4.1. A typical procedure for the preparation of chalcogenophosphates

Dialkyl phosphite **1** (0.24 mmol), dichalcogenide **2** (0.10 mmol), I_2 (0.2 mmol) and CS_2CO_3 (0.3 mmol) were added successively to a mixed solvent MeOH/THF (v/v, 3/1) (4 mL). The mixture was vigorously stirred at r.t. for several minutes (monitored by TLC). Upon completion, the reaction was quenched by addition of sat. aq. $Na_2S_2O_3$ (2 mL) and H_2O (5 mL), respectively. Then the water phase was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic phase was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was finally purified on a silica gel plate (petroleum ether/ethyl acetate, 3/1) to furnish chalcogenophosphate **3**.

4.1.1. O,O-Diethyl Se-phenyl phosphoroselenoate (**3a**) [6a]

Yield: 87%; yellow oil.

1H NMR (500 MHz; $CDCl_3$): δ = 7.68–7.63 (m, 2H), 7.38–7.31 (m, 3H), 4.24–4.15 (m, 4H), 1.34–1.29 (m, 6H).

^{13}C NMR (125 MHz; $CDCl_3$): δ = 135.6 (d, J = 5.0 Hz), 129.5 (d, J = 2.5 Hz), 128.8 (d, J = 2.5 Hz), 123.7, 63.9 (d, J = 5.0 Hz), 16.0 (d,

Table 1
Optimization of the amount of I_2 .

$(EtO)_2\overset{O}{\underset{ }{P}}H + (PhSe)_2 + I_2 \xrightarrow[MeOH/THF (1/3)]{CS_2CO_3 (3.0 eq)} (EtO)_2\overset{O}{\underset{ }{P}}-SePh$			
Entry	I_2 (equiv)	Time (min)	Yield (%) ^a
1	0	1	15
2	0.5	1	38
3	1.0	1	48
4	1.5	1	61
5	2.0	1	87
6	2.5	1	72
7	3.0	1	77
8	2.0	30	85 ^b

^a Isolated yields.

^b 1.0 Equiv of TEMPO was added to the mixture.

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