



Direct synthesis of thiophosphates by reaction of diphenylphosphine oxide with sulfonyl chlorides

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ABSTRACT

A new method for the synthesis of thiophosphates by reductive coupling reaction of diphenylphosphine oxide and sulfonyl chlorides has been developed. The reaction is metal-free and needs no additives, affording various aryl and alkyl substituted thiophosphates in good to excellent yields under mild conditions.

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1. Introduction

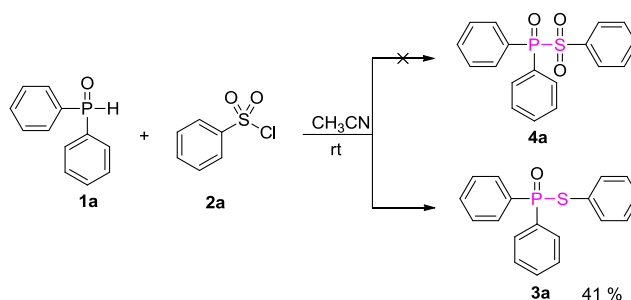
Thiophosphate derivatives have attracted much attention in recent decades due to their widespread application in pharmaceuticals and agrochemicals.¹ Thus, many studies were carried out for the synthesis of thiophosphates. The reported methods for the synthesis of thiophosphates include Michaelis–Arbuzov reaction,² coupling reaction³ and condensation reaction.⁴ Traditional method for the synthesis of thiophosphates is via the nucleophilic substitution of phosphine chlorides with thiols. Recently, Wu and co-workers reported the copper-catalyzed reductive cross-coupling reaction of aryl sulfonyl chlorides with *H*-phosphonates.⁵ Pan and co-workers discovered the reaction of *H*-phosphine oxide or *H*-phosphinate esters with thio/thiophenol using *tert*-butyl peroxybenzoate (TBPB) and KI as additives.⁶ Although many efforts have been made to facilitate the synthesis of thiophosphates, some drawbacks still exist: needing fresh prepared raw materials,^{7,8} using bases,^{9–12} metal catalysts^{13–16} or other additives.^{17,18} Thus, the development of simple and environmental friendly synthesis methods remains unexplored.

2. Results and discussion

Herein, we wish to share our research about the direct synthesis of thiophosphates by the reaction of diphenylphosphine

oxide/*H*-phosphinates/*H*-phosphonates with aryl/alkyl sulfonyl chlorides. Compared with the reported methods for the synthesis of thiophosphates, this reaction is metal-free and needs no additives to afford various substituted thiophosphates under mild conditions.

In the initial work, we attempted the reaction of diphenylphosphine oxide (**1a**) with benzenesulfonyl chloride (**2a**) for the synthesis of sulfonylphosphonate (**4a**) (Scheme 1). To our surprise, we obtained the deoxidized product *S*-phenyl diphenylphosphinothioate (**3a**) instead of **4a** by the MS analysis. To the best of our knowledge, the direct synthesis of thiophosphates by the reaction of diphenylphosphine oxide with sulfonyl chlorides in the absence of metal and additives has not been reported to date. The experiment results enlightened us to further examine the reaction between phosphine oxides and sulfonyl chlorides.

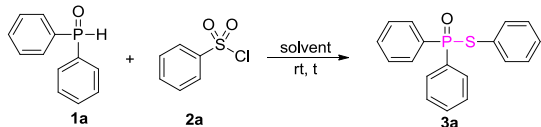


Scheme 1. Reductive coupling reaction of diphenylphosphine oxide with benzenesulfonyl chloride.

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With the consideration in mind, we attempted the reaction of diphenylphosphine oxide (**1a**) with benzenesulfonyl chloride (**2a**) under various conditions (Table 1). Firstly, the reaction was carried out in CH₃CN at room temperature. To our delight, the desired product (**3a**) was obtained in a yield of 41% within 5 h (Table 1, entry 1). We then prolonged the reaction time to 20 h, but the yield of **3a** was only increased by 10% (Table 1, entry 3). It was noted that a main byproduct diphenylphosphinic acid was also isolated, which consumed a portion of the reagent. Therefore, we investigated the effect of the reactant ratio between **1a** and **2a**. When the dosage of **1a** was increased to 2.5 equiv and 3 equiv, the product yields of **3a** were enhanced to 55% and 77%, respectively (Table 1, entries 4 and 5). Consequently, a fairly good yield (88%) of **3a** was obtained when the amount of **1a** was increased to 4 equiv (Table 1, entry 6). It should be noted that the byproduct diphenylphosphinic acid as a flame retardant was readily filtered for other applications. In addition, increasing the temperature from room temperature to 60 °C, the yield of **3a** was increased a bit: from 88 % to 92 % (Table 1, entry 7). Further increase the temperature resulted in no improvement of the yield. For comprehensive consideration, we performed the reaction at room temperature. After screening of the solvents including dichloromethane (DCM), dimethylformamide (DMF), dioxane and toluene, it was found that solvent had a little effect on the reaction (Table 1, entries 8–11) and CH₃CN was selected as the optimal solvent for this reaction.

Table 1
Optimization of reaction conditions^a



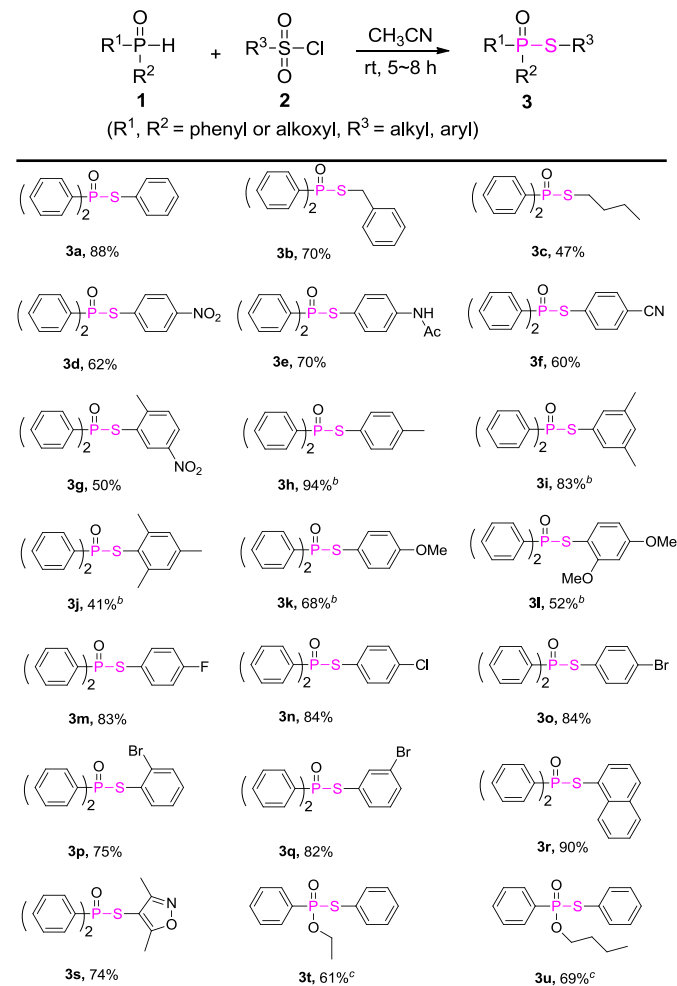
Entry	1a : 2a	Solvent	<i>t</i> (h)	Yield (%)
1	2:1	CH ₃ CN	5	41
2	1.2:1	CH ₃ CN	20	25
3	2:1	CH ₃ CN	20	51
4	2.5:1	CH ₃ CN	20	55
5	3:1	CH ₃ CN	20	77
6	4:1	CH ₃ CN	5	88
7 ^b	4:1	CH ₃ CN	3.5	92
8	4:1	DCM	5	81
9	4:1	DMF	5	86
10	4:1	Dioxane	5	82
11	4:1	Toluene	5	88

^a Unless otherwise noted, the reactions were performed by adding **1a** and **2a** (1 mmol) in solvent (5 mL) at room temperature. Isolated yields.

^b The reaction was performed at 60 °C.

Next, we investigated the scope and limitations of the reaction of diphenylphosphine oxide and *H*-phosphinates with aryl/alkyl sulfonyl chlorides under the optimized reaction conditions. As shown in Scheme 2, various aryl/alkyl sulfonyl chlorides could readily react with diphenylphosphine oxide to form thiophosphates in moderate to good yields. Comparing with the alkyl sulfonyl chloride, aryl sulfonyl chlorides was easier to react with diphenylphosphine oxide (Scheme 2, **3a–3c**). For the substrates of aryl sulfonyl chloride, the strong electron-withdrawing or -donating groups led to lower yields of the desired products (Scheme 2, **3d–3g** and **3k–3l**), while the weak electron-donating and -neutral groups resulted in good yields of thiophosphates (Scheme 2, **3h, 3r**). The steric hindrance also affected the reaction between diphenylphosphine oxide and aryl sulfonyl chlorides. Although the bromine substituted (*o*-, *m*-, *p*-) phenylsulfonyl chloride showed little effect on the reaction (Scheme 2, **3o–3q**), the employment of 2,4,6-trimethylbenzenesulfonyl chloride gave

a much lower yield (Scheme 2, **3j**). In addition, heteroaromatic sulfonyl chloride could also react with diphenylphosphine oxide, affording the product in moderate yield under the standard conditions (Scheme 2, **3s**). Moreover, the reaction of *H*-phosphinates with aryl sulfonyl chlorides proceeded smoothly at 80 °C to give the thiophosphate derivatives in moderate yields (Scheme 2, **3t–3u**).



^a Unless otherwise noted, the reactions were performed by adding diphenyl phosphine oxide or *H*-phosphinates (4 mmol), sulfonyl chlorides (1 mmol) and CH₃CN (5 mL) at room temperature for 5 h. Isolated yields.

^b Reactions were performed for 8 h.

^c Reactions were performed at 80 °C for 9 h.

Scheme 2. Reaction of diphenylphosphine oxide/*H*-phosphinates with sulfonyl chlorides.^a

With the excited and promising results in hand, we envisioned that the reaction of *H*-phosphonates and aryl sulfonyl chlorides could also provide the thiophosphate derivatives (Scheme 3). However, it was found that the reaction between *H*-phosphonate and aryl sulfonyl chlorides showed low efficiency. Although the reaction temperature was increased to 150 °C, the yields of the desired products were still lower (Scheme 3, **3v–3w**). The results indicated that the reaction activity towards aryl sulfonyl chlorides under the standard conditions is as follows: diphenylphosphine oxide > *H*-phosphinates > *H*-phosphonates.

It is also possible to prepare thiophosphates on a gram scale. As shown in Scheme 4, a good yield was provided for the gram-scale synthesis of **3a**, thus offering a reliable and practical access to the synthesis of thiophosphates under mild conditions.

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