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Catalyst-free thiophosphorylation of *in situ* formed *ortho*-quinone methides†

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A metal-, chloride reagent and base-free thiophosphorylation reaction of *in situ* formed *ortho*-quinone methide (*o*-QM) to synthesize functionalized thiophosphates has been developed. The reaction is an atom-economical process, producing water as the sole byproduct. $(EtO)_2P(O)SH$ functions as both a Brønsted acid and nucleophilic thiolate to produce the *o*-QM intermediate and the thiophosphate product, respectively. The aza *o*-QMs were also successfully thiophosphorylated in the presence of catalytic TsOH to form sulfonamido thiophosphates.

Introduction

Over the past few decades, the organophosphorus chemistry field has witnessed a growing research interest since organophosphorus compounds have found widespread applications in medicinal chemistry, organometallic chemistry, agricultural chemistry, and materials chemistry.[1] Specifically, phosphorodithioate compounds bearing the thiophosphoryl bond have useful properties such as insecticides (Fig. 1, **A** and **B**) and neurotoxins (Fig. 1, **C**).[2] They also display important biological activity for the treatment of cancer (Fig. 1, **D**) and glaucoma (Fig. 1, **E**).[3] In addition, thiophosphates have been known for significant antibacterial activities against common strains of bacteria (Fig. 1, **F**).[4]

With a plethora of applications, various methods have been developed to access thiophosphoryl bond motifs. A conventional method to synthesize thiophosphate uses electrophilic $P^{(V)}$ or $P^{(III)}$ compounds such as chlorophosphine oxides and chlorophosphines which undergo a nucleophilic substitution reaction with thiols to produce thiophosphates.[5] Another approach to thiophosphate synthesis employs cross dehydrogenative coupling (CDC) reactions which couple a thiol and pentavalent phosphorous reagent in the presence of a metal catalyst. This CDC synthetic methodology has been extensively explored and various catalysts/activators such as Ni, Cu, Fe, Cs, Pd, NCS, peroxides, Bunte salts, and quaternary ammonium salts have been demonstrated.[6] Photocatalysis and electrochemical process have also been applied to the synthesis of thiophosphates *via* coupling reactions.[7] Nevertheless, catalyst-free methods of thiophosphate synthesis are underdeveloped with a few precedents: a reaction of disulfides with secondary phosphine oxides in the presence of silica gel *via* a radical pathway and the direct substitution reaction between *N*-chalcogenoimides and diethyl phosphites.[8] These methods, however, are limited to a trivalent phosphorus tautomer as an active nucleophile to react with electrophilic sulfur reagents.[9]

An alternative method uses $(EtO)_2P(O)SH$ as a pentavalent nucleophile and a synthon for the thiophosphate group (Scheme 1). $(EtO)_2P(O)SH$ has been utilized in a Michael reaction of activated alkenes to synthesize functionalized thiophosphates at elevated temperatures (Scheme 1a).[10] In addition, the Wu group demonstrated a $Ga(OTf)_3$-catalyzed sulfur substitution reaction on activated alcohols (benzylic or allylic alcohols) with hydrogen phosphorothioates $(EtO)_2P(O)SH$ to generate the thiophosphate compounds (Scheme 1b).[11] They also reported a photochemical method for the synthesis of thiophosphate compounds.[12] The Xiao group also explored the utility of $(EtO)_2P(O)SH$ by coupling with a propargylic alcohol partner to construct *S*-(2*H*-chromen-4-yl) phosphorothioates *via* a cascade reaction and the synthesis of allenyl thiophosphates under elevated thermal conditions (Scheme 1c and d).[13]

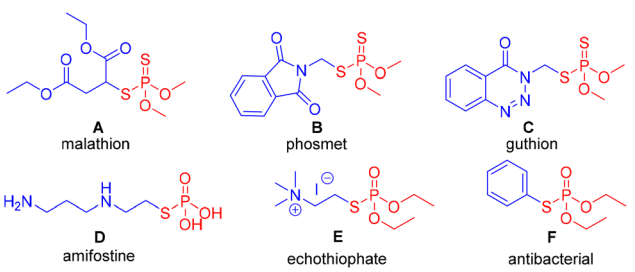

Fig. 1 Applications of phosphorodithioate and thiophosphate.

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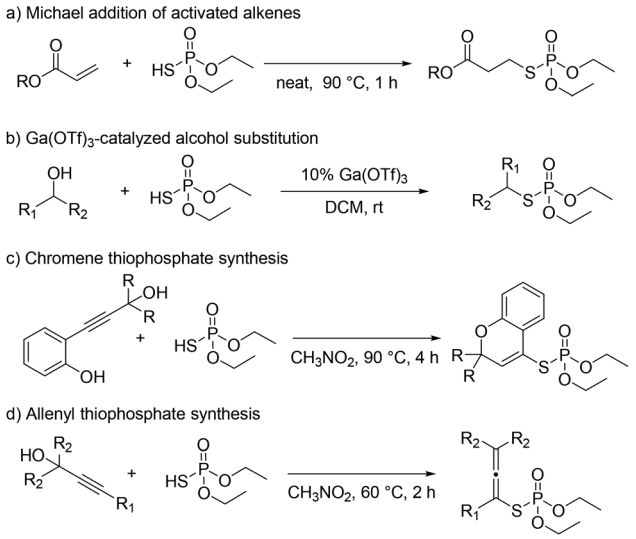


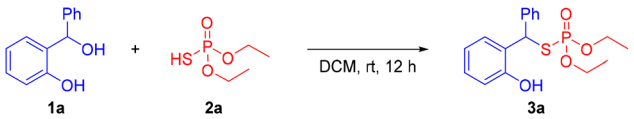
Scheme 1 S–C bond formation using $(EtO)_2P(O)SH$.

Reactive *o*-QM intermediates can be generated under thermal, photochemical, acidic, or basic conditions and they have been employed in various addition reactions.[14] For example, phosphorylation of *o*-QM and *p*-QM using secondary phosphine oxides and H-phosphonates was recently reported.[15] In addition, enantioselective phosphorylation reactions of *o*-QM and aza *o*-QM using bifunctional cinchona catalysts were released.[16] In 2017, we also disclosed the phospha-Michael addition reaction of trialkylphosphites to *in situ* generated *o*-QMs using N-heterocyclic phosphorodiamidic acid (NHPA) catalyst. This transformation demonstrated the formation of carbon–phosphorous bonds employing trivalent phosphorus nucleophiles.[17] Sulfa-Michael addition reaction of thiophosphates to *o*-QMs for the construction of carbon–sulfur bond, however, has remained unexplored. This thiophosphorylation reaction of *o*-QM revealed a dual role of phosphorothioic acid, $(EtO)_2P(O)SH$; a Brønsted acid and thiolate $P^{(V)}$ nucleophile, unrealized yet in *o*-QM chemistry.

Results and discussion

To develop a mild, atom-efficient thiophosphorylation of *o*-QM that avoids a toxic metal, moisture-sensitive chloride reagents, and base, we hypothesized that the phosphorothioic acid, $(EtO)_2P(O)SH$, can serve as both a Brønsted acid to generate *o*-QMs and a phosphorothioate nucleophile to react with the *o*-QMs for the synthesis of functionalized diaryl thiophosphates. To test our hypothesis, we used 2-(hydroxy(phenyl)methyl)phenol **1a** and $(EtO)_2P(O)SH$ **2a** as a model substrate for the reaction optimization (Table 1). The reaction was first tested using a 1 : 1 molar equivalent of **1a** : **2a** and product **3a** was generated in 37% yield (Table 1, entry 1). Next, an increment in the molar ratio of **1a** : **2a** to 1 : 1.5 afforded the desired product **3a** in 91% yield (Table 1, entry 2). Solvent effects were

Table 1 Optimization of the reaction conditions[a]

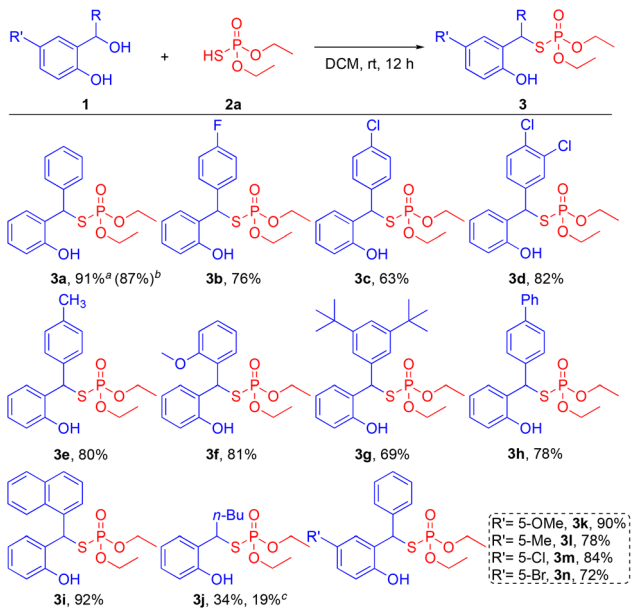


Entry	1a : 2a	Solvent	Yield[b] (%)
1	1.0 : 1.0	DCM	37
2	1.0 : 1.5	DCM	91
3	1.0 : 1.5	THF	0
4	1.0 : 1.5	DCE	45
5	1.0 : 1.5	Toluene	49
6	1.0 : 1.5	ACN	37
7	1.0 : 1.5	Ether	24
8	1.0 : 1.5	Neat	44

[a] Reaction conditions: **1a** (0.1 mmol) and **2a** (0.15 mmol) in solvent (0.5 mL) for 12 h. [b] Isolated yield.

then examined and other solvents (THF, DCE, toluene, ACN, and ether) were inferior to DCM (Table 1, entries 3–7). Finally, the reaction can be performed under neat conditions but a lower yield of 44% was observed (Table 1, entry 8).

With the optimized conditions in hand, the scope of diaryl alcohols was examined for the steric and electronic effects on reaction outcomes (Scheme 2). First, various substituents on the benzylic carbon of the diaryl alcohol substrates were screened. Halogenated diaryl alcohols **1b–1d** (4-F, 4-Cl, and 3,4-diCl) were well tolerated to give the desired products **3b–3d** in moderate to high yields (63–82%). Diaryl alcohols containing electron-donating groups **1e–1g** (4-Me, 2-MeO, and 3,5-*tert*-Bu) furnished the target products **3e–3g** in high yields



Scheme 2 Substrate scope of thiophosphorylation reaction. Reaction conditions: **1** (0.1 mmol) and **2a** (0.15 mmol) in DCM (0.5 mL) for 12 h. [a] Isolated yield. [b] A gram-scale experiment with **1a** (4.5 mmol). [c] Addition of molecular sieves.

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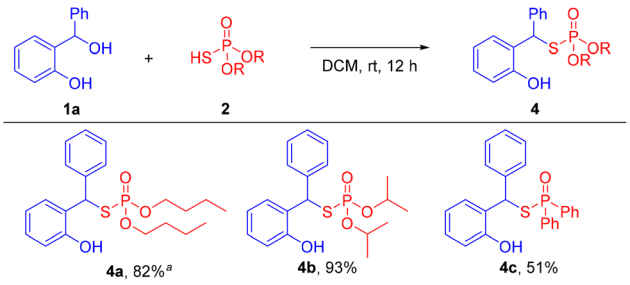
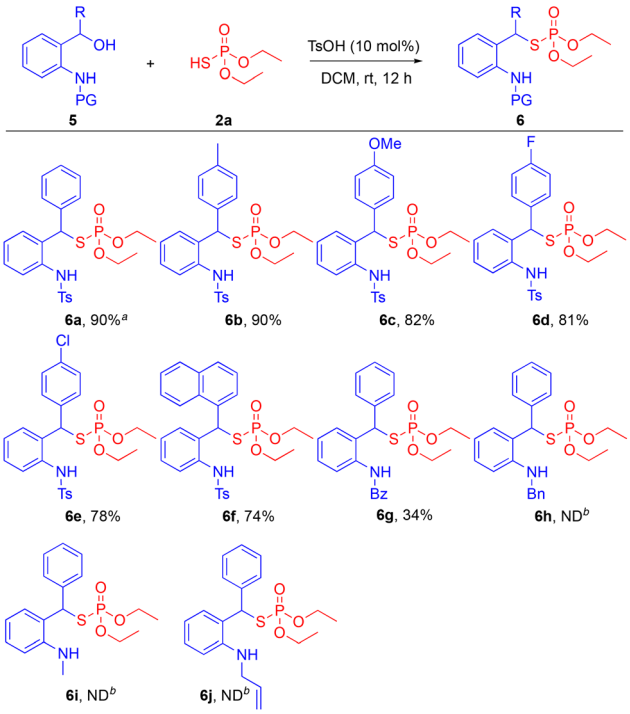
(69–81%). Poly aromatic groups on diaryl alcohols **1h** and **1i** (biphenyl and naphthyl) also smoothly generated the desired products **3h** and **3i** with 78% and 92% yields, respectively. Aliphatic-substituted phenol **1j** (*n*-Bu), however, provided the corresponding product **3j** in a low yield of 34%, presumably due to the reduced stabilization of the *o*-QM intermediate. To inquire about the effect of water molecules in the reaction, a reaction with molecular sieves was performed. The use of molecular sieves, however, did not improve the yield (19%) of **3j**. This result suggests that the water in fact may help to stabilize the *o*-QM intermediate through intermolecular hydrogen bonding.[18] The positive effect of *in situ* generated water molecule on the stabilization of *o*-QM intermediate and the product yield is aligned with our observation on the phospha-Michael reaction.[17] In addition, various substituents on the phenol motif were examined for the substrate scope of the reaction. Electron donating groups on the phenols **1k** and **1l** (5-OMe and 5-Me) were smoothly tolerated to provide the corresponding products **3k** and **3l** in high yields of 90% and 78%, respectively. Phenols with halogenated substrates **1m** and **1n** (5-Cl and 5-Br) also afforded the desired products **3m** and **3n** in 84% and 72% yields, respectively. Furthermore, to demonstrate the scalability of this reaction and its applicability in pharmaceutical processes, a scaled-up experiment with **1a** (4.5 mmol) was demonstrated without sacrificing the reactivity by providing **3a** in 87% yield.

Next, thioacids with different alkoxy substituents were evaluated to test their effects on reaction outcomes (Scheme 3). Various alkoxy-substituted thioacids **2b** and **2c** (*n*-Bu and i-Pr) smoothly provided the target compounds **4a** and **4b** in high yields of 82% and 93%, respectively. In addition, diphenyl thiophosphinic acid **2d** also gave the desired product **4c** in a synthetically useful yield of 51%. These results indicate that the structural variation of thioacids is tolerable.

With promising results of sulfa-Michael addition reaction of thiophosphates to *o*-QMs, we were interested in applying this method to aza *o*-QM intermediates (Scheme 4). In our preliminary screening, it was found that $(EtO)_2P(O)SH$ **2a** was not a strong enough acid to dehydrate sulfonamido alcohol **5a**. With the addition of a 10 mol% TsOH, the reaction proceeded efficiently giving **6a** in 90% yield. Having the optimized reaction conditions, the substrate scope was tested with various

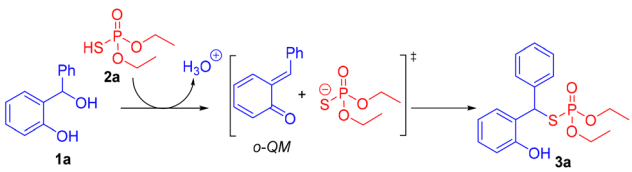


Scheme 3 Substrate scope of thioacid nucleophiles. Reaction conditions: **1a** (0.1 mmol) and **2** (0.15 mmol) in DCM (0.5 mL) for 12 h. [a] Isolated yield.



Scheme 4 Substrate Scope of sulfonamido thiophosphate synthesis. Reaction conditions: **5** (0.1 mmol), **2a** (0.2 mmol), and TsOH (10 mol%) in DCM (0.5 mL) for 12 h. [a] Isolated yield. [b] ND (not determined due to instability).

benzylic aryl substituents. Sulfonamindo alcohols bearing electron-donating groups **5b** and **5c** (4-Me and 4-OMe) furnished the target products **6b** and **6c** in 90% and 82% yields, respectively. Next, halogenated sulfonamido alcohols **5d** and **5e** (4-F and 4-Cl) were examined and they provided the desired products **6d** and **6e** with 81% and 78% yields, respectively. In addition, polyaryl sulfonamido alcohol **5f** generated the naphthyl sulfonamido thiophosphate product **6f** with 74% yield. Furthermore, a different protecting group on the nitrogen atom (Bz) **5g** was investigated, but it provided **6g** in a low yield (34%), presumably due to the weak polarizability of the *o*-QM intermediate compared to a tosyl group on the nitrogen atom.[19] Finally, alkyl-protecting groups on the amine **5h–5j** (benzyl, methyl, and allyl) were screened. It was, however, revealed that the final products **6h–6j** were unstable and rapidly decomposed after isolation. It is noteworthy to mention that attempts to deprotect the tosyl group on the amine moiety **6a** under both basic conditions (4-OMePhSH/DIPEA)[20] and acidic conditions (TFA)[21] were unsuccessful, leaving the decomposition of the substrates.



Scheme 5 Proposed mechanism.

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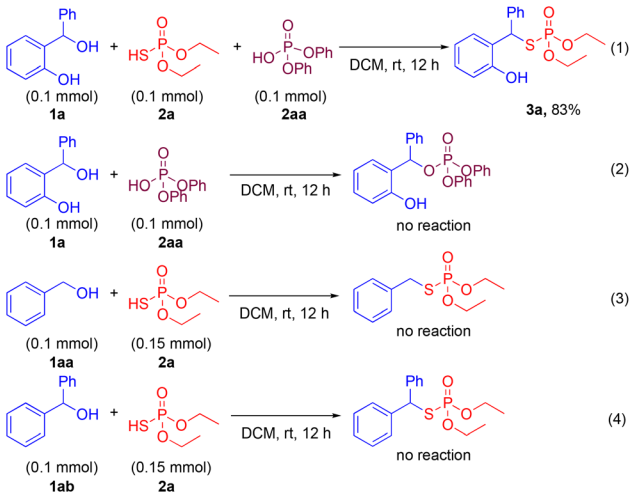

Scheme 6 Control experiments.

On the basis of our experimental data and previous work,[17] a plausible mechanistic pathway is proposed (Scheme 5). Diaryl alcohol **1a** is protonated by $(EtO)_2P(O)SH$ **2a** and then water is released to form *o*-QM intermediate and *O,O*-diethyl phosphorothioate. Subsequently, sulfa-Michael addition reaction of *o*-QM with *O,O*-diethyl phosphorothioate provides the addition product **3a**.

To rationalize the proposed mechanism of this thiophosphorylation reaction, control experiments were performed to gain a mechanistic perspective on this synthetic transformation (Scheme 6). Diaryl alcohol **1a** was treated with $(EtO)_2P(O)SH$ **2a** and $(PhO)_2P(O)OH$ **2aa**, and the reaction provided the thiophosphorylation product **3a** in 83% yield (Scheme 6, eqn (1)). This competition reaction generated only the phosphorothioate product. In another control experiment, the reaction of diaryl alcohol **1a** with diphenylphosphoric acid **2aa** did not generate the desired product which suggests that diphenylphosphoric acid is not acidic enough to generate the *o*-QM intermediate under the reaction conditions (Scheme 6, eqn (2)). These reaction outcomes support the dual role of phosphorothioic acid **2a** as a Brønsted acid and thioate nucleophile; these results also suggest that phosphorothioic acid **2a** is a better nucleophile than the diphenylphosphoric acid **2aa**. It is noteworthy that phosphorothioic acid (pK_a = 1.0) is more acidic than phosphoric acid is (pK_a = 3.88).[22] Additionally, the reaction of benzyl alcohol **1aa** or diphenyl methanol **1ab** with phosphorothioic acid **2a** did not afford the target thiophosphate product (Scheme 6, eqn (3) and (4)). Therefore, these results indicate that a reaction mechanism involving carbocation intermediates is an unlikely pathway.

Conclusions

We have developed a metal-, catalyst-, chloride reagent-, and base-free thiophosphorylation reaction of *o*-QM to synthesize functionalized thiophosphates. The reaction tolerates a wide range of functional groups, proceeds under environmentally benign conditions, and fulfills an atom-economical process. It also demonstrated the dual role of phosphorothioic acid as a Brønsted acid and a thiolate nucleophile in *o*-QM chemistry. Future experiments involving cascade and multicomponent reactions to harness the dual role of phosphorothioic acid, $(EtO)_2P(O)SH$, are underway and will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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