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Organocatalytic Phosphonylation of *in Situ* Formed *o*-Quinone Methides

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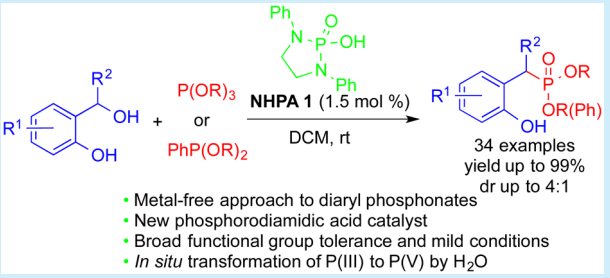
Supporting Information

ABSTRACT: A new class of Brønsted acid catalysts based on *N*-heterocyclic phosphorodiamidic acids (NHPAs) has been developed. The NHPA catalyst promotes phospha-Michael addition reaction of trialkylphosphites to *in situ* generated *ortho*-quinone methides (*o*-QMs) for the construction of diaryl phosphonates in moderate to excellent yields with 1.5 mol % catalyst. Diastereoselective synthesis of *P*-chiral phosphinate esters is achieved with the use of dialkyl phenylphosphonites.



Organophosphonate compounds and their derivatives have shown a wide range of applications in medicinal chemistry,[1] agrochemistry,[2] and organic synthesis.[3] In particular, diaryl phosphonates exhibit a broad spectrum of significant biological activities such as human prostatic acid phosphatase inhibition **A**,[4] leukocyte elastase inhibition **B**,[5] and calcium antagonistic activity **C**[6] (Figure 1). They are also used for the

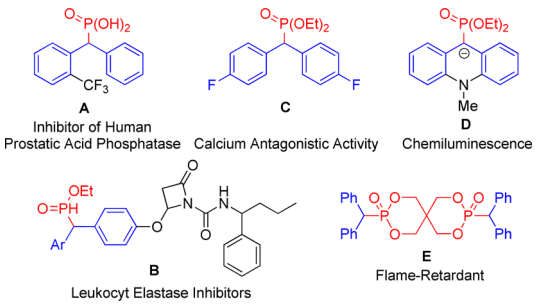


Figure 1. Representative examples of functional diaryl phosphonates and their derivatives.

preparation of chemiluminescence materials **D**[7] and flame retardants **E**[8] (Figure 1). In addition, they serve as versatile building blocks for the synthesis of vinyl-based functional compounds such as fluorescent materials[9] and OLED emitters.[10]

Although the Michaelis–Arbuzov reaction represents a classic method for diaryl phosphonate synthesis, this procedure is limited to alkyl halide substrates and elevated reaction temperature.[11] To overcome these limitations, much effort has been devoted to develop new synthetic methods for constructing diaryl phosphonates. For example, the Chakravarty group reported $FeCl_3$-mediated Friedel–Crafts-type arylation of α-hydroxy phosphonates with various arenes, which requires a stoichiometric amount of $FeCl_3$.[12] On the other hand, Walsh and co-workers disclosed a Pd-catalyzed deprotonative cross-coupling reaction of benzyl phosphonates with aryl halides.[13] This protocol, however, is restricted to only benzyl diisopropyl phosphonate substrate due to the use of a nucleophilic base. Recently, the Anand group[14] and our laboratory[15] revealed 1,6-hydrophosphonylation of *para*-quinone methides (*p*-QMs) for the construction of diaryl phosphonates under metal-free conditions. Nonetheless, for the facile synthesis and inherent instability of *p*-QMs,[16] a di-*tert*-butyl group on *p*-QM derivatives is necessary, which may decrease the synthetic value of the product with extra steps for removal of the protecting group. Considering the prevalent applications in many different fields, the development of an efficient, mild synthetic protocol for diaryl phosphonates under metal-free conditions is highly desirable.

While the *p*-QMs have been extensively used in the phospha-Michael reaction,[14,15] *ortho*-quinone methides (*o*-QMs), isomeric *p*-QM counterparts, have remained underexplored Michael acceptors. Since the pioneering work by Fries and Kann in 1907,[17] *o*-QMs have been regarded as highly versatile synthetic intermediates in organic synthesis.[18] They have been utilized in various synthetic transformations such as the [4 + *n*] cycloaddition reaction,[19] Michael addition reaction,[19c] 6π-electrocyclization,[20] and others.[18b,d] Among the synthetic transformations, Michael addition reaction of *o*-QMs or aza-*o*-QMs with different nucleophiles, including carbon, nitrogen,[21] sulfur, and oxygen nucleophiles,[22] has become an efficient synthetic strategy for the direct synthesis of diverse *ortho*-hydroxybenzyl or 2-aminobenzyl compounds. Despite the successful application of carbon and various heteroatom nucleophiles,[19h,i,23] phospha-Michael reaction of trialkylphosphites with *o*-QMs has remained dormant since its discovery, due to the challenge of *in situ* transformation of P(III) to P(V).[24] This

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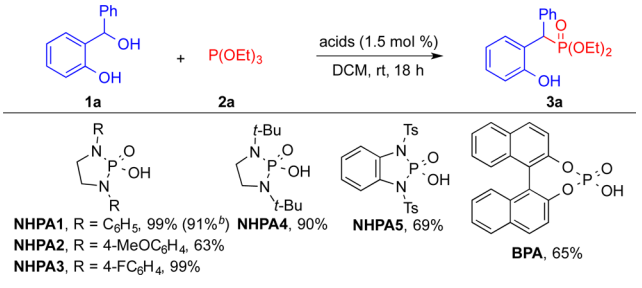
oxidation process is of utmost importance to establish a catalytic cycle and typically requires extra nucleophilic additives,[24] which can make the reaction more complex. In this regard, *in situ* generation of the advantageous nucleophiles for the transformation of P(III) to P(V) would be an ideal strategy.

Our group has a long-standing interest in the development of *N*-heterocyclic phosphines (NHPs) and their derivatives for the discovery of new synthetic transformations.[15,25,26] With the continued efforts to develop NHP-derived catalysts, we recently synthesized *N*-heterocyclic phosphorodiamidic acids (NHPAs) and discovered their exceptional catalytic activity in the phospha-Michael reaction. Herein, we report a novel NHPA-catalyzed phospha-Michael addition reaction of *o*-QMs with trialkylphosphites and dialkyl phenylphosphonites for the synthesis of diaryl phosphonates and phosphinates, respectively. To the best of our knowledge, this transformation demonstrates the first diastereoselective phospha-Michael addition reaction of dialkyl phenylphosphites to *o*-QMs.

With the NHPAs (**NPHA1**−**4**) in hand (see Supporting Information (SI) for the NHPA synthesis), we explored the potential of NHPAs as organocatalysts in the phospha-Michael reaction of 2-(hydroxy(phenyl)methyl)phenol **1a** with triethylphosphite **2a** (Scheme 1). To our delight, the desired diaryl

Scheme 1. Optimization of the Reaction Conditions[a]

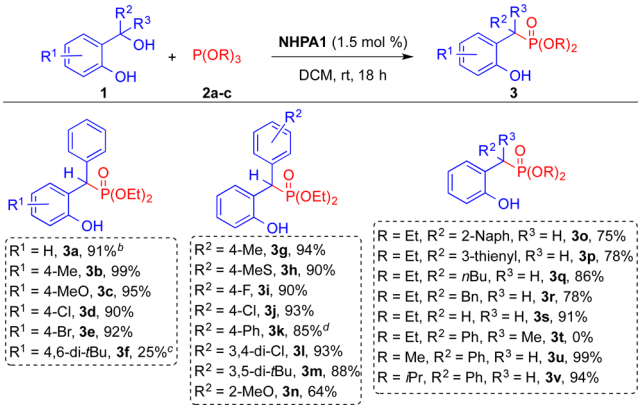


[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), and acids (1.5 mol %) in DCM (0.5 mL) at rt for 18 h. [b]Isolated yield.

phosphonate **3a** was obtained in 99% yield by NMR and 91% isolated yield with only 1.5 mol % **NHPA1**. Further modification of the NHPAs with electron-donating groups on the nitrogen atom (**NHPA2**, **NHPA4**) decreased the catalytic activity whereas that of electron-deficient groups maintained the excellent catalytic reactivity (**NHPA3**). These outcomes strongly support that the pK_a of NHPAs can be systemically modified. We also tested the known Brønsted acids **NHPA5**[27] and **BPA**, but they were inferior to our **NHPA1** (see SI for more conditions).

Having established the optimized reaction conditions, we investigated the scope of the reaction described in Scheme 2. The electronic effects of the substrates on this transformation are negligible whereas the steric effects significantly influence the product yields in this phospha-Michael reaction. For example, the reaction tolerates both electron-donating and -deficient groups, providing the corresponding products in high to excellent yields (Scheme 2, **3a**−**e**, **3g**−**m**). In contrast, *ortho*-substituted substrates **1f** (4,6-*ditert*-Bu) and **1n** (2-MeO) provided the target products in 25% and 64% yields, respectively (Scheme 2, **3f**, **3n**). A polycyclic aromatic compound **1o** also proved to be a suitable substrate, producing 2-naphthyl phosphonate **3o** in 75% yield. A heteroaromatic substrate **1p** also succeeded in providing the desired adduct **3p** in 78% yield. We also explored the scope of alkyl, aryl-mixed substrates. For

Scheme 2. Scope of Phospha-Michael Reaction[a]

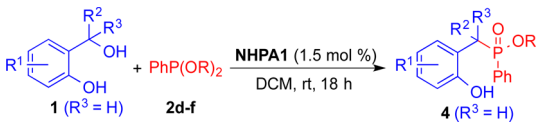


[a]Reaction conditions: **1** (0.1 mmol), **2** (0.1 mmol), and **NHPA1** (1.5 mol %) in DCM (0.5 mL) at rt for 18 h. [b]Isolated yield. [c]Reaction run for 48 h. [d]1.0 mL of DCM was used.

example, **1q** and **1r** with aliphatic substituents were also suitable substrates for this reaction to provide the alkyl-substituted benzyl phosphonates **3q**, **3r** in 86% and 78% yields, respectively. Saligenol **1s** was smoothly converted to benzyl phosphonate **3s** with 91% product yield. In an effort to challenge the synthesis of tetrasubstituted diaryl phosphonates, no target product was observed when diaryl methyl tertiary alcohol **1t** was treated with **2a**, probably due to the steric hindrance (Scheme 2, **3t**). Finally, different alkylphosphites such as P(OMe)$_3$ **2b** and P(O*i*Pr)$_3$ **2c** were evaluated, and they also afforded the corresponding diaryl phosphonates **3u**, **3v** in 99% and 94% yields, respectively.

Having early success in the phosphonylation of *o*-QMs with trialkyl phosphites, we explored the reactivity of dialkyl phenylphosphonites under the same reaction conditions (Table 1). This reaction allows a regio- and diastereoselective transformation, providing only 1,4-addition products with good diastereoselectivity (4:1 dr). First, we investigated the scope of

Table 1. Substrate Scope of Diastereoselective Phospha-Michael Reaction[a]



entry	R	R^1	R^2	product	yield[b] (*dr*)[c]
1	Me	H	C_6H_5	**4a**	85% (4:1)
2	Et	H	C_6H_5	**4b**	84% (3:1)
3	*i*Pr	H	C_6H_5	**4c**	81% (4:1)
4	Me	4-Me	C_6H_5	**4d**	80% (4:1)
5	Me	4-Cl	C_6H_5	**4e**	76% (4:1)
6	Me	4-Br	C_6H_5	**4f**	74% (4:1)
7	Me	H	4-MeC_6H_4	**4g**	84% (4:1)
8	Me	H	4-MeSC_6H_4	**4h**	82% (4:1)
9	Me	H	4-FC_6H_4	**4i**	81% (4:1)
10	Me	H	4-PhenylC_6H_4	**4j**	69% (4:1)
11	Me	H	2-Naph	**4k**	58% (99:1)[d]

[a]Reaction condition: **1** (0.1 mmol), **2** (0.1 mmol) and **NHPA1** (1.5 mol %) in DCM (0.5 mL) at rt for 18 h. [b]Isolated yield. [c]*dr* value determined by ^{1}H NMR on the crude reaction mixture. [d]*dr* value of the isolated product by flash column chromatography on a silica column.

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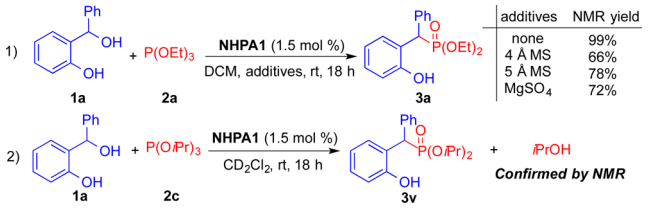
phosphonite nucleophiles. When dimethyl phenylphosphonite **2d** was employed, the target phosphinate product **4a** was isolated in 85% yield with 4:1 dr (Table 1, entry 1). Other nucleophiles such as ethyl and isopropyl phosphonites **2e**, **2f** also provided the desired phosphinate products **4b**, **4c** in 84% and 81% yields with 3:1 and 4:1 dr values, respectively (Table 1, entries 2−3). Next, we examined the scope of Michael acceptors with various substituents and they all yielded the corresponding products in good yields (Table 1, entries 4−10). Finally, a solubility-based purification of diastereomers was successfully demonstrated. Purification via flash column chromatography of a crude mixture of 2-naphthyl phosphinate (**4k**) with 4:1 dr allowed the isolation of the major diastereomer in 58% yield with 99:1 dr (Table 1, entry 11). With the demonstration of an efficient column purification of the diastereomers, we further examined different phosphinate products **4a−e** by performing second column chromatography. In general, they were all succeeded in the isolation of the major diastereomers. This flash column chromatography was particularly useful for the purification of diastereomers **4a**, **4e** (dr >99:1) (see SI for proposed model for diastereoselectivity).

Nucleophilic additives are usually required in the phospha-Michael reaction with trialkylphosphites for the transformation of P(III) to P(V).[24] In contrast, our NHPA-catalyzed phospha-Michael reaction of *o*-QM with $P(OEt)_3$ generates the target Michael adducts without the nucleophile additives. We reasoned that the *in situ* generated H_2O molecule by dehydration of the *o*-hydroxybenzyl alcohols can act as an internal nucleophile to transform P(III) to P(V). To test our hypothesis, control experiments with drying agents such as molecular sieves and $MgSO_4$ were performed, and reduced product yields (66−78%) of **3a** by NMR were observed (Scheme 3, eq 1). These outcomes

Scheme 3. Control Experiments

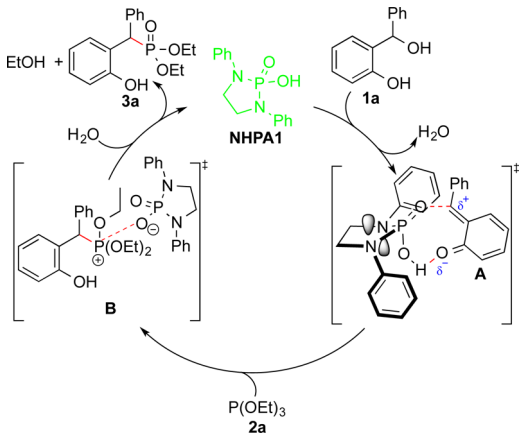


strongly suggest that the H_2O molecule plays an important role in the reaction process. Additionally, an *in situ* NMR study of this phospha-Michael reaction of **1a** with $P(OiPr)_3$ **2c** was conducted in CD_2Cl_2 solvent which also supports that the H_2O molecule serves as an internal nucleophile to generate the target product **3v** and *i*PrOH (Scheme 3, eq 2).

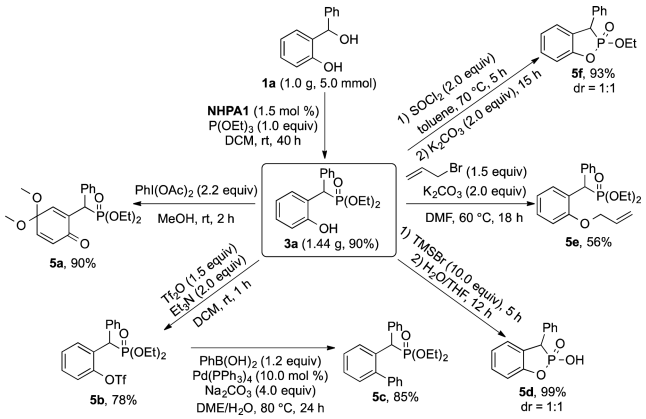
To gain insights into the catalytic cycle of this transformation, a plausible mechanism is proposed on the basis of the results from the control experiments (Scheme 4). The NHPA-catalyzed dehydration of *o*-hydroxybenzyl alcohol **1a** results in the generation of *o*-QM intermediate **A**, which is activated by a hydrogen bond with the **NHPA1**. The following phospha-Michael addition reaction with $P(OEt)_3$ **2a** generates a phosphonium intermediate **B**, which then is attacked by a H_2O nucleophile to produce the diarylphosphonate product **3a** and EtOH.

To demonstrate the synthetic utility of the versatile diaryl phosphonate adducts, we first tested a large-scale experiment with **1a** (1.0 g, 5.0 mmol), and it afforded the target Michael adduct **3a** (1.44 g) in 90% yield (Scheme 5). Next, we explored

Scheme 4. Proposed Mechanism



Scheme 5. Synthetic Utility of Diaryl Phosphonate 3a



the synthetic transformation of **3a**. The phenol group on **1a** was readily oxidized to *γ*-ketophosphonate **5a** with $PhI(OAc)_2$. The conversion of the phenolic hydroxyl group **3a** to the corresponding aryl triflate **5b** in the presence of Tf_2O and Et_3N proceeded smoothly, and the sequential Suzuki cross-coupling reaction of **5b** with $PhB(OH)_2$ delivered the target product **5c** in 85% yield. McKenna reaction conditions[28] for dealkylation of the ethylphosphonate **3a** provided only cyclic phosphonate **5d** as a potential halogen-free flame retardant.[8] The treatment of **3a** with allyl bromide under basic conditions afforded allyloxy substituted diaryl phosphonate **5e** in moderate yield. Finally, considering the significant application of the cyclic phosphonates as precursors of stabilized C-centered radicals,[29] a one-pot cyclization of **3a** in the presence of $SOCl_2$ and K_2CO_3 was conducted and the desired cyclic phosphonate product **5f** was obtained in 93% yield.

In summary, we have developed a novel *N*-heterocyclic phosphorodiamidic acid (NHPA) organocatalyst for the phospha-Michael reaction of *o*-QMs with trialkylphosphites. This NHPA catalyst has demonstrated its high catalytic efficiency (1.5 mol % catalyst) in phosphonylation of *o*-QMs to synthesize versatile diaryl phosphonates under mild reaction conditions. In addition, this organocatalytic system enables diastereoselective synthesis of diaryl phosphinates employing dialkyl phenyl-phosphonites. A series of control experiments and an *in situ* NMR study suggest that a H_2O molecule generated by dehydration of *o*-hydroxybenzyl alcohol serves as an internal nucleophile for the transformation of P(III) to P(V). On the

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basis of these outcomes, a plausible mechanism of the NHPA-catalyzed phospha-Michael reaction is proposed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03019.

Experimental details (PDF)
Spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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