$NaIO_4/NH_2OH$-mediated Efficient Synthesis of Phosphoroamidates from Anilines and Triethyl Phosphite

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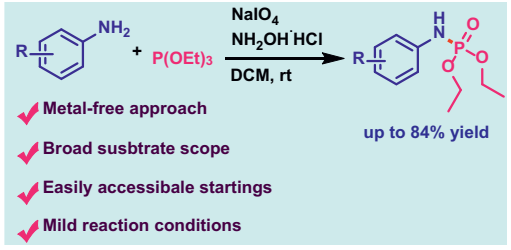
SIGNIFICANCE

- An efficient and metal-free method for the synthesis of phosphoroamidates at room temperature and mild conditions.
- A combination of sodium periodate ($NaIO_4$) and hydroxylamine ($NH_2OH{\cdot}HCl$) effectively accelerates the phosphoramidation reaction of amines and triethyl phosphites.
- A wide variety of anilines bearing mono-, di-, and tri-substituted functional groups have been used for the preparation of phosphoroamidates in moderate to good yields.



Keywords

Metal-free, Sodium periodate ($NaIO_4$), Hydroxylamine ($NH_2OH{\cdot}HCl$), Available starting substrates, Phosphoroamidates, Room temperature

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ABSTRACT

A simple, efficient, and metal-free method was developed for the synthesis of phosphoroamidates. In essence, a mixture of sodium periodate ($NaIO_4$) and hydroxylamine ($NH_2OH{\cdot}HCl$) was used in stoichiometric amounts to

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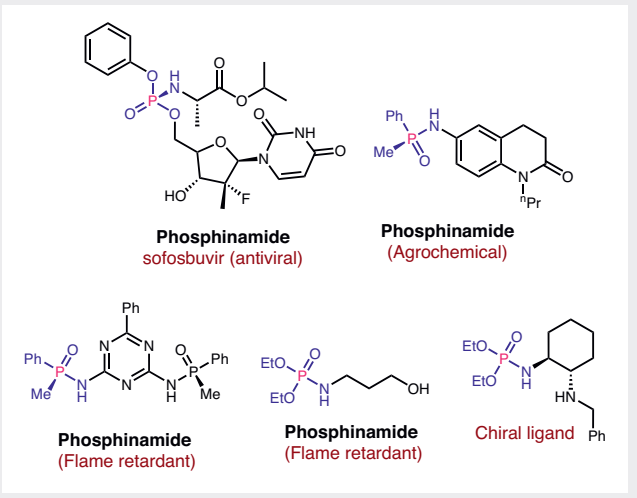
execute the phosphoramidation reaction of aromatic amines and triethyl phosphites at room temperature, in open air. This method offers a practical synthesis route to afford a diverse range of phosphoroamidates via the construction of P–N bonds, with excellent functional group compatibility and good yields under mild conditions.

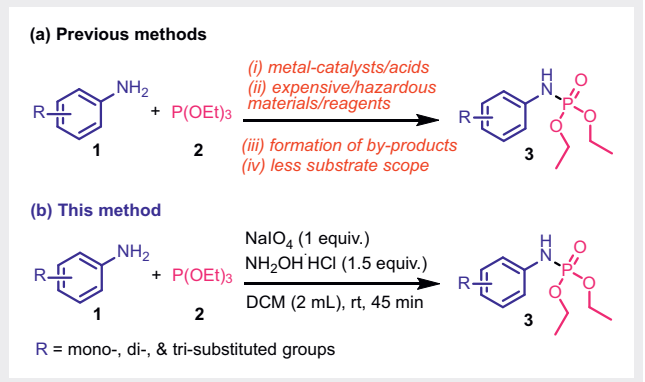
Introduction

Organophosphorus compounds containing P–N bonds have extensive applications in biological chemistry and modern organic synthesis [1]. Molecules with phosphorus–nitrogen bonds are considered to be versatile as the P–N bond attributes distinct bonding modes, electrical configuration, and stereochemical arrangement [2]. Consequently, the P–N bond formation is a dynamic and important research area for the development of useful intermediates in several organic transformations, including coupling reactions, isotope exchange reactions, preparation of phosphonamidates, ligands, etc [3]. Among the classes of various organophosphorus compounds, phosphoroamidates are broadly associated with numerous biologically active molecules, medicinal chemistry, and industrially important products. Remarkably, they have been widely used as prodrugs for the significant improvement of the therapeutic potential of the parent drugs, and in this context, phosphoramides, phosphonamides, and phosphinamides are commonly found in functional materials, pharmaceuticals, and organic synthesis [4]. In particular, a number of nucleoside phosphoramidates such as MK-3682 are used as potential antiviral and antitumor drugs. In 2013, sofosbuvir got FDA approval for the treatment of hepatitis C virus infection (▶**Fig. 1**) [5]. In addition, some of them (MMP-2 and MMP-9) are under clinical trials in terms of a chemotherapy perspective as matrix metalloprotease inhibitors [6]. Recently, phosphoramidates have also been considered effective flame retardants for polyamide, epoxy resins, and cotton cellulose [7]. Phosphoramidates have also been employed as efficient chiral ligands in asymmetric synthesis and as useful precursors to synthesize aziridines, azetidines, amines, imines, and heterocycles [8] Moreover, their application has extended to abscisic acid agonists, antirust additives in lubricating oils, and agents to improve the ionization efficiency in mass spectrometry [9].

Due to having wide application in various fields of research, a number of strategies have been developed in synthesizing phosphoramidates for the last few years. Traditionally, among the phosphorous analogues, H-phosphonates have been largely exploited as a useful precursor to couple with aromatic or aliphatic amines, leading to the formation of phosphoramidates in the presence of an activating agent such as CCl_4 or trichloroisocyanuric acid (TCCA), transition metal catalysts, photocatalysts, molecular iodine or iodine/H_2O_2 [10]. Besides these, phosphoryl chlorides, phosphoryl azide, trialkyl phosphites were also employed as substrates for the direct phosphoramidation [11]. In 2019, Wang et al. reported *tert*-Butyl hydroperoxide (TBHP)/NH_4I-mediated N–H phosphorylation via the cross-dehydrogenative coupling (CDC) reactions between imines/imidates and P(O)H compounds [12]. In 2022, Yu et al. disclosed a copper/photoredox-catalyzed approach to construct P(O)–N bond from P(O)–H compounds and aromatic amines [13]. Remarkably, these previously reported methods are associated with several issues such as the use of expensive metal catalysts, hazardous materials, generation of by-products, limited substrate scope, long reaction time, and harsh reaction conditions [10d], [10g], [10j]. Consequently, a simple and efficient approach regarding the synthesis of phosphoramidates is still relevant in current research progress. In continuation of our study in developing straightforward and practical methods [14], we have proposed a metal-free synthesis route to access phosphoroamidates from readily available and stable starting materials. Herein, the construction of P(O)–N has been achieved by the reaction of trialkyl phosphites, $P(OR)_3$, and aromatic amines in the presence of sodium periodate ($NaIO_4$) and hydroxylamine ($NH_2OH{\cdot}HCl$), as shown in Scheme 1. Interestingly, the mixture of these reagents effectively promoted direct phosphoramidation at ambient conditions. The present protocol reveals an indirect use of molecular iodine to accelerate the conversions using less explored and air-stable triethyl phosphite



▶**Figure 1** Examples of bioactive molecules containing phosphonamide moiety.



Scheme 1 Synthesis of phosphoramidates.

under mild conditions. Furthermore, the in situ generated iodine facilitates the reactions without the formation of possible phosphate side products and affords phosphoramidates in high yields.

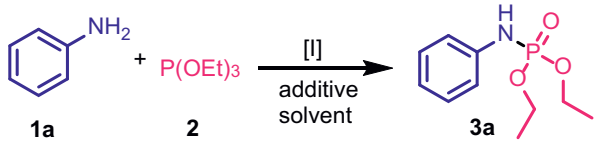
Results and Discussion

Our initial motive was to find the best procedure without the direct interference of molecular iodine. Several strategies were considered suitable for initiating the reaction by generating iodine in the reaction mixture. Thus, we attempted the phosphoramidation reaction of aniline and $P(OEt)_3$ in the presence of NaI and TBHP in a dichloromethane (DCM) medium (▶**Table 1**, entry 1). Unfortunately, the experiment did not yield the product **3aa**. Thereafter, we investigated the reaction with various iodine analogues such as TBAI and $NaIO_4$ to carry out the reaction, which also did not yield the desired product (▶**Table 1**, entries 2 and 3). We then turned our attention to using the oxidants and utilized hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) as a reagent. It is noteworthy that the phosphoroamidate **3aa** product was produced in 67% yield (▶**Table 1**, entry 4). Subsequently, we performed the reaction with an increased amount of $NH_2OH{\cdot}HCl$ (1.5 equiv) to enhance the production, obtaining the compound with an 84% yield (▶**Table 1**, entry 5). However, further increment of the amount (2 equiv) did not make any significant change in the product formation (▶**Table 1**, entries 6 and 7). Next, solvent screening was conducted by employing several organic solvents such as THF, toluene, ethanol, DMF, and acetonitrile (▶**Table 1**, entries 8–12). Notably, among these solvents, only DCM was preferred to furnish the best yield under the optimum conditions. In addition, the experiment was monitored for six hours, leading to a reduced yield (79%) (▶**Table 1**, entry 13). On the other hand, when the reaction was heated to 60 °C, the product formation dropped significantly (▶**Table 1**, entry 14).

With the optimized reaction conditions in hand, we decided to explore the generality of the reaction with various aryl amines (▶**Table 2**). First, we chose a variety of monosubstituted anilines to react with triethyl phosphite. Notably, *p*-toluidine was easily converted to the desired product **3ab** in 82% yield. Then, the reaction was investigated with a number of halogens substituted (2-F, 3-Br, 4-Br, and 2-I) anilines, providing the phosphonamide compounds **3ac–3af** in 64–77% yields. We then used a few anilines with highly electron-deficient groups ($-OCF_3$, $-CF_3$), and the corresponding products **3ag–3ah** formed in moderate yields.

As the next step, we were interested in evaluating the response of di-substituted anilines in the phosphoramidation

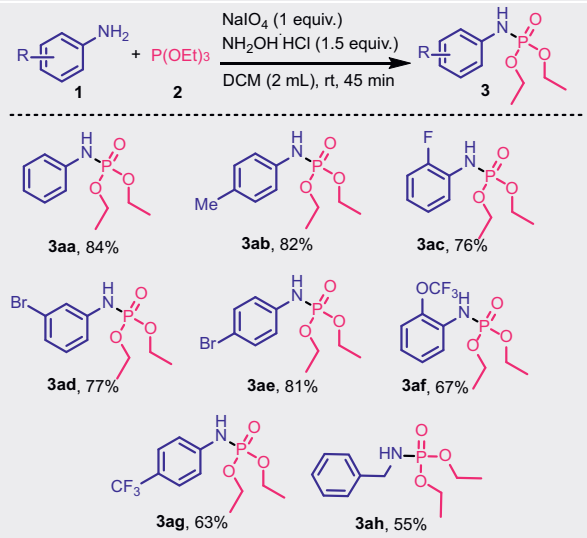
▶**Table 1** Optimization of the reaction conditions.[a,b]



Entry	[I] (equiv)	Reagent (equiv)	Solvent (mL)	Yield[b] (%)
1	NaI (1)	TBHP (1)	DCM	nr
2	TBAI (1)	TBHP (1)	DCM	nr
3	$NaIO_4$ (1)	TBHP (1)	DCM	Trace
4	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1)	DCM	67
5	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1.5)	DCM	84
6	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (2)	DCM	85
7	$NaIO_4$ (2)	$NH_2OH{\cdot}HCl$ (1.5)	DCM	82
8	$NaIO_4$ (2)	$NH_2OH{\cdot}HCl$ (1.5)	THF	18
9	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1.5)	toluene	trace
10	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1.5)	EtOH	trace
11	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1.5)	DMF	nr
12	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1.5)	MeCN	27
13	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1.5)	DCM	79[c]
14	$NaIO_4$ (1)	$NH_2OH{\cdot}HCl$ (1.5)	DCM	66[d]

[a]Reaction conditions: **1** (1.5 mmol), **2** (1.0 mmol), $NaIO_4$ (1.0 equiv), NH_2OH (1.5 equiv), in solvent (2 mL), stirring for 45 min.
[b]Isolated yield.
[c]Reaction carried out for 6 h.
[d]Reaction carried out at 60 °C.

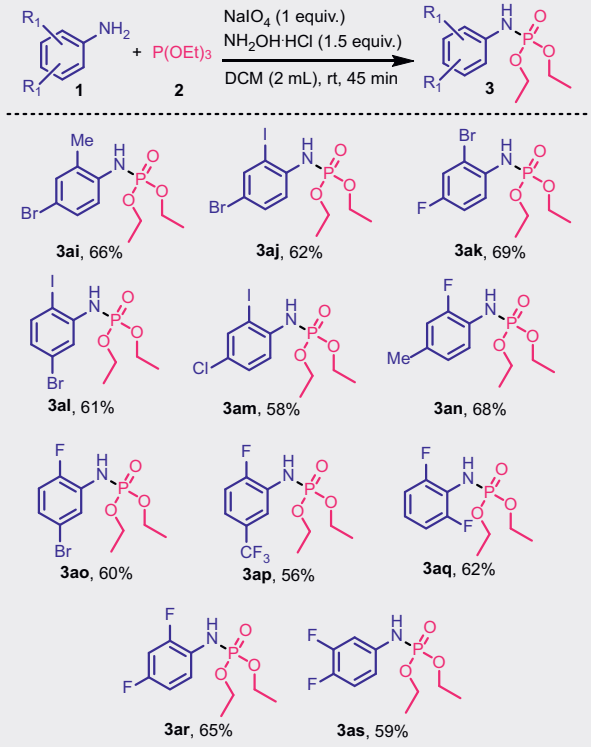
Table 2 Scope of different monosubstituted anilines.[a,b]



[a]Reaction conditions: **1** (1.5 mmol), **2** (1.0 mmol), $NaIO_4$ (1.0 equiv), NH_2OH (1.5 equiv), in DCM (2 mL) stirring at r.t. for 45 min.
[b]Isolated yield.

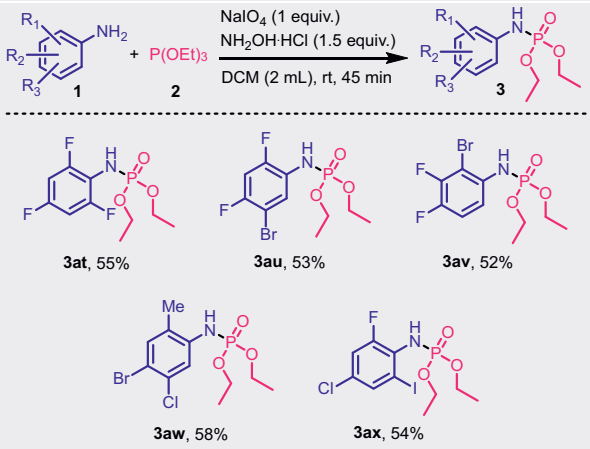
reaction (**Table 3**). Thus, the reaction was started with 4-bromo-2-methylaniline and $P(OEt)_3$. In consequence, the expected product **3ai** was generated with a 66% yield. Thereafter,

Table 3 Scope of different di-substituted anilines.[a,b]



[a]Reaction conditions: **1** (1.5 mmol), **2** (1.0 mmol), $NaIO_4$ (1.0 equiv), NH_2OH (1.5 equiv), in DCM (2 mL) stirring at r.t. for 45 min.
[b]Isolated yield.

Table 4 Scope of different tri-substituted anilines.[a,b]

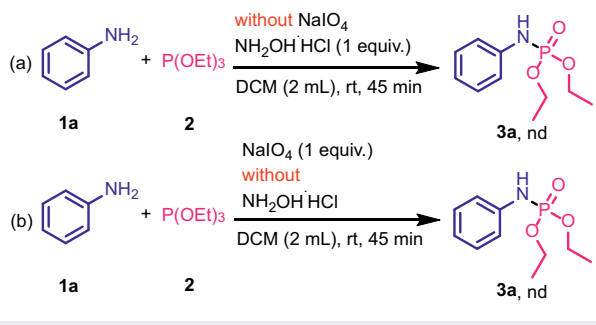


[a]Reaction conditions: **1** (1.5 mmol), **2** (1.0 mmol), $NaIO_4$ (1.0 equiv), NH_2OH (1.5 equiv), in DCM (2 mL) stirring at r.t. for 45 min.
[b]Isolated yield.

various anilines bearing substituents (–F, –Cl, –I, $–CF_3$, –Me) at different positions in the phenyl ring underwent the phosphoramidation reaction to give the corresponding products **3aj–3ap** in moderate yields. Next, we carried out the reactions using di-fluoro-substituted anilines, leading to the desired phosphonamides **3aq–3as** in 59–65% yields.

Following the previous result, we further explored the substrate range by coupling tri-substituted anilines with $P(OEt)_3$ (**Table 4**). First, reactions were attempted with fluoro- and bromo-containing anilines and interestingly, the desired products **3at–3av** in isolated in 52–55% yields. Other aniline derivatives bearing –Me, –Cl, –Br, and –I groups were converted to the corresponding compounds, and **3aw–3ax** were isolated with satisfactory yields. It is noteworthy that mono-, di-, and tri-substituted phenyl rings were compatible with the reaction, affording the desired products.

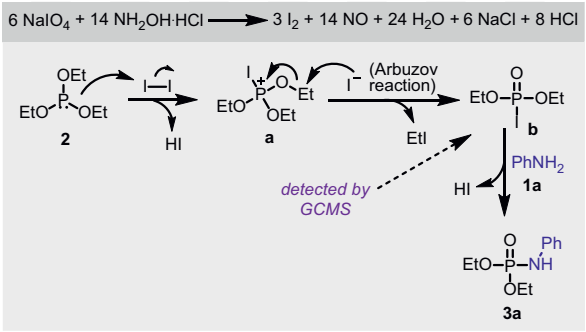
To understand the mechanism, we also carried out a couple of control experiments (Scheme 2). First, the reaction was conducted without $NaIO_4$, but no product was detected. On the other hand, no reaction proceeded in the absence of $NH_2OH{\cdot}HCl$. Therefore, after 15–20 min, stirring these two



Scheme 2 Control experiments.

components produced iodine in the mixture, which assisted in proceeding with the reactions.

Based on the previous literature studies [15] and GCMS analysis (see SI), a probable mechanistic pathway is proposed and displayed in Scheme 3. First, the combination of $NH_2OH{\cdot}HCl$ and $NaIO_4$ released iodine in the reaction mixture. Then this in situ generated iodine attacked the phosphite molecule **2** to produce intermediate **a** and the conversion is further accelerated by the existing acid in the mixture. In the next step, **a** undergoes Arbuzov reaction to provide the iodophosphate **b**, resulting in ethyl iodide as a by-product. Finally, the nucleophilic attack of iodophosphate **b** (detected by GCMS analysis) by aniline **1a** led to the desired phosphoramidate **3a** with the elimination of HI.



Scheme 3 Probable mechanistic pathway.

Conclusions

In conclusion, we developed a $NaIO_4/NH_2OH{\cdot}HCl$-mediated phosphoramidation reaction of commercially available aromatic amines and $P(OEt)_3$, providing a simple and practical protocol for the synthesis of phosphonamides. The metal-free, one-pot reaction was carried out in DCM solvent at room temperature to form a new P(O)–N bond. Moreover, a wide variety of substrates with excellent functional group tolerance, good yields, ease of isolation, and mild reaction conditions are notable features of this method. The strategy offers impressive reliability for the potential applications of phosphoramidates.

Experimental Section

General Information

All starting materials and commercial reagents were purchased from Alfa Aesar (Haverhill, Massachusetts), Sigma-Aldrich (St. Louis, Missouri), Avra (Hyderabad, India), Spectrochem (Mumbai, India), and TCI (Tokyo, Japan). Thin-layer chromatography plates were visualized by exposure to ultraviolet (UV) light with a wavelength of 254 nm and then further analyzed using an iodine chamber. Thin-layer chromatography was performed using precoated plates. Column chromatography was performed in 120–200 mesh size silica gel. The reactions were carried out in a round-bottom flask and sealed tube. and all NMR spectra were recorded on a Bruker Avance 400 spectrometer (^1H at 400 MHz and ^{13}C at 100 MHz). Chemical shifts for ^1H NMR spectra have been reported in parts per million (ppm) from tetramethylsilane (TMS) with solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Similarly, ^{13}C NMR spectra have been reported in parts per million (ppm) relative to TMS with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). The ^1H NMR and ^{13}C NMR spectra of the known products were compared with literature reports.

Procedure for the Preparation of Phosphoroamidates 3

A solution of $NaIO_4$ (1.0 equiv) in DCM (2 mL) was subjected to stirring with the gradual addition of $NH_2OH{\cdot}HCl$ (1.5 equiv) for 10–15 min at r.t. Then, the starting materials namely triethyl phosphite (1.0 mmol) and aniline (1.5 mmol) were added one by one to the mixture, and it was stirred for another 30 min at r.t. The completion of the reaction was monitored by TLC, and the resulting solution was washed with saturated $Na_2S_2O_3$ solution followed by dilution with water (10 mL) and extracted with EtOAc (2×20 mL). Then the combined organic residue was evaporated and dried over anhydrous Na_2SO_4. Finally, the desired pure product **3** was isolated by column chromatography on silica gel with hexane/EtOAc as eluent.

Diethyl phenylphosphoramidate (3aa)

Yield: 0.192 g, 84%.

^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 1H), 7.25 (dd, *J* = 12.9, 4.9 Hz, 1H), 7.05–6.92 (m, 1H), 6.77 (dd, *J* = 29.9, 9.1 Hz, 2H), 4.11 (dt, *J* = 25.0, 17.4 Hz, 4H), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.88 (s), 129.27 (s), 121.57 (s), 117.30 (d, *J* = 7.3 Hz), 62.91 (d, *J* = 4.9 Hz), 16.09 (d, *J* = 7.1 Hz).

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Primary Data

NO.

Contributors' Statement

Data collection: E.V.V.S.R., S.G., R.C., J.S.; design of the study: E.V.V.S.R., S.G., R.C., J.S.; statistical analysis: E.V.V.S.R., S.G., R.C., J.S.; analysis and interpretation of the data: E.V.V.S.R., S.G., R.C., J.S., V.D.; drafting the manuscript: R.C., V.D., R.D.; critical revision of the manuscript: R.C., R.D.

Conflict of Interest

The authors declare that they have no conflict of interest.

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