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Direct Aerobic Oxidative Esterification and Arylation of P(O)−OH Compounds with Alcohols and Diaryliodonium Triflates

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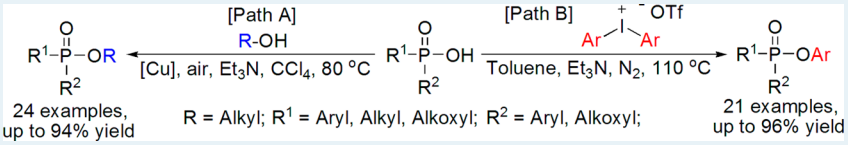
Supporting Information



ABSTRACT: Copper-catalyzed aerobic oxidative esterification of P(O)−OH compounds is achieved using alcohols as efficient esterification reagents, giving the expected products with good to moderate yields. Furthermore, it is shown that the arylation of P(O)−OH compounds proceeds efficiently to produce the corresponding products via the treatment of diaryliodonium triflates under mild reaction conditions. It is a simple way to produce a broad spectrum of functionalized phosphinates, phosphonates, and phosphates from basic starting materials with good to excellent yields. The protocol is convenient for practical application. A plausible mechanism has been proposed for the reaction.

KEYWORDS: *aerobic oxidative esterification, arylation, P(O)−OH compounds, alcohols, diaryliodonium triflates*

1. INTRODUCTION

Organophosphorus compounds are important intermediates in organic synthesis. They are used as structural components in medicinal chemistry as well as intermediates for the preparation of polymers, photoelectric materials, fire retardants, lubricants, and phosphine ligands.[1−6] Due to their broad range of biological properties and presence in bioactive entitles, certain phosphoryl esters are motifs in terms of natural products, pharmacological agents, amino acid analogues, and synthetic precursors.[7,8] In recent years, there is a growing interest in these kinds of compounds. For their preparation, phosphoryl chlorides or P(O)−H rather than P(O)−OH compounds are commonly used as phosphorylation agents.[8,9]

As depicted in Scheme 1, phosphinates, phosphonates, and phosphates are synthesized by treating P(O)−H or P(O)−Cl compounds with nucleophiles by means of nucleophilic substitution.[10,11] In 1962, Pollart et al. disclosed for the first time that P(O)−OH can be easily converted to P(O)−Cl in the presence of sulfuryl chloride. Through a stepwise procedure, P(O)−Cl reacts with nucleophiles (e.g., alcohols, phenols) to give the corresponding phosphates or phosphonates.[11a] In addition, Jang et al. found that in the presence of PPh_3, CCl_3CCN acts as efficient chlorinating agent in the esterification of phosphoric acid with alcohols.[11f] The method, however, suffers from shortcomings such as the lack of tolerance toward functional groups and the high cost of P(O)−H compounds.

In 2005, Ishihara et al. demonstrated that the nucleophilic bases promote the dehydrative condensation of phosphoric acid with alcohols.[9f−h] Later, Kaushik et al. found that the esterification reaction of phosphoric acid with alcohols proceeds efficiently via the assistance of silica chloride.[11g] Furthermore, microwave-promoted esterification of cyclic phosphinic acid with alcohols was reported by Keglevich et al. in 2012, but the direct esterification of diphenyl phosphinic acid with methanol or other alcohols could not occur under the adopted reaction conditions.[11h] It was reckoned that the esterification of phosphinic acids is much more difficult than that of carboxylic acids due to the stronger acidity of the former.[9−11]

Base-promoted arylation of nucleophiles (e.g., O−H, N−H, S−H, P−H) using diaryliosonium salts as arylation reagents is a well-documented process.[12] The arylation of oxygen nucleophiles with diaryliodonium salts was reported by Crowder et al. in 1963 and later by Olofsson and co-workers in 2012,[12a,b,13] whereas the studies on arylation of nitrogen nucleophiles was reported by Kang et al. in 2000 as well as by Carroll and Wood in 2007.[12c−d] In 2013, Xu et al. reported the direct coupling of diaryliodonium salts with P−H containing nucleophiles by means of copper-catalyzed P-arylation.[12f] Recently, Feringa investigated the synthesis of mixed alkyl aryl phosphonates through the reaction of phosphonates with diaryliodonium salts over a copper catalyst.[12g] Although there are a large number of studies on the arylation of nucleophiles, the use of P(O)−OH

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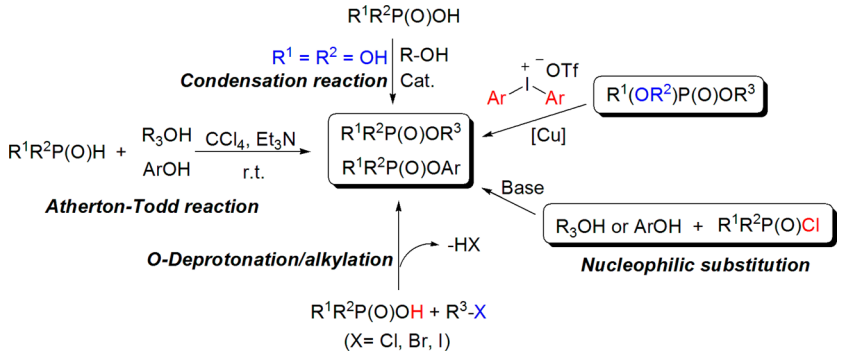
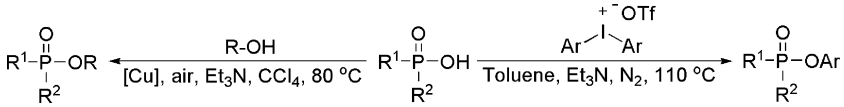
Scheme 1. Methods for the Synthesis of Phosphinates, Phosphonates, and Phosphates[8−11]



Scheme 2. Outline of the Present Study



R = Alkyl; R^1 = Aryl, Alkyl, Alkoxyl; R^2 = Aryl, Alkoxyl;

compounds as starting materials has not been reported. Indeed, reports about the metal-catalyzed cross-coupling reaction of P(O)−OH compounds with aryl halides or arylboronic acids are rare. Thus, to develop an efficient and convenient method for the arylation of P(O)−OH compounds is highly desired in organophosphorus chemistry.

In the present study, we report the copper-catalyzed aerobic oxidative esterification of P(O)−OH compounds with alcohols under mild reaction conditions. We obtain esterification products with good to excellent yields. Further treatment with diaryliodonium triflates results in arylation products with good to excellent yields (Scheme 2). A plausible mechanism is proposed for the copper-catalyzed aerobic oxidative esterification reaction.

2. RESULTS AND DISCUSSION

2.1. Copper-Catalyzed Direct Aerobic Oxidative Esterification of P(O)−OH Compounds with Alcohols. The reaction of diphenyl phosphinic acid with methanol at 80 °C with the assistance of CuI, CCl_4, and Et_3N in the presence of Na_2CO_3 under air atmosphere gives methyl diphenyl phosphinate **3a** in 89% yield (Table 1, entry 1). In the reaction, alcohol was in excess and served as solvent. Then we concentrated on the optimization of reaction conditions. We found that when the reaction was operated under N_2 atmosphere, there is no esterification product. We thus deduce that the presence of oxygen is essential (Table 1, entry 2). Other bases such as K_2CO_3, Cs_2CO_3, NaOAc, and NaOH were also tested. Obviously, Na_2CO_3 is the best, and 89% yield of **3a** is obtained at a "diphenyl phosphinic acid/Na_2CO_3 molar ratio" of 1:2 (Table 1, entries 3−8). Among the copper sources (CuI, CuBr, CuCl, Cu_2O, CuO, $Cu(OAc)_2$, $CuBr_2$, $CuCl_2$, and Cu powder), CuI gives the best result (Table 1, entries 8−16). We studied the effect of CuI loading and found that when the amount of CuI is reduced from 10 to 5 mol %, the product yield decreases from 89% to 66%, and a further decrease of CuI to 1 mol % causes further decline to 21% (Table 1, entries 1, 27−28).

The increase of reaction temperature within the 40−80 °C range is beneficial, but a further increase from 80 to 100 °C results in decrease of product yield (Table 1, entries 17−19). With the optimized reaction conditions in hand, we investigated the effect of additives, and we found that their efficiency is in the order: Et_3N > $(n\text{-Pr})_3N$ > $(i\text{-Pr})_2NEt$ > $(Et)_2NH$ > $n\text{-BuNH}_2$ > *N*,*N*-dimethylbenzenamine > bipyridine (Table 1, entries 1 and 20−25). In the case when there is no additive, there is no generation of product (Table 1, entry 26). Because Et_3N is the best (giving a product yield of 89%) we adopted Et_3N as the additive for further studies.

As shown in Table 2, the copper-catalyzed aerobic oxidative esterification reaction can be applied to a variety of alcohols. Different types of alcohols such as methanol, ethanol, isopropanol, 1-octanol, *n*-butyl alcohol and 3-methylbutan-1-ol react efficiently with diphenyl phosphinic acid (**1a**) under the optimized reaction conditions to afford the corresponding esterification products in good to excellent yields (Table 2, **3a**−**3f**). It is observed that 2,2,2-trifluoroethanol and ethane-1,2-diol also exhibit high reactivity, producing the corresponding products in 93% and 79% yields, respectively (Table 2, **3g**, **3h**). In the case of 2,2-dimethylpropan-1-ol, there is no generation of product, plausibly a result of steric hindrance (Table 2, **3i**). We observed that phenyl methanol and cyclohexanol are inert to the reaction. The phenomenon can be explained by the fact that this type of substrates can be easily oxidized under the present conditions (Table 2, **3j**, **3k**).

As depicted in Table 3, we investigated the reaction of P(O)−OH compounds (**1b**−**1g**) with a number of alcohols under the optimized conditions. It is clear that methanol, *iso*-propanol, *n*-butanol and *n*-octanol react with diphenyl hydrogen phosphate (**1b**) efficiently to give **4a**−**4d** in 82−93% yields. Dibutyl hydrogen phosphate (**1c**) is also a good substrate, and the esterification **4e** product is generated in 88% yield. In addition, differently substituted P(O)−OH compounds such as di-(4-methylphenyl)phosphinic acid, di-(4-trifluoromethylphenyl)phosphinic acid, ethyl hydrogen phenylphosphonate, and 10-hydroxy-9,10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide were tested, and **4f**−**4i** are generated in 81−89% yields as expected. Also, methyl 2-ethylhexyl octan-3-ylphosphonate (**4j**) and methyl *bis*-(2-ethylhexyl) phosphate (**4k**) are obtained through the reaction of **1h** and **1i** with methanol. However, in the cases of phosphoric acid (**1j**) and phosphonic acid (**1k**), there is no detection of the

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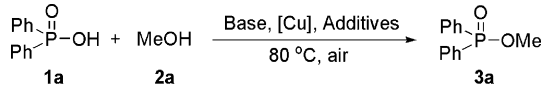
Table 1. Optimization of the Aerobic Oxidative Esterification of P(O)−OH Compounds with Methanol[a]



1a 2a 3a

entry	base	amine	[Cu]	yield (%)[b]
1	Na_2CO_3	Et_3N	CuI	89
2	Na_2CO_3	Et_3N	CuI	N.D.[c]
3	K_2CO_3	Et_3N	CuI	43
4	Cs_2CO_3	Et_3N	CuI	16
5	NaOAc	Et_3N	CuI	5
6	NaOH	Et_3N	CuI	trace
7	Na_2CO_3	Et_3N	CuI	58[d]
8	Na_2CO_3	Et_3N	CuI	71[e]
9	Na_2CO_3	Et_3N	CuBr	52
10	Na_2CO_3	Et_3N	CuCl	45
11	Na_2CO_3	Et_3N	Cu_2O	53
12	Na_2CO_3	Et_3N	CuO	29
13	Na_2CO_3	Et_3N	$Cu(OAc)_2$	52
14	Na_2CO_3	Et_3N	$CuBr_2$	58
15	Na_2CO_3	Et_3N	$CuCl_2$	50
16	Na_2CO_3	Et_3N	Cu powder	51
17	Na_2CO_3	Et_3N	CuI	24[f]
18	Na_2CO_3	Et_3N	CuI	63[g]
19	Na_2CO_3	Et_3N	CuI	36[h]
20	Na_2CO_3	$(n\text{-Pr})_3N$	CuI	79
21	Na_2CO_3	$(i\text{-Pr})_2NEt$	CuI	73
22	Na_2CO_3	$(Me)_2NPh$	CuI	48
23	Na_2CO_3	$(Et)_2NH$	CuI	56
24	Na_2CO_3	$n\text{-BuNH}_2$	CuI	52
25	Na_2CO_3	bipyridine	CuI	26
26	Na_2CO_3	None	CuI	N.D.
27	Na_2CO_3	Et_3N	CuI	21[i]
28	Na_2CO_3	Et_3N	CuI	66[j]

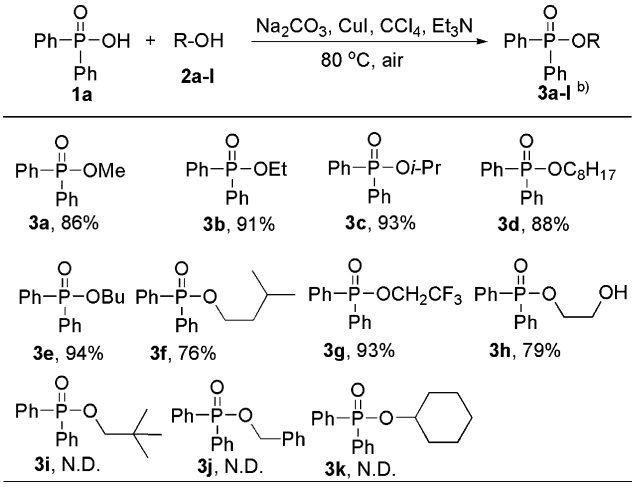
[a]Reactions were carried out with diphenyl phosphinic acid (1 mmol), base (2 mmol), CCl_4 (3 mmol), additive (1 mmol), and [Cu] catalyst (10 mol %) in methanol (1 mL), under air atmosphere stirred at 80 °C for 12 h. [b]Yield was determined by GC analysis, and dodecane was used as the internal standard. [c]Under N_2 atmosphere, N.D. = not detected. [d]Na_2CO_3 (1 mmol). [e]Na_2CO_3 (1.5 mmol). [f]40 °C. [g]60 °C. [h]100 °C. [i]CuI (1 mol %). [j]CuI (5 mol %).

corresponding products methyl dihydrogen phosphate (**4l**) and methyl hydrogen phosphonate (**4m**). According to Keglevich et al, these substrates are unfavorable for the reaction due to their high Gibbs free energy.[11h] It is deduced that phosphoric acid and phosphonic acid are highly reactive toward Na_2CO_3, affording the corresponding inorganic bases which are unreactive toward the aerobic oxidative esterification reaction.

In order to clarify the reaction mechanism, we operated the reaction of diphenyl phosphinic acid with tetracarbon chloride (1 mL) in the presence of CuI (10 mol %) at 80 °C for 16 h in air or in oxygen atmosphere. The excess carbon tetrachloride served as solvent. As confirmed by GC, GC-MS, and ^{31}P NMR analysis, there was no detection of chlorinating product. We hence deduce that the phosphoryl chloride is not generated in situ in the reaction, and the reaction possibly occurs through an aerobic oxidative esterification path (see Supporting Information, Scheme 1).

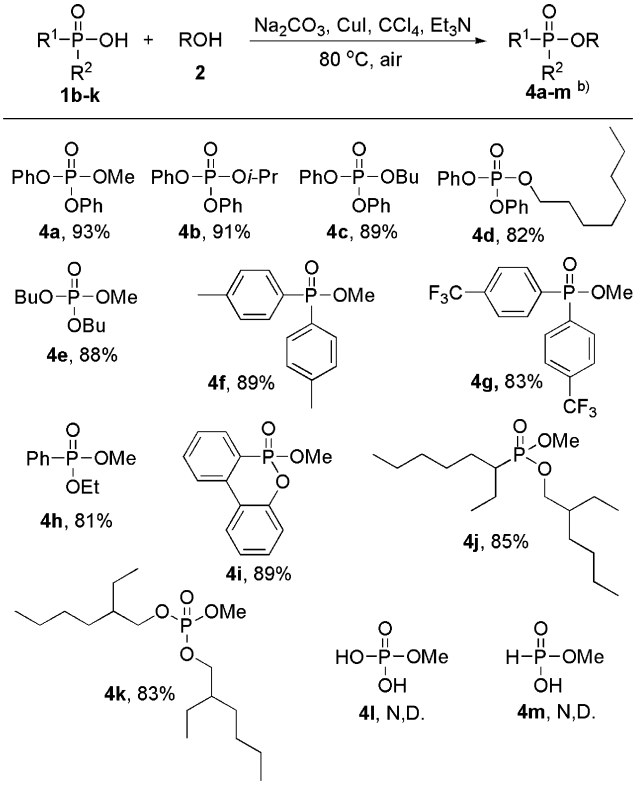
As depicted in Table 1 (entry 2), when the reaction is conducted under N_2 atmosphere with CuI (10 mol %), there is no detection of esterification product after the reaction.

Table 2. Scope of Alcohols[a]



[a]Reaction conditions: diphenyl phosphinic acid (1 mmol), alcohols (1 mL), Na_2CO_3 (2 mmol), CuI (0.1 mmol), CCl_4 (3 mmol), Et_3N (1 mmol), air, 80 °C, 12 h. [b]Isolated yields. [c]GC yield.

Table 3. Scope of P(O)−OH Compounds[a]



[a]Reaction conditions: P(O)−OH compounds (1 mmol), methanol (1 mL), Na_2CO_3 (2 mmol), CuI (0.1 mmol), CCl_4 (3 mmol), Et_3N (1 mmol), air, 80 °C, 12 h. [b]Isolated yields.

However, in a control reaction of diphenyl phosphinic acid with methanol under N_2 atmosphere over 1 equiv (i.e., 1 mmol) of CuI, there is 64% yield of **3a**. It is apparent that the amount of Cu(I) salts play an important role in the catalytic cycle (Scheme 3).

A plausible mechanism for the copper-catalyzed aerobic oxidative esterification of P(O)−OH compounds with alcohols is proposed as illustrated in Scheme 4. In protic solvent, P(O)−

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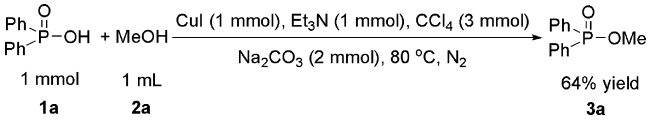
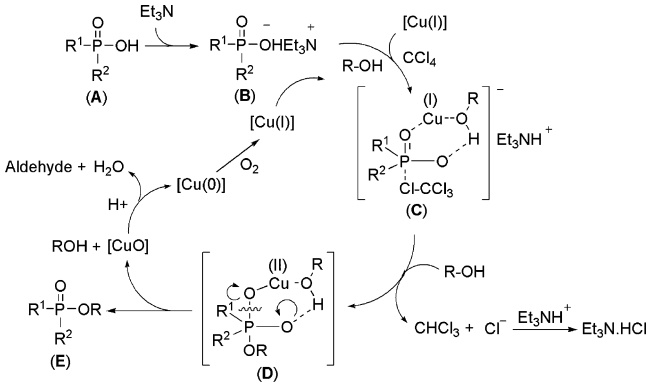
Scheme 3. Control Experiment



Scheme 4. Plausible Mechanism for the Copper-Catalyzed Aerobic Oxidative Esterification of P(O)−OH Compounds with Alcohols

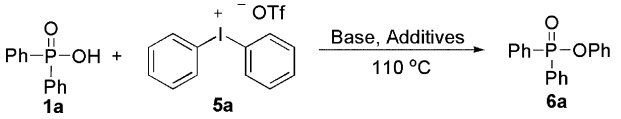


OH compound first combines with Et_3N to form intermediate **B**. With the assistance of CCl_4, there is simultaneous coordination of intermediate **B** with Cu(I) and alcohol, forming transition state **C** as a result. Then a molecule of alcohol attacks **C** to give the transition state **D** together with the elimination of $CHCl_3$ and Cl^-. Finally, with the elimination of CuO and alcohol molecule, there is esterification product **F**. The CuO source is readily reduced to Cu(0) and then oxidized to give back the catalytically active Cu(I) species.

Obviously, with the assistance of a copper salt and oxidant, one can realize the aerobic oxidative esterification reaction of P(O)−OH compounds and alcohols. Furthermore, through the reaction of P(O)−OH compounds with diaryliodonium triflates, one can get the corresponding arylation products with good to excellent yields.

2.2. Base-Promoted Arylation Reaction of P(O)−OH Compounds Diaryliodoniium Triflates. According to the report of Olofsson and co-workers,[13,14] we chose the reaction of diphenyl phosphinic acid (**1a**) with Ph_2IOTf (**5a**) as a model reaction to optimize the reaction conditions. We screened a number of inorganic and organic bases (i.e., KOH, K_3PO_4, *t*-BuONa, Cs_2CO_3, Na_2CO_3, K_2CO_3, $NaHCO_3$, NaOH, Et_3N) (Table 4, entries 1−9) for the arylation reaction, and found that Et_3N is the best, giving 95% yield of phenyl diphenyl phosphinate (**6a**). The phenomenon is ascribed to the intrinsic property of the substrates. It is deduced that the P(O)−OH compounds are highly reactive toward strong inorganic bases (e.g., Na_2CO_3, Cs_2CO_3, and NaOH), generating inorganic bases that are not reactive enough to undergo nucleophilic attack toward the diaryliodonium salts, although the presence of some potassium salts and weak bases results in the moderate results (Table 4, entries 16−18). It is noted that with the addition of CuI, the yield of **6a** is only 21%. When the temperature is decreased from 110 °C to room temperature, only a trace amount of **6a** is generated (Table 4, entries 10−11). Increasing the temperature within the 25−110 °C range is beneficial for the reaction but a further rise from 110 to 130 °C results in a decrease of **6a** yield (Table 4, entries 12−15).

Table 4. Optimization of the Arylation of P(O)−OH Compounds with Diaryliodonium Triflates[a]



entry	base	additive	temperature	yield (%)[b]
1	KOH		110 °C	55
2	K_3PO_4		110 °C	64
3	*t*-BuONa		110 °C	57
4	Cs_2CO_3		110 °C	37
5	Na_2CO_3		110 °C	21
6	K_2CO_3		110 °C	49
7	$NaHCO_3$		110 °C	80
8	NaOH		110 °C	7
9	Et_3N		110 °C	95
10	Et_3N	CuI	110 °C	21
11	Et_3N	CuI	r.t.	trace
12	Et_3N		r.t.	trace
13	Et_3N		40 °C	21
13	Et_3N		60 °C	52
14	Et_3N		80 °C	84
15	Et_3N		130 °C	89
16	Et_3N		110 °C	79[c]
17	Et_3N		110 °C	77[d]
18			110 °C	65
19	Et_3N		110 °C	81[e]

[a]Reactions were carried out with diphenyl phosphinic acid (1 mmol), base (1.1 mmol), diphenyliodonium triflate (1 mmol), and additive (10 mol %) in toluene (1 mL), under N_2 atmosphere stirred at 110 °C for 3 h. [b]Yield was determined by GC analysis, and dodecane was used as the internal standard. [c]Et_3N (0.5 mmol). [d]Et_3N (0.1 mmol). [e]Under air atmosphere.

With the reaction temperature fixed at 110 °C, we investigated the effect of Et_3N amount. When the amount of Et_3N is reduced from 110 to 50 mol %, the product yield decreases from 95% to 79%, and a further decrease of Et_3N to 10 mol % only causes a slight decline of **6a** yield to 77%. When the reaction is conducted without the addition of Et_3N, the **6a** yield is 65%. Hence we took 110 mol % as the optimized amount of Et_3N, and such an amount was adopted for the rest of the study. In addition, further reaction under air atmosphere gives the arylation product **6a** in 81% yield, demonstrating that the use of an inert atmosphere is important.

As shown in Table 5, the arylation reaction can be applied to a variety of P(O)−OH compounds. A number of substituted P(O)−OH compounds such as diphenyl phosphinic acid, diphenyl hydrogen phosphate, dibutyl hydrogen phosphate, di-(methylphenyl) phosphinic acid, di-(trifluoromethylphenyl) phosphinic acid, ethyl hydrogen phenylphosphonate, 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, bis-(2-ethylhexyl) hydrogen phosphate and 2-ethylhexyl hydrogen 2-ethylhexylphosphonate react efficiently with diphenyliodonium triflate (**5a**) to afford the corresponding arylation products with good to excellent yields (Table 5, entries 1−9). Additionally, symmetric diaryliodoniium triflates such as di-(4-methylphenyl)-iodonium triflate, di-(4-tertbutyl-phenyl)-iodonium triflate, di-(4-fluorophenyl)-iodonium triflate, di-(4-bromophenyl)-iodonium triflate and di-(4-iodo-phenyl)-iodonium triflate, exhibit high reactivity toward diphenyl phosphinic acid and diphenyl hydrogen phosphate,

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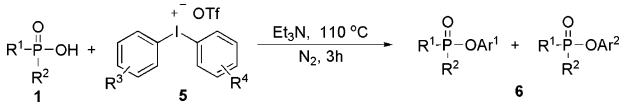
Table 5. Base-Promoted Arylation of P(O)−OH Compounds Diaryliodoniium Triflates[a]



Entry	P(O)-OH	Ar^1Ar^2IOTf	Product	Yield (%) [b]	Entry	P(O)-OH	Ar^1Ar^2IOTf	Product	Yield (%) [b]
1.	**1a**	**5a**	**6a**	91	11.	**1a**	**5c**	**6k**	90
2.	**1b**	**5a**	**6b**	96	12.	**1a**	**5d**	**6l**	94
3.	**1c**	**5a**	**6c**	88	13.	**1a**	**5e**	**6m**	88
4.	**1d**	**5a**	**6d**	91	14.	**1a**	**5f**	**6n**	82
5.	**1e**	**5a**	**6e**	88	15.	**1b**	**5e**	**6o**	91
6.	**1f**	**5a**	**6f**	83	16.	**1a**	**5g**	**6j** (**6j**:**6a** = 47:53) + **6a**	92
7.	**1g**	**5a**	**6g**	94	17.	**1b**	**5g**	**6p** (**6p**:**6b** = 45:55) + **6b**	89
8.	**1h**	**5a**	**6h**	92	18.	**1a**	**5h**	**6l** (**6l**:**6a** = 65:35) + **6a**	88
9.	**1i**	**5a**	**6i**	83	19.	**1a**	**5i**	**6n** (**6n**:**6a** = 72:28) + **6a**	96
10.	**1a**	**5b**	**6j**	87	20.	**1a**	**5j**	**6q** (**6q**:**6a** = 11:89) + **6a**	96

[a]Reactions were carried out with P(O)−OH compound (1 mmol), Et_3N (1.1 mmol) and diaryliodonium triflate (1 mmol) in toluene (1 mL), under N_2 atmosphere stirred at 110 °C for 3 h. [b]Isolated yield.

giving the corresponding products in 82% to 94% yields. For the symmetric diaryliodonium salts, electron-donating groups and electron-withdrawing group on the aryls do not have a significant effect on the yield of products (Table 4, entries 10−15).

The use of unsymmetric diaryliodonium salts was subsequently investigated. When 4-methylphenyl phenyliodonium triflate is applied, the reaction of 4-methylphenyl phenyliodonium triflate with diphenyl phosphinic acid or diphenyl hydrogen phosphate affords the corresponding products of **6j** with **6a** (at a ratio of 47/53) and **6p** with **6b** (at a ratio of 45/55) in 92% and 89% yields, respectively. As for 4-fluorophenyl phosphinate (**6l**) and 4-iodophenyl phosphinate (**6n**), they are obtained in 88% and 96% yields (with a ratio of 65/35 and 72/28 to **6a**), respectively, through the reaction of **5h** and **5i** with **1a**. Moreover, the reaction of **5j** with **1a** proceeds efficiently, giving 4-methoxyphenyl diphenyl phosphinate (**6q**) and **6a** (with a ratio of 11/89) in 96% yield. The phenomenon may be

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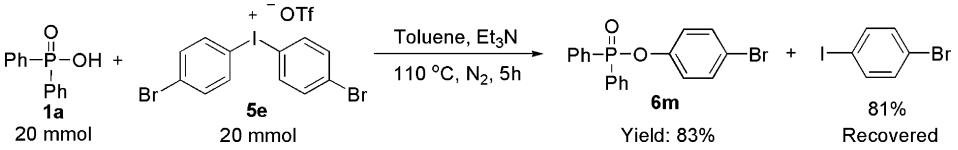
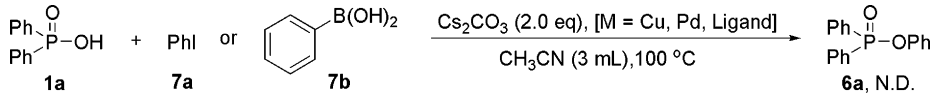
Scheme 5. Large-Scale Production of 6m



Scheme 6. Metal-Catalyzed Cross Coupling Reaction of Diphenyl Phosphinic Acid with Iodobenzene and Phenylboronic Acid[15]



ascribed to the fact that electron-poor aryl groups are transferred more readily than electron-rich aryl groups in the arylation reaction of unsymmetric diaryliodonium salts with P(O)−OH compounds.[12b]

In order to demonstrate the practical application of this method, we performed a large-scale reaction of di-(4-bromophenyl) iodonium triflate **5c** (20 mmol) with **1a** (24 mmol) and obtained **6g** in 83% yield. The byproduct 1-bromo-4-iodobenzene was recovered in 81% yield (Scheme 5).

With traditional metal-catalyzed cross-coupling reaction in mind, we used copper salts (e.g., CuI, CuBr, CuO, $Cu(OAc)_2$) as well as palladium salts (e.g., $Pd(OAc)_2$, $PdCl_2$) to promote the reaction of diphenyl phosphinic acid with iodobenzene or phenylboronic acid under the present reaction conditions but found no generation of coupling products. It is plausibly that there is easy coordination of diphenyl phosphinic acid with the metals to form phosphoryl-metal intermediates rather than the activation of iodobenzene or phenylboronic acid. It is deduced that in comparison with the other nucleophiles, the corresponding cross coupling reaction is much more difficult to undergo due to the strong acidity of the P(O)−OH compounds (Scheme 6).[15]

3. CONCLUSION

We developed a divergent method for the preparation of phosphates, phosphinates and phosphonates via the copper-catalyzed aerobic oxidative esterification and arylation of P(O)−OH compounds using alcohols and diaryliodonium salts as starting chemicals. We first realized the direct esterification of diphenyl phosphinic acid with alcohols under mild reaction conditions. The method avoids the use of air-sensitive reagents, and the reaction can be performed under ambient conditions, rendering the experimental procedure simple. Moreover, the diaryliodonium salts can be readily prepared from the corresponding arene compounds. Therefore, the synthetic method has high potential for the construction biologically active molecules, catalytic ligands, and organophosphorus compounds.

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501523g.

Information of experimental procedures and methods, characterization data, and NMR spectra of organic products (PDF)

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Notes

The authors declare no competing financial interest.

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