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Electrochemically driven P–H oxidation and functionalization: synthesis of carbamoylphosphonates from phosphoramides and alcohols†

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An electrochemical method to achieve carbamoylphosphonates from phosphoramides and alcohols *via* P–H oxidation and functionalization by using *n*-Bu_4NI as a catalyst is reported. A series of carbamoylphosphonates were obtained with good to excellent yields under mild reaction conditions. The electrochemical reaction is carried out under constant current electrolysis, with the alcohol being used as a solvent and a substrate, and is an attractive green synthesis method.

Introduction

In recent years, electrosynthesis has been regarded as an increasingly important method for molecular synthesis, and there have been considerable advances in the activation of C–H functionalizations.[1] The Stahl and Zeng groups have developed indirect electrochemical procedures for the halogenation of C–H, N–H and O–H bonds.[2] In these procedures, they used a halide such as TBAX (X = Cl, Br, I) as the redox mediator and/or electrolyte through halide generation, allowing reoxidation of the halide ions to halogens. Diverse nucleophilic reaction products under the halogenation electrolysis conditions were then obtained. More generally, I^- has been used for anodization and as a catalytic substrate to obtain target products.[3] Generation of a halide in the nucleophilic substitution step has the benefit of allowing reoxidation of the halide to a halogen at the anode and permitting these reactions to be performed with catalytic quantities of halide.[4]

Organophosphorus compounds and their derivatives have important application value in many fields, such as drug pharmacophores, agrochemicals, flame retardants and transition metal catalyst ligands.[5,6] Bisacylphosphonates have influences on tissue calcification, bone resorption, hydroxyapatite (HAP) formation and dissolution activity. The bisacylphosphonate molecules can be fully ionized at physiological pH.[7] Carbamoylphosphonates (CPOs) such as cyclopentylamide phosphate and *cis*-2-aminocyclohexylcarbamoylphosphonic acid (*cis*-ACCP) are potential candidates for matrix metalloproteinase (MMPs) inhibitors.[8,9] In addition, some carbamoylphosphonic acids have anti-tumor necrosis factor alpha (TNFa)[10] and carbonic anhydrase (CA) inhibitory activities.[11] Some typical carbamoylphosphonate derivatives are shown in Fig. 1.

Generally, carbamoylphosphonates are prepared by the substitution reaction of phosphonoformates or phosphonothiolformates with amines (Scheme 1a),[11a,12] and by the addition reaction of dialkyl phosphonates into isocyanates and isothiocyanates (Scheme 1b).[13] Alternatively, they can be synthesized *via* a multistep transformation from an amide derivative and phosphorus halides (Scheme 1c).[14,15] However, several limitations remain in these strategies, including the requirement of excess toxic regents, low yields, substrate limitations and/or harsh reaction conditions. Recently, we reported the synthesis of carbamoylphosphonates by iodine-promoted P–H phosphorylation and oxygenation of phosphinecarboxamides with alcohols (Scheme 1d).[16] We proposed that this transformation was completed by forming a P–I intermediate as the key step.

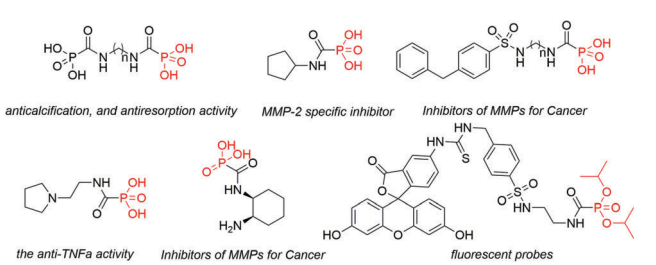

Fig. 1 Pharmaceutically-relevant organophosphorus compounds.

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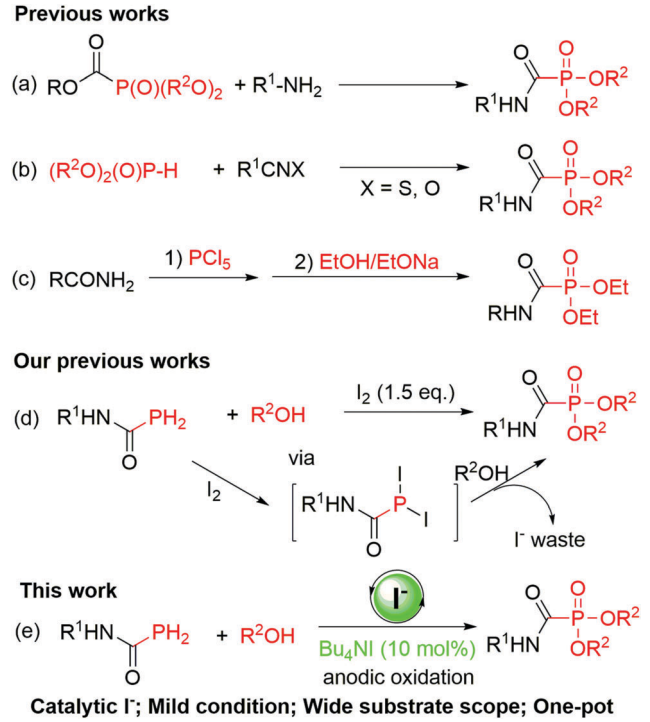
† Electronic supplementary information (ESI) available: Experimental procedures, characterization data, and copies of ^1H, ^{13}C and ^{31}P NMR spectra. See DOI: 10.1039/c8nj05739g



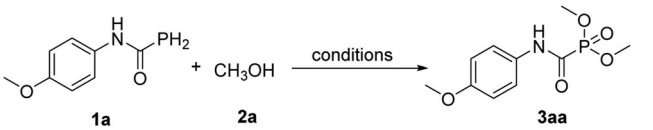
Scheme 1 Phosphonate-forming reactions.

A typical method for the electrochemical functionalization of N–H by C–H activation amination has been reported more recently.[17] We have now unraveled the power of electrochemical P–H activation to enable the first electrochemical domino-reaction of P–H iodination–phosphonation–oxygenation using a catalytic amount of *n*-Bu_4NI as a mediator in an undivided cell under constant current conditions (Scheme 1e). Key features of our approach include: (i) electrochemical P–H iodination/phosphonation/oxygenation, (ii) no toxic sacrificial halide reagents, (iii) a catalytic amount of *n*-Bu_4NI (10 mol%) as an iodine source, and (iv) metal-free P–H functionalization under ambient conditions.

Results and discussion

Initially, methoxyphosphoramide **1a** in methanol **2a** was used as the starting material and electrolyzed by using 1.5 equivalents of KI (1.5 eq.) as electrolyte and CH_3OH as a solvent at a constant current of 0.5 mA cm^{-2} in an undivided cell (Table 1, entry 1). Fortunately, the target product **3aa** was obtained in 26% yield. Then, different electrodes were investigated, and the best choice was found to be platinum electrodes (Table 1, entries 1–3). Notably, when we used 0.1 eq. of KI and 1.5 eq. of $LiClO_4$, the target product **3aa** was obtained in 76% yield (Table 1, entry 4). KI and ^{n}Bu_4NBr underwent the reaction smoothly, and TBAI gave a better result (Table 1, entries 5 and 6); 1.5 eq. of electrolyte loading could maintain good conductivity for the electrolysis, and **3aa** could be achieved in excellent yield. However, ^{n}Bu_4NBF_4 was not compatible with this transformation (Table 1, entry 7). These results showed that the role of the halogen salts was not only as the electrolyte, but also as a redox mediator. The reaction time was

Table 1 Optimization of the reaction conditions[a]

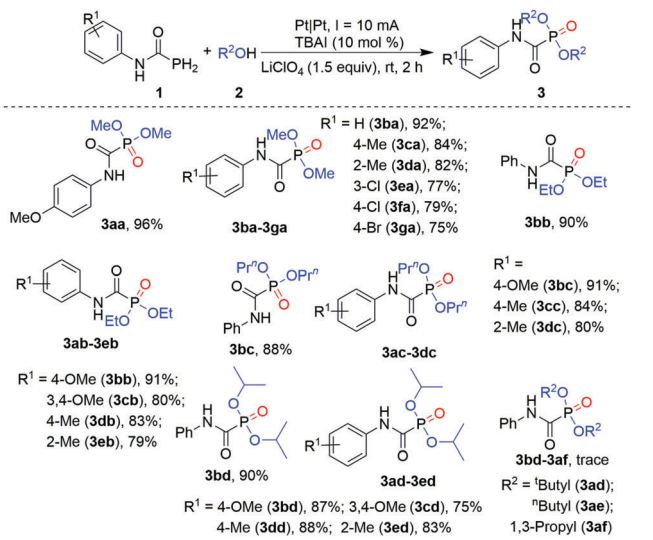


Entry	Anode/cathode	Electrolyte	Current/mA	Solvent	Time/h	Yield[b] (%)
1	C/C	KI (1.5 eq.)	0.5	CH_3OH	20	26
2	C/Pt	KI (1.5 eq.)	0.5	CH_3OH	20	61
3	Pt/Pt	KI (1.5 eq.)	0.5	CH_3OH	20	75
4	Pt/Pt	$KI/LiClO_4$	0.5	CH_3OH	20	76
5	Pt/Pt	^{n}$Bu_4NI/LiClO_4$	0.5	CH_3OH	20	80
6	Pt/Pt	^{n}$Bu_4NBr/LiClO_4$	0.5	CH_3OH	20	77
7	Pt/Pt	^{n}$Bu_4NBF_4/LiClO_4$	0.5	CH_3OH	20	—
8	Pt/Pt	^{n}$Bu_4NI/LiClO_4$	5	CH_3OH	5	91
9	Pt/Pt	^{n}$Bu_4NI/LiClO_4$	10	CH_3OH	2	96
10	Pt/Pt	^{n}$Bu_4NI/LiClO_4$	15	CH_3OH	1	75
11	Pt/Pt	^{n}$Bu_4NI/LiClO_4$	—	CH_3OH	20	—
12[c]	Pt/Pt	^{n}$Bu_4NI/LiClO_4$	10	CH_3CN/CH_3OH	1	—

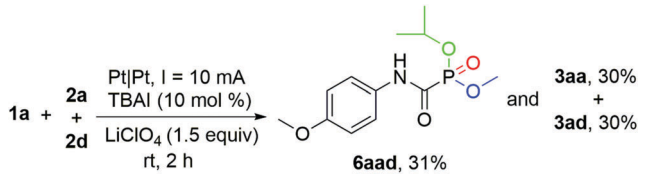
[a] Conditions: **1a** (0.2 mmol), 0.1 eq. of catalyst, 1.5 eq. of electrolyte, solvent (10 mL), and two platinum electrodes (10 × 10 × 0.2 mm), in an undivided cell at room temperature in air. [b] Yield of isolated compound. [c] CH_3CN (10 mL)/CH_3OH (4 eq.).

greatly shortened with increasing current and the yield was also improved (Table 1, entries 8–11). Increasing the current to 15 mA led to a relatively lower yield (Table 1, entry 10). The experimental results demonstrated that using 10 mA of current gave the best results. Of course, the reaction cannot be carried out in the absence of electricity (Table 1, entry 11). Afterwards, different solvents were investigated and MeCN (4 eq.) as the substrate was found to be detrimental to the process (Table 1, entry 12).

After deriving the optimal conditions, we further investigated the range and limitation of the conversion of *N*-arylphosphonamide to *N*-arylaminoformylphosphonate through this electrochemical route (Scheme 2). Various phosphonamides could be smoothly transformed into the corresponding carbamoylphosphonates in good to



Scheme 2 Substrate scope of the phosphinecarboxamide and alcohol.

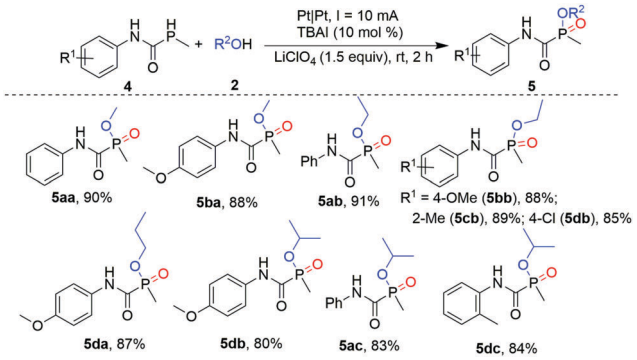


Scheme 3 The reaction of a phosphinecarboxamide and two different alcohols.

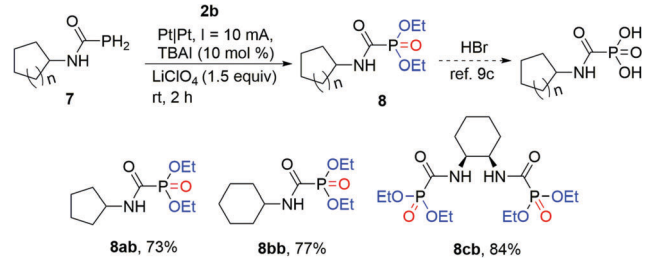
excellent yields. First, the functional group tolerance was studied by using methanol as a solvent and phosphoramides with different substituted functional groups (**3ba–3ga**). Phosphoramides containing electron donating groups (**3ca** and **3da**) or electron withdrawing groups (**3ea–3ga**) were well tolerated. The reaction also exhibited good compatibility with a series of phosphonamide reactants, which have groups in the para or *o*-substituent positions (**3ca**, **3da**). In particular, dimethoxy-substituted phosphonamides also exhibited excellent reactivity (**3cb**, **3cd**). Therefore, steric hindrance has no significant effect on the reaction. Ethanol and *n*-propanol alcohols were also compatible with the reaction with **1** and provided the product in good yield (**3ab–3eb**, **3ac–3dc**). It was found that a high yield of diisopropyl phosphonate (**3ad–3ed**) was also obtained by using isopropanol as the solvent. However, *n*-butanol, *tert*-butanol and propane-1,3-diol (**3ad–3af**) were not viable under the optimized conditions. Herein, the relatively large resistance hampered the completion of the reaction.

Then, the products with two different alcohols were tested. The reaction of **1a** with methanol and isopropanol (1 : 1) gave a mixture of products, **3aa**, **3ad**, and **6aad**, in about 30% yield of each product (Scheme 3). It was shown that the relevant products were not selective.

With the success of the carbamoylphosphonate synthesis, we next attempted to construct methyl phosphinates by applying the electrochemical method (Scheme 4). Gratifyingly, methanol could react with substrate **1** efficiently under the optimal conditions. Similar to what was observed before in the carbamoylphosphonate synthesis, the methyl phosphinate was also largely unaffected by steric or electronic properties. A high yield could be achieved to obtain the methyl methyl phosphinates (**5aa–5dc**). As a result, the diverse phosphoramide substituents



Scheme 4 Substrate scope of the 1-methyl-*N*-phenylphosphanecarboxamides and alcohols.



Scheme 5 Synthesis of aliphatic phosphate carbamoylphosphonates.

that could be used as substrates demonstrated the broad functional-group tolerance of the reaction.

Finally, *N*-cyclopentylphosphanecarboxamide and *N*-cyclohexylphosphanecarboxamide were tested in this transformation and they were well-tolerated in the reaction affording the desired products (**8ab** and **8bb**). Bis(azanediyl)bis(carbonyl)bis(phosphonate) (**8cb**) was also achieved. By using the reported method,[11c] these compounds can be further converted into carbamoylphosphonic acids, which are MMP inhibitors (Scheme 5).

Finally, to further elucidate the role of TBAI, the effect of TBAI on the reaction was investigated by cyclic voltammetry (see Fig. 2). Obviously, a redox wave was observed for TBAI (black curve). The increase in peak (ipa) current is associated with the regeneration of the iodine compound.[18] However, substrate *N*-(4-methoxyphenyl)phosphanecarboxamide **1b** did not display a significant peak (red curve). When we treated the mediator TBAI with substrate **1b** (green curve), the anodization peak (ipa) disappeared significantly, indicating that TBAI participated in the reaction. These results can be clearly interpreted as a single electron transfer mechanism, which suggests that TBAI serves as a mediator and catalyst during the reaction (green curve *vs.* black curve).[19]

According to the results described above and the literature reports, we proposed the following possible mechanisms in Scheme 6.

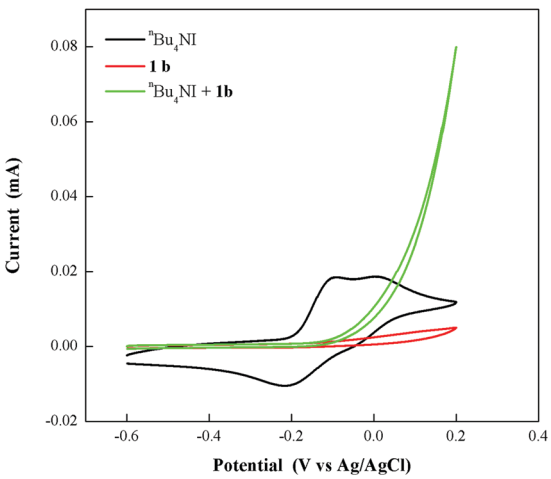
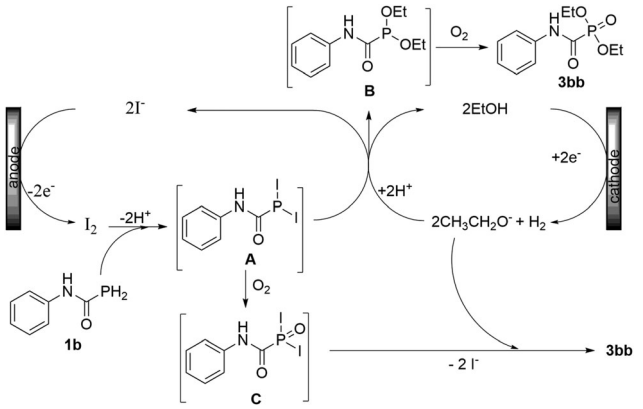


Fig. 2 Cyclic voltammograms: platinum rod (CHI 102) as the working electrode, platinum wire as the counter electrode (CHI 115) and Ag/AgCl as the reference electrode in MeOH (10 mL) with 0.03 M $LiClO_4$ as the supporting electrolyte. (black line) TBAI (0.002 mol L^{-1}), (red line) **1b** (0.2 mmol), and (green line) TBAI (0.002 mol L^{-1}) and **1b** (0.2 mmol). Scan rate: 100 mV s^{-1}.



Scheme 6 Proposed reaction mechanism.

At the anode surface, iodine ions are oxidized to I_2, which reacts with substrate **1** to generate intermediate **A**.[20] Then, intermediate **A** undergoes reaction with an ethoxy anion generated in the cathode to give intermediate **B**,[21] which is oxidized by oxygen in the air to give the target product **3bb**. In another path, it is possible that substance **A** is oxidized by air (O_2) to provide intermediate **C**, followed by nucleophilic attack of intermediate **C** by an ethoxy anion to give **3bb**. At the cathode, EtOH is reduced to provide the ethoxy anion and H_2.[22]

Conclusions

In summary, we disclose an efficient electrochemical route for the synthesis of phosphonates *via* phosphonamides and alcohols under mild conditions by using TBAI as a redox catalyst in an undivided electrochemical cell. This transformation offers a new method for phosphonate formation by oxygenation of phosphonamides and alcohol coupling. During the reaction, the *in situ* electrogenerated I_2 plays a vital role. Only a catalytic amount of TBAI is required, and iodine and its salts have low toxicity and are safe as compared to bromine oxidation catalysts. On the other hand, the alcohol is both a reactant and a solvent. It not only provides a medium for the reaction, but also reacts with the cathode as a reactant, which reduces environmental pollution. This process is simple, and the reaction conditions are mild, green and environmentally friendly.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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