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Exogenous-oxidant-free electrochemical oxidative C–H phosphonylation with hydrogen evolution†

Yong Yuan, ‡[ab] Jin Qiao,‡[a] Yangmin Cao,[a] Jingmei Tang,[a] Mengqin Wang,[a] Guojuan Ke,[a] Yichen Lu,[a] Xue Liu[a] and Aiwen Lei *[ab]

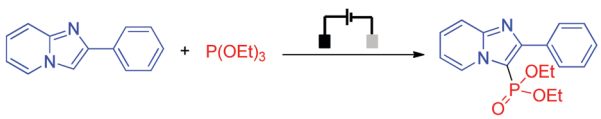
We herein report a versatile and environmentally friendly electrochemical oxidative C–H phosphonylation protocol. This protocol features a broad substrate scope; not only C(sp^2)–H phosphonylation, but also C(sp^3)–H phosphonylation is tolerated well under exogenous-oxidant-free and metal catalyst-free electrochemical oxidation conditions.

Phosphorus containing compounds are of much importance because they are widely found in a vast number of natural products, biological compounds, and agricultural chemicals,[1] as well as represent outstanding synthetic intermediates for the preparation of complex organic molecules.[2] As such, methods for the preparation of these valuable molecules are very important synthetic technologies. Over the past decades, considerable works have been conducted on the synthesis of significant phosphorus containing compounds.[3] Compared with conventional synthetic methods that employed pre-functionalized aryl halides or arylboronic acids as the starting materials,[4] direct C–H phosphonylation represents a much more attractive strategy for C–P bond formation.[5] Although this strategy avoided the use of pre-functionalized starting materials and has achieved considerable development, most of the reported reactions still suffer from some drawbacks, such as the need for metal catalysts or stoichiometric oxidants. Therefore, developing a much more elegant method for producing phosphorus containing compounds under metal catalyst-free and exogenous-oxidant-free reaction conditions is urgently needed.

As an ideal alternative to chemical oxidants, electrochemical anodic oxidation provides an efficient and environmentally benign synthetic method for C–H functionalization.[6] In this context, considerable progress has been made, such as in electrochemical oxidative C–H amination,[7] oxygenation,[8] thiolation,[9] alkylation,[10] *etc.*[11] Nevertheless, electrochemical oxidative C–H phosphonylation is still underexplored.[12] As part of our recent research interest in the area of electrochemical oxidative C–H functionalization, we herein report an elegant and versatile electrochemical oxidative C–H phosphonylation protocol. Overall, the notable features of this reaction include the following: (1) neither a metal catalyst nor an exogenous-oxidant/additive is required; and (2) this protocol features a broad substrate scope – not only C(sp^2)–H phosphonylation, but also C(sp^3)–H phosphonylation is tolerated well under electrochemical conditions.

We initiated our studies by investigating the reaction of 2-phenylimidazo[1,2-*a*]pyridine (**1a**) with triethyl phosphite (**2a**) because the imidazopyridine unit is a widely existing substructure in many commercially available drugs and the resultant C–H phosphonylation products may also have a potential utility in pharmaceutical chemistry (Table 1).[13] To our delight, when the reaction was performed in an undivided cell employing a carbon rod as the anode and a platinum plate as the cathode as well as using ^{n}Bu$_4$NBF$_4$ as electrolyte, the reaction worked smoothly in

Table 1 Optimization of the reaction conditions[a]



1a 2a 3a

Entry	Electrolysis conditions	Yield[b] (%)
1	Carbon rod anode, platinum plate cathode, ^{n}Bu$_4$NBF$_4$	70
2	Entry 1 but ^{n}Bu$_4$NClO$_4$ as electrolyte	54
3	Entry 1 but ^{n}Bu$_4$NPF$_6$ as electrolyte	77, 70[c]
4	Entry 3 but nickel plate cathode	61
5	Entry 3 but carbon cloth anode	49
6	Entry 3 but no electric current	0

[a] Reaction conditions: carbon rod anode, platinum plate cathode, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), ^{n}Bu$_4$NBF$_4$ (0.1 mmol), MeCN (10 mL), 50 °C, 4 mA, 6 h (3 F mol^{-1}). [b] Yields were determined by ^{31}P NMR using PPh$_3$ as an internal standard. [c] Isolated yield.

[a] *National Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang 330022, P. R. China. E-mail: aiwenlei@whu.edu.cn*
[b] *College of Chemistry and Molecular Sciences, Institute for Advanced Studies (IAS), Wuhan University, Wuhan 430072, P. R. China*

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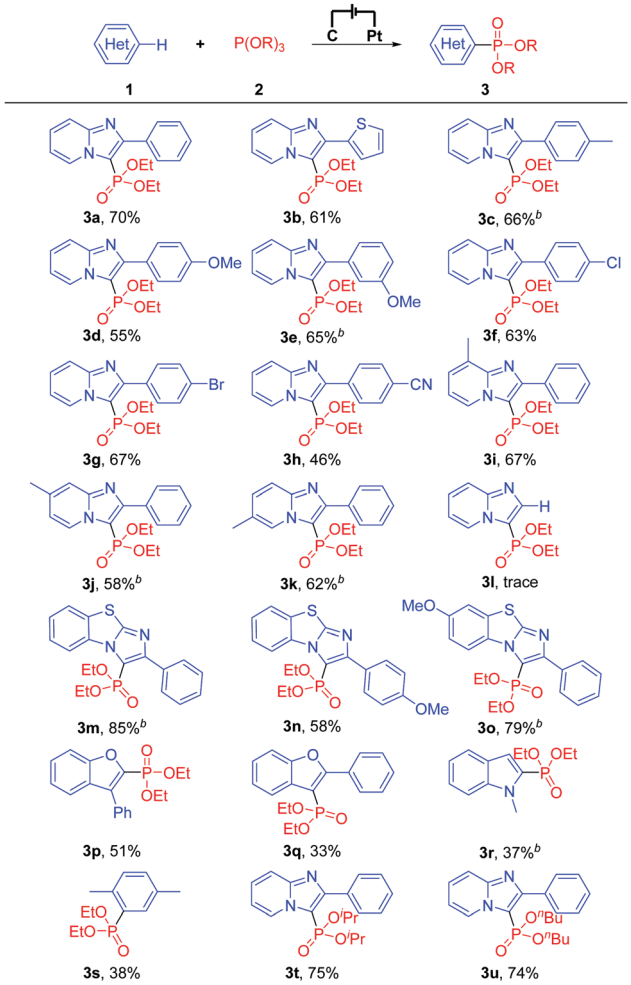
‡ Yong Yuan and Jin Qiao contributed equally to this work.

acetonitrile under a constant current of 4 mA, providing the desired C–H phosphonylation product **3a** in 70% NMR yield (Table 1, entry 1). At the same time, H_2 was also detected by GC-TCD. Further explorations showed that $^{n}Bu_4NPF_6$ was a better choice for electrolyte, affording **3a** in 77% NMR yield and 70% isolated yield (Table 1, entries 2 and 3). In comparison, conducting the reaction with a nickel plate cathode or a carbon cloth anode showed decreased reaction efficiency (Table 1, entries 4 and 5). In addition, a control experiment showed that the constant current was crucial for the reaction (Table 1, entry 6) (for more details about optimization of reaction conditions, see the ESI†). Note that for some conditions with low yields, **1a** and its homo-coupling product were often observed.

With the optimized reaction conditions in hand, the scope of the exogenous-oxidant-free electrochemical oxidative C(sp^2)–H phosphonylation was subsequently explored. Initially, different heteroarenes were investigated. As shown in Table 2, 2-phenylimidazo-[1,2-*a*]pyridine and 2-thiophenylimidazo-[1,2-*a*]pyridine could be transformed into the C–H phosphonylation products in 70% and 61% yields, respectively (Table 2, **3a** and **3b**). 2-Phenylimidazo-[1,2-*a*]pyridines bearing both electron-donating groups and weak electron-withdrawing groups at the 2-phenyl moiety afforded the products in moderate to good yields (Table 2, **3c–3g**). In comparison, 2-phenylimidazo-[1,2-*a*]pyridine with a strong electron-withdrawing group at the 2-phenyl moiety delivered the C(sp^2)–H phosphonylation product in moderate yield (Table 2, **3h**). When 8-methyl, 7-methyl, and 6-methyl substituted imidazopyridines were treated with triethyl phosphite (**2a**), the corresponding products could still be obtained in moderate to good yields (Table 2, **3i–3k**). However, when using imidazo[1,2-*a*]pyridine as the substrate, only a trace amount of the C(sp^2)–H phosphonylation product (Table 2, **3l**) was obtained; the reason for this may be that imidazo[1,2-*a*]pyridine has a relatively high oxidation potential and is not easily oxidized. It is worth noting that other heteroarenes such as important benzo[*d*]-imidazo[2,1-*b*]thiazole derivatives, 3-phenylbenzofuran, 2-phenylbenzofuran, *N*-methylindole, and *p*-xylene were also suitable for this reaction, affording the respective products in 33% to 85% yields (Table 2, **3m–3s**). Other phosphonylation reagents for this electrochemical oxidative C(sp^2)–H phosphonylation protocol were investigated as well. Delightfully, despite the bulky steric hindrance or a long alkyl chain, $P(O^{i}Pr)_3$ and $P(O^{n}Bu)_3$ were well suitable for the reaction and afforded the C(sp^2)–H phosphonylation products in 75% and 74% yields, respectively (Table 2, **3t** and **3u**). Note that for some examples with longer durations of electrolysis (Table 2, **3c**, **3e**, **3j**, **3k**, **3m**, **3o**, and **3r**), the reason for prolonging the duration of electrolysis is mainly to increase the conversion rates, thereby further improving the yields.

Table 2 Substrate scope for electrochemical oxidative C(sp^2)–H phosphonylation[a]

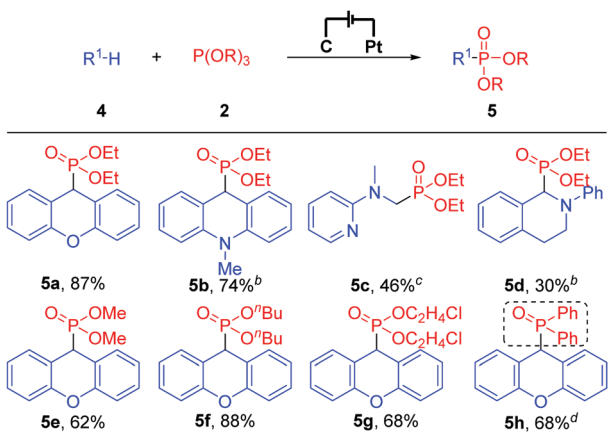


[a] Reaction conditions: carbon rod anode, platinum plate cathode, undivided cell, **1** (0.3 mmol), **2** (0.6 mmol), $^{n}Bu_4NPF_6$ (0.1 mmol), MeCN (10 mL), 50 °C, 4 mA, 6 h (3 F mol^{-1}), isolated yield. [b] 8 h (4 F mol^{-1}).

To demonstrate the practicality of this electrochemical oxidative C–H phosphonylation, reactions of $P(OEt)_3$ with **1a** and **4a** on a 6.0 mmol scale were performed. The reactions worked smoothly and afforded the corresponding C–H phosphonylation products in 55% and 50% yields (for more details about gram scale synthesis, see the ESI†), respectively.

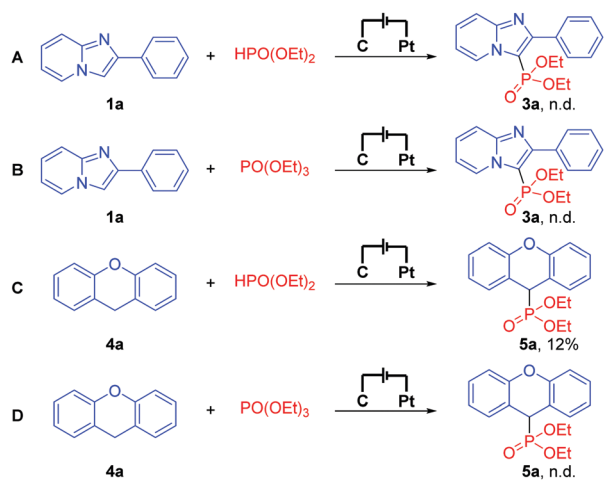
Subsequently, we turned our attention to the more challenging C(sp^3)–H phosphonylation because no examples have been reported in which C(sp^2)–H phosphonylation and C(sp^3)–H phosphonylation were accomplished concurrently under similar or the same reaction conditions. Gratefully, under the electrochemical conditions, C(sp^3)–H phosphonylation was also accomplished. As shown in Table 3, when xanthene and *N*-methyl-9,10-dihydroacridine were employed as substrates, the reaction worked smoothly and afforded the corresponding C(sp^3)–H phosphonylation products in 87% and 74% yields, respectively (Table 3, **5a** and **5b**). Besides, an *N*,*N*-dimethylaniline derivative and *N*-phenyl tetrahydroisoquinoline were also compatible with the reaction conditions (Table 3, **5c** and **5d**). Notably, other phosphonylation reagents such as $P(OMe)_3$, $P(O^{n}Bu)_3$, $P(OC_2H_4Cl)_3$, and even diphenylphosphine oxide all were suitable substrates and afforded the C(sp^3)–H phosphonylation products in good to high yields (Table 3, **5e–5h**). Unfortunately, only a trace amount of the product was detected when $P(O^{i}Pr)_3$ was applied as a substrate, possibly because of its bulky steric hindrance.

Table 3 Substrate scope for electrochemical oxidative C(sp^3)–H phosphonylation[a]

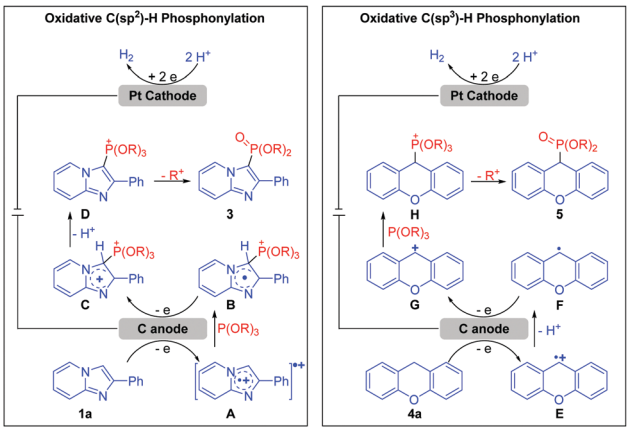


[a] Reaction conditions: carbon rod anode, platinum plate cathode, undivided cell, **4** (0.3 mmol), **2** (0.6 mmol), $^nBu_4NPF_6$ (0.1 mmol), MeCN (10 mL), 70 °C, 4 mA, 6 h (3 F mol^{-1}), isolated yield. [b] 50 °C. [c] Yields were determined by ^{31}P NMR using PPh_3 as an internal standard. [d] **4** (0.6 mmol) and **2** (0.3 mmol).

To shed light on this exogenous-oxidant-free electrochemical oxidative C–H phosphonylation mechanism, cyclic voltammetry (CV) experiments on **1a**, **2a**, and **4a** were performed, respectively. The oxidation peaks of **1a** and **4a** were observed at 1.68 V and 2.28 V, respectively, while no obvious oxidation peak of **2a** was observed at 0–2.5 V (for more details about cyclic voltammetry (CV) experiments, see the ESI†). This result suggests that our electrochemical oxidative C–H phosphonylation might begin with the oxidation of **1a** or **4a** at the anode. To further gain some insights into the mechanism, the reactions of **1a** and **4a** with $HPO(OEt)_2$ or $PO(OEt)_3$ were performed (Scheme 1), respectively. Besides, the reaction of **4a** with $HPO(OEt)_2$ afforded the desired product in 12% yield, and no desired products were detected in any other reactions. These results indicated that neither $HPO(OEt)_2$ nor $PO(OEt)_3$ is the reaction intermediate, and once again indicated that our electrochemical oxidative C–H phosphonylation really begins with the oxidation of **1a** or **4a** instead of **2a**.



Scheme 1 Control experiments.



Scheme 2 Proposed mechanism.

Based on the studies above and previous reports,[3b,5b] a plausible mechanism for this electrochemical oxidative C–H phosphonylation is proposed in Scheme 2. For C(sp^2)–H phosphonylation, **1a** is first oxidized at the anode to form the radical cation intermediate **A**, which is then captured by $P(OR)_3$ (**2**) to deliver adduct **B**. **B** undergoes further anodic oxidation and dehydrogenation, resulting in the formation of phosphorus cation intermediate **D**. Finally, the ensuing dealkylation of **D** forms the C(sp^2)–H phosphonylation product **3**. At the same time, protons were reduced at the cathode to form H_2. With respect to C(sp^3)–H phosphonylation, the generated intermediate **E** does not directly react with $P(OR)_3$ (**2**), but sequentially loses one proton and one electron to afford intermediate **G**; **G** is then captured by $P(OR)_3$ (**2**) to deliver the phosphorus cation intermediate **H**. Subsequently, as with the C(sp^2)–H phosphonylation, the ensuing dealkylation of **H** leads to the C(sp^3)–H phosphonylation product **5**.

In summary, we have disclosed a versatile and environmentally friendly electrochemical oxidative C–H phosphonylation protocol. Under exogenous-oxidant-free and metal catalyst-free electrochemical oxidation conditions, a series of complex and significant phosphorus containing compounds were constructed in moderate to high yields accompanied by hydrogen evolution. Notably, during the reaction, neither an exogenous oxidant nor a metal catalyst is required. With respect to the substrate scope, not only C(sp^2)–H phosphonylation, but also C(sp^3)–H phosphonylation is tolerated well under the electrochemical conditions.

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Conflicts of interest

There are no conflicts to declare.

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