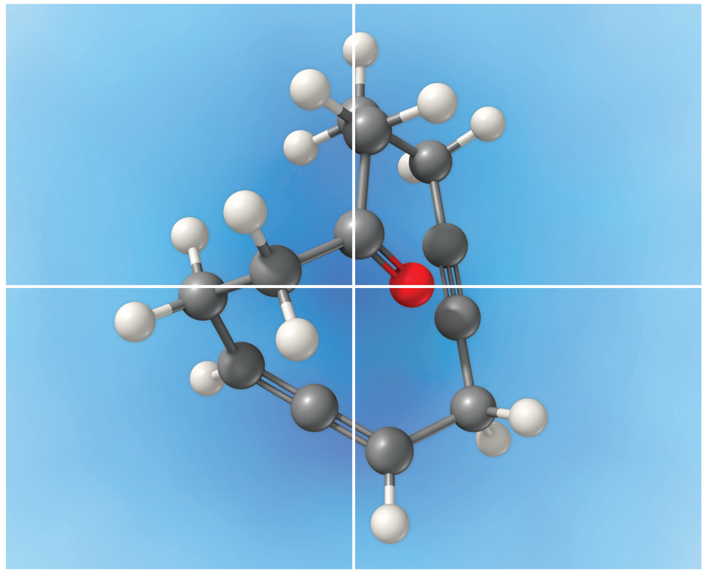

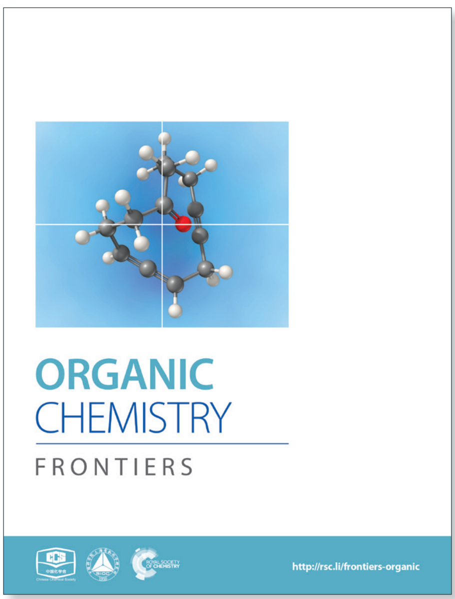

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ARTICLE TYPE

# Metal-free direct difunctionalization of alkenes with $I_2O_5$ and P(O)–H compounds leading to β-iodophosphates†

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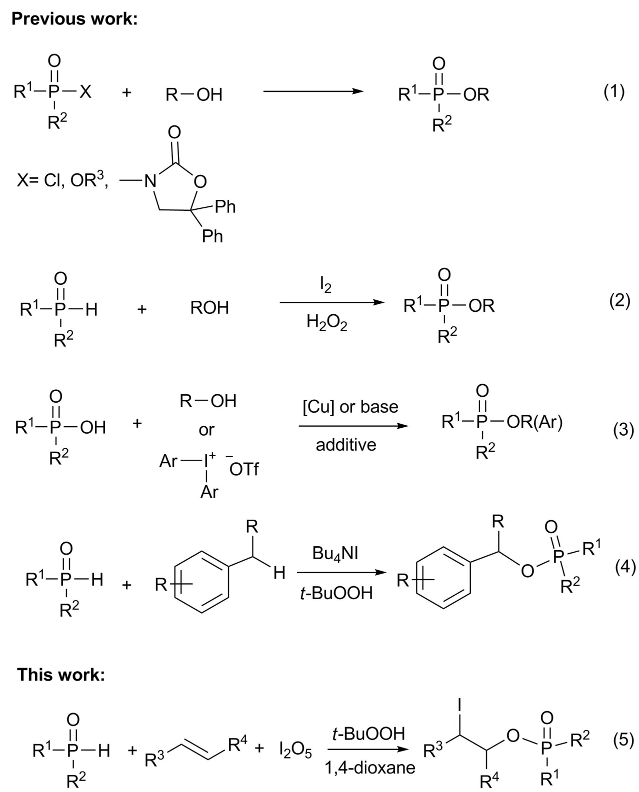
**A novel and efficient procedure for direct difunctionalization of alkenes with $I_2O_5$ and P(O)–H compounds has been developed under metal-free conditions. The present methodology produces a series of substituted β-iodophosphates in moderate to good yields with high regioselectivity and favorable functional group tolerance.**

Alkenes are inexpensive and readily available chemical feedstocks and organic reactants, which difunctionalization represents a class of reactions with significant synthetic potential accessing to many useful and fascinating compounds.[1] In recent years, many transition-metal-catalyzed difunctionalizations of alkenes have been developed, such as diamination,[2] dioxygenation,[3] aminooxygenation,[4] oxyphosphorylation,[5] and aminohalogenation.[6] Nevertheless, the cost, toxicity and environmental impact of these metal-catalysts might thereby limit their applications on a large scale in the field of organic synthesis and pharmaceutical chemistry. The development of a convenient and efficient strategy for difunctionalization of alkenes via metal-free process has become a challenging but highly attractive target. Despite great efforts have been made in this field over past several years, successful metal-free strategies are considerably less than their transition metal-based counterparts.[7] As our continuous interest in metal-free difunctionalization of alkenes,[8] here, we seek to develop a novel and convenient procedure for direct iodophosphorylation of alkenes with $I_2O_5$ and P(O)–H compounds leading to β-iodophosphates under metal-free conditions.

Organophosphates have attracted great interest of chemists and physiologists due to they play significant roles in drug discovery[9] and many major physiological processes such as energy transfer and regulation of ions release.[10] They have also been extensively studied in various organic transformations[11] and many agrochemicals such as insecticides and herbicides.[12] Due to the prominent importance of these compounds in synthetic chemistry and molecular biology, various synthesis methods have been



developed,[13-21] most known as the methods using the nucleophilic substitution reactions of alcohols with highly air-sensitive and hazardous P(O)−Cl compounds in the presence of a base[14] or transesterification of phosphate esters[15] or phosphorylation of alcohol with N-phosphoryloxazolidinones[16] (eqn (1)). Alternative preparation methods such as the reactions of phosphoramidites with the requisite alcohol followed by subsequent oxidation,[17] base mediated ephospha-Brook rearrangement,[18] $I_2/H_2O_2$ mediated phosphorylation of alcohols with P(O)–H compounds (eqn (2)),[19] and copper-catalyzed aerobic oxidative esterification of P(O)−OH compounds with alcohols or diaryliodonium triflates[20] (eqn (3)) have also been developed. However, most of them could suffer from some limitations such as inaccessible starting materials, relatively harsh reaction conditions, poor substrate scope, and use of a large amount of promoters or transition-metal catalysts. Recently, Tang and co-workers described a metal-free $Bu_4NI$-catalyzed phosphorylation of benzyl C-H bonds leading to phosphate esters using TBHP as

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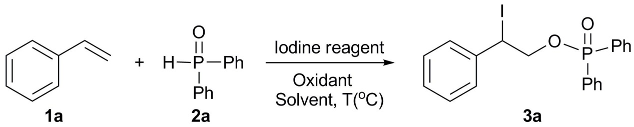
**Table 1** Optimization of the reaction conditions[a]



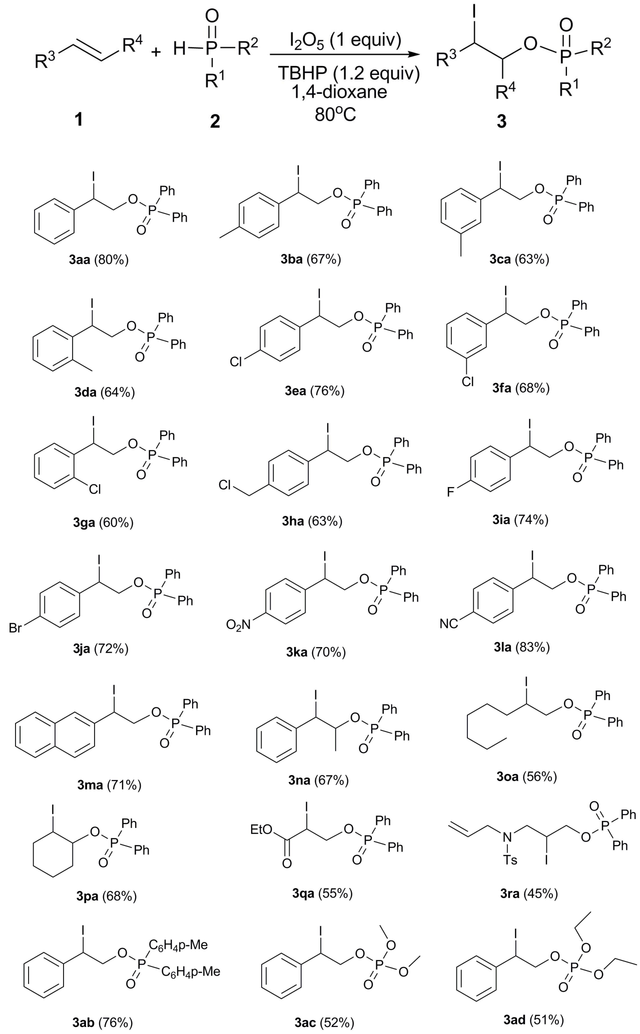

| Entry | Iodine reagent | Oxidant | Solvent | Yield (%)[b] |
|---|---|---|---|---|
| 1 | KI | TBHP | 1,4-dioxane | 0 |
| 2 | NaI | TBHP | 1,4-dioxane | 0 |
| 3 | $I_2$ | TBHP | 1,4-dioxane | 0 |
| 4 | TBAI | TBHP | 1,4-dioxane | 0 |
| 5 | $I_2O_5$ | TBHP | 1,4-dioxane | 80 |
| 6 | $I_2O_5$ | DTBP | 1,4-dioxane | 68 |
| 7 | $I_2O_5$ | $K_2S_2O_8$ | 1,4-dioxane | 23 |
| 8 | $I_2O_5$ | $(NH_4)S_2O_8$ | 1,4-dioxane | trace |
| 9 | $I_2O_5$ | $Na_2S_2O_8$ | 1,4-dioxane | trace |
| 10 | $I_2O_5$ | Oxone | 1,4-dioxane | 43 |
| 11 | $I_2O_5$ | TBHP | THF (reflux) | 58 |
| 12 | $I_2O_5$ | TBHP | DME | 40 |
| 13 | $I_2O_5$ | TBHP | DCE | 26 |
| 14 | $I_2O_5$ | TBHP | $CH_3CN$ | 42 |
| 15 | $I_2O_5$ | TBHP | Toluene | 0 |
| 16 | $I_2O_5$ | TBHP | DMF | 0 |
| 17 | $I_2O_5$ | TBHP | DMSO | 0 |
| 18 | - | TBHP | 1,4-dioxane | 0 |
| 19 | $I_2O_5$ | TBHP | 1,4-dioxane | 61[c] |
| 20 | $I_2O_5$ | TBHP | 1,4-dioxane | 79[d] |
| 21 | $I_2O_5$ | TBHP | 1,4-dioxane | 0[e] |
| 22 | $I_2O_5$ | TBHP | 1,4-dioxane | 71[f] |

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), iodine reagent (0.25 mmol), oxidant (0.3 mmol), solvent (2 mL), 80°C, 16 h. TBAI=(*n*-Bu)$_4$NI; DME: 1,2-Dimethoxyethane, DCE: 1,2-dichloroethane; TBHP: tert-Butyl hydroperoxide, 5.5 M in decane, DTBP: Di-tert-butyl peroxide, Oxone: ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$); [b] Isolated yields based on **1a**. [c] $I_2O_5$ ( 0.5 equiv), [d] $I_2O_5$ ( 1.5 equiv), [e] 25°C, [f] 60°C.

an oxidant (eqn (4)).[21] Nevertheless, the substrate scope of this well developed reaction could be limited to toluene derivatives only. In the present work, a convenient and metal-free procedure has been developed for the synthesis of various β-iodophosphates from diverse and readily-available alkenes and P(O)–H compounds with high regioselectivity and favorable functional group tolerance (eqn (5)).

In an initial experiment, styrene **1a** and diphenylphosphine oxide **2a** were chosen as model substrates to optimize the reaction conditions under air. To our delight, among various iodine reagents tested, $I_2O_5$ was found to be the optimal iodine source for the formation of the desired **3a** (80% yield) in the presence of TBHP (Table 1, entries 1-5), which was further demonstrated to be the best oxidant (Table 1, entries 5-10). Moreover, the screening of solvents showed that 1,4-dioxane was more effective than the others such as THF, DME, DCE, and $CH_3CN$ (Table 1, entries 5, 11-14). Interestingly, no conversion was observed when the reaction was performed in Toluene, DMF, and DMSO (Table 1, entries 15-17). Also, the reaction efficiency was obviously low with the decreasing of $I_2O_5$ loading and reaction temperature (Table 1, entries 18-20). In addition, no product was detected when the reaction was conducted in the absence of $I_2O_5$ or at room temperature (Table 1, entries 18 and 21). After an extensive screening of the reaction parameters, the best yield of **3aa** (80%) was obtained by employing 1.0 equiv of $I_2O_5$ and 1.2 equiv of TBHP in 1,4-dioxane at 80°C (Table 1, entry 5).

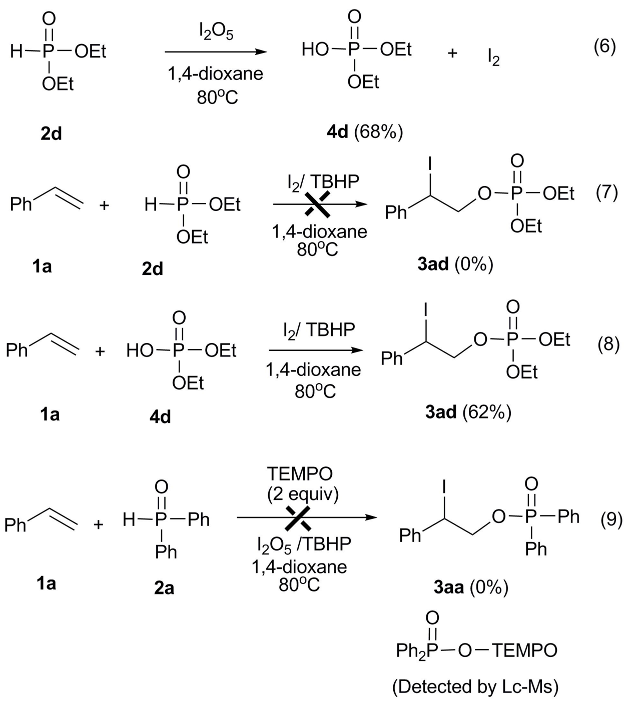
**Table 2** Results for metal-free difunctionalization of alkenes with $I_2O_5$ and P(O)–H compounds[ab]



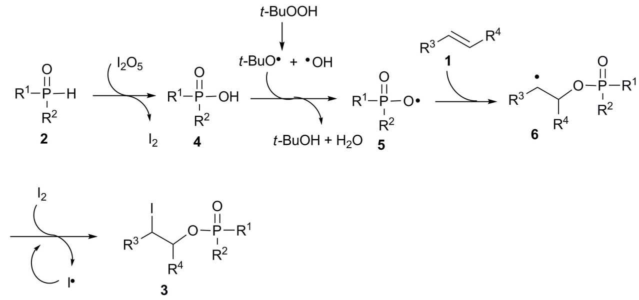

[a] Reaction conditions: **1** (0.25 mmol), **2** (0.5 mmol), $I_2O_5$ (0.25 mmol), TBHP (0.3 mmol), 1,4-dioxane (2 mL), 80°C, 16-24 h. [b] Isolated yields based on **1**.

With the optimized conditions in hand, the scope and generality of this reaction was investigated. As shown in Table 2, both electron-rich and electron-deficient aromatic alkenes were suitable for this reaction, of which the corresponding products were obtained in moderate to good yields (**3aa-3la**). The reaction was not significantly affected by the steric effect. *Ortho*-, *meta*- or *para*-position of the phenyl moieties were compatible with this reaction (**3ba-3ga**). Moreover, various functionalities including halogen, chloromethyl, nitro, and cyano groups were also tolerated in this reaction leading to the products **3ea-3la**, which could be employed for further transformations. 2-Vinylnaphthalene was also used to give the desired product **3ma** in 71% yield. Notably, internal aromatic alkene such as (E)-prop-1-enylbenzene and aliphatic alkenes such as 1-octene, cyclehexene, ethyl acrylate and N,N-diallyl-4-methylbenzenesulfonamide were also suitable for this protocol to generate the corresponding products (**3na-3ra**) in moderate to good yields. In addition to diphenylphosphine oxide, substituted diphenylphosphine oxide, diethyl phosphonates, and dibutyl phosphonates were all suitable substrates, with the corresponding products **3ab-3ad** in moderate to good yields.

In order to obtain further insights into this reaction, several control experiments were conducted as demonstrated in eqns. 6-9. When the reaction of diethyl phosphonate **2d** with $I_2O_5$ was conducted in the absence of styrene, the corresponding diethyl hydrogen phosphate **4d** was obtained in 68% yield (eqn (6)). Meanwhile, the formation of molecular iodine was confirmed by observation of an obvious color change from gray to deep blue when starch was added into the above reaction system.[22] When the reaction of styrene **1a** with **2d** was conducted in $I_2$/TBHP system, none of desired product **3ad** was detected (eqn (7)). Furthermore, the desired product **3ad** was isolated in 62% yield, when the reaction of styrene **1a** with **4d** was performed in the presence of $I_2$/TBHP system (eqn (8)). The above results indicated $I_2O_5$ palyed a key role in the formation of diethyl hydrogen phosphate **4d**, which was the key intermediate in this difunctionalization reaction. Moreover, the iodophosphorylation reaction was completely inhibited when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, a well-known radical scavenger) was added in this reaction system, and TEMPO-trapped complex ($Ph_2P(O)$-O-Tempo) was detected by LC-MS analysis (see ESI.†). This result suggested that P(O)-O radical might exist in this reaction system and the present reaction should proceed through a radical pathway (eqn (9)).




According to the aforementioned information and based on some previous reports,[22-24] a possible reaction pathway for this transformation is outlined in Scheme 1. Initially, the oxidation of $R_2P(O)$–H compound **2** with $I_2O_5$ would produce the corresponding $R_2P(O)$–OH **4** and $I_2$. Subsequently, radical intermediate **5** was formed by the interaction of $R_2P(O)$–OH **4** with an alkoxyl radical and a hydroxyl radical, which were generated from a homolytic cleavage of tert-butyl hydroperoxide.[23,24] Next, selective addition of radical **5** to



**Scheme 1.** Tentative reaction pathway.

alkene **1** afforded alkyl radical **6**, which further interacted with molecular iodine leading to the formation of the desired product **3**.

In conclusion, we have developed a novel and efficient metal-free synthesis method for the construction of β-iodophosphates via the direct difunctionalization of alkenes with $I_2O_5$ and P(O)–H compounds. A variety of biologically important phosphate esters could be obtained in moderate to good yields from readily-available starting materials of alkenes with high regioselectivity and excellent functional group tolerance. This simple and metal-free reaction system is expected to extend the potential applications of functionalized organophosphates in the synthetic and pharmaceutical chemistry.

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