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Iron-Catalyzed and Air-Mediated C(sp^3)–H Phosphorylation of 1,3-Dicarbonyl Compounds Involving C–C Bond Cleavage

Yingcong Ou,[a] Yuanting Huang,[a] Yu Liu,[a] Yanping Huo,[a] Yang Gao,[a] Xianwei Li,[a] and Qian Chen[a,b,*]

[a] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, People's Republic of China
E-mail: qianchen@gdut.edu.cn

[b] Key Laboratory of Functional Molecular Engineering of Guangdong Province, South China University of Technology, Guangzhou 510640, People's Republic of China

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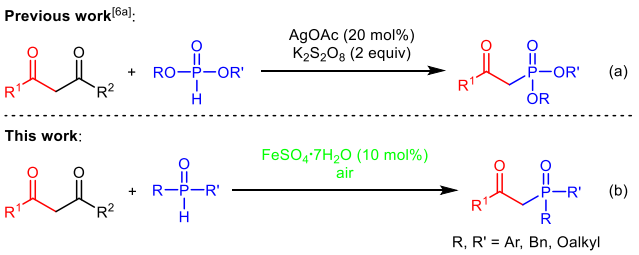
Abstract: A C(sp^3)–H phosphorylation has been achieved via the iron-catalyzed cross-coupling reactions between 1,3-dicarbonyl compounds and P(O)–H compounds involving C–C bond cleavages with air as the oxidant. This transformation provides a straightforward way to construct C(sp^3)–P bonds, leading to the formation of β-ketophosphine oxides in up to 93% yield with good functional group tolerance.

Keywords: phosphorylation; C(sp^3)–H bonds; iron catalysts; air; β-ketophosphine oxides

It is well-known that β-ketophosphine oxides are of great importance in organic synthesis, coordination chemistry and catalysis, and extractants.[1] Notably, β-ketophosphonates have been widely used as key synthetic precursors in the Horner-Wadsworth-Emmons reaction, which is the most popular and reliable method for the preparation of alkenes.[2] Traditional methods such as the Michaelis-Arbuzov reaction for the synthesis of β-ketophosphine oxides are somewhat unsatisfactory (*e.g.*, the use of halides, low efficiency, and harsh reaction conditions).[3,4] Recently, the reactions between phosphoryl radicals and unsaturated compounds such as alkenes, alkynes and enolates for accessing β-ketophosphine oxides have been well-documented.[5] Among them, the C(sp^3)–H phosphorylation of 1,3-dicarbonyl compounds with P(O)–H compounds involving C–C bond cleavages provided a more straightforward way to construct C(sp^3)–P bonds.[6] For example, Dong, Ma, Peng and co-workers reported a silver-catalyzed oxidative C(sp^3)–H/P–H cross-coupling reaction of 1,3-dicarbonyl compounds with H-phosphonates (Scheme 1a).[6a] Most recently, Kim, Wu and co-workers developed a visible-light-induced radical cascade reaction of 1,3-dicarbonyl compounds with diarylphosphine oxides.[6b] However, these methods require the use of excess amounts of strong oxidants (*e.g.*, $K_2S_2O_8$ or dibenzoyl peroxide) and relatively expensive catalysts (*e.g.*, AgOAc or fluorescein). Therefore, the development of a mild and cheap synthetic protocol for the preparation of these important compounds is still highly desirable.

Iron salts, which are considered as the ideal catalysts, have been of particular interest due to their characteristic of low price and low toxicity.[7] In the past decade, iron/O_2-mediated oxidative coupling reactions have attracted increasing attention.[8] The use of air as the more sustainable oxidant instead of chemical oxidants is considered to be an ideal oxidation process.[9] In addition, the generation of phosphoryl radicals from P(O)–H compounds with dioxygen (O_2) as the initiator represents a milder process. However, O_2-initiated phosphoryl radical reactions have received less attention.[10] Based on our recent studies on phosphorylation reactions[10e,11] and air-initiated sulfenylation reactions,[12] we became interested in developing a C(sp^3)–H phosphorylation of carbonyl compounds under mild conditions. Herein, we report an efficient transformation for the synthesis of β-ketophosphine oxides through the cross-coupling reactions between 1,3-dicarbonyl compounds and P(O)–H compounds involving C–C bond cleavages (Scheme 1b). The significant advantages of this report are: 1) A cheap iron salt is employed as a catalyst; 2) Air is used as an oxidant.



Scheme 1. Metal-catalyzed C(sp^3)–H phosphorylation involving C–C bond cleavages.

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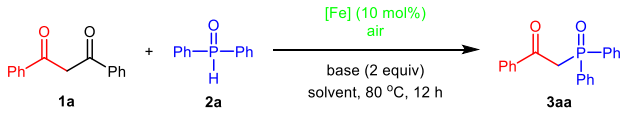
Table 1. Optimization of reaction conditions.[a,b]

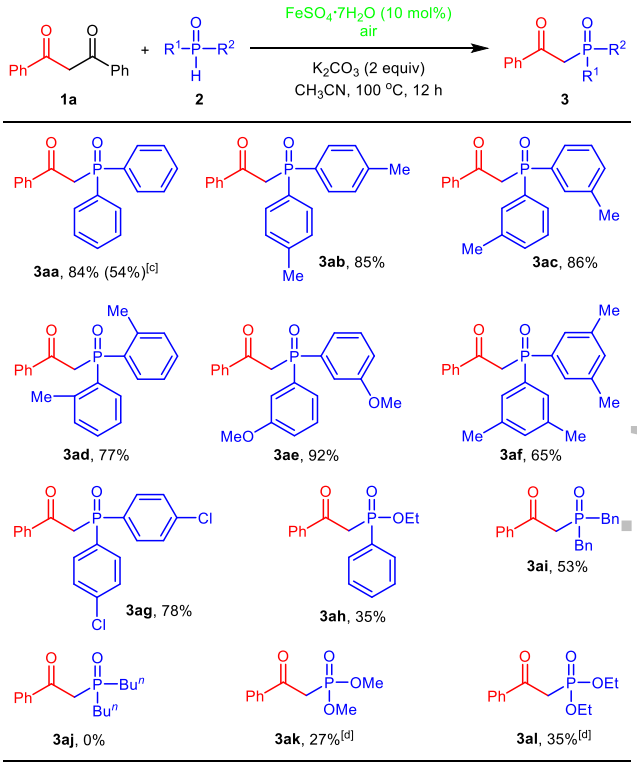


Entry	[Fe]	Base	Solvent	Yield of **3aa** [%]
1	$Fe(OAc)_2$		THF	0
2	$Fe(OAc)_2$	K_2CO_3	THF	45
3		K_2CO_3	THF	Trace
4	$Fe(OAc)_2$	K_2CO_3	DCE	5
5	$Fe(OAc)_2$	K_2CO_3	DMSO	50
6	$Fe(OAc)_2$	K_2CO_3	Toluene	22
7	$Fe(OAc)_2$	K_2CO_3	CH_3CN	62
8	$Fe(OAc)_2$	Cs_2CO_3	CH_3CN	33
9	$Fe(OAc)_2$	K_3PO_4	CH_3CN	55
10	$Fe(OAc)_2$	DBU	CH_3CN	12
11	$FeCl_2$	K_2CO_3	CH_3CN	54
12	$FeCl_3$	K_2CO_3	CH_3CN	39
13	$Fe_2(SO_4)_3$	K_2CO_3	CH_3CN	45
14	$FeCl_2·4H_2O$	K_2CO_3	CH_3CN	46
15	$FeCl_3·6H_2O$	K_2CO_3	CH_3CN	66
16	$FeSO_4·7H_2O$	K_2CO_3	CH_3CN	70
17[c]	$FeSO_4·7H_2O$	K_2CO_3	CH_3CN	54
18[d]	$FeSO_4·7H_2O$	K_2CO_3	CH_3CN	89
19[e]	$FeSO_4·7H_2O$	K_2CO_3	CH_3CN	25

[a] Reaction conditions: a 50 mL vial was charged with **1a** (0.2 mmol), **2a** (0.6 mmol), iron salt (0.02 mmol) and base (0.4 mmol) in solvent (2 mL) and sealed under air atmosphere (1 atm), and the mixture was stirred at 80 °C for 12 h. [b] Yield based on **1a** was determined by ^{1}H NMR analysis using an internal standard. [c] $FeSO_4·7H_2O$ (5 mol%) was employed. [d] The reaction was carried out at 100 °C. [e] The reaction was carried out at 60 °C.

The reaction conditions were tested using a model reaction of 1,3-dicarbonyl compound **1a** with diphenylphosphine oxide **2a** catalyzed by an iron salt (10 mol%) under air, and the results were shown in Table 1. Initially, no reaction occurred when the reaction was carried out in the presence of $Fe(OAc)_2$ at 80 °C in THF (entry 1). To our delight, the desired β-ketophosphine oxide **3aa** was obtained in 45% yield with the addition of 2 equiv of K_2CO_3 (entry 2). When the reaction was performed without a catalyst, only trace amounts of **3aa** were detected (entry 3), which indicated the importance of the iron salt. We then turned our attention to the screening of solvents (entries 4–7), and found that CH_3CN was the optimum solvent, leading to the formation of **3aa** in 62% yield (entry 7). A screening of bases was also carried out (entries 8–10), and K_2CO_3 was proved to be the optimum base. Switching the catalyst from $Fe(OAc)_2$ to a variety of iron salts (entries 11–16) showed that $FeSO_4·7H_2O$ was the optimum catalyst (70% yield, entry 16). A decrease in the amount of $FeSO_4·7H_2O$ (5 mol%) led to a lower yield (54%, entry 17). Pleasingly, a yield of 89% was achieved when the reaction was carried out at 100 °C (entry 18), while the product yield was significantly decreased when the temperature was set at 60 °C (entry 19).

Table 2. Scope of P(O)–H compounds.[a,b]



[a] Reaction conditions: a 50 mL vial was charged with **1a** (0.2 mmol), **2** (0.6 mmol), $FeSO_4·7H_2O$ (0.02 mmol) and K_2CO_3 (0.4 mmol) in CH_3CN (2 mL) and sealed under air atmosphere (1 atm), and the mixture was stirred at 100 °C for 12 h. [b] Isolated yield based on **1a**. [c] The reaction was performed in a 4 mmol scale (0.9 g of **1a**) under an open air atmosphere at reflux for 12 h. [d] $Cu(OTf)_2$ instead of $FeSO_4·7H_2O$.

With the optimized reaction conditions in hand (Table 1, entry 18), we then set out to explore the generality of this C(sp^3)–H phosphorylation. We first applied the optimized conditions to the coupling of **1a** with a variety of P(O)–H compounds **2**, and the results were illustrated in Table 2. Pleasingly, diarylphosphine oxides bearing different groups such as Me, OMe and Cl at the *para*, *meta*, or *ortho* position of aromatic rings were all applicable to the reaction. The corresponding β-ketophosphine oxides **3aa**–**3ag** were isolated in good to high yields (65–92%) yields. It is noteworthy that the reaction of **1a** with ethyl phenylphosphinate afforded the desired β ketophosphinate **3ah** in 35% yield. We then turned to dialkylphosphine oxides. The reaction of **1a** with dibenzylphosphine oxide gave the desired **3ai** in 53% yield, while the employment of dibutylphosphine oxide failed to give the desired **3aj**. In addition, the reactions of **1a** with dialkylphosphites were performed under standard conditions using $Cu(OTf)_2$ instead of $FeSO_4·7H_2O$, and the corresponding β-ketophosphonates **3ak** and **3al** were isolated in moderate yields (see Table S2 in the Supporting Information for more details). The scale-up of the reaction of **1a** with **2a** was also attempted under an

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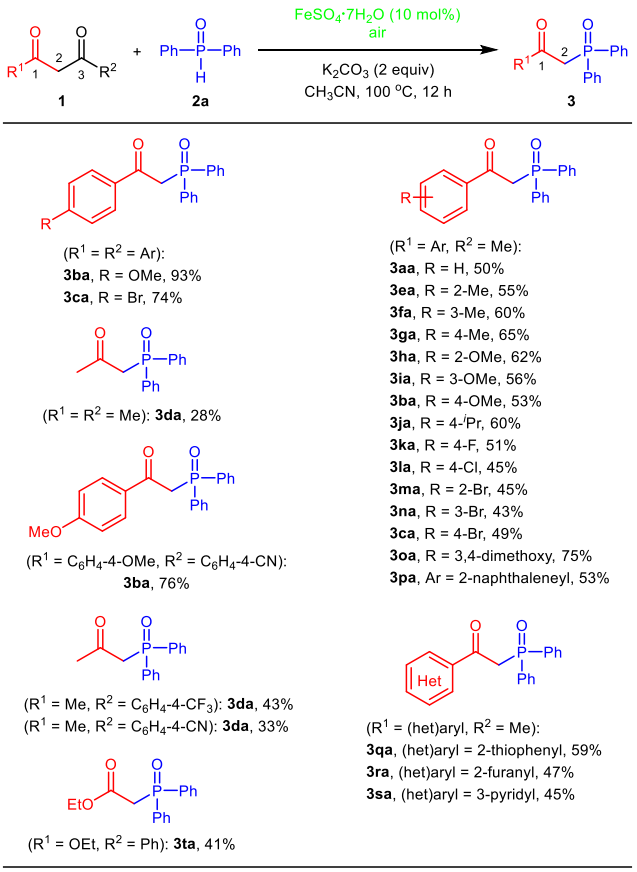
open air atmosphere at reflux. When we increased the scale of the reaction from 0.2 to 4 mmol, **3aa** was isolated in 54% yield (0.69 g).

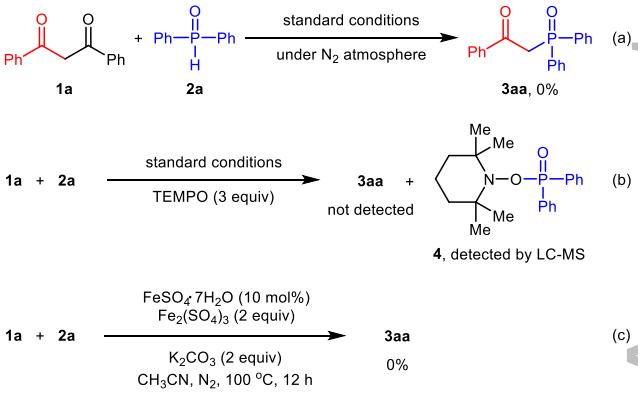
Table 3. Scope of 1,3-dicarbonyl compounds.[a,b]



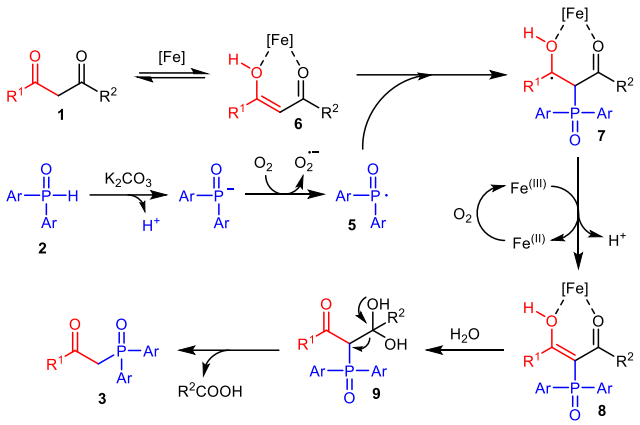
[a] Reaction conditions: a 50 mL vial was charged with **1** (0.2 mmol), **2a** (0.6 mmol), $FeSO_4·7H_2O$ (0.02 mmol) and K_2CO_3 (0.4 mmol) in CH_3CN (2 mL) and sealed under air atmosphere (1 atm), and the mixture was stirred at 100 °C for 12 h. [b] Isolated yield based on **1**.

Next, the C(sp^3)–H phosphorylation of various 1,3-dicarbonyl compounds **1** with **2a** under standard conditions was examined (Table 3). The results showed that symmetric 1,3-diaryl-β-diketones bearing electron-donating groups (*para*-OMe) or electron-withdrawing groups (*para*-Br) were well-tolerated, leading to the formation of **3ba** and **3ca** in 93% and 74% yields, respectively. Unfortunately, the reaction of symmetric 1,3-dimethyl-β-diketone with **2a** afforded the desired **3da** in only 28% yield. Notably, **3ba** was obtained in 76% yield as a single regioisomer when unsymmetric 1,3-diaryl-β-diketone (*para*-OMe and *para*-CN) was employed. The more electron-deficient benzoyl group (*para*-CN) might undergo a more rapid decarboxylation. The employment of unsymmetric 1-aryl-3-methyl-β-diketones bearing different groups (Me, OMe, ^{i}Pr, F, Cl and Br) at the *para*, *meta*, or *ortho* position of aromatic rings, as well as the bulky 2-naphthaleneyl group, selectively gave the corresponding products **3aa**–**3ca** and **3ea**–**3pa** in 43–75% yields as major regioisomers (see Table S2 in the Supporting Information for more details). These results showed that the C–C bond cleavages mainly took place at C2–C3 bonds, suggesting that acetyl group could be preferred in the decarboxylation process. When strong electron-withdrawing groups (CF_3 or CN) were introduced into the aromatic rings of 1-aryl-3-methyl-β-diketones, C1–C2 bond cleavages became predominant, leading to the formation of **3da** in moderate yields as a single regioisomer. In addition, this reaction was successfully applied to heteroaryl-substituted diketones to afford the corresponding products **3qa**–**3sa** in moderate yields. Moreover, in the reaction of ethyl benzoylacetate with **2a**, only a single regioisomer **3ta** was formed in 41% yield involving the decarboxylation of benzoyl group.

To gain more insight into the mechanism of the reaction, a couple of control experiments were conducted (Scheme 2). When the reaction of **1a** with **2a** was carried out under N_2, **3aa** was not detected (Scheme 2a), suggesting that an aerobic oxidation might be involved in the reaction. When the radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxyl) was employed under standard conditions, the desired reaction was completely inhibited, and the TEMPO-P(O)Ph_2 adduct **4** was detected by LC-MS (Scheme 2b), indicating that a phosphoryl radical reaction pathway might be involved. In order to confirm whether phosphoryl radicals were initiated by iron salts, we carried out the reaction of **1a** with **2a** under N_2 using excess amounts of $Fe_2(SO_4)_3$ instead of air (Scheme 2c). The results (**3aa**, 0% yield) showed that iron salts might not be the initiator, suggesting that O_2 (air) should initiate the radical reaction.[10]



Scheme 2. Mechanistic studies.



Scheme 3. Proposed mechanism.

Based on the above experimental results and previous reports,[6,8,10] a plausible mechanism was proposed (Scheme 3). Initially, phosphoryl radical **5** is generated by the autoxidation of P(O)–H compound **2** in the presence of O_2 and K_2CO_3.[10e] Meanwhile, enolate **6** is formed via the complexation of 1,3-dicarbonyl compound **1** with iron salts. Thus, intermediate **7** was produced by the radical addition of **5** to **6**. Then, C-centered radical **7** is oxidized by the iron salt to generate the direct phosphorylation product **8** and Fe(II), which is reoxidized to Fe(III) by O_2.[8] Finally, the decarboxylation via the C–C bond cleavage affords the desired product **3** through the nucleophilic attack of H_2O on the more electron-deficient carbonyl group of **8**.[6]

In summary, we have developed the iron-catalyzed and air-mediated C(sp^3)–H phosphorylation of 1,3-dicarbonyl compounds involving C–C bond cleavages. Compared with previous reports,[6] this process is cheap and mild by using an iron salt as the catalyst and using air as both oxidant and phosphoryl radical initiator. The inexpensive, simple, and efficient synthesis of extremely important β-ketophosphine oxides with good functional group tolerance showcases the potential of this approach in organic synthesis.

Experimental Section

General Procedure for the Synthesis of β-Ketophosphine Oxides

A 50 mL vial was charged with 1,3-dicarbonyl compound **1**[13] (0.2 mmol), P(O)–H compound **2**[14] (0.6 mmol), $FeSO_4{\cdot}7H_2O$ (0.02 mmol) and K_2CO_3 (0.4 mmol) in CH_3CN (2 mL) and sealed under air atmosphere (1 atm), and the mixture was stirred at 100 °C for 12 h. The reaction solution was then cooled to room temperature and quenched with saturated aqueous NaCl solution (20 mL). The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using ethyl acetate in petroleum ether as the eluent to afford pure β-ketophosphine oxide **3**.

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