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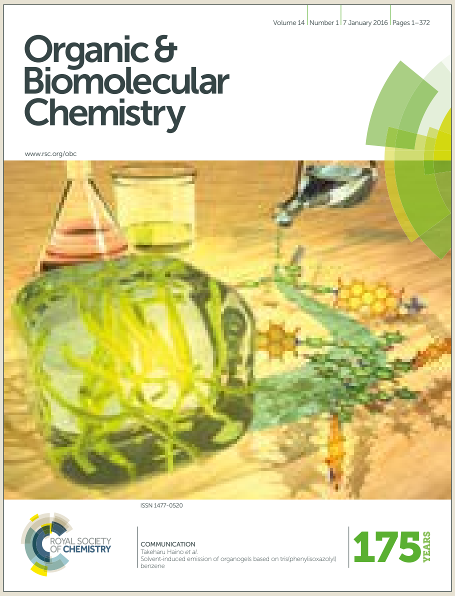

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DOI: 10.1039/C7OB00505A

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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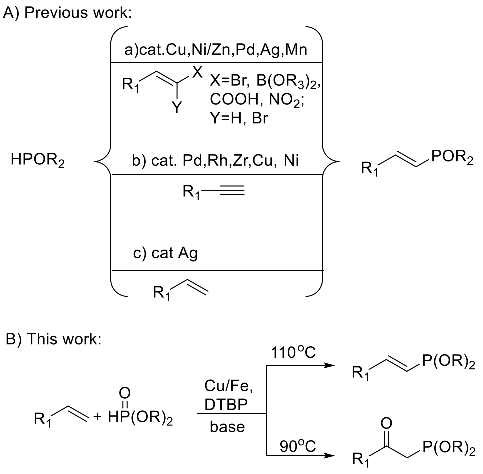
Cu(I)/Fe(III)-Catalyzed C–P Cross-Coupling of Styrenes with H-Phosphine Oxides: A Facile and Selective Synthesis of Alkenylphosphine Oxides and β-Ketophosphonates

Jian Gu,[a] Chun Cai* [a]

Cu(I)/Fe(III)-catalyzed phosphorylation and oxyphosphorylation of styrenes with H-phosphonates which can be controlled by varying the reaction temperature are developed. This study offers a new and expedient strategy for the synthesis of useful alkenylphosphine oxides and β-ketophosphonates in satisfactory yields. Moreover, the transformation is proposed to proceed via a radical process and exhibits a broad substrate scope and good functional group tolerance.

Introduction

The construction of carbon–phosphorus bond is highly important in organic synthesis, since organophosphorus compounds are quite useful in biology, and material sciences.[1] Among them, alkenylphosphine oxides and β-ketophosphonates are extremely useful classes of phosphorous-containing organic compounds, owing to their bioactivity and wide-ranging applications in various synthetically useful transformations.[2] As a result of their importance, wide interest has been generated in the development of new strategies for their preparation. For the synthesis of β-ketophosphonates, the acylation of alkylphosphonates under basic conditions, the hydration of alkynylphosphonates, the oxyphosphorylation of alkenes and alkynes, and oxyphosphorylation of alkynes under different bimetallic synergistically catalyzed aerobic oxidative conditions have been mostly used.[3] And for the synthesis of alkenylphosphine oxides, there are two main strategies particularly noteworthy due to their overall efficiency and selectivity: the phosphorylation of alkynes and functionalized alkenes. Transition-metals such as Cu, Ni/Zn, Ag, Pd, and Mn-catalyzed reactions of 1-bromo- and 1,1-dibromo-1-alkenes, vinylboronate esters, vinylcarboxylic acids, and nitroalkenes with dialkyl phosphites, triethyl phosphite, and diaryl phosphine oxides have been reported to construct Csp2–P bonds (Scheme 1A, a).[4] Transition metals such as Pd, Pt, Rh, Zr, Mo, Cu and Ni catalysts were employed for the direct phosphorylation of alkynes (Scheme 1A, b).[5] Recently, Tan reported the synthesis of vinylphosphonates and phosphine oxides via silver-catalyzed phosphorylation of styrenes with the aid of TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) which can help them get the vinylphosphonates instead of the usually addition product (Scheme 1A, c) [6].



Scheme 1: Strategies for alkenyl Csp2–P bond formation.

As we know, the product selectivity controlled by modification of the reaction conditions represents a significant challenge in organic synthesis.[7] In particular, selective catalysis that leads to different products from the same starting materials is a powerful tool for divergent synthesis.[8] Consequently, on the basis of the above excellent works, we endeavoured to develop effective catalytic processes that exploit selective and controllable way in this C–P bond forming reaction between styrenes and H-phosphonates. To our delight, when we optimal the reaction conditions, we found the main product can be controlled by varying the reaction temperature, so that we can selective synthesis

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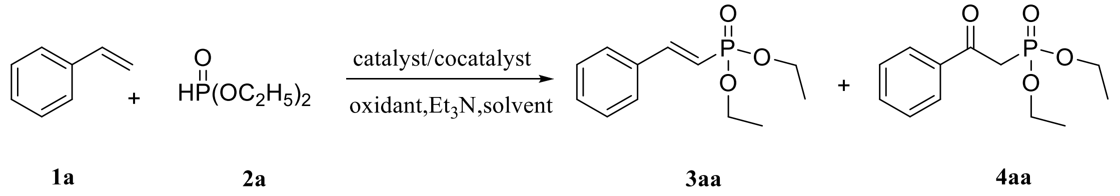
† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data for all products. See DOI: 10.1039/x0xx00000x

alkenylphosphine oxides and β-ketophosphonates by controlling the temperature. We describe herein our successful environmentally benign Cu(I)/Fe(III) catalysts system with DTBP (Di-tert-butyl peroxide) as the oxidant, which can construct the Csp2-P bond directly from styrenes and H-phosphonates without TEMPO and form Csp3-P bond in a different reaction temperature. (Scheme 1B)

Results and discussion

We started our study by investigating the reaction between styrene **1a** and H-diethyl phosphonate **2a** to generate desired alkenylphosphine oxides **3aa** and β-ketophosphonate **4aa** (Table 1). First, a variety of transition-metal salts were investigated, with the finding that CuCl and $FeCl_3$ was the optimal choice for the reaction (entries 1–7). As the next optimization step, we performed an oxidant screening (entries 8–9). When DTBP was replaced by TBHP (tert-Butyl hydroperoxide) or H_2O_2, the significant yield decrease suggested that DTBP was crucial for this reaction. A subsequent survey on the role of solvents revealed that DMSO (Dimethyl sulfoxide) was the optimal candidate (entries 10 −12). Elevating the reaction temperature from 70 °C to 110 °C, the optimal yields for **3aa** and **4aa** seperately were achieved at 110 °C and 90 °C (entries 5, 13−15). When the temperature was 90 °C, the main product was **4aa** and gave an approximate 1:3 mixture of **3aa** and **4aa** respectively. Finally, control experiments showed that both catalysts and DTBP were essential prerequisites for this reaction (entries 16 −19). Thus, the optimal conditions for **3aa** constitute a combination of $FeCl_3$ (20 mol %) and CuCl (10 mol %) in DMSO with TBP as oxidant, NEt_3 as base under Ar atmosphere for 15 h at 110 °C. And when the temperature changed to 90 °C, the reaction condition was optimal for **4aa**.

Table 1. Optimization of the Reaction Conditions [a]



Entry	Catalyst	Cocatalyst	Oxidant	Solvent	T(°C)	Yield of **3aa**(%)[b]	Yield of **4aa**(%)[b]
1	CuCl	$FeSO_4$	DTBP	DMSO	110	--	--
2	CuCl	$Fe(NO_3)_3$	DTBP	DMSO	110	--	--
3	CuCl	$Fe(OTf)_3$	DTBP	DMSO	110	--	--
4	$Cu(OTf)_2$	$FeCl_3$	DTBP	DMSO	110	45	--
5	CuCl	$FeCl_3$	DTBP	DMSO	110	78	--
6	Cu_2O	$FeCl_3$	DTBP	DMSO	110	33	--
7	CuI	$FeCl_3$	DTBP	DMSO	110	--	--
8	CuCl	$FeCl_3$	TBHP	DMSO	110	29	--
9	CuCl	$FeCl_3$	H_2O_2	DMSO	110	--	--
10	CuCl	$FeCl_3$	DTBP	DMF	110	68	--
11	CuCl	$FeCl_3$	DTBP	NMP	110	--	--
12	CuCl	$FeCl_3$	DTBP	toluene	110	--	--
13	CuCl	$FeCl_3$	DTBP	DMSO	70	11	36
14	CuCl	$FeCl_3$	DTBP	DMSO	90	19	61
15	CuCl	$FeCl_3$	DTBP	DMSO	100	30	47
16	CuCl	--	DTBP	DMSO	110	--	--
17	--	$FeCl_3$	DTBP	DMSO	110	22	--
18	CuCl	$FeCl_3$	--	DMSO	110	--	--
19	--	--	DTBP	DMSO	110	--	--

a) Reaction conditions: 1a (0.5 mmol), 2a (2 mmol), catalyst (10 mol%), cocatalyst (20 mol%), base (0.5 mmol), solvent (2 mL), oxidant (1 mmol), 15 h, under Ar atmosphere. b) Isolated yield. DMF is *N,N'*-Dimethylformamide. NMP is N-methyl-2-pyrrolidone.

With these optimized conditions in hand, we next examined the scope of the phosphorylation of alkenyls with H-phosphonates for the synthesis of alkenylphosphine oxides (Table 2). Styrene derivatives in reaction with **2a** were examined first. The reaction worked very well for a range of alkenyls with various substituents at the phenyl ring, and the products were isolated in yields ranging from 63% to 82%. Styrene derivatives with electron-donating substituents at the phenyl ring afforded the desired alkenylphosphine oxides in 63−82% yield (**3ba**-**3ea**), whereas styrene derivatives bearing electron-withdrawing substituents at the phenyl ring provided the desired alkenylphosphine oxides in 63−72% yield (**3fa**-**3ia**). On the whole, the electron-donating substituted alkenyls showed superior reaction efficiency to that of the electron-

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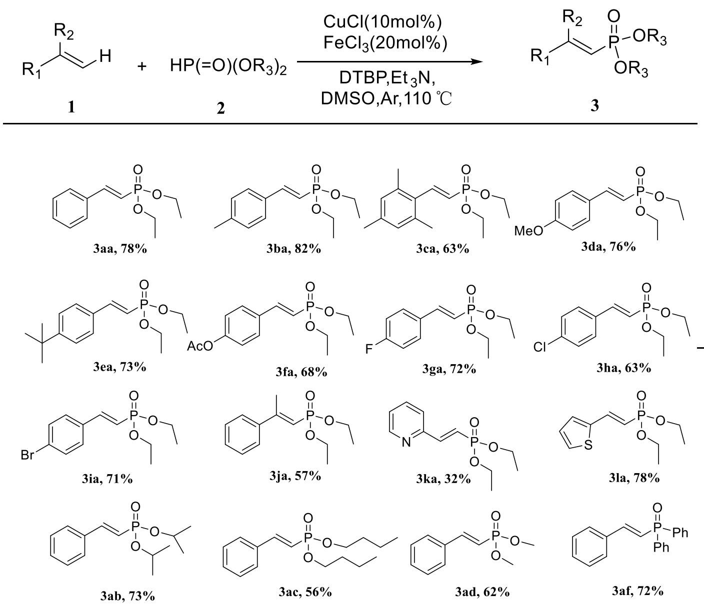
withdrawing ones. In addition to alkyl and alkoxy groups, halo-substituted alkenyls were compatible with the standard conditions (**3ga**-**3ia**). The halo- substituted alkenylphosphine oxides were beneficial for further functionalization. Sterically hindered α-methylstyrene was also suitable for this transformation (**3ja**). Moreover, the arene ring is not limited to benzene rings. Heteroaromatic alkenyls could also be used as suitable substrates, thus providing the corresponding desired products in 32–78% yield (**3ka**-**3la**). This phosphorylation of styrene with H-phosphonates could also be extended to the corresponding alkenylphosphine oxides (**3ab**–**3ad**) when we used other phosphonates as the substrates. In addition to H-phosphonates, we found that diphenylphosphine oxide was applicable under the standard conditions as well and produced the desired products **3af** in a reasonable yield. The wide scope of both the alkenyls and phosphonate partners illustrates the good functional group tolerance and potential applications of this method.

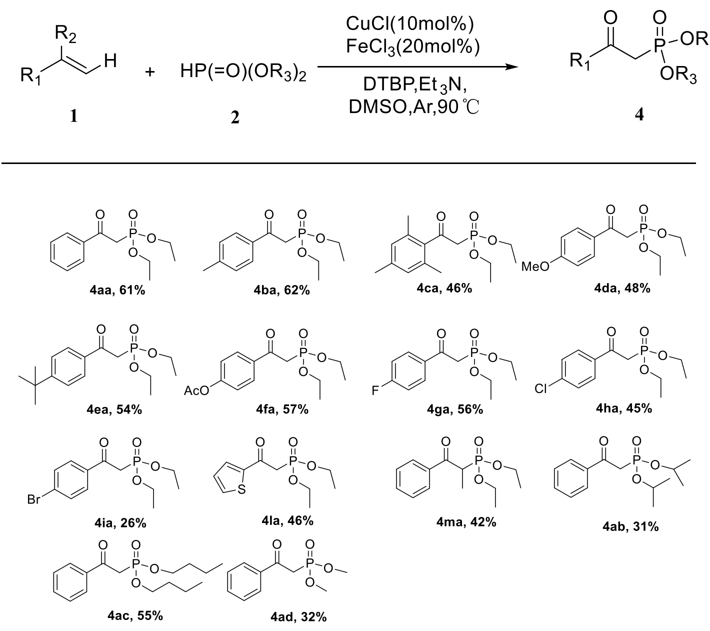
Table 2. Substrate Scope of the Phosphorylation of Alkenyls with H-Phosphonates for the Synthesis of Vinylphosphonates [a]



[a] Reaction conditions: 1 (0.5 mmol), 2 (2 mmol), CuCl(10 mol %), $FeCl_3$(20 mol %), Et_3N (0.5 mmol), DTBP(1 mmol), DMSO (2 mL), 110 ℃, 15 h, Ar, all isolated yields.

Subsequently we tested the application of the developed Cu/Fe catalytic system towards the synthesis of different β-ketophosphonates. When reactions performed at 90°C, the coupling between styrene **1a** and H-diethyl phosphonate **2a** resulted in a 1:3 mixture of the phosphorylation product **3aa** and **4aa**. The selectivity of the coupling process was switched in favor of the synthesis of β-ketophosphonates. Styrene derivatives with electron-donating substituents or electron-withdrawing substituents at the phenyl ring all gave the desired products in satisfactory yields (**4ba**-**4ia**). Sterically hindered β-methylstyrene was also suitable for this transformation (**4ma**). In addition, the reaction was also extended to other electron-rich heteroaromatic and other phosphonates in moderate yield. This phosphorylation of styrene with H-phosphonates could also be extended to the corresponding β-ketophosphonates (**4ab**–**4ad**) when we used other phosphonates as the substrates.

Table 3. Substrate Scope of the oxyphosphorylation of Alkenyls with H-Phosphonates for the synthesis of β-Ketophosphonates[a]

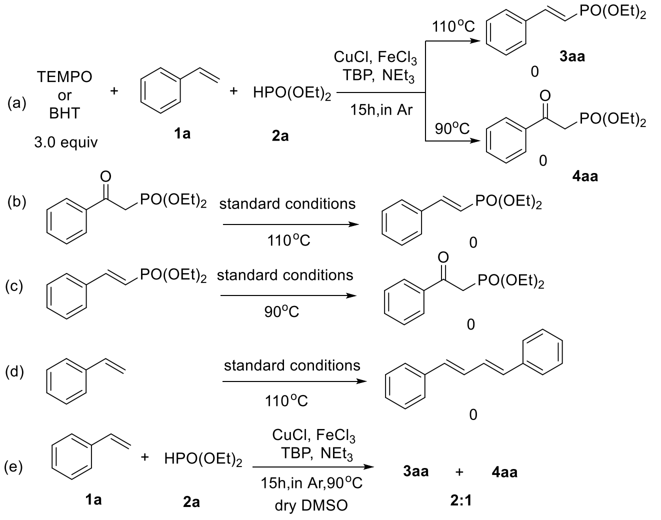


[a] Reaction conditions: 1 (0.5 mmol), 2 (2 mmol), CuCl(10 mol %), $FeCl_3$(20 mol %), Et_3N (0.5 mmol), DTBP(1 mmol), DMSO (2 mL), 90 ℃, 15 h, Ar, all isolated yields.

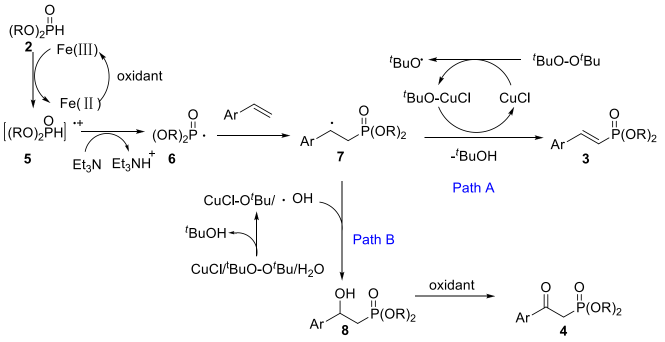
To gain some insight into the mechanism for the Cu/Fe-cocatalyzed oxidative cross-coupling of alkenyls with H-phosphonates, control experiments were carried out (Scheme 2). No target product was observed by the addition of TEMPO or BHT (butylated hydroxytoluene) as a radical inhibitor, indicating that a radial pathway might be involved in the process.(Scheme 2, a) No reaction occurred when only β-ketophosphonates, alkenylphosphine oxides or styrene was employed to the standard reaction conditions under 110°C or 90°C, suggesting that the initial oxyphosphorylation or phosphorylation and styrene radical might not be involved in the reaction mechanism. (Scheme 2, b, c and d) The different temperature may be related to the boiling point of water, so we conducted an experiment with dry DMSO. The proportion of **4aa** decreased significantly when dry DMSO was used, indicating that H_2O might be involved in the production of β-ketophosphonates.(Scheme 2, e)

Although the mechanistic details of this transformation are not clear at the moment, on the basis of the above results and previous reports, a plausible mechanism for the present process can be proposed as shown in Scheme 3.[9,1i,3d]

Phosphonyl radical **6** is generated from dialkyl phosphonate cation radical **5** which is formed through single-electron transfer from iron(II) species to HP(=O)(OR)$_2$ in the presence of TBP. Subsequently, addition of the phosphonyl radical **6** to the double bond of alkenyls produces the alkyl radical **7**. When the reaction temperature is 110^{o}C, the formed radical **7** is believed to undergo direct oxidation by deprotonation to release the final product. Meanwhile, the CuCl was regenerated to continue the catalytic cycle. When the reaction temperature is 90^{o}C, the formed radical **7** interacts with hydroxyl radical that is generated from Cu(I) with DTBP and H$_2$O to form intermediate **8**. Finally, the intermediate **8** would undergo oxidation to give the desired product **4**.



Scheme 2： Control Experiments.



Scheme 3： Proposed mechanism.

Experimental

General

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and compared with previously reported data. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 202 MHz in CDCl$_3$, respectively, and chemical shifts are reported in ppm. High-resolution mass spectra data were obtained on Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

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Synthesis of alkenylphosphine oxides from Alkenyls and H-Phosphonates

A mixture of alkenyls (0.5 mmol), H-phosphonates (2.0 mmol), CuCl (0.05 mmol), FeCl$_3$ (0.1 mmol), DTBP(1.0 mmol) and Et$_3$N (0.5 mmol) in DMSO (2.0 mL) under Ar was stirred at 110^{o}C for 15 h. After the completion of the reaction, the mixture was cooled to 25 ^{o}C and then EtOAc and H$_2$O were added to it. The organic layer was separated and washed with brine, dried over Na$_2$SO$_4$. The volatiles were removed under vacuum to afford the crude product, and analyzed by GC. The crude product was purified by column chromatography on silica gel and eluted with EtOAc/hexanes (25/75) to afford the desired pure product.

Synthesis of β-Ketophosphonates from Alkenyls and H-Phosphonates

A mixture of alkenyls (0.5 mmol), H-phosphonates (2.0 mmol), CuCl (0.05 mmol), FeCl$_3$ (0.1 mmol), DTBP(1.0 mmol) and Et$_3$N (0.5 mmol) in DMSO (2.0 mL) under Ar was stirred at 90^{o}C for 15 h. After the completion of the reaction, the mixture was cooled to 25 ^{o}C and then EtOAc and H$_2$O were added to it. The organic layer was separated and washed with brine, dried over Na$_2$SO$_4$. The volatiles were removed under vacuum to afford the crude product, and analyzed by GC. The crude product was purified by column chromatography on silica gel and eluted with EtOAc/hexanes (25/75) to afford the desired pure product.

Conclusions

In summary, we have developed a copper/iron-catalyzed selective phosphorylation and oxyphosphorylation of alkenyls with H-phosphonates protocol which provided a new and powerful tool for the synthesis of alkenylphosphine oxides and β-ketophosphonates. In addition, radical-trapping experiments indicated that this transformation proceeded through a free-radical process. The inexpensive catalysts (copper and iron salts), good functional group tolerance, and the temperature-controlled selectivity made this protocol more resourceful for future applications.

Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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