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Visible light-promoted metal-free aerobic oxyphosphorylation of olefins: A facile approach to β-ketophosphine oxides

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ABSTRACT

A metal-free direct aerobic oxyphosphorylation of alkenes with *H*-phosphine oxides has been developed utilizing visible light photoredox catalysis. A variety of β-ketophosphine oxides have been obtained in good yields from simple olefins under air with inexpensive rhodamine B as the non-metallic photocatalyst. This method provides a mild, green, and practical synthetic approach to valuable β-ketophosphine oxides.

Introduction

Phosphorus-containing compounds are an important class of chemicals that have broad utilities as pharmaceuticals,[1] agrochemicals,[2] materials,[3] and ligands.[4] Thus, the development of effective strategies for the C-P bond formation has attracted great attention from chemists. Among various organophosphorus compounds, β-ketophosphine oxides are valuable and highly desirable synthetic targets, which can serve as potential ligands[4] and metal-extracting agents due to their excellent metal-complexing ability.[5] Particularly, β-ketophosphine oxides are useful synthetic precursors for the preparation of alkenes through the Horner-Wadsworth-Emmons (HWE) reaction.[6] Furthermore, they can also be used as versatile building blocks in a variety of synthetically useful transformations.[7] Therefore, various efficient methods have been developed to access β-ketophosphine oxides, such as the Arbuzov reaction,[8] the acylation of alkylphosphine oxides with stoichiometric amounts of organometallic reagents as bases,[9] the Pd(II)-catalyzed hydration of alkynylphosphine oxides,[10] and the α-phosphorylation of aryl ketone *O*-acetyloximes.[11] Recently, the oxyphosphorylation of alkenes and their derivatives,[12] cinnamic acids,[13] alkynes,[12b,14] alkynyl carboxylic acids,[14d,15] and cinnamyl/alkynyl carboxylates[16] has proven to be a powerful synthetic protocol to construct β-ketophosphine oxides. Despite great progress in this area, the development of practical, mild, green and efficient methods for the synthesis of β-ketophosphine oxides remains highly desirable.

In recent years, visible light photoredox catalysis[17,18] has emerged as a fascinating and powerful tool in organic synthesis. Compared with ruthenium- or iridium-based photocatalysts, organic dyes have the advantages of lower cost and less toxicity. Photoredox-catalyzed reactions for the construction of C-P bonds have been achieved.[19,20] As part of our continuous efforts to develop alkene difunctionalization reactions,[21] we describe herein a visible light-induced oxyphosphorylation of simple alkenes with *H*-phosphine oxides under ambient air using a very cheap organic dye as the photocatalyst, thus leading to an array of β-ketophosphine oxides in good yields under mild conditions

Results and discussion

Our initial studies commenced with the reaction of 4-methylstyrene (**1a**) and diphenylphosphine oxide (**2a**) in the presence of the commercially available photosensitizer eosin B (5 mol%). The reaction was carried out in DMSO at room temperature under ambient air for 24 h under irradiation with a white LED lamp. To our delight, the desired β-ketophosphine oxide product **3a** was obtained in 34% yield (Table 1, entry 1). Other organic photoinitiators, including eosin Y, methylene blue, fluorescein, rose bengal,

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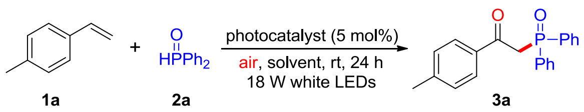
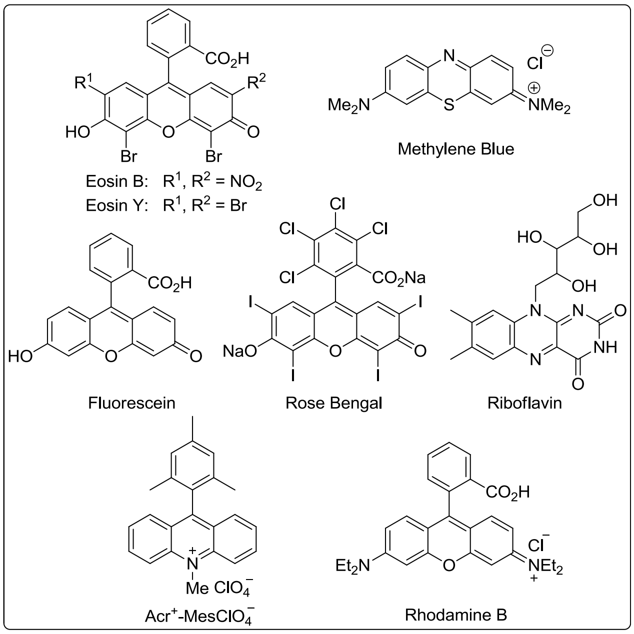
Table 1

Optimization of the reaction conditions.[a]





Entry	Photocatalyst	Solvent	Yield (%)[b]
1	Eosin B	DMSO	34
2	Eosin Y	DMSO	58
3	Methylene blue	DMSO	31
4	Fluorescein	DMSO	42
5	Rose bengal	DMSO	19
6	Riboflavin	DMSO	24
7	Acr$^+$-MesClO$_4^-$	DMSO	27
8	**Rhodamine B**	**DMSO**	**81**
9	Rhodamine B	CH_2Cl_2	53
10	Rhodamine B	$ClCH_2CH_2Cl$	60
11	Rhodamine B	THF	37
12	Rhodamine B	1,4-Dioxane	62
13	Rhodamine B	CH_3CN	53
14	Rhodamine B	DMF	40
15	Rhodamine B	EtOH	52
16	Rhodamine B	*i*-PrOH	58
17[c]	Rhodamine B	DMSO	79
18[d]	–	DMSO	NR
19[e]	Rhodamine B	DMSO	NR

[a] All reactions were carried out with alkene **1a** (0.60 mmol), diphenylphosphine oxide **2a** (0.30 mmol), and photocatalyst (0.015 mmol) in solvent (1.8 mL) at room temperature under ambient air for 24 h under irradiation with a white LED lamp unless otherwise stated.

[b] Isolated yield based on **2a**.

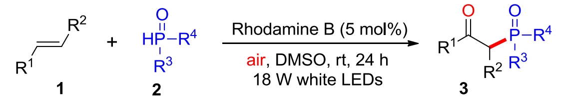
[c] With an oxygen balloon.

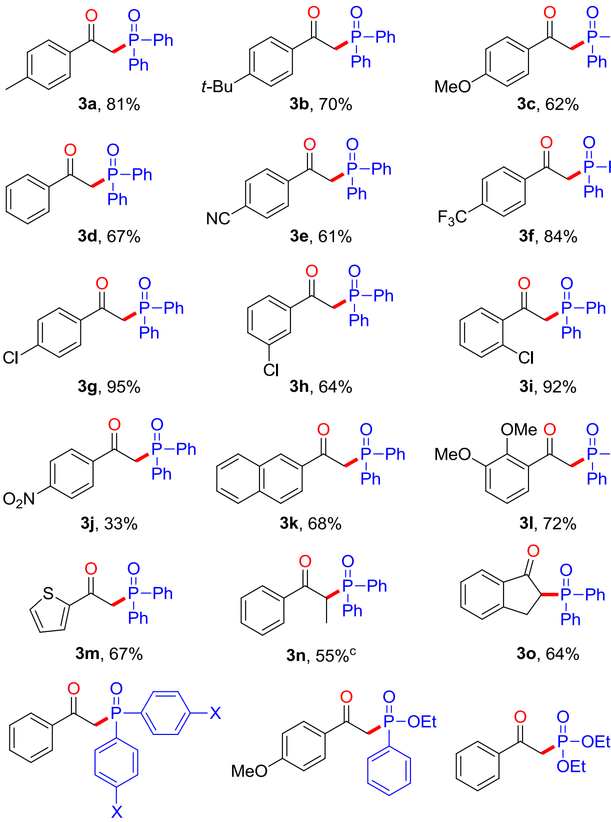
[d] Without photocatalyst.

[e] The reaction was conducted in the dark.

Table 2

Substrate scope.[a,b]





3a, 81%
3b, 70%
3c, 62%
3d, 67%
3e, 61%
3f, 84%
3g, 95%
3h, 64%
3i, 92%
3j, 33%
3k, 68%
3l, 72%
3m, 67%
3n, 55%[c]
3o, 64%
3p, X = OMe, 80%[c]
3q, X = F, 66%
3r, 63%[c]
3s, 0%

[c] Reaction time, 36 h.

[a] All reactions were carried out with alkene **1** (0.60 mmol), phosphine oxide **2** (0.30 mmol), and rhodamine B (0.015 mmol) in DMSO (1.8 mL) at room temperature under ambient air for 24 h under irradiation with a white LED lamp unless otherwise stated.

[b] Isolated yield based on **2**.

riboflavin, Acr$^+$-MesClO$_4^-$, and rhodamine B were also tested (Table 1, entries 2–8). Among the above photocatalysts examined, rhodamine B was found to be the best for this transformation, giving product **3a** in 81% yield (Table 1, entry 8). Further screening of solvents revealed that DMSO was superior to the others such as CH_2Cl_2, $ClCH_2CH_2Cl$, THF, 1,4-dioxane, CH_3CN, DMF, EtOH and *i*-PrOH (Table 1, entries 9–16). A 79% yield of **3a** was obtained when an oxygen balloon was used (Table 1, entry 17). Subsequent control experiments showed that the reaction did not occur without a photocatalyst or visible light irradiation (Table 1, entries 18 and 19).

After determining the optimal reaction conditions, the generality of the visible light-promoted metal-free oxyphosphorylation was investigated. As shown in Table 2, this oxyphosphorylation can be extended to a variety of simple alkenes bearing either electron-donating or electron-withdrawing groups at the *para*, *meta*, and/or *ortho* positions of the phenyl ring, thus affording the corresponding products (**3a–o**) in mostly good to excellent yields (up to 95%). Various functionalities such as CN and Cl were compatible with this reaction, which could be employed for further synthetic transformations. 2-Naphthyl and 2-thienyl substituted olefins were effective substrates, giving the desired *β*-ketophosphine oxides **3k** and **3m** in 68% and 67% yields, respectively. However, the reaction of 4-nitrostyrene with diphenylphosphine oxide (**2a**) gave the expected product **3j** in only 33% yield. It is noteworthy that aromatic internal alkenes were also tolerated in this reaction leading to the corresponding products **3n** and **3o** in satisfactory yields. *β*-Nitrostyrene, a highly electron-deficient internal alkene,