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Metal-Free Visible-Light-Mediated Oxidative Cross-Coupling of Thiols with P(O)H Compounds Using Air as the Oxidant

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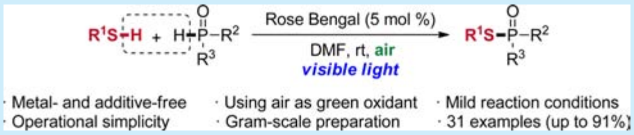
S *Supporting Information*



ABSTRACT: Visible light along with 5 mol % of rose bengal catalyzes the direct S−P(O) coupling between thiols and P(O)H compounds in the presence of air as the green oxidant. The protocol is operationally simple and amenable to gram-scale synthesis. A variety of S−P(O) coupling products can be readily prepared in moderate to excellent yields. The reaction features good functional-group tolerance, operational simplicity, and excellent practicality.

Organophosphorus compounds bearing an S−P(O) bond display important chemical and biological properties that afford utility in various fields, including organic synthesis, medicinal chemistry, and agrochemistry.[1] Studies have disclosed that many sulfur-containing organophosphorus compounds exhibit excellent biological activities.[2] As a consequence, the construction of S−P(O) bonds is an essential issue in organic chemistry and has gained significant attention. Traditional routes for S−P(O) bond formation rely on the nucleophilic substitution reaction of RSX or $R_2P(O)X$ directly or indirectly.[3,4] Nevertheless, the use of toxic and moisture-sensitive P- or S-reagent, multistep reaction processes, and low functional-group tolerance remain impediments of these approaches. In light of the importance of the S−P(O)-substituted moiety in various fields as mentioned above, great efforts have recently been devoted to the development of general and efficient approaches to construct S−P(O) bonds.[5−8] Among these methods, oxidative cross-coupling reactions between an S−H bond and an P(O)−H bond are particularly attractive, since they provide a straightforward and atom-economic protocol for S−P(O) bond formation.[8] Despite significant advances in synthetic methods, the current procedures are associated with one or more limitations such as superfluous usage of strong oxidants, the need for transition-metal catalysts, elevated temperatures, and so on. In this regard, the development of convenient and "greener" protocol is still highly desirable and remains a great challenge.

In recent years, photoredox catalysis enabled by visible light has emerged as a powerful synthetic tool for mild and environmentally benign organic transformations.[9] A variety of elegant photocatalyzed reactions for the construction of C−C and C−heteroatom bonds have been well established.[9−12] However, to the best of our knowledge, S−P bond formation by photocatalysis has not been investigated to date. In this context, we wondered whether an S−H bond could couple with a P(O)−H bond to form an S−P(O) bond via synergistic interactions of visible light stimulation and photosensitizer sensitization. Herein, we report the first visible-light-mediated oxidative cross-coupling of thiols with P(O)H compounds in the presence of cheap organic dye, rose bengal, as the photocatalyst and air as the green oxidant, providing various S−P(O) coupling products in moderate to excellent yields under very mild reaction conditions.

Our initial study was conducted by investigating the reaction of a slight excess (1.2 equiv) of 4-methylbenzenethiol **1a** with diphenylphosphine oxide **2a** in the presence of 5 mol % of $Ru(bpy)_3Cl_2$ in CH_3CN at room temperature under air atmosphere. After 12 h of irradiation with 10 W blue LED lights, the desired coupling product **3aa** was obtained in 57% yield with complete conversion of **2a** (Table 1, entry 1). Encouraged by this promising result, we next surveyed a range of photocatalysts under the same conditions (Table 1, entries 2−7). When *fac*-Ir(ppy)$_3$ was employed as the photocatalyst, **3aa** was formed in 33% yield (Table 1, entry 2). Reactions with various organic dyes including Mes-Acr$^+$, eosin Y, eosin B, rhodamine B, and rose bengal were also examined (Table 1, entries 3−7). These results showed that rose bengal is an effective photocatalyst for this transformation, which afforded **3aa** in 56% yield. To develop a metal-free protocol, further optimization of reaction conditions was conducted by using rose bengal as the photocatalyst. A screening of solvents showed that the yield of **3aa** was significantly improved to 71% when the reaction was performed in DMF (Table 1, entry 8). Other solvents, such as THF, CH_2Cl_2, H_2O, and CH_3CH_2OH, resulted in lower yields (Table 1, entries 9−12). Poorer conversion could be observed when the reaction was carried out in the absence of either photocatalyst or light (Table 1, entries 13 and 14). Notably, the yield was further increased to 74% or 79% by using 1.5 or 2.0 equiv of **1a** (Table 1, entries 15 and 16). Lowering rose bengal loading to 3 or 1 mol % decreased the yield to 69% or 36%, respectively (Table 1, entries 17 and 18). When the reaction was run under 1 atm of O_2, the yield of **3aa** was decreased to 60% due to the formation of byproducts (Table 1, entry 19). The reaction did not work

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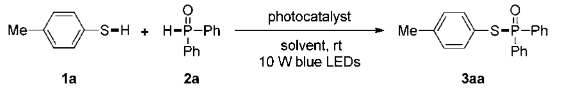
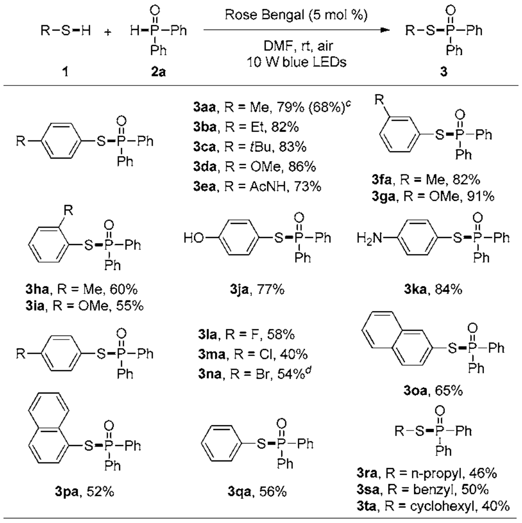
Table 1. Optimization of Reaction Conditions[a]



entry	photocatalyst (mol %)	solvent	yield[b] (%)
1	$Ru(bpy)_3Cl_2$ (5)	CH_3CN	57
2	*fac*-$Ir(ppy)_3$ (5)	CH_3CN	33
3	Mes-Acr^+ (5)	CH_3CN	14
4	eosin Y (5)	CH_3CN	42
5	eosin B (5)	CH_3CN	30
6	rhodamine B (5)	CH_3CN	27
7	rose bengal (5)	CH_3CN	56
8	rose bengal (5)	DMF	71
9	rose bengal (5)	THF	50
10	rose bengal (5)	CH_2Cl_2	35
11	rose bengal (5)	H_2O	22
12	rose bengal (5)	CH_3CH_2OH	20
13	none	DMF	trace
14[c]	rose bengal (5)	DMF	trace
15[d]	rose bengal (5)	DMF	74
16[e]	**rose bengal (5)**	**DMF**	**79**
17[e]	rose bengal (3)	DMF	69
18[e]	rose bengal (1)	DMF	36
19[e,f]	rose bengal (5)	DMF	60
20[e,g]	rose bengal (5)	DMF	10

[a] Reaction conditions: **1a** (0.36 mmol), **2a** (0.30 mmol), and photocatalyst (5 mol %) in solvent (1.5 mL) were irradiated with 10 W blue LEDs at room temperature under air for 12 h. [b] Isolated yields. [c] The reaction was performed in the dark. [d] **1a** (0.45 mmol) was used. [e] **1a** (0.60 mmol) was used. [f] The reaction was conducted under O_2 (1 atm). [g] The reaction was conducted under N_2. Mes-Acr^+ = 9-mesityl-10-methylacridinium perchlorate.

Scheme 1. Scope of Thiols[a,b]



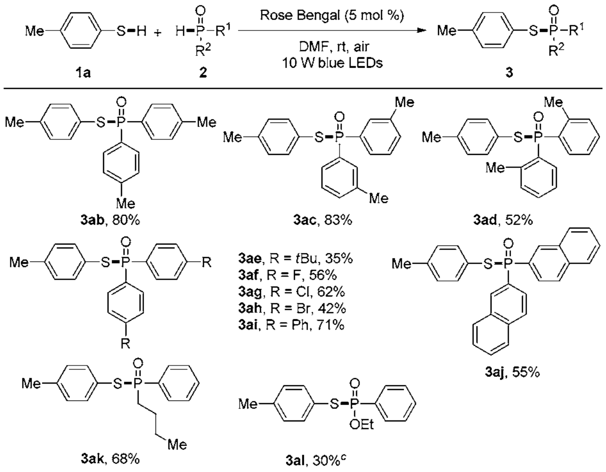
[a] Reaction conditions: see entry 16, Table 1. [b] Isolated yields. [c] 1.11 g of **3aa** prepared. [d] The reaction was conducted for 6 h.

well under a nitrogen atmosphere, giving the product **3aa** in 10% yield (Table 1, entry 20). These experimental results imply that rose bengal, visible light, and O_2 are all necessary for the success of this transformation (Table 1, entries 13, 14, and 20).

With optimized reaction conditions in hand, the scope and limitations of the title procedure were explored. We first investigated the scope of thiols (Scheme 1). Thiophenol derivatives bearing ethyl, *tert*-butyl, methoxyl, and amide groups at the *para*-position of the aromatic ring underwent this transformation smoothly to produce the desired coupling products in good yields (**3ba**−**ea**). *Meta*-substituted congeners of **1a** and **1d** provided similar results (**3fa** and **3ga**). Slightly lower but still good yields were obtained for the *ortho*-substituted systems, probably for steric reasons (**3ha** and **3ia**). To probe the chemoselectivity of this reaction, aromatic thiols with sensitive functional groups such as the free hydroxyl and amine groups were tested. We found that the transformation occurs efficiently with complete chemoselectivity, generating the S−P(O) coupling products in good yields (**3ja** and **3ka**). Thiophenol derivatives carrying halogen substituents such as F, Cl, and Br were shown to be compatible under the current reaction conditions, and the corresponding products **3la**−**na** were isolated in moderate yields. Notably, the halogen substituents such as Cl and Br are very useful for further synthetic elaborations. The naphthyl derivatives coupled readily with diphenylphosphine oxide **2a** to give the corresponding products in good yields (**3oa** and **3pa**). Thiophenol also proved to be a viable substrate and afforded 56% of **3qa**. It is important to note that the current approach is not restricted to the phosphorylation of aromatic thiols. Aliphatic thiols could also be phosphorylated under the optimized reaction conditions. Thus, propane-1-thiol, phenylmethanethiol, and cyclohexanethiol were successfully converted to the targeted products **3ra**−**ta** in moderate yields. To show the practical usefulness of this method, we carried out the reaction of **1a** with **2a** on a gram-scale under the standard conditions and isolated **3aa** in 68% yield (1.11 g).

We next examined the scope of P(O)H compounds (Scheme 2). Diarylphosphine oxides bearing a methyl group at the *para*- or *meta*-position of the arene ring performed well with good yields (**3ab** and **3ac**). The *ortho*-substituted congener of **2a** exhibited less reactivity likely due to the steric hindrance effect (**3ad**). Substrates with a *tert*-butyl group resulted in a low yield due to some side reactions (**3ae**). Halogens like F, Cl, and Br groups were well tolerated in the reaction, leading to the corresponding products **3af**−**ah** in moderate to good yields. The phenyl and naphthyl derivatives were also suitable

Scheme 2. Scope of P(O)H Compounds[a,b]

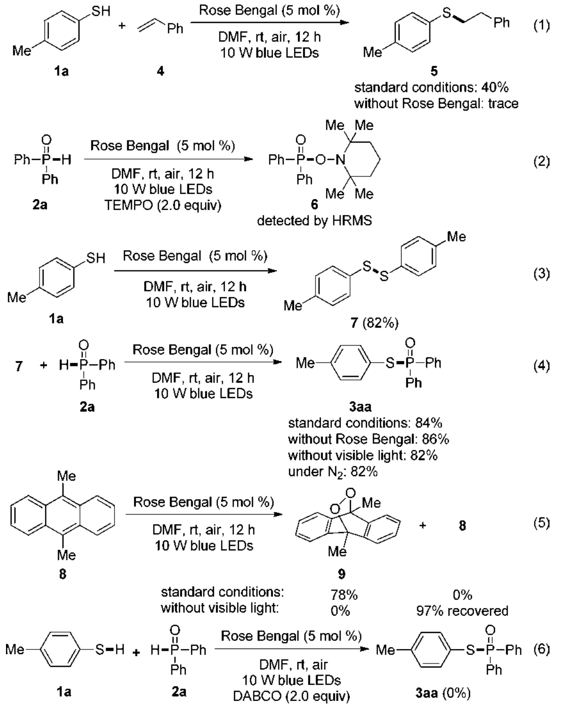


[a] Reaction conditions: see entry 16, Table 1. [b] Isolated yields. [c] The reaction was conducted for 36 h.

substrates for this transformation, and the products **3ai** and **3aj** were obtained in 71% and 55% yields, respectively. Besides symmetric phosphine oxides, unsymmetric phosphine oxides containing an alkyl group coupled readily with 4-methylbenzenethiol **1a** to give the desired coupling products in good yields (e.g., **3ak**). Unfortunately, dialkylphosphine oxides failed to afford the desired products under the applied reaction conditions. Finally, we showed that ethyl phenylphosphinate **2l** is also transformed into the corresponding product **3al** in 30% yield.

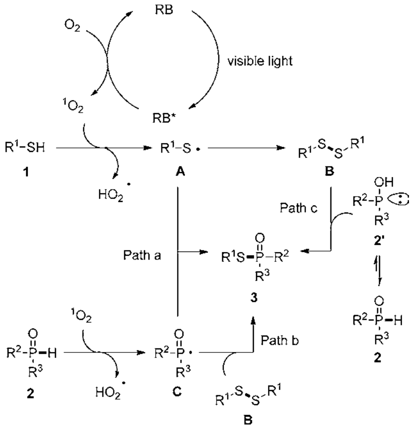
To shed light on the mechanism of this new visible-light-mediated oxidative coupling, some preliminary mechanistic studies were conducted (Scheme 3). Initially, the event for the generation of thiyl radicals from 4-methylbenzenethiol **1a** in the presence of the photocatalyst rose bengal was experimentally supported by trapping the thiyl radicals with styrene **4** to afford the thioether **5** in 40% yield.[13] The background thiol−ene reaction could be excluded because the adduct product **5** could not be obtained in the absence of rose bengal (eq 1). The result from a radical capture experiment with TEMPO on diphenylphosphine oxide **2a** suggested that P-centered radicals are likely involved in the current reaction (eq 2). Moreover, we found that disulfides are formed in all cases, which demonstrated a radical reaction pathway as well.[14] Further investigation showed that the disulfide **7** could be generated from 4-methylbenzenethiol **1a** in 82% yield under the standard conditions (eq 3). To demonstrate the role of disulfide **7**, we ran a reaction using **7** and **2a** as substrates under the standard conditions, leading to **3aa** in 84% yield. This result indicated that the disulfide **7** may be the key intermediate of this transformation. A series of control experiments showed that the formation of **3aa** starting with **7** and **2a** did not require any photocatalyst, visible light, or O_2 (eq 4). Additionally, it is well recognized that rose bengal could react with molecular oxygen under visible light irradiation to generate singlet oxygen ($^1O_2$),[15] which would be the species responsible for this oxidative coupling. In order to verify the presence of $^1O_2$ in the current reaction, we carried out trapping and quenching experiments (eqs 5 and 6). The trapping experiment with 9,10-dimethylanthracene **8**[16] under the standard conditions provided the endoperoxide product **9** that was formed through [4 + 2] cycloaddition involving $^1O_2$, while the adduct product **9** was not observed in the dark. Moreover, the reaction was completely quenched in the presence of 1,4-diazabicyclo[2.2.2]-octane (DABCO), which is known as a strong physical quencher of $^1O_2$.[17] These results indicated that $^1O_2$ is produced from O_2 in our reaction system and is involved in the reaction mechanism.

Scheme 3. Mechanistic Experiments



On the basis of the above experimental observations, we proposed the following mechanism (Scheme 4). First, rose bengal (RB) is excited under visible light irradiation to produce its excited state species RB*, which interacts with O_2 to generate $^1O_2$ via the energy transfer.[15] In this process, the excited state RB* returns to its ground state (RB). Subsequently, the generated $^1O_2$ abstracts a hydrogen atom from thiol **1** to give the thiyl radical **A**,[18] which undergoes homocoupling to form the disulfide **B**. On the other hand, the P-centered radical **C** is generated from the P(O)H compound **2** by a similar oxidation process. Finally, the formed P-centered radical **C** couples with the thiyl radical **A** (path a) or reacts with the disulfide **B** (path b) to afford the product **3**. Alternatively, the product **3** could be produced by nucleophilic attack of the P(O)H compound **2** with the disulfide **B** (path c).

Scheme 4. Proposed Reaction Mechanism



In summary, we have presented the first example of direct oxidative cross-coupling of thiols with P(O)H compounds for the construction of S−P(O) bonds via organic dye-sensitized photocatalysis. In the presence of commercially available and inexpensive organic dye, rose bengal, as the photocatalyst and air as the green oxidant, a range of S−P(O) coupling products can be readily obtained in moderate to excellent yields. Reactions that are easy to conduct exhibit excellent chemoselectivity and good functional-group tolerance. All of these features as well its mild and transition-metal-free conditions make this protocol highly practical. Further studies on synthetic application are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02563.

Experimental details and characterization data for the products (PDF)

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Notes

The authors declare no competing financial interest.

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