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diarylphosphoryl hydrazides

# **New Journal of Chemistry**

# PAPER

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Visible-light-promoted organic dyes-catalyzed sulfidation and

phosphorylation of arylhydrazines toward aromatic sulfides and

The visible-light-promoted sulfidation and phosphorylation of arylhydrazines for the synthesis of aromatic sulfides and diarylphosphoryl hydrazides were developed using the organic dyes rose bengal and Na<sub>2</sub>-eosin Y as photocatalyst, respectively. This strategy offers an efficient and mild transition-metal-free synthetic protocol for the formation of C-S and N-P bonds from arylhydrazines.

Organosulfur molecules, particularly sulfides, are ubiquitous in organic chemicals,<sup>1</sup> pharmaceuticals,<sup>2</sup> medicines,<sup>3</sup> and materials.<sup>4</sup> As a result, the development of efficient methods toward aryl sulfides is a significant subject of research in synthetic chemistry. The traditional methods for aryl sulfides synthesis generally involved transition-metal-catalyzed cross coupling of electrophilic partners with thiols or sulfides (Scheme 1a).<sup>5</sup> For example, Zhao et al reported the synthesis of aryl sulfides through a Pd-catalyzed cross-coupling of arylhydrazines and arenethiols.<sup>6</sup> Alternatively, transition-metal-free strategies for the synthesis of aryl sulfides were also developed.7 For instance, Taniguchi and co-workers reported a transition-metalfree and oxidant-free protocol for the synthesis of unsymmetrical aryl sulfides via the coupling of arylhydrazines with disulfides, but the stoichiometric amount of base was needed.<sup>7b</sup> Very recently, Hajra's group developed an approach to access aryl sulfides starting from arylhydrazines and thiols and under visible-light irradiation.<sup>8</sup> Despite these significant advances, the development of transition-metal-free and basefree procedure for the construction of aryl sulfides under mild conditions are still highly desirable.

On the other hand, phosphorus compounds are of interest in coordination chemistry<sup>9</sup> and homogenous catalysis.<sup>10</sup> Moreover, ligands containing N-P bond can be utilized in asymmetric catalysis.<sup>11</sup> However, only limited cases for the synthesis of phosphorylated hydrazides have been reported. For example, Gholivand *et al* synthesized phosphorylated hydrazides by the coupling of phosphoryl chlorides with arylhydrazines at 0 °C (Scheme 1b).<sup>12</sup> However, phosphoryl chloride compounds are usually unstable and sensitive to water, which will hamper their applications. In this context, the employment of easily handled diarylphosphine oxides to replace phosphoryl chlorides will provide a straightforward method for the synthesis of phosphorylated hydrazides *via* the oxidative coupling of P-H bond.

Visible-light photoredox catalysis has gained much attention for their wide application in organic chemistry.<sup>13</sup> They can act as powerful and inexpensive tools to initiate organic reactions.<sup>14</sup> The classic photocatalysts like ruthenium and iridium polypyridyl complexes have proved to be efficient in various reactions, but the high price, multi-step synthesis and transition-metal contamination issue might limit their applications.<sup>15</sup> Consequently, the application of organophotocatalysts is a significant metal-free alternative, since they are usually less toxic, less expensive and easier to handle.<sup>16</sup>

In the recent years, arylhydrazines have attracted considerable attention as alternative electrophilic partners in cross-coupling reactions.<sup>17</sup> Various chemical bonds including C-



Scheme 1 Transformation of arylhydrazines for C-S and N-P bond formation

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59 60 C,<sup>18</sup> C-N,<sup>19</sup> C-S,<sup>7b, 8, 20</sup> C-Se,<sup>21</sup> and C-P<sup>22</sup> bonds could be constructed from arylhydrazines. Particularly, arylhydrazines can function as arylating agents by releasing nitrogen gas. For instance, in our recent work, the synthesis of arylphosphonates from arylhydrazines and trialkylphosphites was realized under visible-light irradiation with eosin B as photocatalyst.<sup>23</sup> In our continuing research on green chemistry and photocatalytic organic synthesis,<sup>24</sup> we envisioned that the reactivity of arylhydrazines could be tuned by rational designed substrates and judicious selection of catalysts. Herein we report a controllable sulfidation and phosphorylation of arylhydrazines with organic dyes as catalyst by visible-light irradiation under mild conditions with/without the releasing of N<sub>2</sub> (Scheme 1c).

Our studies were initiated by examining the model reaction of phenyl hydrazine **1a** with diphenyl disulfide **2a** under visiblelight irradiation in the presence of various photocatalysts, oxidants and solvents (Table 1). Firstly, various organic dyes including rose bengal, Na<sub>2</sub>-eosin Y, eosin Y, Na<sub>2</sub>-eosin B, rhodamine B, and eosin B were surveyed as photocatalysts (10 mol%) in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant in DMSO (entries 1-6). Among them, Na<sub>2</sub>-eosin Y was found to be the most active catalyst giving the desired product **3a** in 30% yield (entry 2). Then several oxidants were screened employing Na<sub>2</sub>-eosin Y as photocatalyst (entries 7-10). Although the yield of **3a** obtained with TBPB as oxidant was promising, H<sub>2</sub>O<sub>2</sub> was chosen as the

	Ph-NHNH <sub>2</sub> + PhSSPh 1a 2a	Photocatalyst Oxidant → Ph−S−Ph Solvent 3a		
Entry	Photocatalyst	Oxidant	Solvent	Yield <sup>[b]</sup> (%)
1	rose bengal	$H_2O_2$	DMSO	6
2	Na <sub>2</sub> -eosin Y	$H_2O_2$	DMSO	30
3	eosin Y	$H_2O_2$	DMSO	11
4	Na <sub>2</sub> -eosin B	$H_2O_2$	DMSO	18
5	rhodamine B	$H_2O_2$	DMSO	12
6	eosin B	$H_2O_2$	DMSO	15
7	Na <sub>2</sub> -eosin Y	BPO	DMSO	18
8	Na <sub>2</sub> -eosin Y	TBPB	DMSO	30
9	Na <sub>2</sub> -eosin Y	TBHP	DMSO	16
10	Na <sub>2</sub> -eosin Y	DDQ	DMSO	18
11	Na <sub>2</sub> -eosin Y	$H_2O_2$	DMF	15
12	Na <sub>2</sub> -eosin Y	$H_2O_2$	THF	10
13	Na <sub>2</sub> -eosin Y	$H_2O_2$	MeOH	6
14	Na <sub>2</sub> -eosin Y	$H_2O_2$	PhCH₃	0
15 <sup>[c]</sup>	Na <sub>2</sub> -eosin Y	$H_2O_2$	DMSO	10
16 <sup>[d]</sup>	Na <sub>2</sub> -eosin Y	$H_2O_2$	DMSO	46
17 <sup>[e]</sup>	Na <sub>2</sub> -eosin Y	$H_2O_2$	DMSO	58
18 <sup>[f]</sup>	Na <sub>2</sub> -eosin Y	$H_2O_2$	DMSO	62
19 <sup>[g]</sup>	Na <sub>2</sub> -eosin Y	$H_2O_2$	DMSO	70

<sup>[a]</sup> Reaction conditions unless otherwise specified: To a reaction tube, **1a** (0.5 mmol), **2a** (1.0 mmol), photocatalyst (10 mol%), DMSO (1.5 mL), oxidant (1 equiv.) were added, then the tube was capped and stirred under the irradiation of blue LEDs at room temperature for 8 h.  $H_2O_2$  (aq. 30 wt%), BPO = benzoyl peroxide, TBPB = *tert*-butyl peroxybenzoate, TBHP = *tert*-butyl hydroperoxide (aq. 70 wt%), DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. <sup>[b]</sup> GC yields were given by using biphenyl as internal standard. <sup>[c]</sup> **2a** (0.5 mmol). <sup>[d]</sup> **2a** (2.0 mmol). <sup>[e]</sup> **2a** (3.0 mmol). <sup>[f]</sup> **2a** (3.5 mmol), <sup>[g]</sup> **2a** (3.5 mmol), photocatalyst (5 mol%).

# optimal oxidant for further investigation due<sub>Artidoonlits</sub> environmentally friendliness. Subsequently<sup>10</sup> other solvens, such as DMF, THF, MeOH or PhCH<sub>3</sub>, were applied as the reaction media, notable decrease of yields were observed (entries 11-14). Then, we optimized the amount of substrate **2a** and catalyst Na<sub>2</sub>-eosin Y (entries 15-19). To our delight, yields of **3a** were increased significantly with increasing the loading of diphenyl disulfide and lowering the amount of photocatalyst. Therefore, the optimized conditions were established using 5

mol% of Na<sub>2</sub>-eosin Y and 1 equiv of H<sub>2</sub>O<sub>2</sub> under blue LEDs

irradiation for 8 h (entry 19). With the optimal conditions in hand, we explored the scope of visible-light promoted sulfidation of hydrazines (Table 2). As it can be seen, diphenyl sulfide 3a was obtained in 68% isolated yield. The arylhydrazines bearing electron-donating group (-OMe) at the para-position showed good compatibility affording the desired product **3b** in 64% yield. Gratifyingly, arylhydrazines with strong electron-withdrawing group (-NO<sub>2</sub>) at the orthoand para-positions also delivered the corresponding products (3c and 3d) albeit with low yields. The heterocycle containing hydrazine, i.e. 2-hydrazinylpyridine, reacting with 2a also gave the desired product 3e in good yield (71%). Moreover, various diaryl disulfides were subjected into this transformation using phenyl hydrazine 1a as the reaction partner. For example, the diaryl disulfides containing electron-donating groups, such as -OMe and -NH<sub>2</sub>, were converted into the desired products **3f** and 3g in good yields, respectively. In contrast, diaryl disulfides bearing a strong electron-withdrawing group -NO<sub>2</sub> at ortho- and para-positions showed relatively poor reactivities (3h and 3i). To our delight, the heterocyclic and aliphatic hydrazines e.g., di(2-pyridinyl) disulfide and dimethyl disulfide can also afford the desired product 3j and 3k in in yields of 75% and 71%, respectively. The above-mentioned results suggested that the transformation of substrates with strong electron-withdrawing groups into the corresponding sulfides (3c, 3d, 3h, 3i) were not efficient in this procedure, probably due to the lower reactivity of the corresponding radical intermediates.



Reaction conditions: 1 (0.5 mmol), 2 (3.5 mmol), Na<sub>2</sub>-eosin Y (5 mol%), H<sub>2</sub>O<sub>2</sub> (1 equiv.), DMSO (1.5 mL), blue LEDs, room temperature, 8 h. Isolated yields were given.

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Based on the above-mentioned results, we hypothesized that if hydrazine could undergo a direct N-H functionalization without releasing N<sub>2</sub>, the direct formation of hydrazine derivatives might be expected. After extensive optimization, it is pleasing to find that the direct coupling of phenylhydrazine and diphenylphosphine oxide toward phosphorylated hydrazide could be achieved by rose bengal catalysis in the presence of  $Cs_2CO_3$  under the irradiation of white light (for details, see supporting information). It's worth mentioning that in this protocol the desired products could be easily isolated by simply washing and filtration, which avoided the tedious column chromatography (see supporting information for details). Accordingly, the product **7a** can be obtained in isolated yield of 55%.

The substrate scope of the phosphorylation of arylhydrazines was further studied and the results were showed in Table 3. A range of arylhydrazines reacted well with diphenylphosphine oxide, leading to the corresponding products in good yields. The arylhydrazines bearing electron-donating group gave the corresponding products **7b-7d** in moderate to good yields (67-76%). Additionally, the catalytic system also displayed good tolerance to various electron-withdrawing groups, including -F, -Cl, -Br and -CN, affording the corresponding products **7e-7i** in good yields (63-87%). Overall, no significant electron effect was observed in this procedure. Notably, 2-hydrazinylpyridine also worked well in this reaction to give desired product **7j** smoothly.



<sup>[a]</sup> Reaction conditions: 1 (0.55 mmol), 6 (0.5 mmol), rose bengal (10 mol%),  $Cs_2CO_3$  (1 equiv.), CH<sub>3</sub>CN (1.5 mL), white LEDs, room temperature, 9 h. Isolated yields were given. <sup>[b] 31</sup>P NMR yield.

To further understand the mechanism of these transformations, we carried out preliminary mechanistic investigation. As illustrated in Scheme 2a, when the sulfidation reaction was performed in the absence of visible-light, photocatalyst, or oxidant, only trace or lower yield of products **3a** were obtained. The results indicated that visible-light, Na<sub>2</sub>-eosin Y, H<sub>2</sub>O<sub>2</sub> and air were all necessary for the reaction. Then the reaction without H<sub>2</sub>O<sub>2</sub> under the atmosphere of O<sub>2</sub> gave the product **3a** in 66% yield, which is similar with that of the

standard conditions (70% yield, Table 1, entry 19). These cesults suggested that the oxygen molecule  $M^{O}$  the 197/GN  $M^{3}$  suggested from  $H_{2}O_{2}$  might play an important role in this transformation.

Additionally, when the sulfidation reaction was treated with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-tertbutyl-4-methyl-phenol (BHT), only trace amount of **3a** was detected based on GC analysis (Scheme 2b-c). The adducts **4a** and **5a** were detected using HRMS (Figure S2-3), demonstrating the radical intermediates Ph<sup>•</sup> and PhS<sup>•</sup> were involved in the reaction. Similarly, the phosphorylation reaction was supressed by adding TEMPO, and the adduct of phosphorous-centred radical and TEMPO was observed by HRMS (Figure S4), indicating the phosphoryl radical was involved in this photocatalyzed phosphorylation reaction.



Furthermore, luminescence quenching studies were carried out to gain a deeper insight into the reaction mechanism. The studies were conducted by mixing Na<sub>2</sub>-eosin Y (Na<sub>2</sub>-EY) with **1a**, **2a** and H<sub>2</sub>O<sub>2</sub>, respectively. As a result, the significant luminescence quenching effect was detected when Na<sub>2</sub>-eosin Y was mixed with **2a** (Figure 1a). While the quenching effect of **1a** and H<sub>2</sub>O<sub>2</sub> was not obvious (Figure S5). As shown in Figure 1b, a linear relationship between the concentration of **2a** and I<sub>0</sub>/I (I<sub>0</sub> and I are the fluorescence intensity before and after adding **2a**) was observed. The results indicated that **2a** was an effective quencher of Na<sub>2</sub>-eosin Y (for details, see supporting information).

Based on the above experimental observations and related reports,<sup>25</sup> a plausible mechanism was proposed in Scheme 3. First, the photocatalyst Na<sub>2</sub>-eosin Y was irradiated to the excited state PC\*, which then was converted into PC<sup>•-</sup> through a single electron transfer (SET). Then the oxidation of PC<sup>•-</sup> by dioxygen (from  $H_2O_2$  and air) afforded the ground state photocatalyst and

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 $O_2^{\bullet}$ . Meanwhile, phenyl hydrazine **1a** was oxidized to afford radical cation **9**. The deprotonation of radical cation **9** by  $O_2^{\bullet}$  or base afforded radical **10**. Then via a SET process followed by deprotonation rendered radical **10** converted into radical **11**, which then was converted into radical **12**. Subsequently, the elimination of nitrogen from **12** formed the phenyl radical **13**. On the other hand, the phenyl sulfide radical **14** was generated through homolytic cleavage of **2a** under the irradiation of visible-light. Finally, the radical coupling of **13** and **14** delivered the target product diphenyl sulfide **3a**. Similarly, the mechanism of the phosphorylation reaction was also proposed (See supporting information, Scheme S2).



Figure 1. Luminescence quenching experiments: (a) the emission spectra of a 0.05 mM solution of Na<sub>2</sub>-EY with various concentrations of reactant 2a in degassed anhydrous DMSO excited at 490 nm; (b) The linear relationship between the increasing concentration of 2a and  $I_0/I$ .



Scheme 3 Proposed mechanism of sulfidation reaction

## Conclusion

In summary, we have developed a novel visible-light promoted method to realize controllable sulfidation and phosphorylation of arylhydrazines under metal-free conditions. In these protocols, a series of diaryl sulfides and phosphorylated hydrazides were obtained in moderated to good yields via C-S bond and N-P bond construction from the easily available arylhydrazines under mild conditions. Particularly, for the synthesis of phosphorylated hydrazides column chromatography is avoided. Such a simple and controllable photocatalytic strategies might pave the way for it herit related transformation of arylhydrazines.

## **Conflicts of interest**

There are no conflicts to declare.

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Visible-light-promoted organic dyes-catalyzed sulfidation and phosphorylation of arylhydrazines toward aromatic sulfides and diarylphosphoryl hydrazides

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The visible-light-promoted sulfidation and phosphorylation of arylhydrazines for the synthesis of aromatic sulfides and diarylphosphoryl hydrazides were developed using the organic dyes rose bengal and Na2-eosin Y as photocatalyst, respectively. This strategy offers an efficient and mild transition-metal-free synthetic protocol for the formation of C-S and N-P bonds from arylhydrazines.