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# Eosin Y-catalyzed photooxidation of triarylphosphines under visible light irradiation and aerobic conditions†

Yanbin Zhang,<sup>b</sup> Cong Ye,<sup>b</sup> Shijie Li,<sup>b</sup> Aishun Ding,<sup>b</sup> Guangxin Gu<sup>\*a</sup> and Hao Guo<sup>\*b</sup>

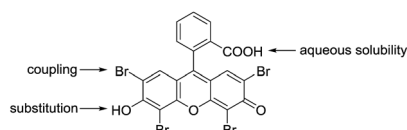
We report herein a novel method for Eosin Y-catalyzed photooxidation of triarylphosphines under visible light irradiation and aerobic conditions. This new approach employed visible light as the energy source and air as the oxidant, showing great advantages in environmental benignness and operational easiness with a wide functional group tolerance.

Photochemistry is an important branch in modern chemistry.<sup>1</sup> Distinct from traditional thermal reactions, the key intermediates in photo-reactions are the electronically excited state of organic molecules. Photochemical sensitization of triplet oxygen to singlet oxygen is one of the appealing aspects of photochemistry.<sup>2</sup> Compared with chemical decomposition, electro-chemical, bio-chemical and other methods,<sup>3</sup> photochemical sensitization is cheap, easy to handle, efficient and environment-friendly. More importantly, organic photocatalysts are easy to functionalize, which means the catalyst could be attached to advanced materials<sup>4</sup> and bio-materials.<sup>5</sup> Several photocatalysts were used in singlet oxygen generation.<sup>6</sup> Among them, the structure of Eosin Y showed good features, such as aqueous solubility and easiness to modify (Scheme 1). Thus, much attention has been paid to Eosin Y-catalyzed singlet oxygen generation.<sup>7</sup>

Phosphine oxide is an important fragment in medicine,<sup>8</sup> and functional supramoleculars.<sup>9</sup> It also plays an important role in organic synthesis.<sup>10</sup> It has been used as a catalyst for the Wittig reaction,<sup>11</sup> a ligand for transitional metals,<sup>12</sup> and as a gentle oxidant.<sup>13</sup> Numerous methods have been developed for the

preparation of phosphine oxides from phosphines *via* direct oxidations,<sup>14,15</sup> among which some photocatalysts, such as 9,10-dicyanoanthracen,<sup>15b</sup> 9-mesityl-10-methylacridinium perchlorate,<sup>15c</sup> and sensitizers generating singlet oxygen<sup>15d</sup> showed nice catalytic activity.<sup>15</sup> However, in many cases, external environmentally harmful oxidants,<sup>14a</sup> expensive additives,<sup>14b</sup> or harsh conditions<sup>14c</sup> were required. Moreover, stoichiometric oxidants will generate stoichiometric wastes, which makes the purification process much more complicated.<sup>14b</sup> An efficient, environmentally friendly, and convenient method for the oxidation of phosphines is desirable as part of an overall effort to develop “Green Chemistry”. With our continuous interest in this field,<sup>16</sup> we turned to study the Eosin Y-catalyzed photo oxidation of triarylphosphines based on the following considerations. Firstly, Eosin Y is cheap and the loading of the catalyst is generally low. Secondly, harsh irradiation conditions can be avoided, since Eosin Y absorbs visible light. Thirdly, Eosin Y is stable in air and absorbs visible light, thus, special glassware and protective gas is no more required. This will provide operational convenience. Here in, we wish to report our recent results in the photooxidation of triarylphosphines using Eosin Y as the catalyst under visible light irradiation and aerobic conditions.

Our initial attempts were carried out using triphenylphosphine **1a** as the model substrate, 15 mol% of Eosin Y as the catalyst, a 23 W household lamp as the light source, and oxygen as the oxidant. A quantitative yield of the corresponding triphenylphosphine oxide **2a** was obtained in all tested solvents (entries 1–6, Table 1). Given that the reaction in methanol showed the highest reaction speed (entry 6, Table 1), methanol was chosen as the standard solvent. However, when we tried to explore the substrate scope, some reactants were not dissolved in methanol. Thus, a mixture of dichloromethane (DCM) : methanol (MeOH) = 5 : 1 was used as the optimal solvent (entry 7, Table 1). Further studies showed that the loading of catalyst could be dramatically reduced (entries 7–10, Table 1). We were delight to see that only 1 mol% of Eosin Y was enough to efficiently catalyze this transformation (entry 10, Table 1). Air was then used as oxidant



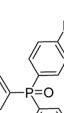
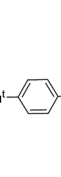
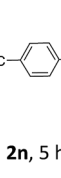
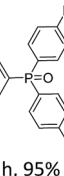
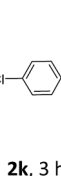
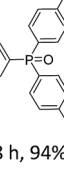
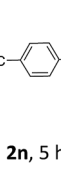
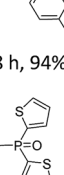
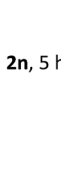
Scheme 1 Structure feature of Eosin Y.

<sup>a</sup>Department of Materials Science, Fudan University, 220 Handan Road, Shanghai, 200433, P. R. China. E-mail: guangxingu@fudan.edu.cn; Fax: +86-21-65648837; Tel: +86-21-65648837

<sup>b</sup>Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, 200433, P. R. China. E-mail: Hao\_Guo@fudan.edu.cn; Fax: +86-21-55664361; Tel: +86-21-55664361

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Table 2 Photooxidation of **1** under condition A<sup>a</sup>

|                                                                                                               |                                                                                                                 |                                                                                                                 |
|---------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|
| $\text{Ar}_3\text{P}$<br><b>1</b>                                                                             | $\xrightarrow[\text{DCM:CH}_3\text{OH} = 5:1, \text{ rt}]{\text{visible light, air (1 atm) Eosin Y (1 mol\%)}}$ | $\text{Ar}_3\text{P=O}$<br><b>2</b>                                                                             |
| <br><b>2a</b> , 3.5 h, 95%   | <br><b>2b</b> , 4 h, 92%      | <br><b>2c</b> , 2 h, 99%     |
| <br><b>2d</b> , 4 h, 89%   | <br><b>2e</b> , 4 h, 95%    | <br><b>2f</b> , 6 h, 91%   |
| <br><b>2g</b> , 2.5 h, 83%  | <br><b>2h</b> , 3.5 h, 87%   | <br><b>2i</b> , 3 h, 95%    |
| <br><b>2j</b> , 3 h, 95%   | <br><b>2k</b> , 3 h, 92%    | <br><b>2l</b> , 8 h, 99%   |
| <br><b>2m</b> , 8 h, 94%   | <br><b>2n</b> , 5 h, 95%    | <br><b>2o</b> , 3.5 h, 90% |
| <br><b>2p</b> , 3.5 h, 90% |                                                                                                                 |                                                                                                                 |

<sup>a</sup> A solution of **1** (0.2 mmol), Eosin Y (1 mol%), DCM (2.5 mL), and MeOH (0.5 mL) was irradiated by a 23 W household lamp at rt under air atmosphere (1 atm). Isolated yield was reported.

tolerance for a wide range of arylphosphines was achieved in this photooxidation methodology.

To gain insight to the mechanism, singlet oxygen quenching experiments were carried out using 9,10-dimethylantracene as singlet oxygen quencher.<sup>2b</sup> The results were shown in Fig. 1. The whole reaction process was inhibited by 1 equivalent of 9,10-dimethylantracene (triangle symbol). The reaction rate was even lower with the addition of 2 equivalents of 9,10-dimethylantracene (square symbol). Since 9,10-dimethylantracene was a typical singlet oxygen quencher,<sup>2b</sup> we reasoned that singlet oxygen might be the key oxidative species in the triarylphosphine

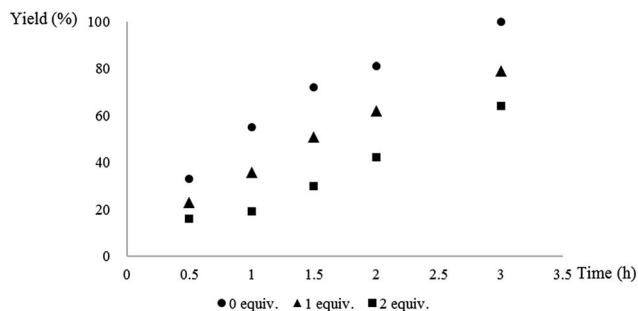
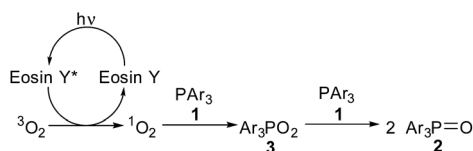


Fig. 1 Singlet oxygen quenching experiments. (Reactions were carried out under optimized conditions with 0, 1 or 2 equivalents of 9,10-dimethylantracene.)



Scheme 2 Proposed mechanism.

oxidation process. The trapping product, 9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene, was also observed in crude  $^1\text{H}$  NMR analysis.<sup>17</sup> Styrene and cyclohexene was also added to the reaction system to trap phosphadioxirane, but no trapping species was detected.<sup>18a</sup>

On the basis of the above results and literature precedence,<sup>18</sup> a possible mechanism was proposed in Scheme 2. Upon the irradiation of visible light, Eosin Y reaches its excited state.<sup>2c</sup> Then energy transfer between Eosin Y\* and oxygen ( $^3\text{O}_2$ ) gave singlet oxygen ( $^1\text{O}_2$ ), and Eosin Y went back to ground state.<sup>2a</sup> Triarylphosphine **1** and singlet oxygen ( $^1\text{O}_2$ ) combined to afford triarylphosphadioxane **3**.<sup>18a</sup> **3** and another molecule of **1** finally furnished **2** as the product.<sup>18b</sup>

## Conclusions

In conclusion, a visible light-induced metal-free photo oxidation of triarylphosphines was developed. Eosin Y was employed as the catalyst and air was used as the oxidant. Considering that this protocol is cheap, environmental friendly, easy to operate, and the substrate scope is broad, this method may be widely used in the oxidation of phosphine derivatives.

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