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ORIGINAL ARTICLE

Catalyst-free photooxidation of triarylphosphines under aerobic conditions



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Abstract A new method for the photooxidation of triarylphosphines into the corresponding oxides is developed. In this new protocol, neither a catalyst nor an additive is required. The greenest oxidant, oxygen in air atmosphere, is used. After a short period of photo irradiation at rt, stoichiometric amounts of the oxides can be easily afforded by simply recycling the solvent under vacuum. No waste is formed in the whole process of this reaction. The substrate scope of this reaction is broad, showing very good application prospects in both organic chemistry and industrial processes.

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1. Introduction

The oxidation of phosphines into phosphine oxides is not only an interesting topic in organic chemistry, but also a challenging goal for industrial processes especially in pollution control [1]. Thus, it has been a fundamentally important subject in chemistry. For these reasons, a large number of methods have been developed in this field [2–16]. Despite their remarkable

achievements, the current phosphine oxidation reactions suffer from some drawbacks. First of all, catalytic or stoichiometric amounts of catalysts [2,3,5,11,14] or additives [4,9,10] should be applied to catalyze or initiate this reaction. Thus, lots of toxic metal or organic waste are generated. Secondly, in many cases, the oxidant is not oxygen, which means that more than one equivalent of waste from the oxidant should be produced [4,7,8]. Finally, in most cases, the formation of byproducts cannot be avoided [8,16], which results in problems on the purification. And waste may be formed in the workup of purification. The above mentioned problems indicate that large amounts of waste are generated, which are obviously not environmentally friendly. Thus, more efficient reactions that can be performed under ambient conditions are in urgent need considering increasing environmental concerns. Photooxidation [10–16] provides an efficient way to realize this reaction, which normally uses oxygen as the oxidant [12–14]. However, transition metal catalyst [11,12,15] or organic photo

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sensitizer [13,14] is still required. And their workup for purification also produces waste. New photooxidations without catalysts will be a better way for this transformation. Herein, we wish to report our recent observation on the catalyst-free photooxidation of phosphines under aerobic conditions at ambient temperature. In this work, we have found for the first time that under simple photo irradiation, triarylphosphines can be easily oxidized into the corresponding oxides in the absence of any catalyst. This reaction uses oxygen in the air atmosphere as the oxidant, which is green and abundantly available. Very importantly, after full conversion, stoichiometric amounts of the oxides are afforded without any byproduct formed, which means that no waste will be generated during the workup step, since simply recycling the solvent under vacuum is enough for purification.

2. Methods

2.1. General experimental methods

All reactions were carried out using a PLS-SXE300UV reactor with Xe lamp (300 W) as the irradiation source. Melting points were determined on a WRS-2 apparatus. ^1H (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz), and ^{31}P (162 MHz) NMR spectra of samples in CDCl_3 (unless stated otherwise) were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics micrOTOF II spectrometer. HRMS (EI) determinations were carried out on a Water GCT CA176 spectrometer.

Table 1 Optimization of the reaction conditions.^a

$\text{Ph}_3\text{P} \xrightarrow[\text{solvent, rt}]{\text{air (1 atm), } h\nu} \text{Ph}_3\text{P=O}$ <p style="text-align: center;">1a 2a</p>			
Entry	Solvent	Time (h)	Yield (%)
1	CH_2Cl_2	1	100 ^b
2	DMC	2	100 ^b
3	CCl_4	2	100 ^b
4	CH_3OH	2	100 ^b
5	EtOH	2	100 ^b
6	CH_3CN	2	100 ^b
7	THF	3.5	100 ^b
8	Acetone	7	100 ^b
9	Benzene	14	100 ^b
10	DMC	2	100 ^c
11 ^d	DMC	12	NR
12 ^e	DMC	12	NR

^a A solution of **1a** (0.2 mmol) in the tested solvent was irradiated by Xe lamp (300 W) at rt under air atmosphere (1 atm).

^b Isolated yield by column chromatography.

^c Isolated yield by directly recycling the solvent under vacuum.

^d The reaction was carried out using visible light.

^e The reaction was carried out without light.

2.2. Typical procedure for the photooxidations

Triarylphosphine and dimethyl carbonate (DMC) were added to a dry quartz reaction flask which was equipped with a magnetic stirrer. The mixture was irradiated by a Xe lamp (300 W) at rt under air atmosphere. After the photoreaction was completed as monitored by TLC (eluent: ethyl acetate). The solvent was directly recycled under vacuum to afford triarylphosphine oxides as a solid.

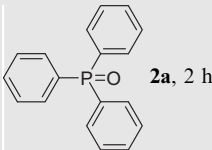
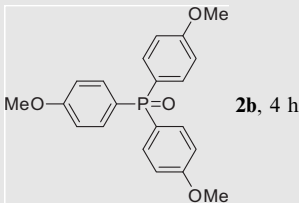
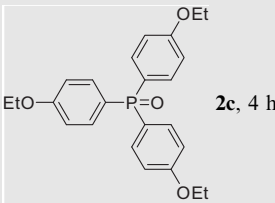
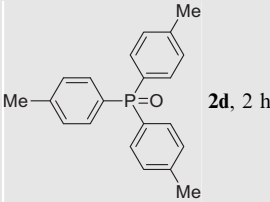
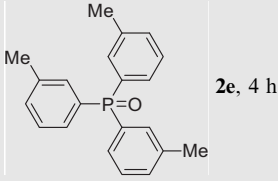
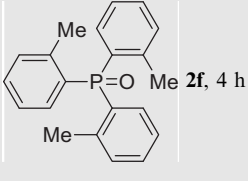
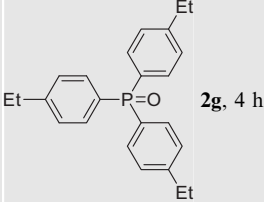
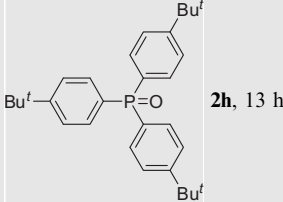
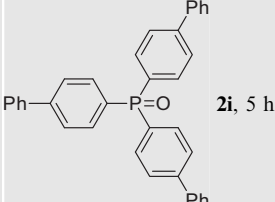
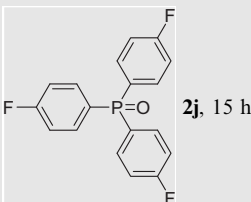
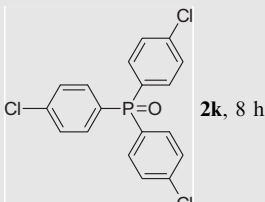
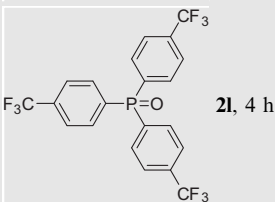
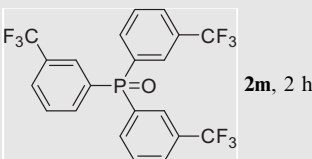
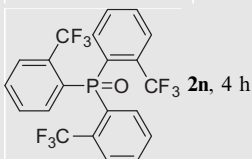
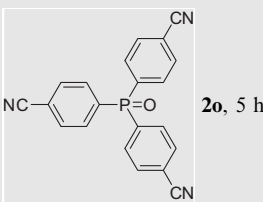
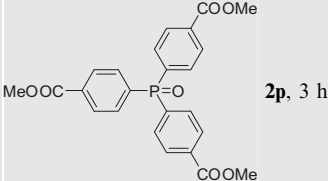
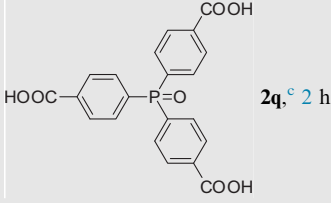
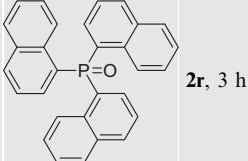
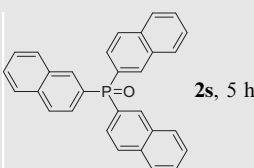
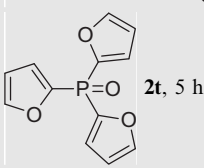
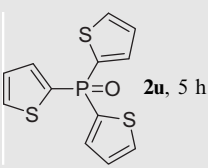
3. Results and discussion

At the beginning of our study, triphenylphosphine **1a** was chosen as the model substrate to explore the feasibility of the reaction. After lots of attempts, we were happy to see that under the irradiation of Xe lamp, without any catalyst, the photooxidation of **1a** in all the tested solvents under air atmosphere gave triphenylphosphine oxide **2a** in 100% isolated yields after purification by column chromatography (entries 1–9, Table 1). Considering that no byproduct was formed, we believed that directly recycling the solvent under vacuum should be enough to get the pure final products. Thus, we chose dimethyl carbonate (DMC) as the standard solvent (entry 2, Table 1), since this solvent is very green [17] and its boiling point is low enough to be recycled under vacuum. Indeed, after a short period of photo irradiation and direct recovery of the solvent under vacuum, the desired product was generated in a 100% yield (entry 10, Table 1). This result indicated that no chemical waste would be produced by this photo chemical method. Then the reaction was carried out under visible light irradiation or in dark conditions, no reaction took place at all (entries 11 and 12, Table 1). These results confirmed that the Xe lamp irradiation played a key role in this photooxidation. Thus, Condition A (air (1 atm), Xe lamp, DMC, and rt) was applied for the following studies.

With the above optimized conditions in hand, the substrate scope of this photooxidation with a series of triarylphosphines under Condition A was investigated carefully. The results are summarized in Table 2. It was observed that the reactions of both electron-rich and deficient phenylated phosphine derivatives proceeded in high efficiency, affording the corresponding oxides (**2a–q**). No clear electronic effect on the phenyl ring was observed. The relative position of the substituents on the phenyl ring showed no influences, either (**2d–f** and **2l–n**). Notably, naphthyl (**2r–s**) and heteroaryl groups, like furyl (**2t**) and thienyl (**2u**), were also tolerant in this transformation. It was also worthy to note that 100% isolated yields were observed for all the above test substrates. And the solvent was efficiently recycled in all cases.

On the basis of these results and the corresponding mechanism studies [12,14,15] in the field of photooxidation, a possible mechanism is proposed as shown in Fig. 1. Under photo irradiation, a single electron transfer (SET) from triarylphosphine to oxygen results in a triarylphosphine radical cation and an oxygen radical anion. Their following coupling reaction led to the formation of intermediate **3** which might react with another molecule of triarylphosphine to yield the final product.

Table 2 Photooxidation of **1** under Condition A.^{a,b}

$\text{Ar}_3\text{P} \xrightarrow[\text{DMC, rt}]{\text{air (1 atm), Xe lamp}} \text{Ar}_3\text{P=O}$ <div> <div>1</div> <div>2</div> <div>100%</div> </div>		
 2a , 2 h	 2b , 4 h	 2c , 4 h
 2d , 2 h	 2e , 4 h	 2f , 4 h
 2g , 4 h	 2h , 13 h	 2i , 5 h
 2j , 15 h	 2k , 8 h	 2l , 4 h
 2m , 2 h	 2n , 4 h	 2o , 5 h
 2p , 3 h	 2q , ^c 2 h	 2r , 3 h
 2s , 5 h	 2t , 5 h	 2u , 5 h

^a A solution of **1** (0.2 mmol) in DMC was irradiated by Xe lamp (300 W) at rt under air atmosphere (1 atm).^b Isolated yield by directly recycling the solvent under vacuum.^c DMSO-*d*₆ (1 mL) was used as the solvent.

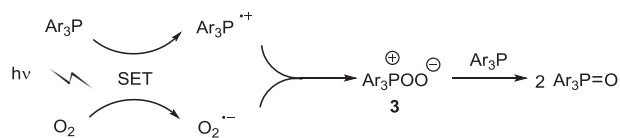


Figure 1 Possible mechanism.

4. Conclusions

In conclusion, we have successfully developed a novel photooxidation of triarylphosphines. In this new protocol, photo irradiation shows a great effect on the activation of the whole reaction system. Oxygen in the air atmosphere, which is green and abundantly available, is used as the oxidant. Neither a catalyst nor an additive is required. This reaction can be carried out directly under air atmosphere at rt, which is a very simple operation. After full conversion, stoichiometric amounts of the oxides are afforded without any byproduct formed. The solvent can be easily recycled and no further purification is needed. All the above advantages indicate that no waste will be produced by this new reaction, which is very environmentally friendly. Considering that its scope is broad, this reaction will contribute a lot in both organic chemistry and industrial processes.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jscs.2015.07.004>.

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