

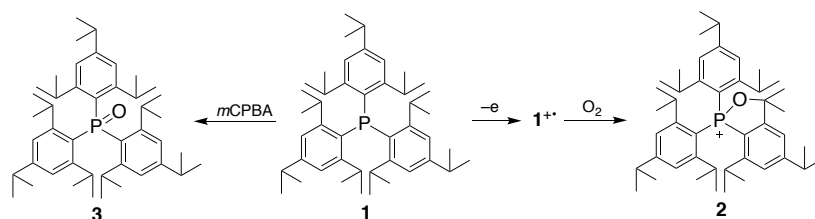
## Phosphorus–oxygen bond formation reactions of sterically crowded triarylphosphines

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Sterically crowded triarylphosphines represented by tris(2,4,6-triisopropylphenyl)phosphine (**1**) and their radical cations undergo characteristic phosphorus–oxygen bond formation reactions (**Scheme 1**).<sup>1</sup> Radical cation **1**<sup>•+</sup> reacts with molecular oxygen to afford heterocyclic phosphonium salt **2** resulting from the participation of the *ortho* substituent. The oxidation of phosphine **1** with *m*CPBA gives phosphine oxide **3**, but the initial color change of the reaction suggests radical cation **1**<sup>•+</sup> as an initial product as well as a reaction intermediate. Interestingly, triarylphosphines having trityl cation moiety undergo reactions similar to the radical cations.<sup>2</sup> Herein, we report the details of the phosphorus–oxygen bond formation reactions of the sterically crowded triarylphosphines and discuss the reaction mechanisms.

Oxidation of trivalent phosphines to phosphine oxides by peroxides have been theoretically studied and reported to proceed by nucleophilic attack of the phosphine to the oxygen atom of the peroxide.<sup>2</sup> The DFT study of the oxidation of trimethyl-, triphenyl- and trimesityl-phosphines with peracetic acid showed the mechanism similar to the previous studies, and limited effect of the steric hindrance to the activation energies due to the compensation by increasing HOMO energy level.<sup>3</sup> One electron oxidation of phosphine **1** with various oxidants was investigated and *in situ* generated carbocations were found to oxidize **1** to radical cation **1**<sup>•+</sup>. Reaction of the resultant radical cation **1**<sup>•+</sup> with molecular oxygen afforded **2** without formation of **3**. In order to clarify the reaction mechanism for the formation of **3**, reactivities of **1**<sup>•+</sup> were further studied and will be presented.



**Scheme 1.** Phosphorus–oxygen bond formation reactions of triarylphosphine **1**.

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