

Photocatalytic Arylation of White Phosphorus with Aryl Bromides and Chlorides

R. Wolf¹, M. Gawron¹, J. Rüchel¹

¹Department of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany

E-Mail: jannes.ruechel@ur.de

White phosphorus (P₄) is the main feedstock material for the synthesis of industrially significant organophosphorus compounds (OPCs). Research into the synthesis of OPCs is driven by the desire to develop efficient and direct routes toward phosphines and phosphonium salts. However, such direct and catalytic procedures converting P₄ into valuable monophosphorus compounds remain to be scarce.^[1] The visible light-mediated photocatalytic transformation of P₄ into triarylphosphines (Ar₃P) and tetraarylphosphonium salts ([Ar₄P]⁺) has been previously reported by our group.^[2] This method utilized an iridium-based photocatalyst, aryl iodides as substrates, and triethylamine as both a sacrificial electron and H-atom donor. While the expensive iridium photocatalyst could be replaced by an organic alternative, the exclusive use of expensive and less available aryl iodides presented a major limitation of this protocol.^[3] Herein, we present the photocatalytic synthesis of Ar₃P and [Ar₄P]X (X = Br, Cl) directly from P₄ and readily available aryl bromides and chlorides. We have developed two independent protocols either using an acridinium-based or a 5-deazaflavin-based photocatalyst. The properties and scope of these new P₄ arylation systems have been studied. Furthermore, a reaction mechanism is proposed based on NMR spectroscopic monitoring studies and model reactions.

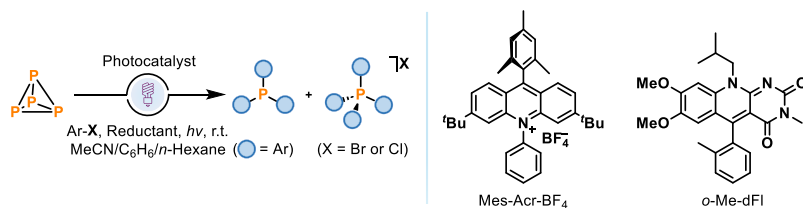


Figure 1: Photocatalytic functionalization of P₄ with arylbromides and -chlorides.

[1] D. J. Scott, *Angew. Chem. Int. Ed.* 2022, **61**, e202205019, DOI: 10.1002/anie.202205019.

[2] U. Lennert *et al.*, *Nat. Catal.* 2019, **2**, 1101-1106, DOI: 10.1038/s41929-019-0378-4.

[3] P. B. Arockiam *et al.*, *Chem. Eur. J.* 2020, **26**, 16374-16382, DOI: 10.1002/chem.202002646.