



# Photocatalytic stannylation of white phosphorus†

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Organophosphorus compounds (OPCs) are highly important chemicals, finding numerous applications in both academia and industry. Herein we describe a simple photocatalytic method for the stannylation of white phosphorus ( $P_4$ ) using a cheap, commercially-available distannane,  $(Bu_3Sn)_2$ , and anthraquinone as a simple photocatalyst. Subsequent 'one pot' transformation of the resulting stannylated monophosphine intermediate  $(Bu_3Sn)_3P$  provides direct, convenient and versatile access to valuable OPCs such as acylated phosphines and tetraalkylphosphonium salts.

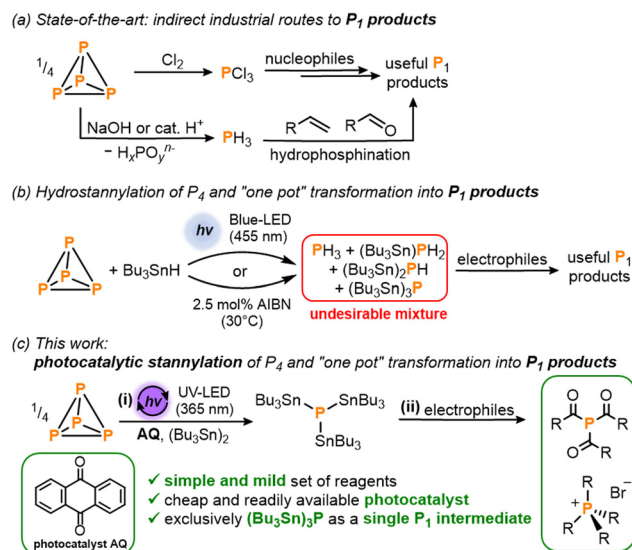
White phosphorus ( $P_4$ ) – the most chemically important allotrope of this ubiquitous and abundant element – acts as the common precursor from which all commercially valuable and academically important organophosphorus compounds (OPCs) are prepared. The current methods used for the industrial synthesis of these myriad useful  $P_1$  products include the oxidation of  $P_4$  with toxic  $Cl_2$  gas to generate  $PCl_3$  which can subsequently be transformed into a variety of OPCs by reaction with nucleophiles (Scheme 1a). As an alternative route, initial acid- or base-mediated disproportionation of  $P_4$  can be used to generate highly toxic  $PH_3$  gas which is then employed for the hydrophosphination of unsaturated organic substrates.<sup>1</sup>

Given the drawbacks of these methods, a highly prominent aim has long been to find ways of bypassing these multi-step procedures. In particular, there is a longstanding desire to develop more step-efficient *direct* – and, ideally, *catalytic* – methods to functionalize  $P_4$  and generate OPCs in a single reaction.

As a result, for several decades comprehensive efforts have been made to better understand the fundamental reactivity of  $P_4$ .<sup>2</sup> However, it is only very recently that it has finally become

possible to successfully transform  $P_4$  directly into a variety of useful  $P_1$  products.<sup>3</sup> Moreover, and despite these extensive investigations, the number of successful examples remains extremely low, and those that do exist still suffer from substantial limitations.<sup>4</sup> As such, there remains a clear need to expand the range of strategies available for direct, productive  $P_4$  activation, with new catalytic methods being particularly desirable.<sup>4a</sup>

In one of our own contributions to this area, we recently reported a simple 'one pot' method in which the classical radical reagent tri-*n*-butyltin hydride ( $Bu_3SnH$ ) is used for initial hydrostannylation of



**Scheme 1** (a) Current state-of-the-art industrial methods for the synthesis of valuable  $P_1$  products.<sup>1</sup> (b) Recently reported hydrostannylation of white phosphorus ( $P_4$ ) using  $Bu_3SnH$  followed by reaction with electrophiles to generate useful  $P_1$  products in a 'one-pot' fashion.<sup>5</sup> (c) This work: (i) photocatalytic stannylation of  $P_4$  using the photocatalyst anthraquinone (AQ) and hexabutylstannane ( $Bu_3Sn)_2$ ; and (ii) subsequent functionalization of the intermediate  $(Bu_3Sn)_3P$  with electrophiles into products such as triacylphosphines and tetraalkylphosphonium salts.

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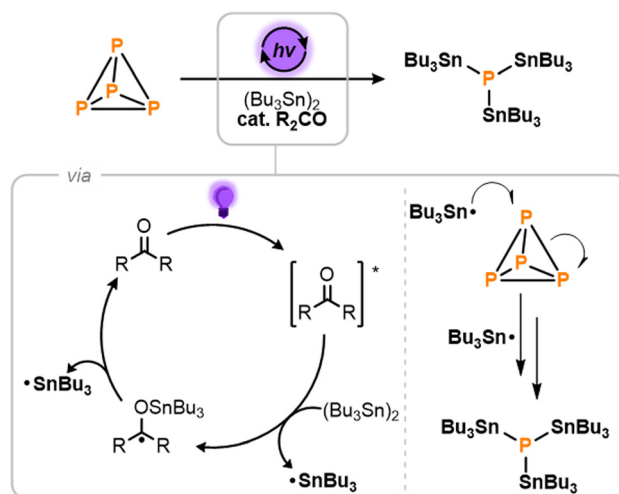
$P_4$  (Scheme 1b).<sup>5</sup> This reductive  $P_4$  activation is mediated either by light or by a chemical radical initiator such as AIBN (azobis(isobutyronitrile)) which can initiate a radical chain reaction that breaks down the  $P_4$  tetrahedron, yielding a mixture of hydrostannylated phosphines  $(Bu_3Sn)_xPH_{3-x}$  ( $x = 0-3$ ). Key to this mechanism is the attack of stannyl radicals ( $Bu_3Sn^\bullet$ ) on the P-P bonds of  $P_4$ . The resulting  $(Bu_3Sn)_xPH_{3-x}$  mixture can then be converted into a number of important and useful OPCs by reaction with electrophiles.<sup>5</sup>

Unfortunately, one significant disadvantage of this hydrostannylation strategy is the complexity of the  $(Bu_3Sn)_xPH_{3-x}$  mixture, which complicates 'downstream' reaction development by requiring functionalization of two different types of bond (P-Sn and P-H), both of which are distributed over four distinct molecules. Moreover, the presence of gaseous  $PH_3$  as a component of this mixture has been suggested to have a limiting effect on overall yields as it can easily be lost during subsequent manipulations,<sup>4a</sup> and it is also problematic from a safety perspective.

These drawbacks would be overcome if the initial  $P_4$  reduction step could instead furnish a single species with just one functionalizable motif, but with reactivity otherwise similar to  $(Bu_3Sn)_xPH_{3-x}$ . To achieve this, we describe herein a simple photocatalytic strategy for the atom-precise stannylation of  $P_4$  using the cheap, commercially-available distannane  $(Bu_3Sn)_2$  and simple benzophenone derivatives as photocatalysts (Scheme 1c). This new procedure generates exclusively the stannylated monophosphine  $(Bu_3Sn)_3P$  and subsequent, simplified 'one pot' transformations with electrophiles afford valuable OPCs including acylated phosphines and alkylated phosphonium salts.

Based on the analysis above, we sought to develop a new method by which  $P_4$  could be selectively transformed into  $(Bu_3Sn)_3P$  as the sole product.<sup>6</sup> It is worth noting that the closely related product  $(Ph_3Sn)_3P$  has previously been prepared from  $P_4$  using  $Ph_3SnCl$  as the stannylating reagent, but this required use of a relatively elaborate Ti(III) reagent as a halogen atom abstractor.<sup>3f</sup> Instead, we imagined that an ideal reagent for such a reaction would be the distannane  $(Bu_3Sn)_2$ , which is cheap to purchase and could in principle provide the target phosphine with perfect atom economy.<sup>7</sup> Indeed, Sn-Sn homolysis of  $(Bu_3Sn)_2$  is known to furnish  $Bu_3Sn^\bullet$  radicals, which previous work has shown are capable of adding to  $P_4$ .<sup>3f,5</sup> However, achieving this homolysis directly requires extreme temperatures or very high energy UV light irradiation that is known to lead to unselective reactivity, and is also unlikely to be compatible with  $P_4$ .<sup>8-10</sup> Fortunately, it has been reported that simple ketones can be used as photocatalysts to access  $Bu_3Sn^\bullet$  radicals by Sn-Sn bond cleavage under much lower energy irradiation.<sup>11</sup>

The light-driven photocatalytic stannylation of  $P_4$  was therefore targeted, based on the mechanistic proposal outlined in Scheme 2.<sup>9</sup> It was anticipated that photoirradiation of the ketone  $R_2CO$  would first provide an excited state,  $[R_2CO]^*$ ,<sup>12</sup> capable of reacting with  $(Bu_3Sn)_2$  to generate a stannylated ketyl radical and a free  $Bu_3Sn^\bullet$  radical.<sup>11</sup> The former could then



**Scheme 2** Proposed mechanism for the light-driven, photocatalytic stannylation of  $P_4$  in the presence of hexabutyldistannane,  $(Bu_3Sn)_2$ , and a ketone photocatalyst,  $R_2CO$ .

thermally release a second  $Bu_3Sn^\bullet$  radical to close the catalytic cycle. Once formed, these  $Bu_3Sn^\bullet$  radicals would then add to the P-P bonds of  $P_4$ , ultimately breaking it down to generate  $(Bu_3Sn)_3P$  as the only  $P_1$  product.<sup>13</sup>

To begin, benzophenone (**BP**) was chosen as a proof-of-principle photocatalyst due to both its simplicity and the fact that its photoreactivity towards hexaalkyldistannanes has been studied previously.<sup>11d</sup> Gratifyingly, after an initial optimization the photocatalytic stannylation of  $P_4$  could successfully be achieved, with use of 25 mol% **BP** (all stoichiometries, in both equiv. and mol%, are defined per P atom) and a 3.3-fold excess (5 equiv.) of  $(Bu_3Sn)_2$  providing 50% conversion to the target stannylated phosphine  $(Bu_3Sn)_3P$  after stirring under near UV LEDs overnight (Scheme 3; see also ESI,† S3). Control experiments confirmed that all reaction components ( $P_4$ ,  $(Bu_3Sn)_2$ , **BP**, irradiation) were necessary for the reaction to proceed productively (see ESI,† S3, Table S1).

These initial results provided a clear proof-of-principle for the proposed mechanistic strategy. Notably, the observed conversion indicates the activation of at least three Sn-Sn bonds per available equivalent of **BP**,<sup>14</sup> making this a rare example of a system where  $P_4$  activation has been achieved catalytically, using an otherwise inert substrate.<sup>5,9a,9b,9e,15</sup> Nevertheless, in order to improve the reaction outcome further, a broader range of benzophenone derivatives was subsequently screened, with several found to provide markedly improved performance (see ESI,† S5). Particularly impressive results were achieved using



**Scheme 3** Initial conditions for the direct, photocatalytic stannylation of  $P_4$  into  $(Bu_3Sn)_3P$  optimized using benzophenone (**BP**) as photocatalyst. Stoichiometries in equiv. and mol% are defined per P atom.





**Scheme 4** Optimized conditions for the direct, photocatalytic stannylation of  $P_4$  into  $(Bu_3Sn)_3P$  using anthraquinone (AQ) as photocatalyst. Stoichiometries in equiv. and mol% are defined per P atom.

anthraquinone (AQ) and following brief further optimization (see ESI,† S5 and S7) 79% conversion to  $(Bu_3Sn)_3P$  could be achieved using significantly reduced loadings of both AQ (12.5 mol%) and  $(Bu_3Sn)_2$  (3 equiv.) over the same timeframe (Scheme 4; see also ESI,† S7). Based on the catalytic cycle proposed in Scheme 2, this would correspond to a turnover number (TON) of 10.0 for AQ. Further reductions in catalyst loading to 6.3 mol% or 2.5 mol% were found to lead to even higher TONs (16.8 and 28.2, respectively), albeit at the cost of lower overall conversions (see ESI,† S7, Table S11).

With the stannylation of  $P_4$  optimized, attention was then shifted to its subsequent, 'one pot' transformation into other useful  $P_1$  products. Having previously developed procedures for the analogous transformation of the phosphine mixture  $(Bu_3Sn)_xPH_{3-x}$ , which includes  $(Bu_3Sn)_3P$  as a minor component, it was anticipated that addition of electrophiles to photocatalytically-generated  $(Bu_3Sn)_3P$  should be similarly productive,<sup>4,5</sup> especially since neither the AQ photocatalyst nor the  $(Bu_3Sn)_2$  starting material is expected to show appreciable reactivity towards such substrates. And, indeed, *in situ* addition of a variety of acid chlorides yielded the corresponding triacylphosphines  $(R(O)C)_3P$  ( $R = Ph, Cy, Ad, tBu, iPr, nBu, Me$ ) with good conversions of up to 75% (Scheme 5a(i)).<sup>5,16</sup> Notably, and in comparison to our previously-reported hydrostannylation system, no exclusion of light and no additional base were required for this step, highlighting both the robustness and simplicity of  $(Bu_3Sn)_3P$  as a " $P^3-$ " synthon, relative to  $(Bu_3Sn)_xPH_{3-x}$ .

Similarly, reaction of  $(Bu_3Sn)_3P$  with alkyl bromides  $RBr$  ( $R = Bn, Et$ ) under moderate heating successfully provided

'one pot' access to the corresponding phosphonium salts,  $[R_4P]Br$ , including tetrabenzylphosphonium bromide,  $[Bn_4P]Br$ , which is a known precursor for useful Wittig chemistry (Scheme 5a(ii)).<sup>17</sup> Again, no auxiliary base was required for these reactions, in contrast to the analogous procedures *via*  $(Bu_3Sn)_xPH_{3-x}$  where the absence of base leads to a 50% reduction in yield.<sup>5</sup>

Finally, another industrially important class of  $P_1$  products was targeted. Hydroxymethyl-substituted phosphine derivatives are used as flame-retardant materials (among a number of other applications),<sup>18</sup> and could be accessed by reacting the stannylated monophosphine  $(Bu_3Sn)_3P$  with paraformaldehyde in EtOH to furnish tris(hydroxymethyl)phosphine, THP ( $THP$ ; Scheme 5a(iii)).<sup>18a</sup> Subsequent exposure to air then yielded the corresponding phosphine oxide,  $(HOCH_2)_3PO$  ( $THPO$ ; Scheme 5a(iv)),<sup>18b</sup> while the phosphonium salt tetrakis(hydroxymethyl)phosphonium chloride,  $[(HOCH_2)_4P]Cl$  ( $THPC$ ),<sup>18c,18d</sup> could be accessed by quenching the *in situ* generated THP with HCl, all in one pot (Scheme 5a(v)).

To demonstrate the viability of these reactions on a preparative scale the triacylphosphine  $(Ph(O)C)_3P$  and the phosphonium salts  $[Bn_4P]Br$  and THPC were selected as representative examples for isolation (Scheme 5b; see ESI† S9). At 0.8 mmol scale  $(PhC(O))_3P$  could be isolated in 55% yield,<sup>19</sup> which compares well with our previously-reported hydrostannylation method (51%).  $[Bn_4P]Br$  could also be isolated in good 56% yield, and THPC in a more modest yield of 33%.<sup>19</sup>

For this last reaction, efforts were also made to recover the Sn-containing compounds present at the end of the reaction. We have previously shown that for the analogous synthesis of THPC *via*  $(Bu_3Sn)_xPH_{3-x}$  recovery of the  $Bu_3SnCl$  byproduct allows for convenient regeneration and recycling of the  $Bu_3SnH$  starting material, thus minimizing the formation of organotin-containing waste.  $Bu_3SnCl$  can also be used to regenerate  $(Bu_3Sn)_2$  through a net one-electron reduction,<sup>8</sup> meaning similar recycling should be feasible for this newer system, provided  $Bu_3SnCl$  can again be cleanly recovered. Satisfyingly,  $Bu_3SnCl$  could indeed be recovered during THPC workup through simple washing with diethyl



**Scheme 5** (a) One-pot synthesis directly from  $P_4$ , via photocatalytically generated  $P_1$  intermediate  $(Bu_3Sn)_3P$ , of (i) triacylphosphines  $(R(O)C)_3P$  (4 equiv.  $RC(O)Cl$ ,  $R = tBu, Ph, Me, nBu, Cy, iPr, Ad$ ), (ii) phosphonium salts  $[R_4P]Br$  (5 equiv.  $RBr$ ,  $R = Bn, Et$ ,  $60-80^\circ C$ ), (iii) tris(hydroxymethyl)phosphine, THP ( $EtOH$ , 3 equiv. paraformaldehyde), (iv) tris(hydroxymethyl)phosphine oxide, THPO (as for (iii) then air,  $80^\circ C$ ), and (v) tetrakis(hydroxymethyl)phosphonium chloride, THPC (as for (iii) using 12.5 equiv. paraformaldehyde, then 10 equiv.  $HCl$ ); and (b) Isolated yields for reactions on preparative scale (0.8 mmol). Stoichiometries in equiv. are defined per P atom.





ether, being isolated as part of an otherwise clean mixture with unreacted  $(\text{Bu}_3\text{Sn})_2$  in an excellent overall yield of 92% (1.3:1 molar ratio, see ESI† S9).

In conclusion, we have developed a simple, new method for the direct transformation of  $\text{P}_4$  into a variety of commercially and academically interesting OPCs. The reaction proceeds through a photocatalytic stannylation of white phosphorus, which generates  $(\text{Bu}_3\text{Sn})_3\text{P}$  with perfect atom economy as a single, convenient  $\text{P}_1$  intermediate using an inexpensive, commercially available distannane and a simple photocatalyst. This method can be used to prepare a variety of different products through inclusion of a range of different electrophilic substrates, and we have demonstrated that the Sn-containing byproducts of the reaction can in principle be recovered and recycled. These results expand the currently very limited range of strategies that are available for the direct functionalization of  $\text{P}_4$ , and suggest the intriguing possibility that  $\text{P}_4$  activation might also be achievable by reaction with other weak E–E bonds under similar photocatalytic conditions.

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## Conflicts of interest

There are no conflicts to declare.

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