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## Water mediated synthesis of dialkylphosphine oxides from white phosphorus and *N*-(acyloxy) phthalimides†

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The multicomponent synthesis of dialkylphosphine oxides from  $P_4$  without a chlorination step is reported. With the use of *N*-(acyloxy)phthalimides (NHPI esters) as the alkylation reagents,  $H_2O$  as the oxygen source, tris(2,2'-bipyridine)ruthenium dichloride as a photocatalyst, 2,6-lutidine as a base, and *N,N*-dimethylacetamide as a solvent, the reactions are performed under green light irradiation, yielding the desired products in moderate to good yields. Notably, this catalytic system is also capable of synthesizing  $\alpha$ -hydroxy phosphine oxides from  $P_4$  in one-pot. This two step-economic approach, which directly utilizes  $P_4$  as the P-atom source, avoids the traditional chlorination stage and oxidation processes.

## Introduction

Organophosphorus compounds (OPCs) containing C-P bonds are ubiquitous in both industrial and academic fields, such as materials science, pharmaceutical chemistry, catalysis, and coordination chemistry.<sup>1</sup> In general, the preparation of OPCs predominately relies on white phosphorus ( $P_4$ ) as the source of P atoms.<sup>2</sup> However, the conversion of  $P_4$  to OPCs involves (oxy) chlorination process and uses corrosive chlorine gas ( $Cl_2$ ) and intermediates such as  $PCl_3/PCl_5/POCl_3$ . Another approach toward OPCs is the hydrophosphinylation of alkenes with toxic and explosive  $PH_3$ .<sup>3</sup> To circumvent the use of  $PCl_3$  and  $PH_3$ , significant progress has been made in forming of heteroatom-P bonds, such as S-P bonds<sup>4</sup> or O-P bonds<sup>5</sup> from  $P_4$  (Scheme 1).

Dialkyl phosphine oxides [ $R_2P(O)H$ ] containing reactive P(O)-H bonds are versatile building blocks for synthesizing trialkyl phosphine oxides such as  $\alpha$ -hydroxy phosphine oxides. The direct transformation of  $P_4$  into tertiary phosphines ( $PR_3$ ) and their oxides containing the same three alkyl/aryl groups was investigated by the Cummins, Wolf, and Zhang groups

and others.<sup>6</sup> Due to the complex P-P bond breaking patterns, it is still challenging to construct  $R_2P(O)H$  containing both C-P and P(O)-H bonds directly from  $P_4$  with good selectivity. In 2022, our group made a breakthrough and published the paper entitled “Decarboxylative Selective Phosphorylation of Aliphatic Acids: A Transition-Metal- and Photocatalyst-Free Avenue to Dialkyl and Trialkyl Phosphine Oxides from White Phosphorus”.<sup>7a</sup> Since then, we have reported the selective construction of  $R_2P(O)H$  from  $P_4$  with alkyl bromides and iodides.<sup>7b,c</sup> All these experiments required excess alkylation reagents. Furthermore, strict anhydrous operation and subsequent oxidation workup were needed (Scheme 1B).

One-pot multicomponent reactions enable the efficient and atom-economical synthesis of OPCs directly from  $P_4$ . Significant progress has been made in multicomponent reactions for the synthesis of P-heteroatom bonds (Scheme 1A).<sup>8</sup> In 2020, the first general synthesis of mixed phosphorothioates involving  $P_4$ , disulfides, KOH, and alkyl halides was presented.<sup>8a</sup> In 2022, we described a four-component functionalization of  $P_4$  with disulfides, amines and KOH to synthesize phosphoramidodithioates.<sup>8b</sup> In 2023, we published a one-pot direct synthesis of tetra-thiophosphates from  $P_4$ , NaSH, disulfides and alkyl halides with sodium alkyltetra-thiophosphates as the key intermediates.<sup>8c</sup> In 2024, we presented the first copper-catalyzed three-component reaction for generating phosphorothioates from  $P_4$ , disulfides, and alcohols in a single reaction step.<sup>8d</sup>

To construct C-P bonds, many novel phosphorus transfer reagents have been developed in recent years.<sup>9</sup> From the perspective of step-economy, it is highly appealing to directly convert  $P_4$  into OPCs in one-pot process without the use of phosphorus transfer reagents. Compared to the research of P-heteroatom bonds formation, few multicomponent reactions

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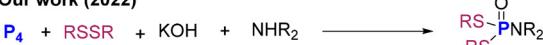
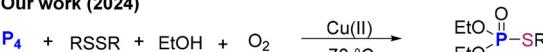
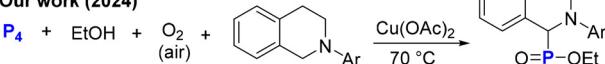
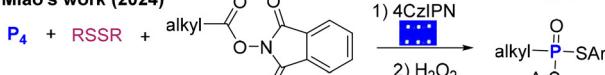
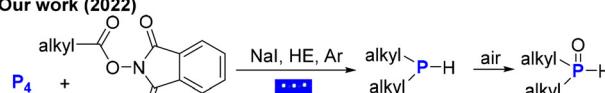
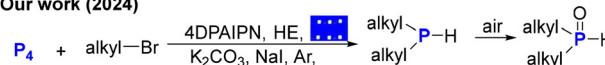
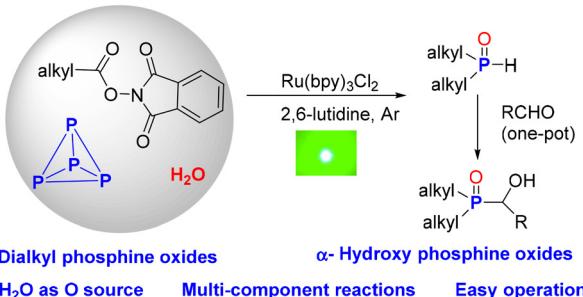
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† Electronic supplementary information (ESI) available: Experimental procedures for the synthesis, spectral data and NMR spectra of compounds 3a-3o and 4a-4l. See DOI: <https://doi.org/10.1039/d4qo02447h>

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**A) Multi-component reactions for P-Hetero bonds****Our work (2020)****Our work (2022)****Our work (2023)****Our work (2024)****B) Multi-component reactions for P-Carbon bonds****Our work (2024)****Miao's work (2024)****C) Synthesis of dialkyl phosphines****Our work (2022)****Our work (2023)****Our work (2024)****D) This work: Multi-component reactions for dialkyl phosphine oxides****Scheme 1** Multi-component reactions with  $\text{P}_4$ .

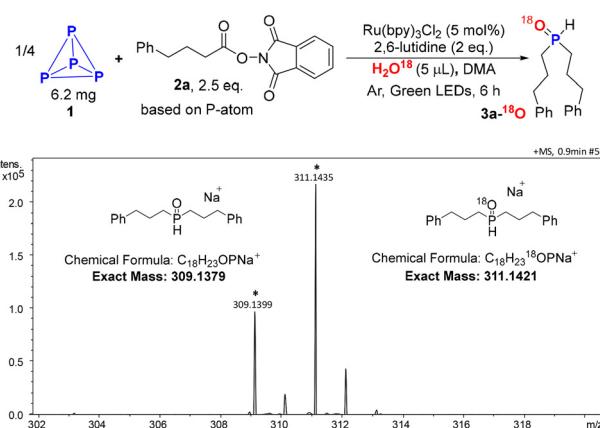
for the construction of C-P bonds have been explored (Scheme 1C). In 2024, the first multicomponent oxidative  $\alpha$ -phosphonylation of amines with  $\text{P}_4$  and alcohols was developed.<sup>10a</sup> In the same year, Miao *et al.* reported a visible light-induced three-component reaction integrating  $\text{P}_4$ , disulfides, and *N*-(acyloxy)phthalimides (NHPI esters) to produce alkyl-substituted phosphonodithioates.<sup>10b</sup>

As a continuum of our efforts in  $\text{P}_4$  chemistry, we envisioned that with the use of  $\text{H}_2\text{O}$  as the oxygen source, and *N*-(acyloxy)phthalimides as the carbon source,  $\text{R}_2\text{P}(\text{O})\text{H}$  could be directly synthesized from  $\text{P}_4$  under an argon atmosphere without additional oxidation processes (Scheme 1D).

**Results and discussion**

To verify our conjecture, we commenced our project by employing  $\text{H}_2^{18}\text{O}$ , and 4-phenylbutanic acid NHPI ester (**2a**) as model substrates to direct functionalization of  $\text{P}_4$  (**1**). When a solution of **1** (6.20 mg),  $\text{H}_2^{18}\text{O}$  (5  $\mu\text{L}$ ), **2a** (0.5 mmol, 2.5 equivalents per P-atom), 2,6-lutidine in *N,N*-dimethylacetamide (DMA) was irradiated by green LEDs at room temperature for 6 h in the presence of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  under argon atmosphere, **3a-18O** was obtained as the main product (Scheme 2).

Inspired by this result, we began optimizing the conditions for the synthesis of  $\text{R}_2\text{P}(\text{O})\text{H}$  **3a** using  $\text{H}_2\text{O}$  as the oxygen source. After extensive screening of bases, solvents, and catalysts, the desired product **3a** was obtained in 90% yield (entry 1 in Table 1). No  $\text{R}_2\text{P}(\text{O})\text{H}$  and  $\text{R}_2\text{PH}$  were obtained in the

**Scheme 2** Water-<sup>18</sup>O as the O-resource.**Table 1** Synthesis of  $(\text{PhCH}_2\text{CH}_2\text{CH}_2)_2\text{P}(\text{O})\text{H}$  (**3a**)<sup>a</sup>

Entry	Deviation from standard conditions	Yield (%)
1 <sup>b</sup>	Standard conditions	94 (90)
2	Without $\text{H}_2\text{O}$	Trace
3	$\text{H}_2\text{O}$ (0.5 eq.)	13
4	DIPEA, DABCO instead of 2,6-lutidine	60–70
5	NMP instead of DMA	89
6	DMF, DMSO, MeCN instead of DMA	32–49
7	Other organo-PC	0–70
8	Air instead of Ar	0
9	No light or PC	0

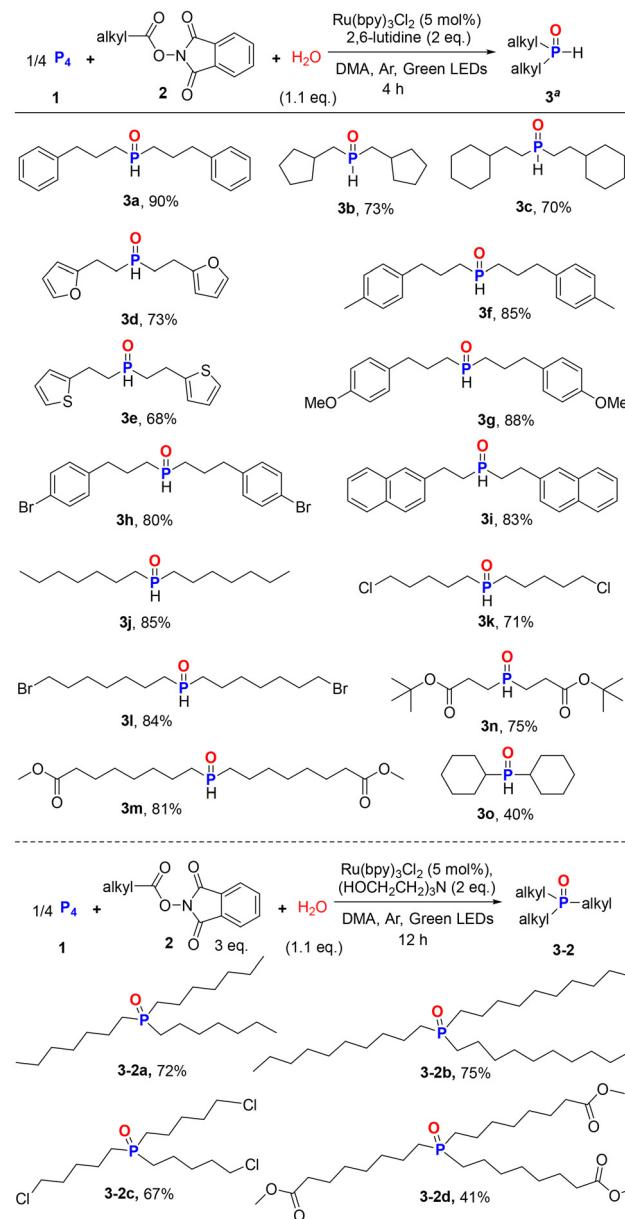
<sup>a</sup> Reaction conditions: **1** (6.20 mg, 0.20 mmol of P atom, a 0.74 M solution of **1** in toluene, 0.27 mL), **2a** (2.5 equivalents per P-atom),  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (0.01 mmol, 5 mol%),  $\text{H}_2\text{O}$  (1.1 eq., 4  $\mu\text{L}$ ), 2,6-lutidine (0.40 mmol, 2 eq.) in DMA (1 mL) irradiated by green LEDs (2  $\times$  3 W, 565–575 nm) at room temperature for 6 h under argon atmosphere. Yield of **3a** was determined by the  $^{31}\text{P}\{^1\text{H}\}$  NMR analysis of the crude reaction mixture using  $(\text{C}_6\text{H}_5\text{O})_3\text{P}(\text{O})$  as an internal standard. <sup>b</sup> Isolated yield in parenthesis. PC = photocatalyst.

absence of  $\text{H}_2\text{O}$  (entry 2). Increasing the amount of  $\text{H}_2\text{O}$  to 0.5 equivalents gave **3a** but in only 13% yield (entry 3). Using  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2\text{O}$  as the *O*-resources verified that water was the key starting material in this transformation. Other bases, such as DIPEA and DABCO, resulted in lower yield of **3a** (entry 4). DMA and NMP were found to be good solvents for this reaction (entry 5), while other polar solvents, such as DMF, DMSO, and MeCN, led to much lower yields (entry 6). When transition-metal-free photocatalysts were tested, most performed poorly (entry 7), although  $\text{Na}_2\text{-eosin Y}$  gave the product in 70% yield. No C-P bond formation was observed when the reaction was conducted under air conditions (entry 8). The reaction was inhibited in the absence of either photocatalyst or light (entry 9).

After optimizing the reaction conditions for the synthesis of **3a**, we explored the scope of carboxylic acids for the synthesis of structurally diverse  $\text{R}_2\text{P}(\text{O})\text{H}$  **3** (Scheme 3). Under photoirradiation conditions, various alkyl acid NHPI esters can participate in this process, providing the desired products in good yields. 2-Cyclopentylacetic acid and 3-cyclohexylpropanoic acid NHPI esters gave products **3b** and **3c** in 73% and 70% yields, respectively. Linear acid NHPI esters with heterocyclic rings such as O-heterocycle (**3d**), S-heterocycle (**3e**) underwent phosphorylation without difficulty. Aryl-substituted linear acid NHPI esters with electron donating groups (methyl, methoxy, naphthalene) or electron withdrawing group (bromo) on the benzene ring gave **3f**–**3i** in 80–88% yields. Simple primary saturated fatty acid ester gave **3j** in 85% yield. Furthermore, a range of synthetically useful functional groups, such as  $\text{C}(\text{sp}^3)\text{-Cl}$ ,  $\text{C}(\text{sp}^3)\text{-Br}$ , and ester (**3m** and **3n**), were also compatible with the mild conditions, providing respective dialkyl phosphine oxides in 71–85% yields. Due to steric hindrance, cyclohexanecarboxylic acid ester produced dicyclohexylphosphine oxide in a low yield (**3o**, 40%). When linear secondary or tertiary carbon radical precursors were employed, no C-P bonds were formed. In these failed experiments, white phosphorus remained completely ( $\delta = -529$  ppm). It is speculated that the sharp decrease in the yield of secondary and tertiary carbon free radical reactions may be due to the stability and steric hindrance effect of their free radicals.

We then speculated about whether this water mediated multicomponent strategy could be used to produce valuable trialkyl phosphine oxides (Scheme 3). With  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  as the best catalyst and trolamine as the best base, the reaction was performed for 12 h to afford the desired product **3-2a** in 72% yield. A series of chain primary fatty acid ester selected as substrates provided the corresponding trialkyl phosphine oxides **3-2b**–**3-2d** in satisfactory yields.

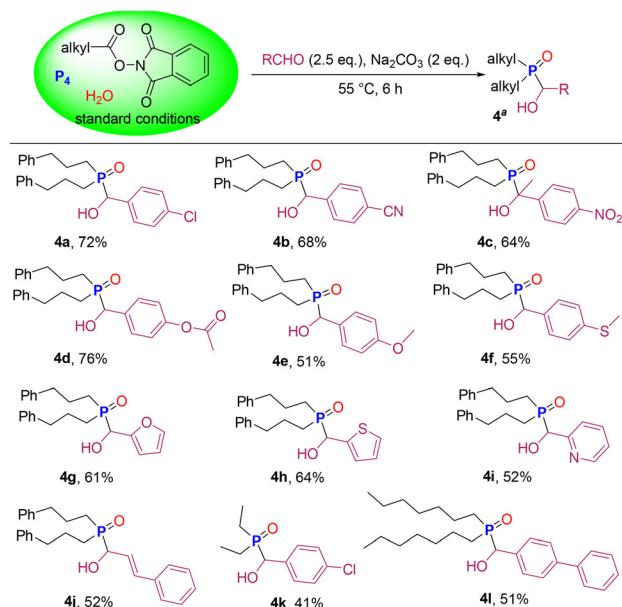
Dialkyl phosphine oxides are often used as starting materials for the preparation of various organophosphorus compounds. Encouraged by the findings described above, we continued to explore the one-pot synthesis of  $\alpha$ -hydroxy phosphine oxides from  $\text{P}_4$ , avoiding the purification process of  $\text{R}_2\text{P}(\text{O})\text{H}$  and the use of dangerous  $\text{Cl}_2$  and  $\text{PCl}_3$ . Pleasingly, we added aldehydes and  $\text{Na}_2\text{CO}_3$  to the crude product **3a** solution to produce  $\alpha$ -hydroxy phosphine oxides in good yields



**Scheme 3** Scope of alkyl acid *N*-hydroxyphthalimide esters for the synthesis of dialkyl/trialkyl phosphine oxides.

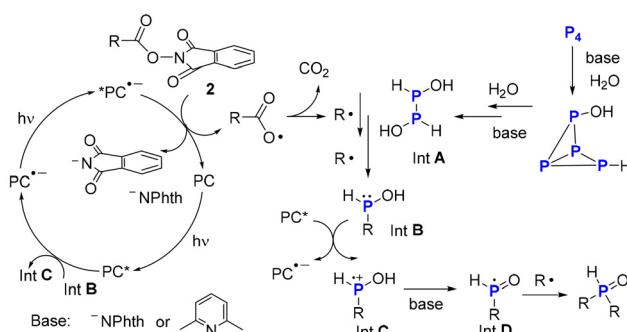
(Scheme 4). Benzaldehyde with electron withdrawing group ( $-\text{Cl}$ ,  $-\text{CN}$ , and  $-\text{NO}_2$ ) and electron donating groups ( $-\text{OCOCH}_3$ ,  $-\text{OCH}_3$ , and  $-\text{SCH}_3$ ) provided the corresponding products in yields of 51–76% (**4a**–**4f**). When aromatic heterocyclic formaldehydes such as furan-2-carbaldehyde, thiophene-2-carbaldehyde and pyridine-2-carbaldehyde were employed as substrates, products **4g**–**4i** were obtained in the range of 52–64%. Cinnamaldehyde, with a double bond, afforded the product **4j** in 52% yield. This method was found to be compatible with primary saturated fatty acid esters. Decarboxylative phosphorylation of propionic acid NHPI ester followed by nucleophilic addition reaction of aldehyde gave product **4k** in 41% yield. Long-chain *n*-octoic acid NHPI ester



Scheme 4 One-pot synthesis of  $\alpha$ -hydroxy phosphine oxides from  $P_4$ .

successfully participated in this one-pot synthesis of  $\alpha$ -hydroxy phosphine oxide **4l**.

Furthermore, *in situ* NMR studies on the reaction of NHPI ester **2a** and  $P_4$  were conducted and the corresponding  $^{31}P\{^1H\}$  NMR spectra were shown in Fig. 1–3 (see ESI $\dagger$ ). When the reaction mixture was irradiated by white light-emitting diodes (LEDs) for 30 min, the signal of the product **3a** and byproduct ( $RP(O)(OH)H$ ) appeared. No  $RPH_2$  or  $R_2PH$  was detected. Based on these results and previous studies,<sup>7</sup> a tentative mechanism for the photoinduced functionalization of  $P_4$  was proposed (Scheme 5). Initially, water breaks the P–P bond of  $P_4$  in a manner like super-basic systems ( $OH^-$  in DMSO) to yield intermediate **A**.<sup>11</sup> Subsequently, the alkyl radical breaks the P–P bond of intermediate **A** to give an unstable intermediate **B**, which then reacts with excited  $PC^*$  and base to form the phosphinoyl radical **D**. Radical **D** can directly combine with another  $R^*$  yields  $R_2P(O)H$  as the main product of the reaction.



Scheme 5 Proposed reaction mechanism.

## Conclusions

In conclusion, we developed the first water mediated multi-component synthesis of dialkylphosphine oxides and  $\alpha$ -hydroxy phosphine oxides from  $P_4$  without a chlorination step. With the use of *N*-(acyloxy)phthalimides as the alkylation reagents,  $H_2O$  as the oxygen source, the reactions are performed under green light irradiation. The desired dialkylphosphine oxides [ $R_2P(O)H$ ] can be directly synthesized from  $P_4$  under argon atmosphere without additional oxidation processes in moderate to good yields. Advantageously, the catalytic system can also synthesize  $\alpha$ -hydroxy phosphine oxides from  $P_4$ . These step-economic approaches use  $P_4$  as the P-atom source, avoiding the traditional chlorination stage and oxidation processes.

## Experimental

### Synthesis of dialkyl phosphine oxides from white phosphorus

A Schlenk tube containing  $Ru(bpy)_3Cl_2$  (6.4 mg, 0.01 mmol, 5 mol%) and *N*-(acyloxy)phthalimides (0.50 mmol, 2.5 eq.) was evacuated and purged with argon three times.  $P_4$  (6.20 mg, 0.20 mmol of P atom, a 0.74 M solution of  $P_4$  in toluene, 0.27 mL),  $H_2O$  (1.1 eq., 4  $\mu$ L), 2,6-lutidine (0.40 mmol, 2 eq.) and DMA (1 mL) were sequentially added to the system at room temperature. Then the reaction mixture was stirred at room temperature under the irradiation of 6 W green LEDs (565–575 nm) for 6 h. Afterwards, the reaction mixture was quenched with the addition of saturated brine (0.5 mL), and extracted with ethyl acetate ( $3 \times 10$  mL). The combined organic layer was dried over anhydrous  $Na_2SO_4$  and then removed in a vacuum. The residue was purified by flash chromatography using DCM/MeOH (from 40:1 to 20:1, v/v) as the eluent to afford the desired dialkyl phosphine oxides **3a–3o**.

### One-pot synthesis of $\alpha$ -hydroxy phosphine oxides from white phosphorus

After the above-mentioned reaction mixture was stirred at room temperature under the irradiation of 6 W green LEDs (565–575 nm) for 6 h without any work-up, aldehyde (0.50 mmol, 2.5 eq.) and  $Na_2CO_3$  (42.40 mg, 0.4 mmol, 2.0 eq.) were added in air. The reaction mixture was stirred for 22 hours at 55 °C for 6 hours. After completion, saturated brine (0.5 mL) was added; the mixture was diluted by EtOAc (10.0 mL). The mixture was extracted with ethyl acetate ( $3 \times 10$  mL). The combined organic layer was dried over anhydrous  $Na_2SO_4$  and then removed in a vacuum. The residue was purified by flash chromatography using DCM/MeOH (from 40:1 to 10:1, v/v) as the eluent to afford the desired  $\alpha$ -hydroxy phosphine oxides **4a–4l**.

## Data availability

The data supporting this article have been included as part of the ESI. $\dagger$



## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## References

- 1 H. Guo, Y. C. Fan, Z. Sun, Y. Wu and O. Kwon, Phosphine organocatalysis, *Chem. Rev.*, 2018, **118**, 10049–10293.
- 2 (a) D. J. Scott, Recent breakthroughs in P4 chemistry: towards practical, direct transformations into P1 compounds, *Angew. Chem.*, 2022, **134**, e202205019; (b) X. Huangfu, Z. Wang, Y. Chen, J. Wei, W. Liu and W. Zhang, Recent progress on the functionalization of white phosphorus in China, *Natl. Sci. Rev.*, 2024, **11**, nwae162.
- 3 R. Rothfelder, V. Streitferdt, U. Lennert, J. Cammarata, D. J. Scott, K. Zeitler, R. M. Gschwind and R. Wolf, Photocatalytic arylation of P<sub>4</sub> and PH<sub>3</sub>: reaction development through mechanistic insight, *Angew. Chem., Int. Ed.*, 2021, **60**, 24650–24658.
- 4 (a) G. Lu, J. Chen, X. Huangfu, X. Li, M. Fang, G. Tang and Y. Zhao, Visible-light-mediated direct synthesis of phosphorotriethioates as potent anti-inflammatory agents from white phosphorus, *Org. Chem. Front.*, 2019, **6**, 190–194; (b) X. Huangfu, Y. Wang, G. Lu, Y. Cao, G. Tang and Y. Zhao, Direct synthesis of phosphorotriethioites and phosphorotriethioates from white phosphorus and thiols, *Green Chem.*, 2020, **22**, 5303–5306.
- 5 (a) Z. Cai, X. Zeng, Y. Zhang, Y. Liu, G. Tang and Y. Zhao, Direct synthesis of dialkylphosphites from white phosphorus, *Adv. Synth. Catal.*, 2022, **364**, 2916–2921; (b) Z. Cai, Y. Zhang, Y. Cao, Y. Liu, G. Tang and Y. Zhao, Ternary photoredox/nickel/halide catalysis for the phosphorylation of alcohols with white phosphorus, *ACS Catal.*, 2023, **13**, 8330–8335; (c) Y. Zhang, Z. Cai, Y. Chi, X. Zeng, S. Chen, Y. Liu, G. Tang and Y. Zhao, Diphenyl diselenide-catalyzed synthesis of triaryl phosphites and triaryl phosphates from white phosphorus, *Org. Lett.*, 2021, **23**, 5158–5163.
- 6 (a) B. M. Cossairt and C. C. Cummins, Radical synthesis of trialkyl, triaryl, trisilyl and tristannyl phosphines from P<sub>4</sub>, *New J. Chem.*, 2010, **34**, 1533–1536; (b) U. Lennert, P. B. Arockiam, V. Streitferdt, D. J. Scott, C. Rödl, R. M. Gschwind and R. Wolf, Direct catalytic transformation of white phosphorus into arylphosphines and phosphonium salts, *Nat. Catal.*, 2019, **2**, 1101–1106; (c) M. Till, V. Streitferdt, D. J. Scott, M. Mende, R. M. Gschwind and R. Wolf, Direct catalytic transformation of white phosphorus into arylphosphines and phosphonium salts, *Chem. Commun.*, 2022, **58**, 1100–1103; (d) X. Huangfu, W. Liu, H. Xu, Z. Wang, J. Wei and W. Zhang, Photochemical benzylation of white phosphorus, *Inorg. Chem.*, 2023, **62**, 12009–12017; (e) Y. Chen, W. Liu, X. Huangfu, J. Wei, J. Yu and W. Zhang, Direct synthesis of phosphoryltriacetates from white phosphorus via visible light catalysis, *Chem. – Eur. J.*, 2023, **29**, e202302289.
- 7 (a) F. Chen, M. Bai, Y. Zhang, W. Liu, X. Huangfu, Y. Liu, G. Tang and Y. Zhao, Decarboxylative selective phosphorylation of aliphatic acids: a transition-metal- and photocatalyst-free avenue to dialkyl and trialkyl phosphine oxides from white phosphorus, *Angew. Chem., Int. Ed.*, 2022, **61**, e202210334; (b) F. Chen, J. Peng, Y. Ying, Y. Cao, P. Xu, G. Tang and Y. Zhao, Metal-free visible-light-induced phosphorylation of unactivated alkyl iodides with white phosphorus as the P-atom source, *Green Chem.*, 2023, **25**, 6629–6634; (c) J. Peng, A. Wang, Y. Liu, F. Chen, G. Tang and Y. Zhao, Selective functionalization of white phosphorus with alkyl bromides under photocatalytic conditions: a chlorine-free protocol to dialkyl and trialkyl phosphine oxides, *Org. Lett.*, 2024, **26**, 9316–9321.
- 8 (a) X. Huangfu, Y. Zhang, P. Chen, G. Lu, Y. Cao, G. Tang and Y. Zhao, Synthesis of mixed phosphorotriethioates from white phosphorus, *Green Chem.*, 2020, **22**, 8353–8359; (b) Y. Zhang, Y. Cao, Y. Chi, S. Chen, X. Zeng, Y. Liu, G. Tang and Y. Zhao, Formation of N-P(O)-S bonds from white phosphorus via a four-component reaction, *Adv. Synth. Catal.*, 2022, **364**, 2221–2226; (c) J. He, S. Shi, Y. Zhang, Y. Zhang, P. Xu, G. Tang and Y. Zhao, Synthesis of tetrathiophosphates from white phosphorus, *Chin. J. Chem.*, 2023, **41**, 2311–2316; (d) Y. Cao, M. Bai, J. Huang, F. Chen, Y. Liu, G. Tang and Y. Zhao, Three-component coupling reaction of white phosphorus, alcohols and diaryl disulfides: A chlorine-free avenue for accessing phosphorothioates, *Green Chem.*, 2024, **26**, 477–482.
- 9 (a) D. J. Scott, J. Cammarata, M. Schimpf and R. Wolf, Synthesis of monophosphines directly from white phosphorus, *Nat. Chem.*, 2021, **13**, 458–464; (b) M. Till, J. Cammarata, R. Wolf and D. J. Scott, Photocatalytic stanylation of white phosphorus, *Chem. Commun.*, 2022, **58**, 8986–8989; (c) M. Donath, K. Schwedtmann, T. Schneider, F. Hennersdorf, A. Bauza, A. Frontera and J. J. Weigand, Direct conversion of white phosphorus to versatile phosphorus transfer reagents via oxidative onioation, *Nat. Chem.*, 2022, **14**, 384–391; (d) Y. Mei, Z. Yan and L. L. Liu, Facile synthesis of the dicyanophosphide anion via electrochemical activation of white phosphorus: An avenue to organophosphorus compounds, *J. Am. Chem. Soc.*, 2022, **144**, 1517–1522.
- 10 (a) M. Bai, Y. Cao, J. Huang, Y. Liu, G. Tang and Y. Zhao, Direct synthesis of  $\alpha$ -aminophosphonates from amines, alcohols and white phosphorus, *CCS Chem.*, 2024, **6**, 91–99; (b) F. Wang, X. Zhang, J. Xu, Q. Shen, B. Jiang and



Z. Miao, Metal-free visible-light-induced direct synthesis of alkyl-substituted phosphonodithioates from white phosphorus ( $P_4$ ), *Adv. Synth. Catal.*, 2024, DOI: [10.1002/adsc.202401355](https://doi.org/10.1002/adsc.202401355).

11 B. A. Trofimov and N. K. Gusarova, Elemental phosphorus in strongly basic media as phosphorylating reagent: a dawn of halogen-free 'green' organophosphorus chemistry, *Mendeleev Commun.*, 2009, **19**, 295–305.

