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## Organophosphorus compounds

## A Direct Catalytic Synthesis of Sodium Diarylphosphinates and Their Corresponding Acids from Sodium Phosphinate

Laurian Botez,<sup>[a,b]</sup> G. Bas de Jong,<sup>[b]</sup> J. Chris Slootweg,<sup>[b]</sup> and Berth-Jan Deelman<sup>\*[a]</sup>

**Abstract:** In this contribution we present the direct conversion of sodium phosphinate ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ) to symmetrical sodium diarylphosphinates and their corresponding acids by using pal-

ladium catalysis. This route eliminates the need for chlorinated precursors, such as  $\text{PCl}_3$  and intermediate alkyl- or ammonium-phosphinates.

## Introduction

Organophosphinic acids  $\text{R}_2\text{P}(\text{O})\text{OH}$  ( $\text{R}$  = hydrocarbonyl group) and their esters and salts are relevant compounds in many fields: from flame retardants to solar cells and from ligands for catalysis to pharmaceutical applications and metal extraction.<sup>[1,2]</sup> They are interesting intermediates in the synthesis of other P-derivatives such as phosphines through reduction and/or functionalization.<sup>[3]</sup>

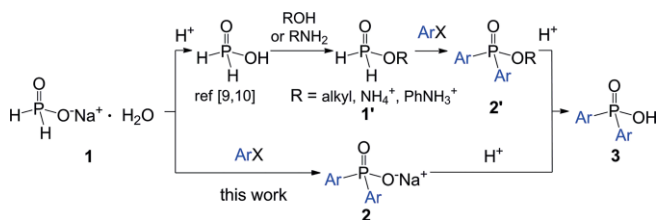
Current processes for the industrial production of organophosphinic acids and derivatives involve the use of phosphorus trichloride ( $\text{PCl}_3$ ) as starting material. Its availability is often taken for granted, but it should be realized that its production is energy-intensive and requires the use of chlorine gas, which carries inherent risks. Furthermore, arylation or alkylation is accomplished by using Grignard-, Michaelis–Arbuzov- or Michaelis–Becker-type coupling. These couplings start from *N,N*-dialkylphosphoramidic dichlorides ( $\text{R}_2\text{NP}(\text{O})\text{Cl}_2$ ) or *N,N*-dialkylphosphoramidic dichlorides [ $\text{R}_2\text{NP}(\text{O})\text{Cl}_2$ ] or alternatively involve the reaction of aryldiazonium fluoroborates with  $\text{PCl}_3$  in the presence of a catalyst ( $\text{CuBr}$ ).<sup>[4]</sup> These methods generally give suboptimal yields, often lead to mixtures, and also generate significant amounts of waste salts.

In an attempt to develop a more efficient and environmentally friendly<sup>[5]</sup> synthetic pathway for diarylphosphinic acids, we considered the direct arylation of sodium phosphinate [also known as sodium hypophosphite,  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  (**1**)]. By starting from this raw material, the use of chlorine gas can be eliminated, which potentially improves overall atom efficiency and reduces the risks associated with the process. Sodium phosphinate and its monohydrate are odorless, air- and water-stable solids, produced industrially at a multiton scale through basic hydrolysis of white phosphorus ( $\text{P}_4$ ) and mainly used in elec-

troless plating.<sup>[2]</sup> They are registered under REACH as non-hazardous compounds.<sup>[6]</sup> In synthesis, sodium phosphinate has been applied as a reducing agent<sup>[7]</sup> and for the hydrophosphination of alkenes and terminal alkynes.<sup>[8]</sup>

## Results and Discussion

Inspired by previous work on diarylphosphinate synthesis,<sup>[9,10]</sup> we investigated the direct arylation of sodium phosphinate **1** to sodium diarylphosphinates **2** (Scheme 1, bottom route). Diarylphosphinates **2'** have been prepared from **1** before, but only indirectly through the corresponding esters or ammonium salts **1'**, which require at least two additional steps to generate diarylphosphinic acids **3** (top route). Direct arylation of **1** has only been mentioned so far as a side reaction in the monoarylation of *H,H*-phosphinates.<sup>[11]</sup>



Scheme 1. Synthesis of diarylphosphinic acids through arylation of *H,H*-phosphinate esters or ammonium salts (**1'**)<sup>[9,10]</sup> and directly from  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  (**1**; this work).

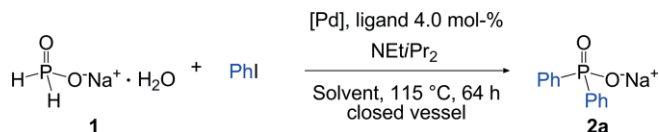
To explore the feasibility of converting **1** ( $\delta(^{31}\text{P}) = 2.2$  ppm in toluene/methanol (1:1)) directly into **3**, we chose  $\text{Pd}(\text{OAc})_2$  or  $\text{Pd}_2(\text{dba})_3$  (dibenzylideneacetone) combined with the large-bite-angle bidentate phosphine ligands dppf [1,1'-bis(diphenylphosphino)ferrocene], dppp [1,3-bis(diphenylphosphino)propane], and xantphos [4,5-bis(diphenylphosphino)-9,9-dimethylxanthene] as catalysts to promote rapid reductive elimination during the P–C coupling reaction. Initially, with iodobenzene as substrate (Pd loading: 4.0 mol-%), we only observed low yields of sodium diphenylphosphinate **2a** [2–7 % by in situ NMR spectroscopy;  $\delta(^{31}\text{P}) = 20.6$  ppm in toluene/methanol (1:1)].<sup>[12]</sup>

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Monohydrate **1** performed better than water-free sodium phosphinate (Scheme 2).<sup>[13]</sup> Analysis of the crude reaction mixture by <sup>31</sup>P NMR spectroscopy indicated that significant amounts of unreacted **1** were present along with small amounts of sodium monophenylphosphinate [ $\delta(^{31}\text{P}) = 15.0$  ppm in toluene/methanol (1:1)].<sup>[14]</sup>



Scheme 2. Direct diarylation of  $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$  (**1**) with PhI.

We then continued our studies by using bromobenzene as substrate,  $\text{NEt}_3\text{Pr}_2$  as the base, and  $\text{Pd}(\text{OAc})_2/\text{dppf}$  or  $\text{Pd}(\text{OAc})_2/\text{dppp}$  as catalysts, which gave much higher conversions (Table 1, entries 1–3). The choice of solvent [toluene/DME (dimethoxyethane) or DMF (dimethylformamide)] is crucial, as there was little or no conversion in protic solvents (methanol, acetic acid, water; not shown). More interestingly, the catalyst derived from the low-valent Pd precursor  $\text{Pd}_2(\text{dba})_3/\text{xantphos}$  gave even higher conversions (Table 1, entries 5–7).

Table 1. Direct diarylation of  $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$  (**1**) with PhBr.<sup>[a]</sup>

Entry	Catalyst	Ligand	Solvent	<sup>31</sup> P NMR yield [%] <sup>[b]</sup>
1	$\text{Pd}(\text{OAc})_2$	dppf	toluene/DME (9:1)	40
2	$\text{Pd}(\text{OAc})_2$	dppp	toluene/DME (9:1)	25
3	$\text{Pd}(\text{OAc})_2$	dppp	DMF	35
4	$\text{Pd}(\text{OAc})_2$	xantphos	DME	63
5	$\text{Pd}_2(\text{dba})_3$	xantphos	DMF	50
6	$\text{Pd}_2(\text{dba})_3$	xantphos	DME	82
7	$\text{Pd}_2(\text{dba})_3$	xantphos	toluene	90 (100 <sup>[c]</sup> )

[a] Reaction conditions:  $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$  (1.0 mmol) in solvent (5 mL); entries 1–4: PhBr (2 equiv.),  $\text{Pd}(\text{OAc})_2$  (4.0 mol-%), ligand (4.4 mol-%),  $\text{NEt}_3\text{Pr}_2$  (2.3 equiv.); entries 5–7: PhBr (2.5 equiv.),  $\text{Pd}_2(\text{dba})_3$  (2.0 mol-%), xantphos (4.4 mol-%);  $\text{NEt}_3\text{Pr}_2$  (3.5 equiv.). [b] Determined in situ by <sup>31</sup>P NMR spectroscopy. [c] Separate experiment with 10 mmol of  $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ .

Following these in situ studies, we used the set of conditions with reduced Pd concentration (2.0 mol-%) for preparative work (Table 1, entry 7). To isolate diphenylphosphinic acid **3a** in pure form and to extend the scope of the reaction,<sup>[15]</sup> a simple purification protocol was devised. This involved evaporation of the volatiles after the reaction, dissolving the residue in diethyl ether, extracting the ether solution with aqueous sodium hydroxide followed by acidification, and back extraction into dichloromethane. Evaporation of the solvent afforded disubstituted phosphinic acids **3a–j** (see Table 2 and the Supporting Information for more details).

This method afforded **3a**<sup>[16]</sup> [ $\delta(^{31}\text{P}) = 23.4$  ppm in  $[\text{D}_6]\text{DMSO}$  (dimethyl sulfoxide)] in 86 % isolated yield. Good yields (75–83 %) were also obtained when using the substrates 4-bromotoluene (**3b**<sup>[17]</sup>), 5-bromo-1,3-xylene (**3c**<sup>[18]</sup>), 4-bromobiphenyl

Table 2. Direct diarylation of  $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$  (**1**), scope extension.<sup>[a]</sup>

Compound	$\text{Ar}_2\text{P}(\text{O})\text{OH}$	Isolated yield [%] <sup>[b]</sup>	$\delta(^{31}\text{P})$ [ppm] <sup>[d]</sup>
<b>3a</b>		86	23.4
<b>3b</b>		78	24.1
<b>3c</b>		81	24.1
<b>2d</b> <sup>[c]</sup>		83	20.1 <sup>[g]</sup>
<b>3e</b> <sup>[d]</sup>		66	27.0 <sup>[h]</sup>
<b>3f</b>		61	22.8
<b>3g</b>		81	21.6
<b>3h</b>		65	21.2
<b>3i</b> <sup>[e]</sup>		41	21.5
<b>3j</b>		75	18.3

[a] Reaction conditions:  $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$  (5.0 mmol), ArBr (2.5 equiv.),  $\text{Pd}_2(\text{dba})_3$  (1.0 mol-%), xantphos (2.2 mol-%),  $\text{NEt}_3\text{Pr}_2$  (3.5 equiv.), toluene (25 mL); reaction time: 20 h. [b] After acidic work-up and corrected according to HPLC purity. [c] Isolated as the  $[\text{Ar}_2\text{POO}]\text{Na}$  salt. [d] 1 mmol scale. [e] From the corresponding diethyl ester due to hydrolysis during work-up. [f] In  $[\text{D}_6]\text{DMSO}$  unless otherwise specified. [g] In  $[\text{D}_4]\text{methanol}$ . [h] In  $[\text{D}_1]\text{acetic acid}$ .

(**2d**, new compound), 4-bromofluorobenzene (**3g**<sup>[19]</sup>), and even 4-bromonitrobenzene (**3j**<sup>[20]</sup>). A reduction in the yield (41–66 %)

was observed for the deactivated 3- and 4-bromoanisoles (**3e**<sup>[21]</sup> and **3f**<sup>[22]</sup>) and for bromoarenes containing groups sensitive to reduction and/or aldol condensation [ethyl 4-bromobenzoate (**3i**<sup>[23]</sup>) and/or 4-bromoacetophenone (**3h**, new compound), respectively]. In all cases the mass balance was completed by unconsumed starting material. The reaction can be run in air with only a 15 % drop in yield (**3a**).

Our new method outperforms the known procedures for making these phosphinic acids, certainly when considering the fact that the reaction times were not optimized (to allow better comparison between different substrates).

With the exception of poorly soluble **2d**, the reaction products were isolated as the acids [Ar<sub>2</sub>P(O)OH], all of which are stable towards air and moisture. They were obtained as white (**3a–c**, **3e–i**), yellow (**3j**), or grayish (**2d**) solids. They generally dissolve well in methanol, ethanol, alkaline solutions, and DMSO (except for **2d**, which only dissolved with difficulty in alcoholic and alkaline solutions).

The reaction intermediate, monoarylated phosphinate [Ar(H)P(O)O]Na, has a higher solubility in organic solvents compared to that of **1**. Thus, consumption of [Ar(H)P(O)O]Na to form [Ar<sub>2</sub>P(O)O]Na is faster than the first aryl introduction on **1**. In this way, the disubstituted phosphinates are selectively formed over the monosubstituted ones, which were only observed in small amounts as intermediates.

## Conclusion

In summary, the novel Pd-catalyzed direct formation of symmetrical diarylphosphinic acids [Ar<sub>2</sub>P(O)OH] and their sodium salts [Ar<sub>2</sub>P(O)O]Na from the inexpensive, hazard-free sodium phosphinate NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O and bromoarenes is achieved. The method is well-suited for the synthesis of diarylphosphinic acids and derivatives with a wide variety of aryl groups and tolerates functional groups, such as keto and carboxyl moieties, that are incompatible with the classical approach that employs Grignard or organolithium reagents.

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**Keywords:** Phosphinates · Homogeneous catalysis · Cross-coupling · Palladium · Sustainable chemistry · Industrial chemistry

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- [13] Variations in Pd catalyst, ligand, base (triethylamine, ethyldiisopropylamine, propylene oxide), and solvent (toluene, DME, toluene/DME = 9:1) gave only modest improvements. A quick test to achieve a catalytic Ullmann coupling<sup>[10c]</sup> gave no conversion.
- [14] Lower yields of aryl iodides vs. aryl bromides have been observed previously in the context of P–C coupling.<sup>[10d,10e]</sup>
- [15] The influence of different bases was briefly studied: potassium carbonate did not afford any transformation (most likely because of limited solubility) while pyridine, NEt<sub>3</sub>, NEt<sub>3</sub>Pr<sub>2</sub> provided similar results, NEt<sub>3</sub>Pr<sub>2</sub> being the best.
- [16] For comparison, the reported total yield for compound **3a**, starting from PCl<sub>5</sub> appears to be at best 49–52 % [76 % in B. Quanxing, C. Jiagang, F. Riqing (Huangshi Lifuda Medicine Chemical Co. Ltd.), CN105001258A, **2015**] in three steps: diphenylphosphinic acid from chlorodiphenylphos-

- phine in 90–96 % yield,<sup>[4b]</sup> chlorodiphenylphosphine from *N,N*-diisopropylphosphoramidate dichloride and phenyl Grignard in 80 % yield, *N,N*-diisopropylphosphoramidate dichloride from  $\text{PCl}_3$  in 68 % yield and the yield of phenyl Grignard from bromobenzene assumed to be quantitative.<sup>[4c]</sup> The reported yield of **3a** through P–C coupling is 85 %.<sup>[10d]</sup>
- [17] Chlorotoluene also afforded **3b** in 10 % yield; For comparison, the best reported yield for compound **3b** is 75 % through Grignard reaction (G. M. Kosolapoff, *J. Am. Chem. Soc.* **1949**, *71*, 369–370).
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- [22] For comparison, the best reported yield for compound **3f** is 59 % through Grignard reaction (J. Cornforth, A. F. Sierakowski, T. W. Wallace, *J. Chem. Soc. Perkin Trans. 1* **1982**, 2299–2315).
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