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Sustainable Phosphorus Chemistry: A Silylphosphide Synthron for the Generation of Value-Added Phosphorus Chemicals

J. Chris Slootweg*

alternative synthesis · industrial chemistry ·
phosphoric acid · sustainability · white phosphorus

The phosphorus chemical industry heavily depends on elemental, white phosphorus, which is produced in the energy-intensive Wöhler process (12.5–14 MWh per metric ton of P_4) by reduction of phosphate rock in an electric arc furnace at 1500–1600 °C with coke (C; reducing agent) and silica (SiO_2 ; for $CaSiO_3$ slag formation).^[1] This so-called “thermal process” functions as an element separator by removing impurities present in phosphate rock deposits (e.g., fluorine, cadmium, uranium, radium, mercury, lead, chromium, zinc, iron, copper, and rare-earth elements) and produces P_4 in high purity.^[2] The reduction of phosphates to white phosphorus (P_4) is the route to many high-grade phosphorus products (Figure 1),^[3] but now Cummins and Geeson provide an alternative pathway.^[4] To date, P_4 is thermally converted into its allotrope red phosphorus (P_{red}),^[1a] and reacts with sulfur to phosphorus sesquisulfide (P_4S_3) and phosphorus pentasulfide (P_4S_{10}).^[1b] In addition, white phosphorus is oxidized by combustion using dry air to produce phosphorus pentoxide (P_4O_{10}).^[1b] Subsequent hydrolysis produces high-purity phosphoric acid (H_3PO_4), which is applied as a food additive, for metal treatment, water treatment, and converted into phosphates for foodstuffs, pharmaceuticals, and animal feeds.^[1a,d] Thermally generated phosphoric acid hardly contains any impurities; only arsenic (5–30 ppm; present in P_4) is removed in a further purification step using hydrogen sulfide to precipitate arsenic sulfide.^[1b,d,2]

Current industrial processes also rely on phosphorus trichloride (PCl_3), which is obtained by treating molten white phosphorus with gaseous chlorine.^[1b] Subsequent addition of chlorine, oxygen, sulfur, or water readily produces the key derivatives phosphorus pentachloride (PCl_5), phosphoryl chloride ($P(O)Cl_3$), thiophosphoryl chloride ($P(S)Cl_3$), and phosphonic acid (H_3PO_3 ; Figure 1).^[1b] Phosphorus trichloride

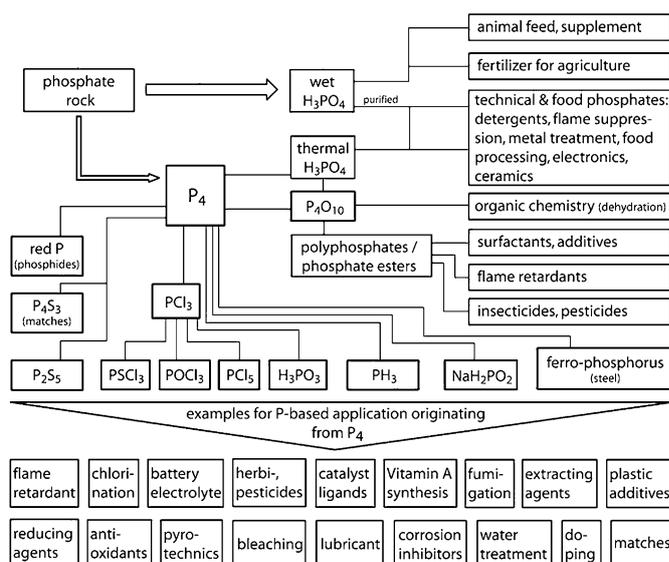


Figure 1. Use of phosphorus in the chemical industry, an overview provided by Weigand and co-workers.^[3] Reproduced (and slightly adapted) with permission from Springer Nature.

is an important intermediate in the production of, for example, the battery electrolyte lithium hexafluorophosphate ($LiPF_6$; from PCl_3), glyphosate (a herbicide), organophosphate triesters (phosphorus-based flame retardants), and a plethora of organophosphorus compounds, such as triphenylphosphine (PPh_3 ; vitamin A synthesis).^[3] Yet, in all cases, the production of these value-added phosphorus compounds is accompanied by the formation of copious amounts of Cl waste. An alternative approach that avoids the use of chlorine gas and the generation of Cl waste is the alkaline hydrolysis of P_4 with sodium hydroxide, which affords phosphine (PH_3)^[1b] and sodium hypophosphite (NaH_2PO_2), which can both undergo atom-economic P–C bond formations (by hydrophosphination of alkenes and alkynes) to afford organophosphorus compounds^[1c] and phosphinates,^[5] respectively.

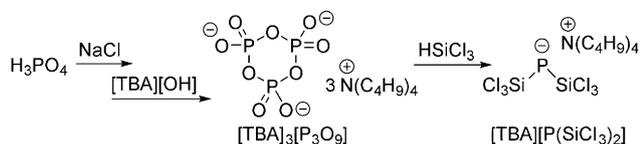
To further improve the sustainability of these chemical processes, it would be desirable to bypass the need for elemental white phosphorus (Figure 1).^[6,7] Approximately 95 % of all phosphoric acid (H_3PO_4 ; fertilizer for agriculture) is produced directly from phosphate rock in the “wet process”

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by treatment with sulfuric acid (H_2SO_4) and subsequent removal of large amounts of gypsum (CaSO_4) by filtration.^[1d,2] Many of the impurities in the phosphate rock are still present in the wet phosphoric acid, which can be rigorously purified by several processes, the most common being extraction and precipitation. After intensive treatment, the purity of the phosphoric acid is comparable with the food-grade phosphoric acid produced by the thermal process.^[1d,2]

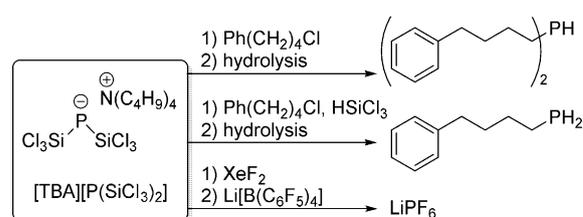
Cummins and Geeson have now unveiled that phosphoric acid is a suitable precursor for chemicals traditionally synthesized from white phosphorus (P_4).^[4] Their discovery is based on the use of commercially available sodium trimetaphosphate ($\text{Na}_3[\text{P}_3\text{O}_9]$), which can be obtained in a one-pot procedure by the dehydration of phosphoric acid using sodium chloride (600 °C, 2 h), with hydrochloric acid (HCl) as the only byproduct.^[8] Subsequent ion exchange with tetra-*n*-butylammonium hydroxide ([TBA][OH]) affords the more soluble cyclic phosphate trimer $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$ (76 %; $\delta(^{31}\text{P}) = -19.8$ ppm; Scheme 1), which was used by Cummins and Gleeson as the starting material.^[4,8b]



Scheme 1. Synthesis of $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$ and $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$ from phosphoric acid. TBA = tetra-*n*-butylammonium, $\text{N}(\text{C}_4\text{H}_9)_4$.

Trimetaphosphate is an interesting anionic $\kappa^3\text{-O}$ ligand for organometallic chemistry,^[8b] and was recently applied, also by Cummins and co-workers, for the synthesis of cobalt and vanadium trimetaphosphate polyanions, which have favorable properties for non-aqueous redox-flow battery applications.^[9] Cummins and Geeson now developed the direct conversion of trimetaphosphate, $[\text{P}_3\text{O}_9]^{3-}$, into valuable phosphorus compounds. Namely, $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$ can be reduced in a steel pressure reactor with trichlorosilane as the solvent (HSiCl_3 ; 33:1 Si/P molar ratio) at 110 °C for 72 hours to afford the novel bis(trichlorosilyl)phosphide anion in the form of its tetrabutylammonium salt $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$ (65 %; $\delta(^{31}\text{P}) = -171.7$ ppm, $^1J_{\text{P,Si}} = 156$ Hz; Scheme 1).^[4] Note that the industrial-scale production of HSiCl_3 requires elemental silicon, which is, just like P_4 , prepared in a high-energy process.^[10] Cummins and Geeson discovered that the phosphorus–silicon bonds of $[\text{P}(\text{SiCl}_3)_2]^-$ can be converted into phosphorus–carbon, phosphorus–hydrogen, or phosphorus–fluorine bonds by substitution (Scheme 2).^[4]

Treatment of $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$ with (4-chlorobutyl)benzene ($\text{Ph}(\text{CH}_2)_4\text{Cl}$ (5 equiv), 105 °C, 108 h) in toluene afforded the corresponding dialkylsilylphosphine ($\text{Ph}(\text{CH}_2)_4)_2\text{PSiCl}_3$, which was converted into the desired bis(4-phenylbutyl)phosphine ($\delta(^{31}\text{P}) = -69.2$ ppm, $^1J_{\text{P,H}} = 199.5$ Hz; Scheme 2) by treatment with aqueous sodium hydroxide or basic alumina. Selective monoalkylation was also feasible and produced the primary phosphine $\text{Ph}(\text{CH}_2)_4\text{PH}_2$ (Scheme 2), even by using trimetaphosphate



Scheme 2. Reactivity of $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$; hydrolysis to PH_3 not shown.

directly and in situ generation of the silylphosphide anion. Namely, heating a mixture of $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$, $\text{Ph}(\text{CH}_2)_4\text{Cl}$, and trichlorosilane at 110 °C for 96 hours gave the alkylsilylphosphine $\text{Ph}(\text{CH}_2)_4\text{P}(\text{SiCl}_3)\text{H}$, which afforded the corresponding phosphine $\text{Ph}(\text{CH}_2)_4\text{PH}_2$ (64 %; $\delta(^{31}\text{P}) = -136.2$ ppm, $^1J_{\text{P,H}} = 195$ Hz) after work-up (Scheme 2). Furthermore, Cummins and Geeson showed that this primary phosphine can be easily oxidized with hydrogen peroxide to afford (4-phenylbutyl)phosphinic acid ($\text{Ph}(\text{CH}_2)_4\text{P}(\text{O})(\text{OH})\text{H}$, 90 %; $\delta(^{31}\text{P}) = 38.8$ ppm, $^1J_{\text{P,H}} = 542$ Hz), which is a key building block in the reported synthesis of the prodrug fosinopril.^[4]

$[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$ can also be hydrolyzed directly to produce phosphine (PH_3 , ≥ 63 %; $\delta(^{31}\text{P}) = -241.1$ ppm, $^1J_{\text{P,H}} = 188$ Hz). Oxidation of the silylphosphide with a fluorine source is feasible, too. Treatment of $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$ with xenon difluoride (XeF_2 , 8 equiv) in dichloromethane gave $[\text{TBA}][\text{PF}_6]$, which yielded the prevalent electrolyte lithium hexafluorophosphate (LiPF_6 , 70 %; $\delta(^{31}\text{P}) = -144.6$ ppm, $^1J_{\text{P,F}} = 706$ Hz) after salt metathesis with lithium tetrakis(pentafluorophenyl)borate ($\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$, 1 equiv; Scheme 2).

The seminal work by Cummins and Geeson highlights the use of a novel silylphosphide synthon, which offers a route between phosphoric acid (H_3PO_4) and value-added phosphorus chemicals that had previously only been available from white phosphorus (P_4). This breakthrough will undoubtedly stimulate the development of more atom-economic synthetic methods that will safeguard our precious resources, and in particular promote the sustainable use of phosphorus.^[5,6]

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Conflict of interest

The authors declare no conflict of interest.

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