Let’s Make White Phosphorus Obsolete
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ABSTRACT: Industrial and laboratory methods for incorporating phosphorus atoms into molecules within the framework of Green Chemistry are in their infancy. Current practice requires large inputs of energy, involves toxic intermediates, and generates substantial waste. Furthermore, a negligible fraction of phosphorus-containing waste is recycled which in turn contributes to negative environmental impacts, such as eutrophication. Methods that begin to address some of these drawbacks are reviewed, and some key opportunities to be realized by pursuing organophosphorus chemistry under the principles of Green Chemistry are highlighted. Methods used by nature, or in the chemistry of other elements such as silicon, are discussed as model processes for the future of phosphorus in chemical synthesis.

1. INTRODUCTION: THE PHOSPHORUS INDUSTRY
The colors often associated with phosphorus are red and white, these being representative of the two most common allotropes of the element.1 Green is uncommon,2–4 although with global issues surrounding waste, environmental pollution, sustainability, and climate change perhaps the concept of “green phosphorus” warrants serious consideration. The 12 principles of Green Chemistry are a blueprint for performing chemistry with high efficiency, while minimizing energy inputs, waste outputs, and potential for harm to the environment or indeed personal safety.5 In the case of synthesis surrounding the element phosphorus, these criteria are met infrequently.

Phosphorus atoms that exist in man-made chemicals and materials began their life cycles, almost exclusively, in phosphate ores such as fluorapatite, Ca₅(PO₄)₃F. This is a relatively modern phenomenon: up until the end of the 19th century much of the world’s phosphorus came from guano, the excrement of birds and bats. Prior to guano, farmers relied on the scrupulous reuse of phosphate-containing materials, including mud from rivers where phosphorus from agriculture and sewage accumulates. The discovery of the “wet process” for producing phosphoric acid from phosphate rock and sulfuric acid (Figure 1) has led to an “anthropogenically broken natural-phosphorus cycle”,6 where phosphorus atoms now run from deposits of high concentrations on land to high dilution in the seas and soils.

Approximately 95% of mined phosphate rock is destined for the wet process, and the resulting phosphoric acid is used to produce phosphate fertilizers.8 Sulfuric acid, required stoichiometrically to operate the wet process, is produced from combustion of elemental sulfur which is in turn obtained from fossil fuel refining (or historically, from volcanic deposits).9

Figure 1. Summary of the synthesis of some key phosphorus-containing compounds and their formal oxidation states. Compounds in the green box are “redox-neutral” products derived from the wet process. Compounds in the red box are derived from P₄ and the thermal process. Orange phosphorus atoms are in the +3 oxidation state and are useful intermediates in chemical synthesis.
The wet process is the principal reason for sulfuric acid production, and in this scheme the industrial chemistries of phosphorus, sulfur, and fossil fuels are intertwined. As refinement of fossil fuels declines, future methods for obtaining useful products directly from phosphate rock or the use of acids other than sulfuric would therefore be desirable. The remaining 5% of phosphate rock is converted to white phosphorus in what is known as the “thermal process”. This involves reduction with carbon in an electric arc furnace, in the presence of silica as an oxide acceptor (Figure 1). The thermal process predates the wet process, tracing its routes back to 1669 when Hennig Brand obtained white phosphorus by heating deposits of urine to high temperatures in a blast furnace. In this early setup, organic matter present in the urine, such as creatine, played the role of reducing agent for phosphorus which is present in relatively high concentrations in urine. This abundant natural source of phosphorus is once again being exploited today by those interested in phosphorus sustainability (Section 3). The modern thermal process requires large inputs of energy for continuous electric arc furnace operation, and so production facilities are often centralized and close to cheap sources of power such as hydrothermal or nuclear.

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At present, via white phosphorus is the only industrially practicable way to obtain phosphorus-containing fine chemicals. This is achieved through intermediates such as PCl3 which have phosphorus–chlorine bonds that can be functionalized readily by reduction or salt metathesis. Both white phosphorus and PCl3 (made from the reaction of P4 and Cl2) have limitations as reagents within the framework of Green Chemistry. White phosphorus is a high-energy and toxic substance. For its military applications (smokescreens, incendiary bombs) white phosphorus goes by the nickname “Willie Pete”. The use of chlorine to make PCl3 requires special measures to mitigate the hazards and reactivity of Cl2 toward personnel and reactor construction materials. Neither P4 nor PCl3 have any significant direct applications, and so they could in principle be omitted in the preparation of phosphorus-containing chemicals if alternative routes are discovered.

2. FINE CHEMICAL SYNTHESIS FROM PHOSPHORUS(V) PRECURSORS

Phosphate Esters from Phosphoric Acid. Advantages of beginning the synthesis of phosphorus-containing chemicals with phosphoric acid include its widespread availability, omitted energy inputs required for the thermal process, and the absence of chlorine-containing byproducts generated when using PCl3. Furthermore, phosphoric acid can be produced from recycled sources of phosphorus (Section 3). Procedures for incorporating phosphoric-acid-derived phosphorus atoms directly into molecules are scarce, though they emerged as early as the 1950s including the pioneering work on nucleoside polyphosphate synthesis by Khorana.

One recent procedure involves treating an alcohol with 1.1 equiv of phosphoric acid in the presence of a catalyst under azotropic reflux in order to remove water (Figure 2). This allows for the phosphorylation of simple alcohols such as stearoyl alcohol in high yields. One drawback of the procedure is the use of long-chain substrates, presumably imposed by the high reaction temperatures that would remove low-boiling alcohol substrates by distillation. Nevertheless, use of nearly equimolar amounts of alcohol and phosphoric acid, increasingly complex substrates such as 2′,3′-0-isopropylidene ribonucleosides, and production of water as the only stoichiometric byproduct is impressive.

These reactions involve loss of water, and so, naturally, reagents used to induce dehydration reactions have been investigated for their ability to promote phosphorylation of alcohols. The use of acetic anhydride or trichloroacetoni-trile to activate phosphoric acid toward attack by a nucleophile allows for milder temperatures and the use of lower-molecular-weight alcohols such as allyl alcohol. However, from an atom-efficiency standpoint, the formation of water as the sole byproduct is the most attractive method for preparing organophosphate monoesters. The use of solid-state catalysts is also being investigated, potentially leading to improved separation procedures.

Another strategy for preparing esters of phosphoric acid is the use of polyphosphoric acid which, as a dehydrated form of phosphoric acid, already includes the anhydride functionality necessary for phosphorylation of nucleophiles. A variety of methods exist for obtaining polyphosphoric acid, and these can be broadly divided according to their reliance on either P4 or H3PO4 for the input of phosphorus, although a third method involves the action of microbes on wastewater (Section 3). Methods that utilize H3PO4 require dehydration which is accomplished by heating, using either combustion of natural gas, electrothermal, or microwave irradiation as the input of thermal energy. Polyphosphoric acid is used a catalyst or reagent in organic synthesis, for example, in cyclization or dehydration reactions. Treatment of polyphosphoric acid
with alcohols leads to the formation of a mixture of mono- and diesters of phosphoric acid which find applications in cleaning agents, cosmetics, and in the paper and textile industries.24

Phosphorylation reactions using oligophosphates, the conjugate bases of polyphosphoric acids, to produce phosphoester linkages25,26 have been extended in recent years, with particular focus on the trimetaphosphate trianion or its derivatives which incorporate some P(V) centers derived from phosphoric acid.26 The sodium salt of trimetaphosphate is produced by dehydration of phosphoric acid in the presence of sodium chloride at 300 °C and is therefore a useful starting material for synthesis of phosphorus-containing compounds in a manner that bypasses P4.27 The sodium cations can be exchanged for organic alternatives such as bis(triphenylphosphine)iminium ([PPN]+) or tetra-n-butylammonium ([TBA]+) which endow favorable solubility properties to the resulting salts in organic solvents. Taylor has disclosed the synthesis of nucleotide triphosphates using [TBA]3[P3O9],28 while our group has isolated a triphosphorylating agent from the reaction of [PPN]3[P3O9] with the peptide coupling reagent PyAOP ([(pyrr)3PON4C5H3][PF6], pyrr = pyrrolidino, NC4H8, Figure 3), and used it to prepare triphosphorylating derivatives of carbon-, nitrogen-, and oxygen-based nucleophiles.29

Figure 3. (A) Procedure for triphosphorylation of nucleoside bases using [TBA]3[P3O9]. TBA, tetra-n-butylammonium; MstCl, 2-mesitylenesulfonyl chloride; DABCO, 1,4-diaza-bicyclo-[2.2.2]-octane; PyAOP, see text. (B) Isolation of a triphosphorylating reagent and subsequent reaction with C-, N-, and O-based nucleophiles.

Using the Bis(trichlorosilyl)phosphide Anion. In an effort to bypass white phosphorus and phosphorus(III) chloride in the synthesis of phosphorus-containing fine chemicals, we recently reported a method for preparing the bis(trichlorosilyl)phosphide anion directly from trimetaphosphate and trichlorosilane (Figure 4).30 The new compound was converted to other products such as phosphonium salts, primary phosphines, alkyl phosphinic acids, and phosphine (PH3). One attractive aspect of the reducing agent, trichlorosilane, is that it is a high-production-volume chemical used to produce high-purity silicon metal for use in photovoltaics. However, silicon (from which HSiCl3 is commonly derived) is prepared by the reduction of silica in a process resembling the thermal process for phosphorus. Fortunately, exciting progress is being made toward the production of SiCl4 and HSiCl3 using redox-neutral or sustainable processes, respectively (Section 6).

In addition to trimetaphosphate, we also showed that it is possible to prepare n-octylphosphine from n-octyl chloride and crystalline phosphoric acid, via the same phosphide anion which is generated in situ by trichlorosilane (Figure 4).31 Mass balance studies showed that the main byproducts of the reduction of phosphate sources with trichlorosilane were H2 gas and chlorosiloxanes, such as O(SiCl3)2.31

3. PHOSPHORUS SUSTAINABILITY AND STEWARDSHIP

Methods for Recovering Phosphorus from Waste. The phosphorus industry presents many opportunities for optimization under the guiding principles of Green Chemistry, particularly with regard to minimizing energy inputs and avoiding the use of toxic or hazardous intermediates. However, most of the opportunities for minimizing harm to the environment lie with phosphate pollution. As can be seen from the Sankey diagram (Figure 5), phosphorus is approximately evenly distributed between the natural and anthropogenic phosphorus cycles.32 The latter has been described as a “broken cycle” because phosphate mining occurs on the order of Mt/y while the formation of new reserves occurs over thousands of millennia.33 Prior to large quantities of phosphate available from the wet process, phosphorus atoms would be cycled from the soil, to plants and animals, to manure, and back to the soil with high efficiency before substantial losses to surface body waters.33 Nowadays, excessive application of phosphate fertilizers leads to substantial runoff into surface body waters and contributes to eutrophication.34

Another source of phosphate that contributes to eutrophication is sewage arising from human and animal excrement.34 Not all sewage is processed, and in some regions it proceeds directly to surface body waters without treatment. In places where wastewater treatment is practiced, there are obvious opportunities for recovering and recycling phosphorus. In several countries, legal limits on the concentration of phosphate in wastewater have led to the adoption of processes for recovering phosphate. In Germany, a recent amendment...
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requires recovery of 50% of the phosphorus from major sewage treatment plants. A leading method for phosphate recovery is precipitation by the addition of magnesium salts to give struvite (magnesium ammonium phosphate, Mg(NH₄)PO₄·6H₂O) which can be used as a slow-release fertilizer. Struvite precipitation is practiced by at least 40 full-scale installations worldwide. Two potential drawbacks of using struvite are (i) its direct contact with wastewater, raising concerns about the accumulation of pharmaceuticals, and (ii) the accumulation of magnesium ions in soil where struvite is used extensively which could lead to fixation of subsequently dosed phosphate. At least with the former concern, Slootweg and co-workers have shown that bioaccumulation of micropollutants such as ibuprofen in tomato crop fruit is of no significance toward human health concerns, although investigations into other micropollutants and crops are necessary given the debate in the literature. In part due to the low values for total phosphorus recovery by struvite precipitation (25–45%), other methods for removing phosphate from sewage sludge are under active investigation and involve extraction using carbon dioxide, mineral acids, or alkaline conditions.

A second method of phosphorus recovery involves incineration of sewage to produce sewage sludge ash (SSA). This produces a product with high phosphorus content and destroys organic pollutants, such as bacteria and drug residues. Another advantage of the process is that the product is a dry powder, suitable for industrial recycling to phosphoric acid. Beginning in 2013, a variation on the wet process was adopted in Japan that uses phosphate rock blended with 2.5% SSA. This ratio is needed to guarantee the quality of both the phosphoric acid and the phosphogypsum products. The two main drivers for incorporating SSA into the process were cited as (i) minimizing risks associated with the volatility of phosphate rock price and (ii) recycling phosphate available from wastewater treatment plants. In The Netherlands, a process for producing triple superphosphate fertilizer (Ca(H₂PO₄)₂·H₂O) allowed the ratio of SSA to phosphate rock to be pushed to 10%. Extending the idea of using recycled phosphorus in known industrial processes, pilot studies are underway to produce white phosphorus from SSA in a process known as RecoPhos.

Biological processes for removing phosphate from sewage sludge are also under development. In a process known as Heatphos, microorganisms capture phosphate and accumulate it in the form of polyphosphate (polyP), featuring phosphonoxyhydroxide bonds and chain lengths of up to 1000 residues. In laboratory experiments, polyP is released from cells by heating to 70 °C for 1 h, and under these conditions shorter chains of polyP and species such as trimetaphosphate are detected. Approximately 65% of the total phosphorus can be precipitated by the addition of CaCl₂ without adjusting the pH. Interestingly, trimetaphosphate is not precipitated under these conditions and remains soluble even up to a pH of 10. If separated from the mixture, trimetaphosphate could have potential commercial value or be employed in chemical synthesis using known methods (Section 2). A pilot-scale plant study showed good assimilation (90–95%) of total phosphate intake by microorganisms; however, the precipitation step using CaCl₂ led to recovery of only about 3% of P input, although this could be improved to 40% by adjusting the pH.

Although recycling phosphorus from sewage presents a low barrier to entry, Scholz and Wellmer have identified significant waste of phosphorus before it enters either the wet or thermal processes (Figure 5). The two main mechanisms for these losses arise during mining and beneficiation. The former involves selecting rock of sufficient phosphorus content while the latter concerns upgrading of phosphate rock prior to processing in order to increase its economic value, principally via flotation. Scholz and Wellmer note that these can be classed as possible or delayed losses, in theory recoverable if ore of lower phosphorus content becomes economically viable to extract in a future where highly concentrated reserves are exhausted.

Are Phosphorus Reserves Running out? The term “peak phosphorus” has been used to describe the phenomenon...
of phosphate rock production volumes reaching a maximum, resulting from exhaustion of high-quality reserves. Recent analysis suggests that there are sufficient reserves for the next few centuries, although quality or accessibility will diminish (for example, of low phosphorus content or located on the sea floor). On land, phosphate reserves are not geographically evenly distributed, with the majority of reserves concentrated in a handful of countries. As a result, 90% of countries are phosphate importers, and thus are not self-sufficient for this resource. Recycling and reuse provides a domestic supply chain for phosphorus, desirable for food security. Therefore, the question of long-term phosphate supply is perhaps of little consequence to the future of the phosphorus industry; moving to a circular phosphorus economy through decreased usage, increased recycling, and engaging in less energy-intensive processing methods all provide significant benefits independent of global supply.

**A Transition to Phosphite?** A recent breakthrough in biotechnology has afforded genetically modified (GM) crops (soybeans, corn, cotton) to be developed that are capable of growth using phosphite, a phosphorus(III) compound, as fertilizer rather than the traditional phosphates. This has major implications for both controlling weeds and eliminating the water pollution that leads to eutrophication. Because only the GM crops can grow on phosphite fertilizer, weed killers such as glyphosate are not needed to control weeds. Additionally, if there is rain and runoff, the non-GM marine algae also cannot grow on the phosphite such that the marine ecosystems are protected from the harmful effects of algae blooms.

One potential drawback of this method is that under earth's oxygen-rich atmosphere, phosphate is preferred thermodynamically over phosphite, and it is known that phosphite is oxidized naturally to phosphate either under atmospheric conditions or under the catalysis of microorganisms. Despite this, the method could still present an advantage because phosphite has the potential to be more easily sensed using devices due to its electrochemical response. Thus, even if phosphite is eventually oxidized to phosphate, it would provide a source of fertilizer that could be accurately monitored in the short term and applied more strategically than is currently the case for phosphate fertilizers.

An issue hindering the implementation of such a process is the relatively high cost of phosphorous acid (H₃PO₃) and its derivatives, which are at present produced from P₄ (Figure 1). The development of scalable and efficient methods for producing phosphite from phosphate would therefore be desirable. Another strategy would be to recover phosphite from phosphorous streams, such as those from electroless nickel plating.

At present, the P(III) waste from this process is chemically oxidized to phosphate and is not utilized further, although research is being conducted into the utilization of this phosphite waste in a biological setting. Another source of phosphite waste is from PH₃ production from the reaction of P₄ with Cl₂; the major byproduct of the reaction is hypophosphite (H₂PO₂⁻), although some phosphite also forms (Scheme 1) and can be precipitated as the calcium salt.

**4. P(III) COMPOUNDS AS THE BOTTLENECK**

**Phosphorus(III) Chloride.** Phosphorus(III) chloride (PCl₃) is produced by the strongly exothermic reaction of P₄ with Cl₂. The heat generated is sufficient to vaporize the PCl₃, which leads to its distillation and purification. Clearly, chemical energy is stored in the P–P and Cl–Cl bonds of the starting materials, energy that ultimately comes from the large-scale industrial processes used for their production: the thermal and chloralkali processes, respectively. The oxidation states of phosphorus and chlorine in the starting materials are both zero, while in the product they are +3 and −1, respectively. Chloride exemplifies the only naturally occurring oxidation state of chlorine, while P(+3) is only two formal oxidation states away from naturally occurring phosphate (+5). With these considerations in mind, is it possible to design a process that minimizes redox reactions of the substituent atoms? If minimization of oxidation state change is considered a proxy for the energy requirements to produce a chemical, then such a process would be highly desirable.

This idea was investigated by Nordschild and Auner, who investigated the carbochlorination of calcium phosphate, Ca₃(PO₄)₂, with hydrogen chloride and carbon under microwave conditions. Phosphorus(III) chloride was collected in a cold trap and identified by its ³¹P NMR chemical shift. The authors observed "white flashes," attributed to electrical discharges or arcs, and assumed to be the reaction zones in which carbochlorination occurs. Further experiments for this interesting reaction are required to analyze the efficiency of the inputs of microwave energy and the nature of reaction intermediates: do phosphorus-containing species in an oxidation state lower than +3 form? How much of the carbon reductant is converted to CO or CO₂?

Besides this report, processes that lead from a phosphate source to PCl₃ omitting the intermediary of white phosphorus are scarce. However, clues as to how such a transformation could be achieved may lie in chemistry that is being actively developed for upgrading silicates and silica to silicon-containing chemicals of industrial importance (Section 6).

**Phosphine (PH₃).** Phosphine is used for the synthesis of alkyl phosphines by the atom-efficient hydrophosphination of olefins. Phosphine itself is produced by oxidation of P₄ using sodium hydroxide, a process that also results in the formation of hypophosphite ([H₂PO₂⁻]⁻) and phosphate ([HPO₄²⁻]) as byproducts (Scheme 1). The use of phosphine as opposed to PCl₃ for the synthesis of organophosphorus compounds is
beneficial from a waste perspective because it does not result in stoichiometric halogen-containing byproducts. However, PH₃ does not offer access to product classes such as arylphosphines.\textsuperscript{24} Additionally, the control of product distribution between mono-, di-, and trialkylphosphines represents a difficulty as a result of the presence of three P–H bonds in PH₃.\textsuperscript{24} The other major phosphorus-containing product, hypophosphite, has been pioneered by Montchamp as an alternative reagent in synthesis that ordinarily requires PCl₃.\textsuperscript{61}

**Phosphorous Acid (H₃PO₃) and Its Derivatives.** Phosphorous acid (H₃PO₃), its conjugate base phosphite ([HPO₄]²⁻), and their many organic derivatives are typical phosphorus compounds in the +3 oxidation state (Scheme 2).

**In brackets: tautomerization of phosphorous acid between the pentavalent and trivalent isomers.**

![Scheme 2. Thermal Disproportionation of Phosphorous Acid to Phosphine and Phosphoric Acid\textsuperscript{44}](image)

In an effort to avoid the use of high temperatures and phosgene (which is toxic and gives CO₂ as a byproduct of the chlorination reaction), electrochemical methods for the reduction of triphenylphosphine oxide to triphenylphosphine are under active investigation.\textsuperscript{70} Interested in utilizing H₂ as the reducing agent, frustrated Lewis pair (FLP) catalysis enabled the reduction of triphenylphosphine oxide to triphenylphosphine in the presence of H₂ (4 bar) and oxalyl chloride (Scheme 3).\textsuperscript{71} Remarkably, increasing the pressure of H₂ (80 bar) led to a variant of the reaction in which the borane component was not required, and triphenylphosphine could be obtained in 93\% yield.

In addition to stoichiometric recycling, a complementary approach is the use of organophosphorus catalysts, in conjunction with sustainable stoichiometric reducing agents.\textsuperscript{72} Such efforts have been disclosed for several classes of organic reactions that typically generate stoichiometric quantities of phosphate oxides, such as the Wittig,\textsuperscript{73} Aza-Wittig,\textsuperscript{74} Mitsunobu,\textsuperscript{75} Appel,\textsuperscript{76} and Staudinger\textsuperscript{77} reactions, as well as several others.\textsuperscript{78}

An intriguing report, focused on plausible sources of reduced phosphorus in the Archean ocean, details the observation of phosphite by the action of iron(II) salts on phosphate at 180 °C.\textsuperscript{65} Although the reported yield of phosphite was low (4%), the process corresponds to being a selective reduction of phosphate to phosphite. Related geochemical occurrences of phosphite have been attributed to lightening strikes\textsuperscript{67} and reducing environments within volcanic hydrothermal systems.\textsuperscript{68}

**P(V) to P(III) Recycling in Chemical Synthesis.** The case made thus far entails elimination of P₄ and PCl₃ in the synthesis of phosphorus-containing chemicals. However, another aspect of phosphorus sustainability that offers an opportunity for improvement is recycling chemicals that already contain phosphorus. Organophosphorus compounds such as triphenylphosphine are used in chemical synthesis as stoichiometric reagents, for example, in the Wittig or Mitsunobu reactions, where a common theme is the formation of a strong P=O double bond as a thermodynamic driving force. Therefore, an economically feasible method for the reduction of triphenylphosphine oxide back to triphenylphosphine has the potential to minimize waste. BASF achieved this by chlorination of Ph₂PO with phosgene to Ph₂P(O)Cl\textsubscript{2} followed by reduction using aluminum metal at 130 °C (Scheme 3).\textsuperscript{59}

**Scheme 3. Stoichiometric Reductions of Triphenylphosphine Oxide to Triphenylphosphine**

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Another commodity chemical that has the potential to be recycled is lithium hexafluorophosphite (Li[P₄F₁₀]), present in lithium-ion batteries as an electrolyte. Industrial processes for recycling certain components of lithium-ion batteries such as lithium, nickel, and cobalt are already practiced, while recycling of additional components is of increasing interest.\textsuperscript{79} One promising procedure describes the extraction of LiPF₆ from discharged Li-ion cells using mixtures of supercritical CO₂ and organic solvent.\textsuperscript{80} Besides recycling, another reason for removing LiPF₆ from end-of-life batteries is that it can react with organic carbonate solvents during thermal recycling methods to give alkylfluorophosphates that bear a strong
structural resemblance to toxic nerve agents and are thus of environmental and safety concerns.82

5. HOW DOES BIOLOGY MAKE PHOSPHORUS–CARBON BONDS?

Assimilation of Inorganic Phosphate. The wet-process strategy of lowering pH to access otherwise insoluble phosphate is, of course, predated by nature. Phosphate solubilizing bacteria (PSB) achieve uptake of phosphate by the release of small-molecular-weight organic acids, such as citric or lactic acid.83 These acids improve phosphate solubility by lowering the pH of the soil and by chelation of metal cations such as Ca2+ or Mg2+. In addition to providing inspiration for our own methods of processing phosphate, PSB are also being investigated as biofertilizers that could lead to decreased application of synthetic fertilizers.84

Phosphoenolpyruvate as the Entryway. Natural product biosynthesis is a proven source of inspiration for reaction discovery. So how do P–C bonds form in nature? The key phosphorus–carbon bond-containing compounds in biology are phosphonates (RPO3H2), typically used by nature as antibacterial agents. The starting point for biological P–C bond formation (Scheme 4) is phosphoenolpyruvate (PEP), which serves as a key intermediate to numerous P–C bond-containing compounds via subsequent functionalization.85

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Scheme 4. Biosynthesis of Phosphorus–Carbon Bonds (See Text for Abbreviations)

Most natural P–C bond-containing compounds

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Linking biological intermediates to chemical synthesis, a recent study employed the potassium salt of PEP in conjunction with [TBA]HSO4 as a catalyst for the phosphor-ylation of alcohols to give phosphate esters.87 Currently, commercially available PEP is accessed using chemistry derived from P4. If obtained instead using enzymatic methods or via reactions starting from wet-process P(V) precursors, this would constitute a method for the synthesis of phosphate esters in a manner that avoids reduction of phosphorus from its preferred oxidation state of +5.

6. LESSONS FROM GROUP 14

Redox-Neutral Processing of Silicate Minerals to Silicon(IV) Chloride. Silicon also enters commercial products through the intermediacy of the elemental form, the production of which is analogous to the thermal process for obtaining white phosphorus. Industrially important silicon-containing polymers can be produced from chlorosilanes such as SiCl4, and so the same arguments around redox-neutral processing can be made for both silicon and phosphorus.88

With these goals in mind, Goodman and Kenney showed in 1988 that tetraethoxysilane (Si(ΟEt)4, TEOS) could be obtained by treating silicate-containing minerals with ethanolic hydrogen chloride (Scheme 5). More recently, Choi described the preparation of TEOS from silica and ethanol, using molecular sieves to drive the dehydration reaction to completion.91 The molecular sieves could be reactivated by heating (300 °C, 15 h), allowing the reaction to be cycled six times with no loss to the TEOS yield. Furthermore, rice hull ash (RHA), a product of agricultural rice production, could also be used as the source of silica to give TEOS in 60% yield. Further improvements to the procedure involve use of calcium oxide instead of molecular sieves as the desiccant, resulting in the formation of Ca(OH)2.92 A full technoeconomic and environmental assessment suggests that the new procedure could result in a reduction of 7% to production costs and 34% to green house gas (GHG) emissions if the new process were implemented.92

Tetraalkoxyxilanes such as TEOS are important chemical feedstocks for a variety of zeolites, ceramics, and silica-based organic–inorganic hybrid materials. Industrially, they are produced from SiCl4 and an alcohol, with the liberation of HCl. Researchers at Dow have taken steps toward producing SiCl4 in a redox-neutral process by using tetraalkoxyxilanes as their starting point. A first report dealt with the production of SiCl4 from tetramethoxysilane (Si(ΟMe)4, TMOS) and HCl, in the presence of lithium chloride as a catalyst.93 Acetonitrile and additional equivalents of HCl were required in order to trap the methanol byproduct as an imidate salt and prevent its back reaction with SiCl4 (Scheme 5). Using this procedure, the reported yield of SiCl4 was 99%, as determined by 29Si NMR spectroscopy.

Scheme 5. Examples of Redox-Neutral Reactions Using Silicon(IV) Compounds

A  
\[ \text{Ca}_2\text{SiO}_4 \xrightarrow{\text{HCl/ethanol}} \text{Si(ΟEt)}_4 \]

B  
\[ \text{Si(ΟMe)}_4 + 8 \text{HCl} + 4 \text{MeCN} \rightarrow \text{SiCl}_4 + 4 \text{MeCN} \]

C  
\[ \text{Si(ΟMe)}_4 + 4 \text{SOCl}_2 \xrightarrow{[\text{TBA}]\text{Cl} (40 \text{ mol \%})} \text{SiCl}_4 + 4 \text{SO}_2 + 4 \text{MeCl} \]
In a second report, the chlorination reagent was changed from hydrogen chloride to thionyl chloride. Thionyl chloride has several advantages over HCl; it can be used in smaller excess, it is easier to handle, and the absence of protons reduces the likelihood of condensing orthosilicates. A catalytic amount of a chloride salt such as tetra-n-butylammonium chloride was required for the success of the reaction, intended to activate the tetraalkoxysilane toward reaction with SOCl₂ by forming a hypervalent anionic silicon species. The main byproducts of the reaction are SO₂ and chloromethane, the latter being potentially recyclable to produce other useful silicone products via the Direct Process.

Diverging Requirements for Elemental P vs Si. Despite the similarities between the industrial processes for obtaining elemental silicon and phosphorus, a key difference is the subsequent applications of the two products. Elemental silicon has large-scale applications in the photovoltaics and electronics industries. Elemental phosphorus, on the other hand, has no major direct applications and is instead converted to compounds such as PCl₃ or H₃PO₄. Thus, elemental silicon can be regarded as an industrial product whereas elemental phosphorus is an intermediate. As such, there is no nonmilitary requirement for P₄ production, should alternative methods utilizing phosphate become available. Elemental silicon, however, will continue to be required in a future that is increasingly reliant on solar electricity. This has spurred research into the production of elemental silicon using green methods, such as electrochemical reduction of silica, or by the reduction of recycled SiCl₄ with sustainably generated H₂, through the intermediacy of HSICl₃.

Toward Chlorine-Free Processing of Elements. A chlorine-free protocol for processing germanium was reported in 2017. Treatment of germanium dioxide or germanium metal with either a catechol or ortho-quinone, respectively, led to the formation of germanium(IV) bis(catecholates), supported by two pyridine ligands (Scheme 6). The catecholate groups could be replaced with carbon-based nucleophiles to prepare tetraorganogermeses (GeR₄) in good yields (>91%). The argument made for processing germanium in a chlorine-free manner can also be applied to phosphorus or indeed any element chloride: Cl₂ is a highly toxic substance, is corrosive toward many materials, and is derived from an energy-intensive process. Additionally, the germanium(IV) bis(catecholates) are bench-stable solids, while germanium tetrachloride is a moisture- and air-sensitive liquid that produces HCl upon hydrolysis. Thus, the use of comparatively stable germanium catecholates represents an advance in terms of toxicity and potential for harm to the environment. Another benefit of the reported procedure was the use of mechanochemistry to perform the reactions, a methodology of growing interest due to low solvent usage, scalability, and fast reaction times.

One challenge posed by the objective of replacing chloride for organooxo groups in element processing is the relatively low cost of the halides. In this regard, future success on a large scale is likely to be met where the organic group is cheap and abundant, for example, methyl, ethyl, or phenyl.

Developing chlorine-free protocols for processing white phosphorus has been an active area of research for decades, and exciting new reactions are still emerging. Improvements to the methods for preparing phosphonic acids, alkylphosphines, and arylphosphines directly from P₄ have benefited from the generation of carbon-based radicals in situ. The recent stabilization of white phosphorus in activated carbon raises the possibility of decreasing the hazards associated with this pyrophoric intermediate, which is likely to feature in chemical synthesis for some time to come.

7. OUTLOOK: CHALLENGES AND OPPORTUNITIES

Clearly, there are many aspects of phosphorus chemistry that could be improved, as judged from the perspective of green chemistry. Here, we lay out some of the key challenges and opportunities for synthetic chemists.

1. Develop selective reductions from P(V) to P(III). While these are known for the reduction of organic molecules (e.g., OPPb₃ to PPh₃), selective reductions of inorganic P(V) to P(III) compounds are scarce. A selective reduction of phosphate to phosphite has the potential to make white phosphorus obsolete and minimize halogen-containing waste in the production of phosphorus-containing chemicals.

2. Use of electrochemical methods for phosphate reduction. Ideally, reduction of phosphate would be performed electrochemically where electricity can be supplied sustainably, and the half reaction corresponding to phosphate reduction is balanced by the formation of O₂ from water oxidation.

3. Use of renewable sources of phosphorus in chemical synthesis. Such products include struvite, sewage sludge ash, or materials obtained from biological extraction processes such as polyphosphates.

If met, overcoming these challenges would provide the following opportunities:

1. Decreased energy consumption and CO₂ emissions. The thermal process requires large inputs of costly electricity. The chemistry of the thermal process requires the oxidation of carbon, eventually to CO₂, a greenhouse gas.

2. Extraction of phosphate rock is minimized. Phosphate rock is considered a nonrenewable resource over very long time scales. Over short time scales, recycling of phosphorus materials minimizes supply risks.

3. Transition to a “circular” or “conical” phosphorus economy. Waste products such as phosphogypsum are minimized, leading to reduced processing costs and potential for harm to the environment. The term “conical economy” refers to a circular economy that emphasizes reducing the consumptive footprint of the value chain, i.e., a circle with a smaller diameter.

4. Discovery of new methods in organophosphorus chemistry. Reaction discovery has the potential to
increase “chemical space” among phosphorus compounds, which are important herbicides and pharmaceutical agents.

(5) Application of discoveries to other elements. In the same way that the chemistry of silicon can shape a greener phosphorus industry, findings made as a result of research into phosphorus chemistry may have the ability to symbiotically improve the processing of other element oxides, such as those of silicon, boron, and germanium.

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