Chemical Recycling of Phosphoric Acid Recovered from Sewage Waste via Direct Esterification with Organosilicate

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Abstract

Global concerns regarding the depletion and strategic importance of phosphorus resources have increased demand for the recovery and recycling. However, waste-derived phosphorus compounds, primarily as chemically inert phosphoric acid or its salts, present a challenge to their direct conversion into high-value chemicals. We aimed to develop an innovative technology that bypasses the use of white phosphorus and enables direct esterification of phosphoric acid to produce widely applicable phosphate triesters. Tetraalkyl orthosilicates emerged as highly effective reagents for the direct triple esterification of 85% phosphoric acid, as well as the esterification of organophosphinic and phosphonic acids. Furthermore, we achieved direct esterification of recovered phosphoric acid with tetraalkyl orthosilicate, thus pioneering a recycling pathway from sewage waste to valuable phosphorus chemicals. Experimental and theoretical investigations revealed a novel mechanism, wherein tetraalkyl orthosilicates facilitate multimolecular aggregation to achieve alkyl transfer from tetraalkylorthosilicate to phosphoric acid via multiple proton shuttling.

INTRODUCTION

Phosphorus plays a vital role in the production of a diverse range of materials in multiple industrial fields and is of utmost importance in agriculture. However, phosphorus resource is limited to the Earth's deposits of phosphorus-containing minerals.[1] Approximately 20 million tons of phosphorus are mined each year, with an estimated 8.5 to 9.5 million tons of it flowing into the ocean. This exceeds the limit defined for a safe operating space, known as the planetary boundary.[2] Therefore, phosphorus recovery and recycling are crucial not only for mitigating resource risks but also for reducing phosphorus pollution and ensuring food security to achieve a sustainable global environment. This concept is now recognized as one of the most important and urgent challenges within the international framework.[1,3-10]

The industrial route to produce phosphorus-containing chemicals generally begins from the production of white phosphorus (P_4) via the energy-intensive reduction of phosphate rock as a nonrenewable natural resource using large amounts of electrical power, approximately 12.5 to 14 MWh per ton of P_4 (Figure 1a).[3,7,11,12] Owing to this method, there have been repeated instances in the past, such as a global price spike of phosphorus resources, that have also raised concerns about the sustainability of P_4 production.[13,14] To address this issue, technologies to recover phosphorus sources from various wastes, such as sewage sludge ash, steel slag, manure and biowaste, have been developed, enabling the production of phosphate salts as fertilizer from recovered phosphoric acid (H_3PO_4, **1**).[1,7] However, the absence of technology for the direct molecular transformation of **1** restricts the range of recycling options for fertilizer applications.[8] Therefore, there is an urgent need to develop new methods to synthesize high-value added phosphorus compounds from recovered **1**.[3,4] This progress is crucial for establishing sustainable phosphorus resource cycles.

Phosphate triesters ($PO(OR)_3$) are industrially distributed as flame retardants[15] and plasticizers.[16] In particular, flame retardants possessing phosphate triester structures are normally synthesized in large quantities (360,000 tons in 2020)[5] via alcoholysis of $POCl_3$ prepared from P_4 (Figure 1a, conventional route).[6] In this context, we focused on the chemical recycling of sewage waste by a direct molecular transformation of **1** to provide phosphate triesters (Figure 1a, this work).[17]

The bottleneck in developing a direct molecular transformation for **1** lies in the high chemical and thermodynamic stability of **1** as a strong acid.[4,18] As described in basic organic textbooks for undergraduate students, typical direct condensation of acids and alcohols (Fischer esterification) rarely proceeds with strong acids that decrease the nucleophilicity of alcohol.[19,20] To overcome this issue, pioneering studies have been reported by several groups (Figure 1b). Azeotropic processes using specific metal- or amine-based catalysts enable the direct esterification of **1** with alcohols.[21-24] Alternatively, the use of stoichiometric activating reagents[25,26] or microwave reactors[27,28] has also been possible methods. These procedures successfully enable facile production of phosphate monoesters and/or diesters from **1**. In contrast, the synthesis of phosphate triesters is still more energetically difficult in comparison with the synthesis of monoesters and diesters.[27] Several alternative methods for the preparation of phosphate triesters using copper catalysts,[29,30] iodonium salts[29] and electrophilic alkylating reagents[27,28,31] have been developed. However, these reactions require phosphate diesters as the starting materials, as well as toxic or expensive reagents.

In this study, we developed an efficient synthetic method for the synthesis of phosphate triesters from **1** via direct triple esterification without water removal by azeotropic processes (Figure 1c). This was achieved by utilizing tetraalkyl orthosilicate as an alkylating agent and successfully applied to crude **1**, obtained from sewage sludge ash that includes water and other impurities; thus, we established an innovative and efficient recycling process for recovered phosphorus resources.

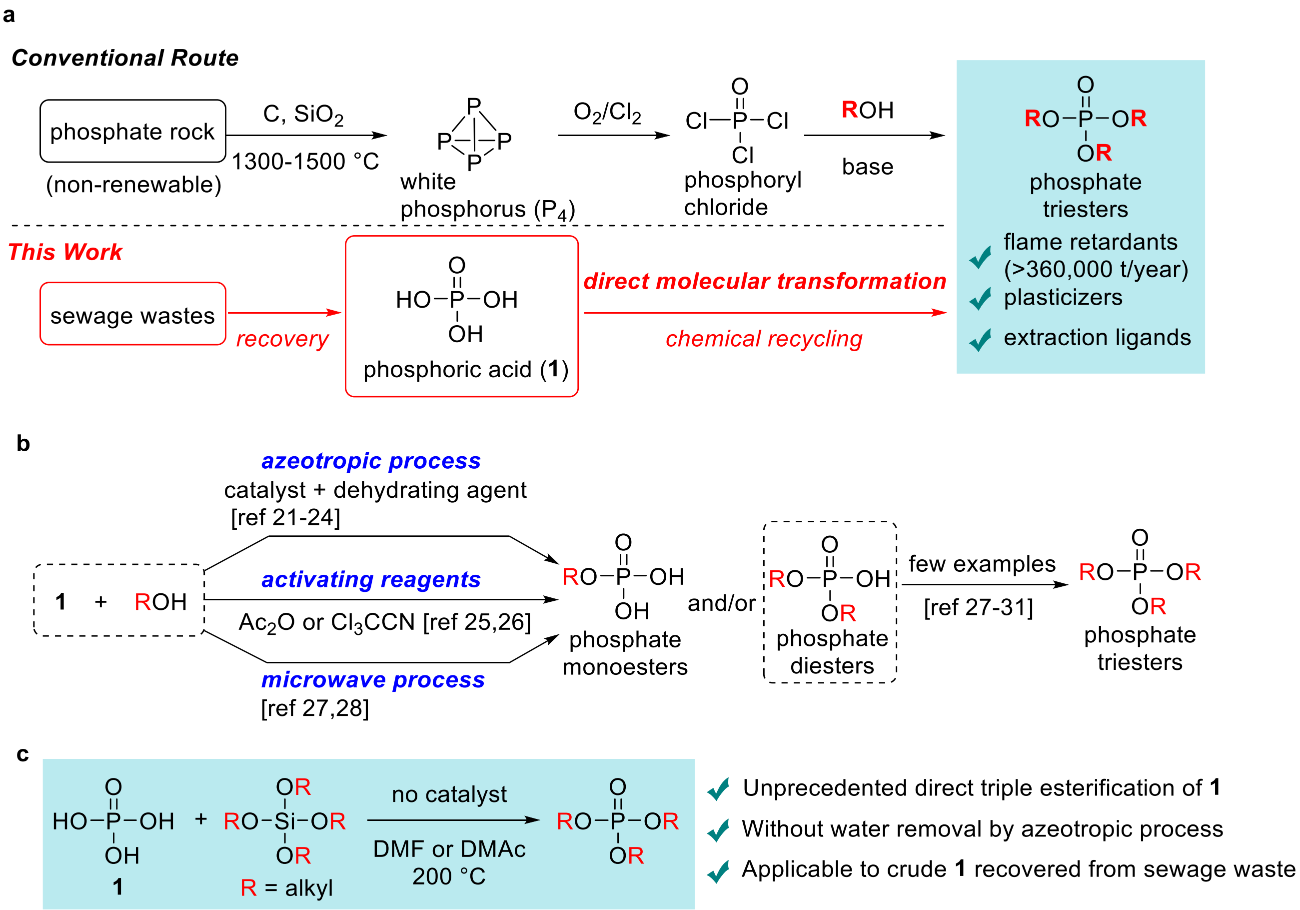


Figure 1. Direct transformation of 1 to phosphate triesters. a. Conventional route and the route developed in this work to produce phosphate triesters. **b.** Reported examples of esterification of **1** to form phosphate esters. **c.** Direct triple esterification of **1** with tetraalkyl orthosilicate.

RESULTS AND DISCUSSION

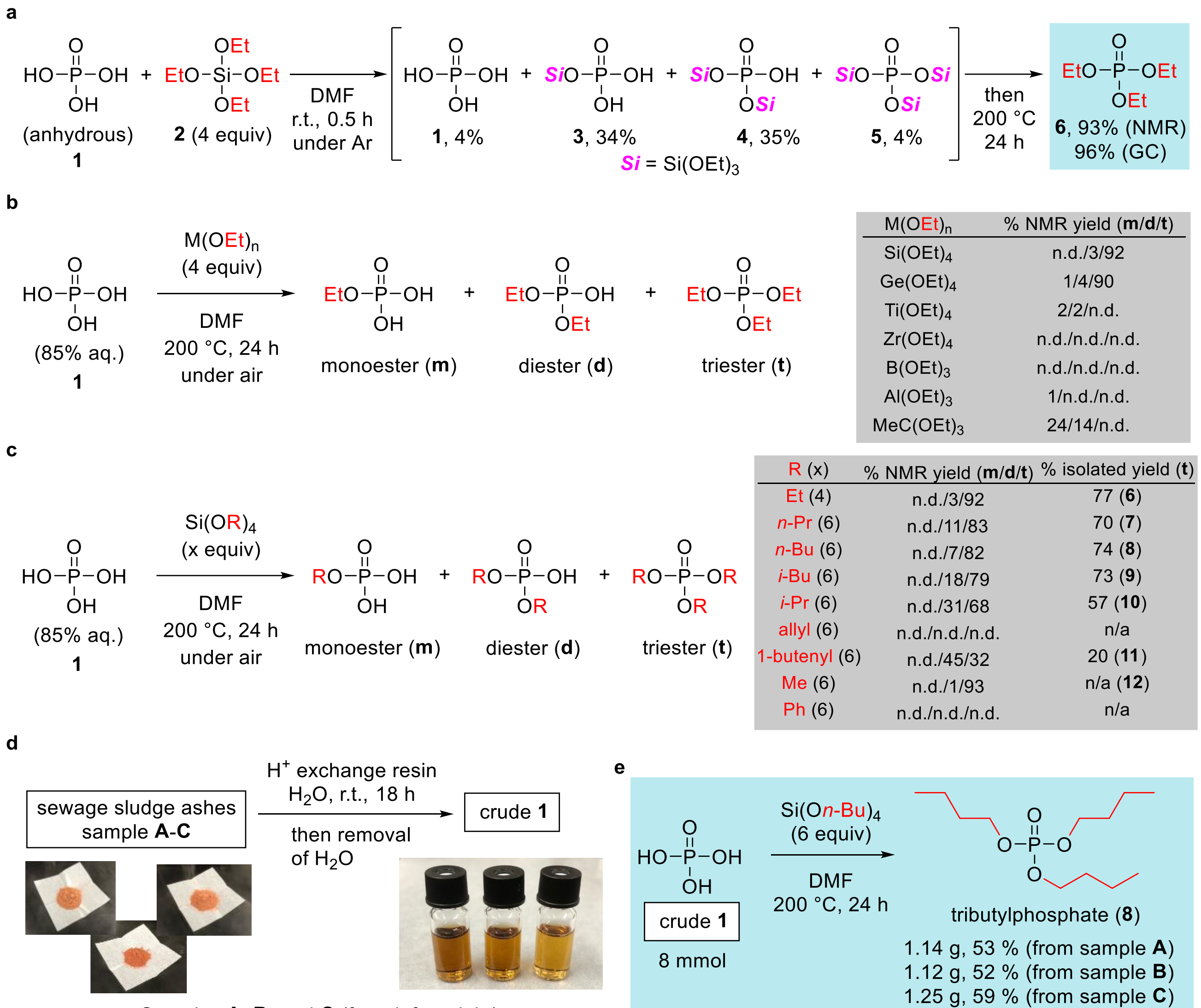
The concept developed in this work originated from an entirely different project in our laboratory, dedicated to the development of silicon-based materials.[32] Specifically, we focused on silicone which is obtained through the condensation of tetraalkyl orthosilicate in the presence of an acid catalyst (curing process). During the curing process of tetraethyl orthosilicate (**2**), **2** was immediately converted to insoluble polymeric silicophosphate upon treatment of **1**, as reported previously.[33-35] On the other hand, we found that the reaction of anhydrous **1** with 4 equivalents of **2** in DMF, as a polar solvent, resulted in the formation of a soluble mixture of triethoxysilyl phosphate esters, **3** (34%), **4** (35%) and **5** (4%) (Figures 2a and S1).[36] To promote additional condensation to form a siloxane bonded (–Si–O–Si–) network, this mixture was heated at 200 °C. Unexpectedly, this process resulted in the exclusive formation of triethyl phosphate (**6**) (93% yield determined by ^{31}P NMR and 96% yield determined by GC). Thus, direct esterification of **1** was achieved using a commercially available simple reagent, tetraalkyl orthosilicate. More surprisingly, the reaction using a versatile 85% aqueous solution of **1** with excess **2** under air also afforded **6** in 92% NMR yield (Figure 2b). According to the literature survey,[37-41] the efficient esterification of phosphinic acid has been reported by using alkoxysilanes, but no application of this method to the synthesis of triesters from **1** has been reported. Motivated by this result, we further investigated other metal ethoxides and found that only $Ge(OEt)_4$, which is also in group 14, similar to $Si(OEt)_4$, was suitable for esterification, while the other Lewis acids, such as $Ti(OEt)_4$, $Zr(OEt)_4$, $B(OEt)_3$ and $Al(OEt)_3$, were completely ineffective (Figure 2b). We also conducted a reaction using triethyl orthoacetate, a reagent known for its effectiveness in esterifying carboxylic acids and phosphinic acids reported by Togo[42] and phosphonic acid by Ostaszewski.[43] The reaction of **1** with triethyl orthoacetate gave the mixture of phosphate monoester and diester in low yields (24% and 14%, respectively) (Figure 2b). The results of these experiments revealed that the inexpensive and readily available tetraalkyl orthosilicate is a useful reagent for the esterification of **1** to directly form phosphate triesters (for details regarding the further examination of the reaction conditions, see Tables S1 and S2).

From a cost-effectiveness perspective, it should be also noted that the typical preparation of tetraalkyl orthosilicates requires tetrachlorosilane ($SiCl_4$) as a starting compound, inexpensively produced as a by-product of the polysilicon industry or from the chlorination of ferrosilicon with chlorine.[44,45] To avoid the use of $SiCl_4$, alternative syntheses of tetraalkyl orthosilicates starting from silica (SiO_2) and alcohols have also been investigated toward the industrial applications.[46-51]

The scope of tetraalkyl orthosilicate reagents was then examined (Figure 2c). When employing orthosilicates other than tetraethyl orthosilicate, it was generally necessary to use 6 equivalents of the tetraalkyl orthosilicate to attain satisfactory yields in the reactions. The reaction of **1** with organosilicates possessing a linear alkyl chain (ethyl, *n*-propyl and *n*-butyl groups) or a branched primary alkyl chain (isobutyl) resulted in the formation of the corresponding trialkyl phosphates **6-9** in 70-77% isolated yields. The reaction of an organosilicate containing a bulky isopropyl group afforded the corresponding triester **10** in 68% NMR yield (57% isolated yield) along with the formation of a diester in 31% NMR yield. The esterification using tetraallyl orthosilicate failed due to gel formation. Instead, the reaction of tetra(1-butenyl) orthosilicate with a terminal olefin gave **11** in 20% isolated yield, even though the partial gel formation was observed. Trimethyl phosphate (**12**) was generated in 93% NMR yield, while the isolation by extraction into organic phase failed due to the high polarity. An attempt to introduce a phenyl substituent using tetraphenyl orthosilicate also failed, resulting the reaction unsuitable for the synthesis of aromatic phosphates.

With this methodology for the direct transformation of **1** into phosphate triesters in hand, our next endeavor was to investigate the utilization of phosphorus resources recovered from actual sewage wastes. Notably, sewage sludge ash has been estimated to contain approximately 15-30 wt% phosphorus as P_2O_5,[1] which is comparable to the composition of phosphate rocks and makes this material attractive as an unused phosphorus resource. Phosphorus recovery from sewage sludge ash has been demonstrated in recent years, and phosphorus extraction through the dissolution of metal phosphates using inorganic acids is a prevalent approach.[17] We evaluated a straightforward, one-step method to efficiently recover **1** from sewage sludge ash labelled **A**, **B** and **C**, which were provided from three different Japanese local sewage treatment plants (Figures 2d and S4). After numerous attempts, we successfully achieved selective phosphorus extraction from these sewage sludge ash samples by treating samples **A-C** with hydrogen-form ion exchange resin in H_2O. This method resulted in extraction of solutions with negligible metal ion contamination,[52] which is inevitable in the acid-extraction procedure.[17] Specifically, the suspension of samples **A-C** and the ion exchange resin was stirred at room temperature for 18 hours, followed by filtration to remove insoluble residues and the resin, affording the extracted aqueous solution of **1**. The results of wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) indicated a phosphorus concentration exceeding 115 mmol/L in the extracted solution (Figure S5). The concentrations of metal cations in the extract were found to be quite low: even the highest iron concentration was less than 1.4 mmol/L (Figure S5). Small quantities of silicon and sulfur, which behave as anions, were detected in the extracted solution, although their concentrations were all less than one-tenth of the phosphorus concentration (Figure S5).

After the removal of water in vacuo from the extract, we obtained three samples of crude **1** at approximately 80 wt% (Figure 2d). These crude samples were subsequently utilized in orthosilicate-mediated esterification without any further purification (Figure 2e). Encouragingly, when we conducted gram-scale reactions of all the crude samples, 6 equivalents of tetrabutyl orthosilicate successfully generated the corresponding product **8** (52-59% isolated yields), which is commonly utilized as a flame retardant and had an annual production volume of 14,907 tons in 2020.[5,53]



$M(OEt)_n$	% NMR yield (**m/d/t**)
$Si(OEt)_4$	n.d./3/92
$Ge(OEt)_4$	1/4/90
$Ti(OEt)_4$	2/2/n.d.
$Zr(OEt)_4$	n.d./n.d./n.d.
$B(OEt)_3$	n.d./n.d./n.d.
$Al(OEt)_3$	1/n.d./n.d.
$MeC(OEt)_3$	24/14/n.d.

R (x)	% NMR yield (**m/d/t**)	% isolated yield (**t**)
Et (4)	n.d./3/92	77 (**6**)
n-Pr (6)	n.d./11/83	70 (**7**)
n-Bu (6)	n.d./7/82	74 (**8**)
i-Bu (6)	n.d./18/79	73 (**9**)
i-Pr (6)	n.d./31/68	57 (**10**)
allyl (6)	n.d./n.d./n.d.	n/a
1-butenyl (6)	n.d./45/32	20 (**11**)
Me (6)	n.d./1/93	n/a (**12**)
Ph (6)	n.d./n.d./n.d.	n/a

Samples **A**, **B**, and **C** (from left to right)

Figure 2. Synthesis of phosphorus-containing chemicals from sewage sludge ash. a. Condensation reaction between anhydrous **1** and **2** at room temperature and the subsequent transformation to **6** at 200 °C. **b.** The screening of metal ethoxides and tetraethyl orthoacetate with **1**. **c.** Scope of tetraalkyl orthosilicate reagents. **d.** Selective extraction of **1** from sewage sludge ash samples **A-C** and preparation of crude **1**. **e.** Gram-scale synthesis of **8** from crude **1**.

To further broaden the applicability of orthosilicate-mediated direct esterification, we next examined the reaction of phosphinic acids and phosphonic acids with various organic substituents (Figure 3). Initially, the scope of tetraalkyl orthosilicate reagents was examined in the reaction of diphenylphosphinic acid to furnish the corresponding phosphinates **13**-**16** with methyl and primary alkyl groups in 54-76% yields. The reactions with organosilicates containing bulky secondary alkyl groups proceeded with lower yields of **17** (18%) and **18** (22%), which was consistent with the observations for the reaction of **1** (Figure 2c). Compound **19** bearing a branched 2-ethylhexyl group was obtained in better yield, suggesting that the steric environment around the silicon centre had a significant influence on the reactivity. The reaction of the substrate containing an olefin moiety generated **20** in 77% yield. The reaction of phenylphosphonic acid with several tetraalkyl orthosilicates resulted in the formation of dialkyl phosphonates **21**-**26** in 62-92% yields, which were much better results than that achieved with diphenylphosphinic acid.

When reacting tetraethyl orthosilicate with various linear aliphatic phosphonic acids, we obtained the corresponding diethyl phosphonates **27**-**33** in 69-87% yields. A decrease in yield was observed for the esterification of sterically hindered *tert*-butyl phosphonic acid (**34**, 27% yield). The reaction of aliphatic phosphonic acid containing phenyl groups also proceeded successfully (**35**-**37**, 61-84% yields). Regarding the impact of substituents on the aromatic rings in the organophosphonic acids, electron-withdrawing groups (e.g., bromo and pentafluoro groups), electron-donating groups (e.g., hydroxy, methoxy and amino groups), and *N*-hetero aromatic rings (e.g., pyridyl and carbazolyl groups) were all tolerated to afford target compounds **38**-**45** in moderate to good yields. In the case of other functional groups, phosphonic acids possessing cinnamyl and perfluoroalkyl groups were tested to confirm their applicability (**46** and **47**, 82 and 89% yields). Finally, diphosphonic acids with 1,4-phenylene and 1,6-hexyl groups were converted to the corresponding diphosphonates **48** (53%) and **49** (53%).

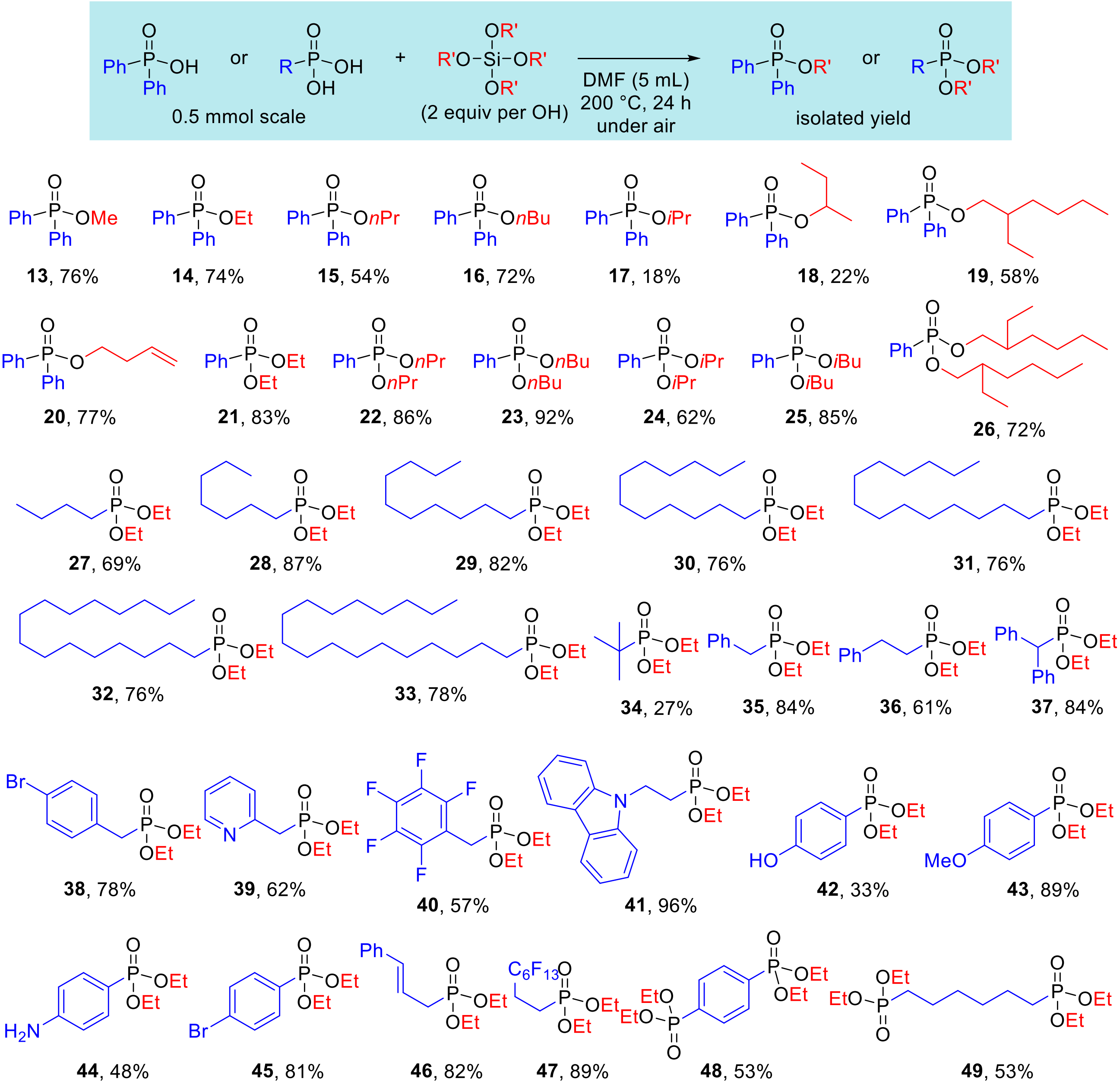
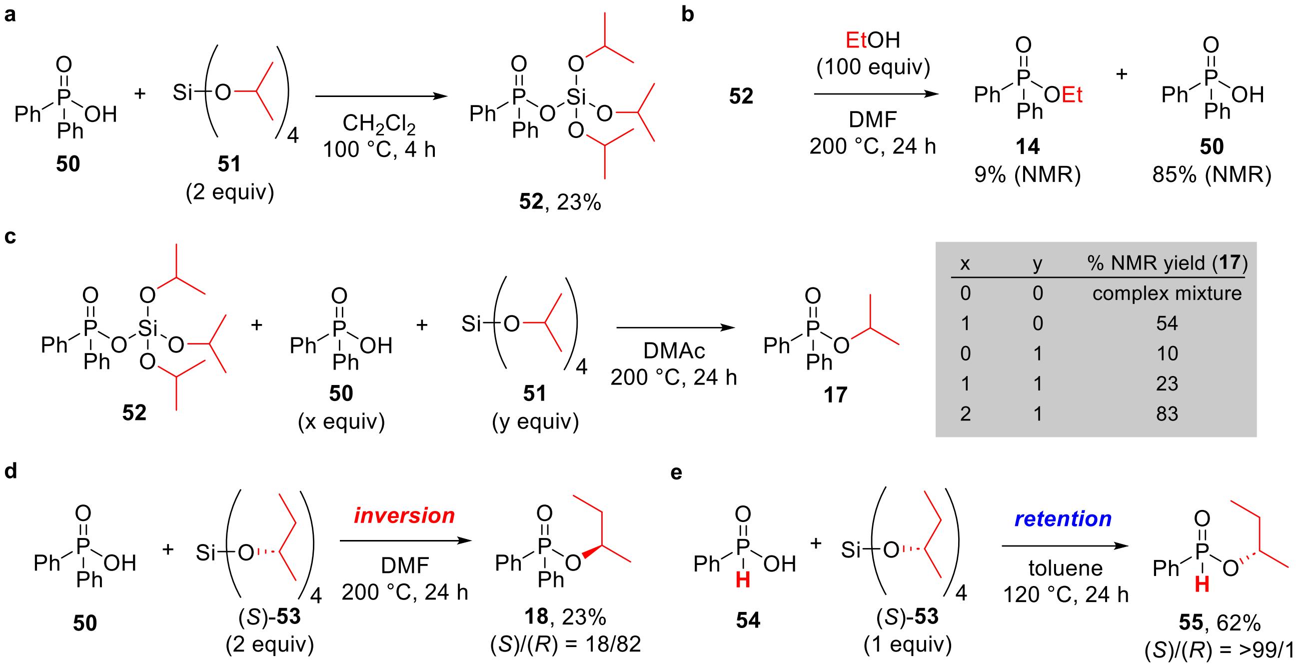


Figure 3. Orthosilicate-mediated direct esterification of organophosphinic acids and phosphonic acids.

The remaining challenge lies in elucidating the reaction mechanism underlying the orthosilicate-mediated esterification of **1**. First, given that condensation between **1** and **2** occurs even at room temperature, it is reasonable to assume that the corresponding triethoxysilyl phosphate products **3-5** serve as reaction intermediates (Figure 2a). It has been reported that the esterification of phosphinic acids, phosphonic acids and phosphoric acids typically proceeds through nucleophilic substitution by an alcohol on the phosphorus atom, often involving the formation of pentacoordinate phosphorus species.[27,54-56] Since the isolation of **3-5** proved challenging due to the instability of the compounds, we synthesized a more stable triisopropoxysilyl phosphinate **52** with bulky substituents from diphenyl phosphonic acid (**50**) and tetraisopropyl orthosilicate (**51**) (Figure 4a). The reaction of **52** with 100 equivalents of ethanol in DMF at 200 °C resulted in a mere 9% yield of the corresponding ethyl ester **14**, with the predominant decomposition leading to the recovery of **50** (Figure 4b). This outcome excludes the possibility that silyl phosphate acts as an activating reagent to facilitate nucleophilic substitution by the alcohol. While the treatment of **52** in DMAc at 200 °C resulted in the formation of a complex mixture, it was found that **50** and **51** were effective as additives (Figure 4c). In particular, the reaction of **52** with 2 equivalents of **50** and 1 equivalent of **51** afforded **17** in 82% yield.

Next, we conducted the reaction of **50** with orthosilicate **53** bearing a chiral (*S*)-*sec*-butyl group. During the reaction, stereoinversion occurred to provide **18** with (*R*)-*sec*-butyl group in 23% yield (Figure 4d). Therefore, this observation strongly suggests that the esterification step proceeds through the cleavage of carbon–oxygen bonds in the orthosilicate and subsequent S_N2-type alkyl transfer. This plausible mechanism is also consistent with the failure of aromatic esterification with tetraphenyl orthosilicate (Figure 2c). Although the inversion was not exclusive, with a ratio of *S*/*R* = 18/82, this partial racemization might occur via the formation of pentacoordinate phosphorus species (see the Supporting Information).

Previously, Montchamp reported the tetraalkyl orthosilicate-mediated esterification of H-phosphinic acids.[37-41] While this method is firmly established for the synthesis of H-phosphinate esters, it has been shown to be applicable to starting compounds containing reactive P-H bonds. Indeed, the reactions of phosphinic acid or phosphonic acid without P-H bond were both failed,[37] and thus the application of **1** to this method should be considered analogically impossible. Considering the possibility that the reaction investigated in the current study might proceed via a similar mechanism, we carried out the esterification of phenylphosphinic acid (**54**) containing a P-H bond with (*S*)-**53**. To our satisfaction, the reaction proceeded smoothly even at 120 °C, and the stereochemistry of the *sec*-butyl group in **55** remained unchanged (Figure 4d). This result strongly suggests that the direct esterification reaction of **1** with orthosilicate proceeds through a reaction mechanism completely distinct from Montchamp's method.



x	y	% NMR yield (**17**)
0	0	complex mixture
1	0	54
0	1	10
1	1	23
2	1	83

Figure 4. Mechanistic studies on the organosilicate-mediated esterification of 1. a. Preparation of silyl phosphinate **52** from **50** and **51**. **b.** Reaction of **52** with excess ethanol. **c.** Reaction of **52** with **50** and **51**. **d.** Stereoinversion during the reaction of **50** and (*S*)-**53**. **e.** Stereoretention during the reaction of **54** with (*S*)-**53**.

To further investigate this point, density functional theory (DFT) calculations were performed using dimethyl phosphate (**56**) and tetramethyl orthosilicate (**57**) as model substrates. Initially, we postulated that the silyl phosphate product, which is formed at the initial stage of the reaction (Figure 2a), serves as a potential intermediate. Therefore, we examined the direct internal alkyl transfer from the siloxy moiety to the phosphoryl moiety of dimethyl(trimethoxysilyl) phosphate (**58**) (see section 3.2 in the Supporting Information). However, as summarized in Figure S17, this process exhibited a high energy barrier (42.7 kcal/mol), even after considering the assistance of additional **56** and **1**, which prevents the formation of an energetically unstable silanone derivative.[57] As shown in Figure S18, this reaction pathway proceeds via the formation of a rigid six-membered ring, which hampers the S_N2-type backside attack at the C^1 atom by the phosphoryl moiety to achieve stereoinversion of the carbon atom. In light of this finding, we next focused on the indirect alkyl transfer in which the formation of multimolecular aggregates using **58** as a template. A related multimolecular aggregate was proposed to form during the esterification of phopshinic acid with alcohols via nucleophilic substitution.[55] To construct a realistic computational model for the methyl group transfer from **57** to **56**, phosphoric acids (**1**) were also introduced to the model on the basis of the experimental fact shown in Figure 4c. We expect that the alkoxide-like structure, which appears during the methyl transfer, is stabilized by the proton transfer from the phosphoric acid. The resultant phosphate is stabilized by another phosphoric acid in a concerted manner mediated by multiple proton shuttling. The structures of the key intermediates and transition state for the methyl transfer are schematically shown in Figure 5a. This process is slightly exergonic by -0.5 kcal/mol with the energy barrier of 29.8 kcal/mol. Detailed information about the structures of the intermediates and transition state are shown in Figure S19. In this reaction, **58** behaves as a template so that the reactants, $Si^2(OMe)_4$ (**57**) and two phosphoric acids (**1**) could easily aggregate via the formation of a pentacoordinate silicon atom (Si^1) to allow the C^1H_3 group of **57** to access the O^5 atom of **58** without structural restraints. In addition, the two additional phosphoric acids (**1**) assist the C^1H_3 group transfer via proton shuttling by forming a multimolecular aggregate.

As **57** interacts with **58**, the C^1-O^6 bond length continuously decreases along the reaction coordinate from 3.58 Å (in the reactant state, **R**) to 1.44 Å (in the product state, **P**) (Figure 5b). On the other hand, the O^1-Si^1 bond length, initially 3.78 Å, significantly decreases to 2.03 Å upon the formation of **I1** from **R**, forming a pentacoordinate Si^1 atom. This event triggers the proton shuttling of two phosphoric acids (**1**), facilitating the transfer of the H^1 and H^2 atoms to the O^3 and O^5 atoms, respectively, upon the formation of **TS1**. This process proceeds stepwise and two representative structures, **X1** and **X2**, were selected, as shown in Fig. 5b. The first transfer of H^1 is completed at **X1** and the second transfer of H^2 ends at **X2** (see Figure S22). The O^5-C^1 bond is slightly elongated to 1.91 Å at **TS1** and then cleaved to form **I2**. Finally, the O^7-Si^1 bond length is cleaved to form trimethyl phosphate (**12**) and new **58** at **P**. Overall, it is likely that after the access of the $P^1(O^1)$ moiety to the Si^1 atom, two sequential proton (H^1 and H^2) transfers facilitate methyl transfer to form a C^1-O^6 bond.

We also confirmed that the reaction proceeds with a higher energy barrier, 34.7 kcal/mol (Figure S20), when compound **58** is absent as a template (Figure S21). This observation provides further evidence that **58** serves as the template to catalyse the proton shuttle reaction process.

Natural population analysis (NPA) revealed that the C^1H_3 group maintains a positive charge throughout the reaction, with this positive charge notably intensifying upon the formation of **TS1** (Figure 5c). Concomitantly, the O^5 atom become negatively charged. These results strongly supported that the C^1H_3 group is transferred as a methyl cation, facilitated by proton shuttling within the multimolecular aggregate. The changes in population among the oxygen (O) atoms are closely associated with the stepwise proton transfer process. From **I1** to **X1**, where the first proton (H^1) transfer proceeds from O^2 to O^3, the population of O^2 decreases and that of O^3 simultaneously increases. From **X1** to **X2**, where the second proton (H^2) transfer proceeds from O^4 to O^5, similar population changes are observed for both O^4 and O^5 atoms. Finally, the cationic C^1H_3 group transfer proceeds from **X1** and **X2**, leading to significant population changes at the O^5 and O^6 atoms. Overall, this observation also supported the template-facilitated multimolecular aggregate mechanism, which is closely associated with the multiproton shuttle process via a network of multiple hydrogen bonds.

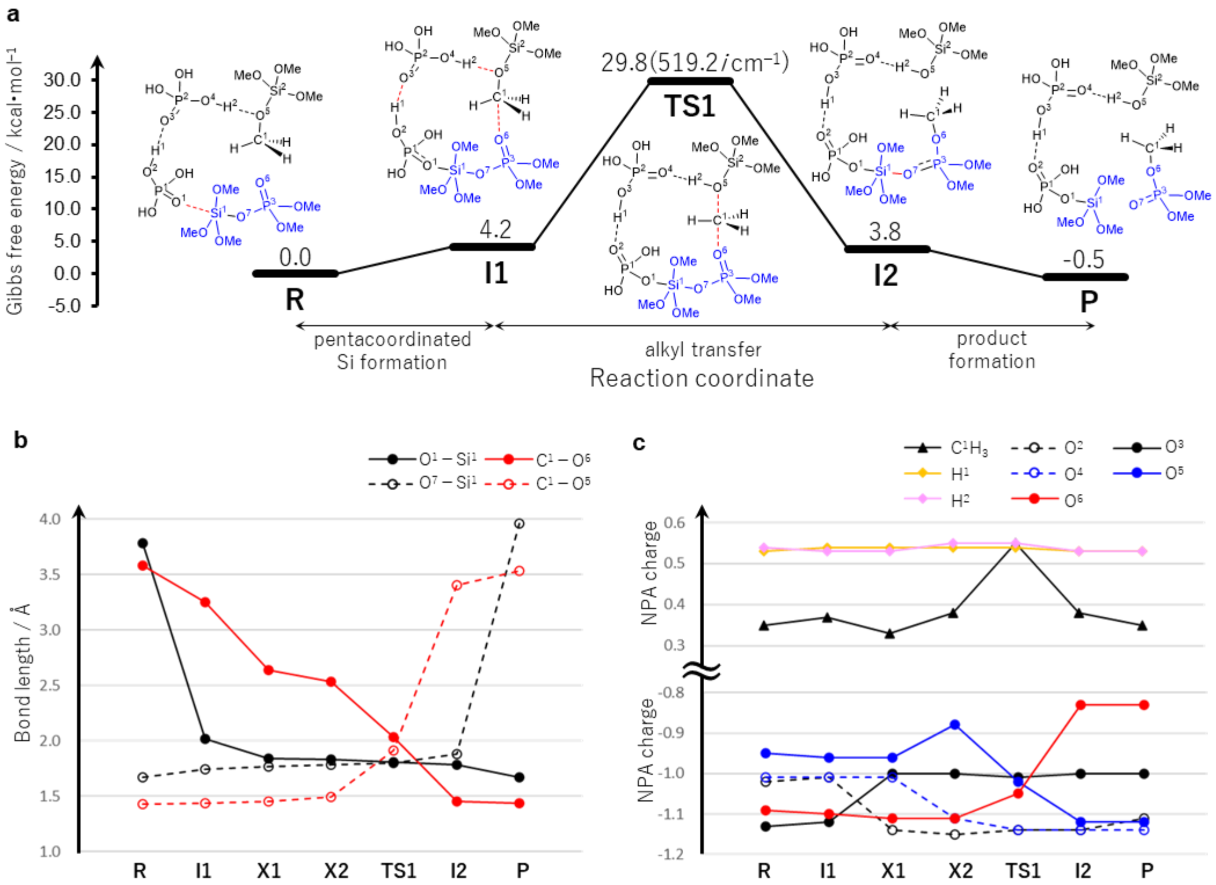


Figure 5. Results of DFT calculations for mechanistic study. a. Energy profile of the multimolecular aggregate mechanism and the structures of the reaction complex along the reaction coordinate. **b.** Variations in bond lengths of significant bonds throughout the reaction pathway. **X1** and **X2** represent characteristic structures after the sequential proton transfer H^1 and H^2, respectively. **c.** Shifts in NPA charges along the reaction pathway.

CONCLUSIONS

The direct triple esterification of **1**, a process previously considered impossible,[21-28] was successfully achieved using tetraalkyl organosilicates. This molecular transformation represents one of notable advancements in the synthesis of phosphorus chemicals, eliminating the need for white phosphorus.[3,4] Moreover, the reaction exhibits tolerance to contaminants such as water and other elements, facilitating the chemical recycling of crude **1** recovered from sewage sludge ash. Regarding the scope of acids, organic phosphonic and phosphinic acids could be effectively converted into the corresponding esters. Mechanistic investigations employing diphenylphosphinic acid (**50**) indicated that the esterification proceeds via alkyl group transfer from tetraalkyl orthosilicate, accompanied by the carbon-oxygen bond cleavage. Theoretical calculations proposed a template-facilitated multimolecular aggregate mechanism, which expands the conventional esterification reaction using tetraalkyl orthosilicate.[39-43]

Considering the cost efficiency of employing stoichiometric organosilicates, current protocols for phosphorus recycling require further improvement to replace the preparative methods of phosphorus chemicals based on white phosphorus. Nevertheless, this discovery utilizing silicon compounds should be promising as a key technology for transforming phosphorus-rich wastes into valuable chemical products, marking a significant milestone in sustainable phosphorus utilization.

ASSOCIATED CONTENT

Data Availability Statement

The data that support the findings of this study are available within the paper and its Supporting Information and from the corresponding author upon reasonable request.

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Author Contributions

Y. Naganawa., M.Y., K. Sato., and Y. Nakajima conceptualized the phosphorus chemical recycling project. Y. Naganawa developed and designed the entire experimental plan with support from K.M. and Y. Nakajima. K. Sakamoto and A.F. conducted the synthetic experiments. K.M. designed and carried out the recovery experiment for phosphoric acid from sewage sludge ash. M.R., J.H., and Y. Nakajima performed the computational studies. Y. Naganawa, K.M., J.H., and Y. Nakajima collectively wrote the manuscript, incorporating contributions from all other authors.

Competing Interests

The authors declare no competing interests.

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