Chemical upcycling of phosphoric acid recovered from sewage waste

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Summary

Global concerns regarding the depletion and strategic importance of phosphorus resources have increased demand for the recovery and recycling.[1] 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[2,3] and enables direct esterification of phosphoric acid to produce widely applicable phosphate triesters.[4] 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 groundbreaking upcycling 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.

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. 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 huge electricity (Fig. 1a).[2,5,6] Owing to this method, there have been repeated instances in the past, such as a global price spike of phosphorus resources, that have raised concerns about the sustainability of P_4 production.[7,8] Another issue is that phosphorus emissions have already been estimated to exceed the limit defined for a safe operating space, that is, the Planetary Boundary.[9] Hence, phosphorus recovery and recycling are crucial in terms of not only resource risk avoidance but also achieving a sustainable global environment.[1,3,10,11] 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] However, these technologies suffer from poor cost profitability due to the low transaction price of fertilizer (Fig. 1a). Therefore, the development of a new method to synthesize high-value added phosphorus compounds from recovered phosphorus is highly desired to establish sustainable phosphorous resource cycles.

Phosphate triesters are industrially distributed as flame retardants, plasticizers and extraction ligands. In particular, flame retardants possessing phosphate triester structures are normally synthesized in large quantities (360,000 tons in 2020)[10] via alcoholysis of $POCl_3$ prepared from P_4 (Fig. 1a, conventional route).[11] In this context, we aimed to develop a direct esterification reaction of **1** to establish a new methodology for the production of phosphate triesters (Fig. 1a, this work).[4]

The bottleneck in developing an upcycling process for **1** lies in the high chemical and thermodynamic stability of **1** as a strong acid.[3,12] 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.[13,14] To overcome this issue, pioneering studies have been reported by several groups (Fig. 1b). Azeotropic processes using specific metal- or amine-based catalysts enable the direct esterification of **1** with alcohols.[15-18] The use of stoichiometric activating reagents[19,20] or microwave reactors[21,22] has also been reported. However, these methods are still limited to the formation of phosphate monoesters and/or diesters. To efficiently form phosphate triesters, which has been estimated to be more energetically difficult,[21] several alternative strategies using copper catalysts,[23,24] iodonium salts[23] and electrophilic alkylating reagents[21,22,25] have been developed, although these methods require phosphate diesters as starting materials.

In this study, we devised an efficient synthetic method for the direct production of phosphate triesters from **1**, employing tetraalkyl orthosilicate as an alkylating agent. Significantly, this method can be successfully applied to crude **1**, obtained from sewage sludge ash that includes water and other impurities; thus, we established an innovative and efficient upcycling process for recovered phosphorus resources.

The concept developed in this work originated from an entirely different project in our laboratory, dedicated to the development of silicon-based materials.[26] 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.[27-29] 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%) (Figs. 2a and S1).[30] 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**) in a remarkable NMR yield of 93%. 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 (Fig. 2b). Motivated by this result, we further screened 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 (Fig. 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 and co-workers,[31] and formed a phosphate monoester and diester in low yields (24% and 14%, respectively) (Fig. 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).

The scope of tetraalkyl orthosilicate reagents was then examined (Fig. 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 60-74% isolated yields. The reaction of an organosilicate containing a bulky isopropyl group afforded the corresponding triester **10** in 68% NMR yield (39% isolated yield) along with the formation of a diester in 31% NMR yield. In the case of tetra(1-butenyl) orthosilicate with a terminal olefin, **11** was obtained in 20% isolated yield due to partial gel formation. Trimethyl phosphate (**12**) was generated in 93% NMR yield, while the isolation failed due to the high polarity.

With this methodology for the direct transformation of **1** into phosphate triesters in hand, our next endeavour 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.[4] 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 (Figs. 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,[32] which is inevitable in the acid-extraction procedure.[4] 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 (Fig. 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 (Fig. 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 (Fig. S5).

After the removal of water in vacuo from the extract, we obtained three samples of crude **1** at approximately 80 wt% (Fig. 2d). These crude samples were subsequently utilized in orthosilicate-mediated esterification without any further purification (Fig. 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.[10,33]

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 (Fig. 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** (Fig. 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%).

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 (Fig. 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.[21,34-36] 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**) (Fig. 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** (Fig. 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 (Fig. 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 an (*R*)-*sec*-butyl group in 23% yield (Fig. 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. 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 Supplementary information).

Previously, Montchamp's group reported the tetraalkyl orthosilicate-mediated esterification of H-phosphinic acids to form H-phosphinate esters.[37-41] 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 (Fig. 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.

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 forms at the initial stage of the reaction (Fig. 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 Supplementary information). However, as summarized in Fig. 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.[42] As shown in Fig. 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 formation of multimolecular aggregates using **58** as a template. A related multimolecular aggregate was proposed to form during the esterification of phoshinic acid with alcohols via nucleophilic substitution.[35] After a series of attempts, we finally found that two additional phosphoric acids (**1**) assist methyl group transfer from **57** to **56** 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 Fig. 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 Fig. 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**). 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 (Fig. 5b). 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 Fig. 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 a 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 (Fig. S20), when compound **58** is absent as a template (Fig 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** (Fig. 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 formation mechanism, which is closely associated with the multiproton shuttle process via a network of multiple hydrogen bonds. The triple esterification of **1**, a process previously considered impossible,[15-22] was successfully achieved through this newly discovered mechanism. This breakthrough represents one of a few achievements associated with the synthesis of phosphorus chemicals without using white phosphorus[2,3] and a pivotal molecular transformation for sustainable phosphorus utilization.

Data availability

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

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Figure legends

Fig. 1. Direct transformation of 1 to phosphate triesters. a. Conventional route and the route developed in this work for the production of phosphate triesters. **b.** Reported examples of esterification of **1** to form phosphate esters.

Fig 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**.

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

Fig 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**.

Fig. 5 Results of DFT calculations for mechanistic study. a. Energy profile of the multimolecular aggregate formation 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.

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Author contributions

Y. Naganawa., M.Y., K. Sato., and Y. Nakajima conceptualized the phosphorus upcycling 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.

Additional information

Supplementary information is available for this paper at XXXXX.

Figures

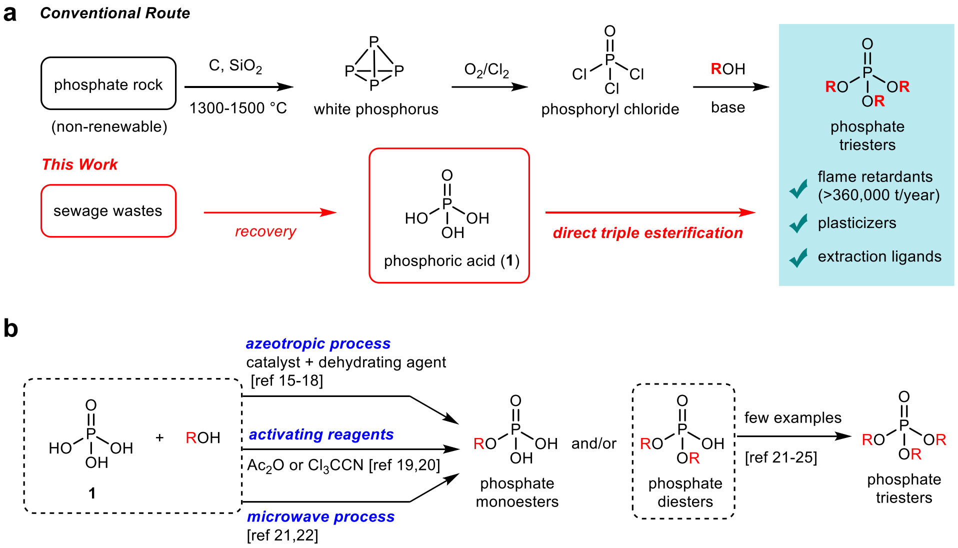
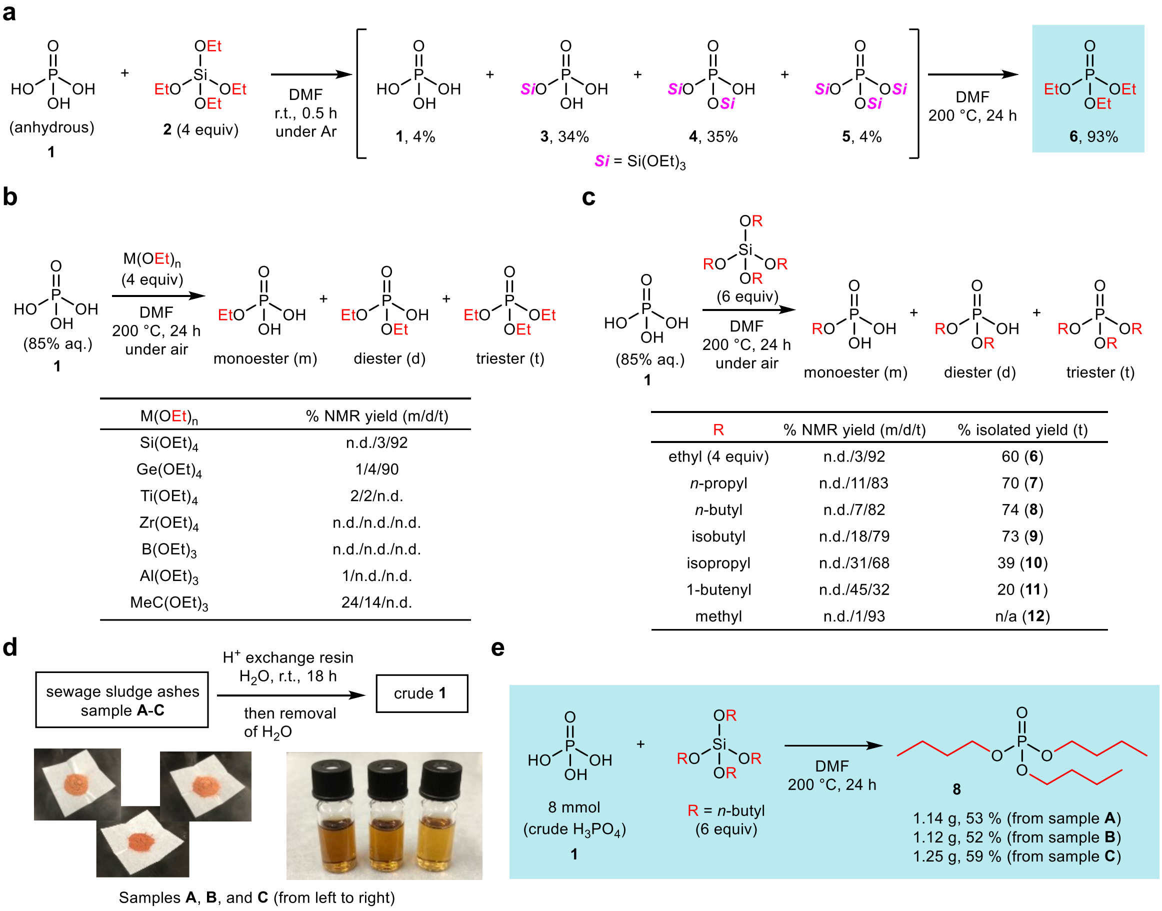


Fig. 1



$M(OEt)_n$	% 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	% NMR yield (m/d/t)	% isolated yield (t)
ethyl (4 equiv)	n.d./3/92	60 (**6**)
n-propyl	n.d./11/83	70 (**7**)
n-butyl	n.d./7/82	74 (**8**)
isobutyl	n.d./18/79	73 (**9**)
isopropyl	n.d./31/68	39 (**10**)
1-butenyl	n.d./45/32	20 (**11**)
methyl	n.d./1/93	n/a (**12**)

Fig. 2

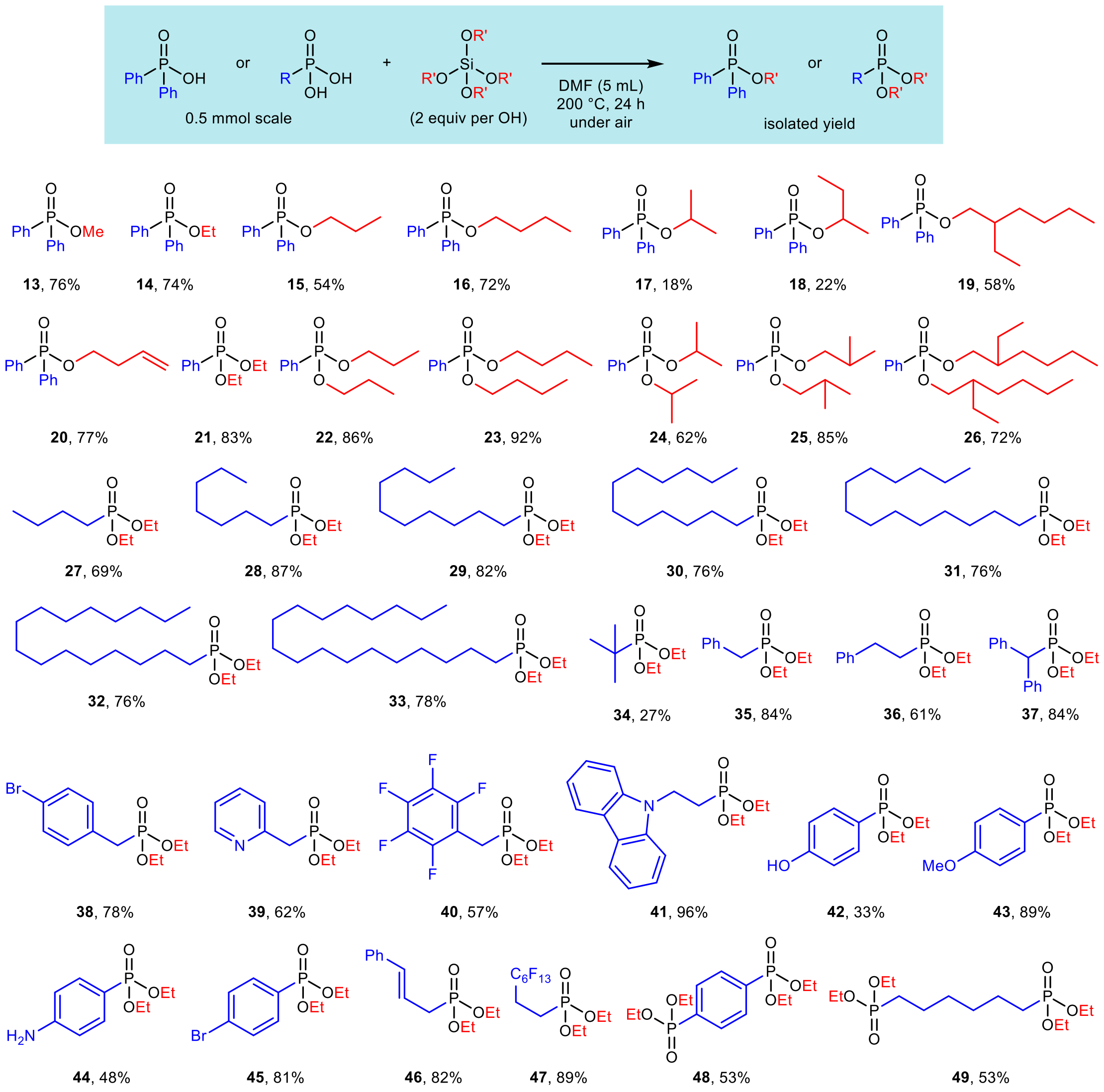
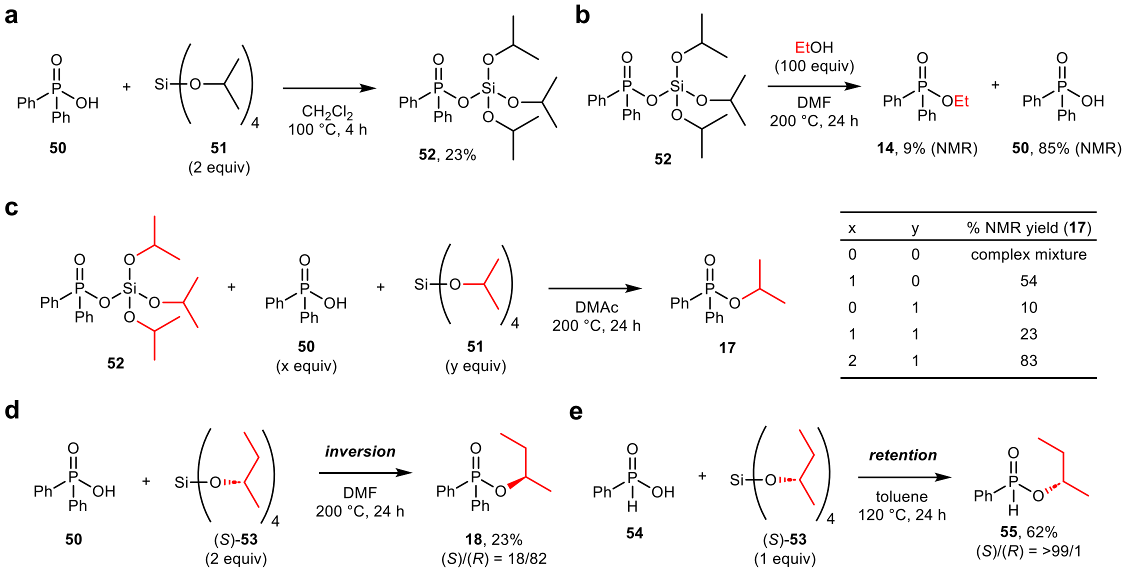

0.5 mmol scale
(2 equiv per OH)
DMF (5 mL)
200 °C, 24 h
under air
isolated yield
13, 76%
14, 74%
15, 54%
16, 72%
17, 18%
18, 22%
19, 58%
20, 77%
21, 83%
22, 86%
23, 92%
24, 62%
25, 85%
26, 72%
27, 69%
28, 87%
29, 82%
30, 76%
31, 76%
32, 76%
33, 78%
34, 27%
35, 84%
36, 61%
37, 84%
38, 78%
39, 62%
40, 57%
41, 96%
42, 33%
43, 89%
44, 48%
45, 81%
46, 82%
47, 89%
48, 53%
49, 53%

Fig. 3



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

Fig. 4

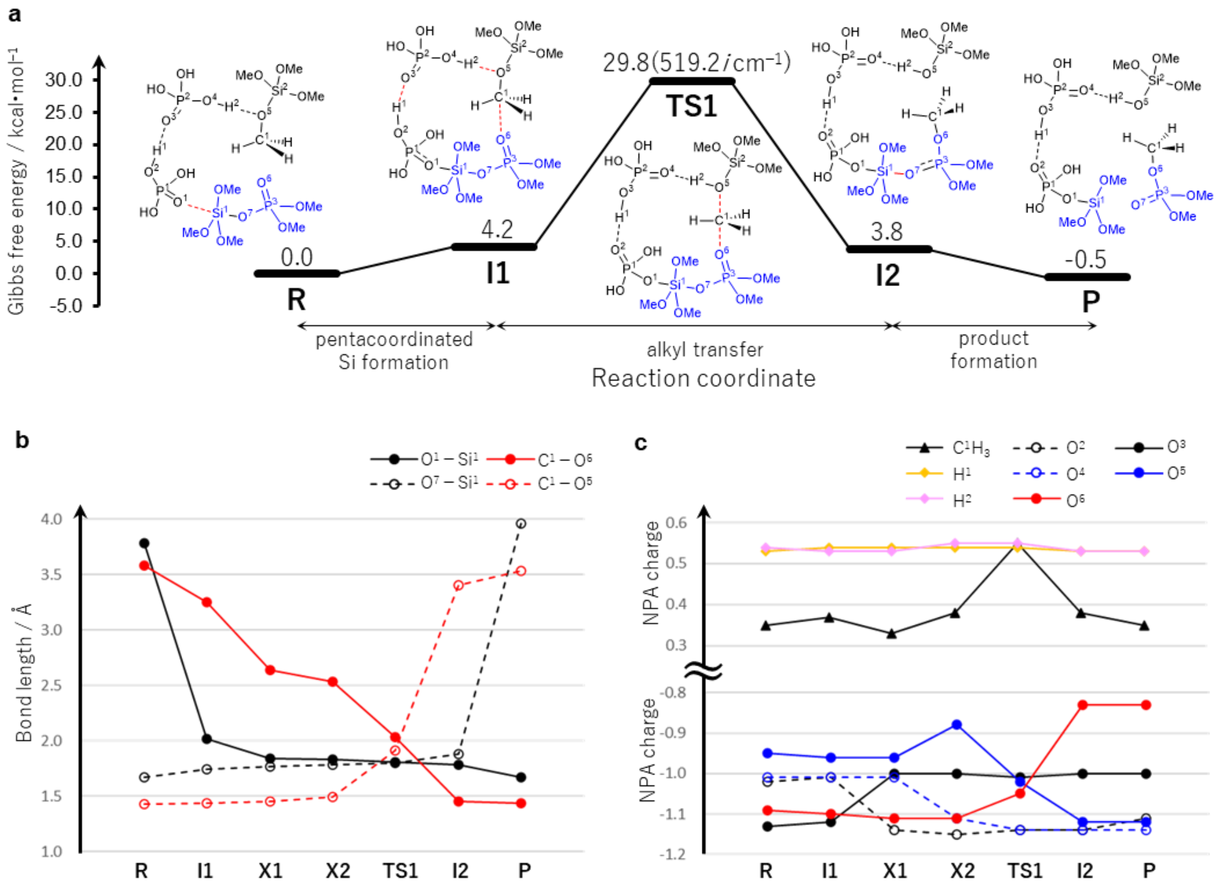

a
Gibbs free energy / kcal•mol⁻¹
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
0.0
R
4.2
I1
29.8(519.2 i cm⁻¹)
TS1
3.8
I2
-0.5
P
pentacoordinated Si formation
alkyl transfer
product formation
Reaction coordinate
b
O¹ – Si¹
C¹ – O⁶
O⁷ – Si¹
C¹ – O⁵
Bond length / Å
4.0
3.5
3.0
2.5
2.0
1.5
1.0
R
I1
X1
X2
TS1
I2
P
c
C¹H₃
O²
O³
H¹
O⁴
O⁵
H²
O⁶
NPA charge
0.6
0.5
0.4
0.3
-0.8
-0.9
-1.0
-1.1
-1.2
R
I1
X1
X2
TS1
I2
P

Fig. 5