

Diphenyl Diselenide-Catalyzed Synthesis of Triaryl Phosphites and Triaryl Phosphates from White Phosphorus

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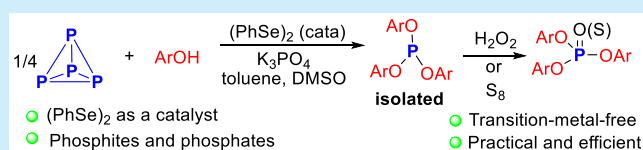
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ABSTRACT: Industrially important triaryl phosphites, traditionally prepared from PCl_3 , have been synthesized by a diphenyl diselenide-catalyzed one-step procedure involving white phosphorus and phenols, which provides a halogen- and transition metal-free way to these compounds. Subsequent oxidation of triaryl phosphites produces triaryl phosphates and triaryl thiophosphates. Phosphorotrithioates are also prepared efficiently from aromatic thiols and aliphatic thiols.



The phosphorus–oxygen bond is widely found in many biologically active organic phosphorus compounds (OPCs), among which triaryl phosphites and triaryl phosphates are already widely used in industry (Figure 1).

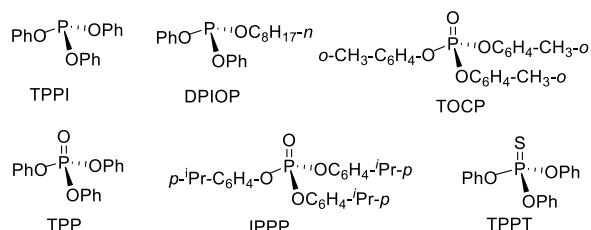
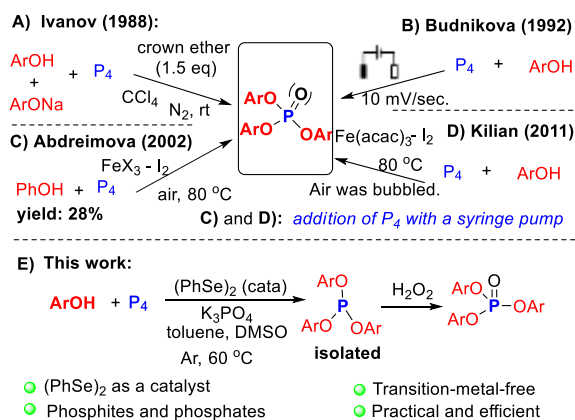


Figure 1. Selected industrially important OPCs.

Triphenyl phosphite (TPPI) is used as the antioxidant stabilizer in polyethylene, polyvinyl chloride, ABS resin, and epoxy resin.¹ Triphenyl phosphate (TPP) is commonly used as a flame retardant and nonflammable plasticizer for lubricating oil, nitrocellulose, and cellulose acetate.² Triphenyl phosphorothioate (TPPT) is an excellent extreme pressure agent even at a small dose in lubrication oil.³ The industrial preparation of TPPI proceeds in two steps. (1) Chlorine gas is continuously introduced into the phosphorus trichloride solution of white phosphorus (P_4) under reflux conditions to generate PCl_3 . (2) PCl_3 is functionalized by phenols at high temperatures accompanied by the release of 3 equiv of HCl . The main disadvantages of this process are transport of chlorine and PCl_3 , large amounts of waste (HCl or metal halides), a large amount of energy consumed, and harsh reaction conditions.⁴ Therefore, it is very important to develop an environmentally friendly P_4 activation for these molecules to avoid the $\text{P}-\text{Cl}$ compounds, so Cl_2 , PCl_3 , or POCl_3 could be omitted in principle.⁵

In the past several decades, the catalytic method for the synthesis of OPCs from P_4 has rarely been reported,⁶ and only four methods for the direct preparation of triaryl phosphates from P_4 have been developed (Scheme 1). Compared to

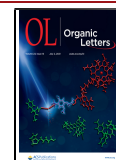
Scheme 1. Synthesis of $(\text{ArO})_3\text{P}(\text{O})$



$\text{R}_{\text{alkyl}}\text{O}^-$ anions, ArO^- anions are difficult to react with P_4 because of the low nucleophilicity in solution.⁷ Attempts to construct $\text{P}-\text{OAr}$ bonds by using CCl_4 as the electrophilic component were made by Ivanov and co-workers with an excess of crown ether to increase the actual concentration of ArO^- anions in CCl_4 (Scheme 1A).⁸ The isolation of triaryl

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phosphites from the reaction mixtures containing crown ether is very difficult.⁸ In 1992, Budnikova investigated the phosphorylation of ArOH with P₄ by an electrochemical method to give triphenyl phosphite in 82% yield (Scheme 1B).⁹ In 2005, the Abdreimova group reported the FeCl₃-I₂-catalyzed reaction of phenol with P₄ to produce (PhO)₃PO with some interesting results (Scheme 1C).¹⁰ In 2011, an efficient Fe-catalyzed method was found by the Kilian group. With the use of Fe(acac)₃-I₂ as the catalysts, the air (30–45 mL/min) and white phosphorus solutions (0.34–0.78 mmol of P₄/h) were introduced into the reaction mixture through needles, making certain the 100% conversion of white phosphorus and synthesis of (ArO)₃PO with high selectivity (Scheme 1D).¹¹ To the best of our knowledge, the separation of OPCs from the mixtures containing a transition metal proved to be difficult because of their strong coordination ability. On the contrary, triphenyl phosphite [(PhO)₃P] could not be obtained by using this method. Thus, there is a pursuit for the synthesis of such organophosphorus compounds in organic chemistry and industrial process, i.e., directly from white phosphorus and without the assistance of a transition metal.

Our continued interest in the green synthesis of phosphorothioates from P₄ prompted us to explore the possibility of using organic sulfur/selenium compounds as the catalysts for the direct catalytic synthesis of triaryl phosphites/phosphates involving white phosphorus and ArOH.¹² We envisioned that the catalytic activation of P₄ with (RSe)₂ might produce P–SeR species, which would undergo a further nucleophilic substitution reaction with ArOH, eventually leading to P–OAr bonds.

Initial investigations into the synthesis of triaryphosphites were carried out with P₄ and *p*-methoxyphenol (**1a**) as reaction partners (Table 1). A mixture of both compounds, K₃PO₄, and a catalyst was heated at 60 °C under argon. In the presence of diphenyl diselenide (**A**) as a catalyst, the reaction in a mixed solvent of toluene and DMSO afforded the desired product (*p*-CH₃OC₆H₄O)₃P **2a** in 85% yield (entry 1). Inspired by this result, we next examined other readily available diaryl disulfides such as diphenyl disulfide (**B**), 4,4'-dinitrodiphenyl disulfide (**C**), 4,4'-dimethyldiphenyl disulfide (**D**), 4,4'-dimethoxydiphenyl disulfide (**E**), and 4,4'-dichlorodiphenyl disulfide (**F**) (entries 2–6), and diphenyl diselenide (**A**) was the best choice (entry 1). Toluene or DMSO alone was used as the solvent, affording product **2a** in very low yield (entries 7 and 8). Other mixed solvents such as toluene with DMF, EtOAc, acetone, 1,4-dioxane, CH₃CN, or THF were less effective (entry 9). Screening the reaction temperature revealed that 60 °C provided the best result (entries 1, 10, and 11). Other alkali metal salts (KOH, NaOH, *t*-BuOK, Cs₂CO₃, K₂CO₃, and Na₂CO₃) were also suitable bases, affording product **2a** in slightly lower yields (entry 12). With the use of DBU as a base, product **2a** was obtained in 64% yield (entry 13). Pyridine and NEt₃ could not promote this process (entry 13). Further increasing the amount of K₃PO₄ to 100 mol %, however, resulted in **2a** with a yield of 35% (entry 14). When the loading of K₃PO₄ or diphenyl diselenide (**A**) was decreased, the yield of **2a** also decreased. The catalyst and base are both indispensable for this phosphorylation of *p*-methoxyphenol (**1a**) (entries 14 and 15). The reaction under oxygen or air gave neither **2a** nor (*p*-CH₃OC₆H₄O)₃PO **3a**, and only some unknown complicated byproducts were observed by ³¹P NMR

Table 1. Optimization of Reaction Conditions^a

entry	base ^b	catalyst ^b	solvent	T (°C)	yield (%)
1	K ₃ PO ₄	A	SS	60	85
2	K ₃ PO ₄	B	SS	60	45
3	K ₃ PO ₄	C	SS	60	0
4	K ₃ PO ₄	D	SS	60	43
5	K ₃ PO ₄	E	SS	60	43
6	K ₃ PO ₄	F	SS	60	27
7	K ₃ PO ₄	A	PhMe	60	trace
8	K ₃ PO ₄	A	DMSO	60	20
9	K ₃ PO ₄	A	solvent ^c	60	trace
10	K ₃ PO ₄	A	SS	40	52
11	K ₃ PO ₄	A	SS	80	67
12	inorganic ^d	A	SS	60	67–80
13	organic ^e	A	SS	60	5–64
14	K ₃ PO ₄ (x %) ^f	A	SS	60	0–85
15	K ₃ PO ₄	A (y%) ^g	SS	60	0–85
16 ^h	K ₃ PO ₄	A	SS	60	<5
17 ⁱ	K ₃ PO ₄	A	SS	60	>95, ^j 42 ^j

^aConditions: *p*-MeO-C₆H₄OH (5 equiv), P₄ (5.6 mg, 0.045 mmol of P₄, 0.18 mmol of P atom, a 0.09 M solution of P₄ in toluene, 0.5 mL), a catalyst, and a base in solvent (1 mL) were stirred for 4 h under an Ar atmosphere. The yield of **2a** was determined by ³¹P NMR analysis of the crude reaction mixture using Ph₃P(O) as an internal standard.

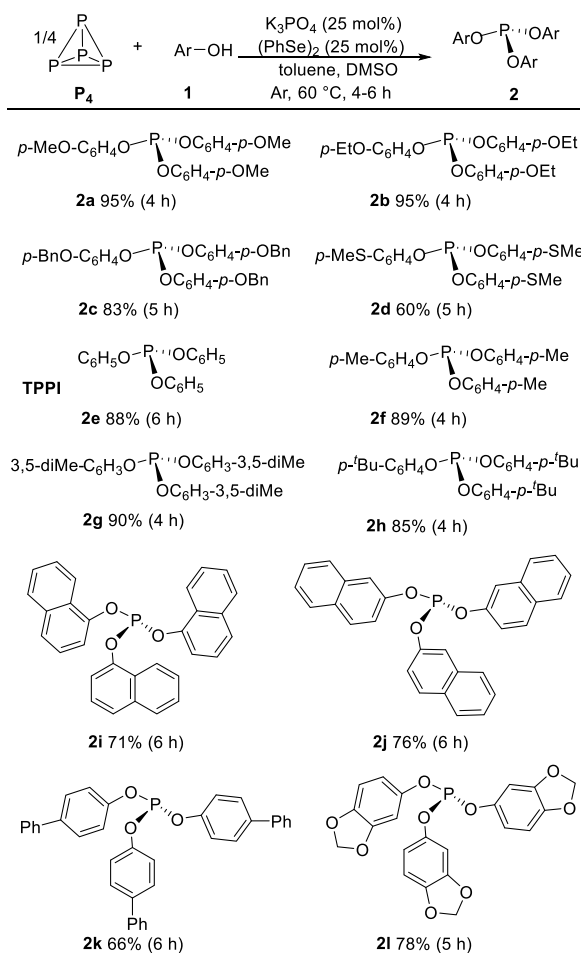
^bIn mole percent per P atom. ^cPhMe (0.5 mL), solvent (0.5 mL), and a solvent (DMF, EtOAc, acetone, 1,4-dioxane, CH₃CN, and THF).

^dInorganic base, yield: KOH, 76%; NaOH, 80%; *t*-BuOK, 79%; Cs₂CO₃, 67%; K₂CO₃, 69%; Na₂CO₃, 77%. ^eOrganic base, yield: DBU, 64%; pyridine or (Et)₃N, <10%. ^fK₃PO₄ (mol %, yield): 0 mol %, 0%; 10 mol %, 75%; 25 mol %, 82%; 50 mol %, 78%; 100 mol %, 35%. ^gA (y mol %, yield): 0 mol %, 0%; 10 mol %, 56%; 20 mol %, 82%; 25 mol %, 85%. ^hO₂ balloon or open to air (**2a**, <5%; **3g**, <5%). ⁱ**1a** (6 equiv). ^j**1a** (3 equiv).

analysis (entry 16). Furthermore, an almost quantitative yield was achieved with 6 equiv of **1a** (entry 17).

We next evaluated the scope of this diphenyl diselenide (**A**)-catalyzed coupling reaction of white phosphorus and phenols for the synthesis of triaryl phosphites [P(III)] (Scheme 2). It was found that phenols bearing an electron-donating group (MeO, EtO, BnO, or MeS) at its *para* position reacted efficiently with P₄, and the corresponding products **2a–2d** were obtained in 60–95% yields. It is noteworthy that triphenyl phosphite (TPPI, **2e**), a famous antioxidant stabilizer, was obtained in 88% yield. Phenols bearing Me or *tert*-butyl groups furnished the desired products in high yields (**2f–2h**). In addition, 1-naphthalenol, 2-naphthalenol, and 4-phenyl phenol also proceeded with good efficiency (**2i–2k**). Phenol with an acetal group afforded the corresponding product **2l** in a yield of 78%.

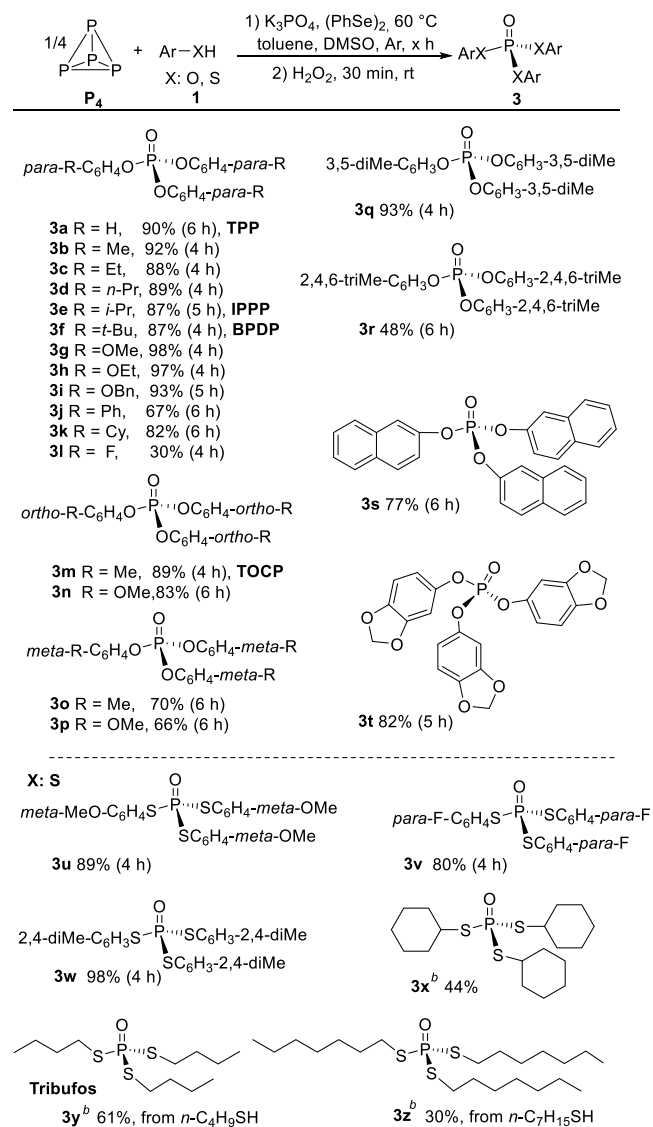
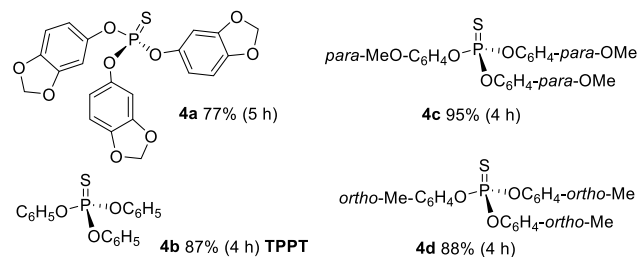
Inspired by these results, we decided to further explore the diphenyl diselenide-catalyzed reaction for the synthesis of triaryl phosphates [P(V)] (Scheme 3). Triphenyl phosphate (TPP, **3a**), a famous fire retardant, was obtained in 90% yield. Phenols bearing an alkyl group (Me or Et) at the *para* position of the phenyl ring gave the corresponding products **3c** and **3d**

Scheme 2. Synthesis of Triaryl Phosphites [P(III)]^a

^aConditions: ArOH (6 equiv), P₄/toluene solution (P₄, 5.6 mg, a 0.09 M solution of P₄ in toluene, 0.5 mL), DMSO (0.5 mL), K₃PO₄ (0.045 mmol, 9.6 mg), diphenyl diselenide (0.045 mmol, 14.1 mg), 60 °C, under argon, 4–6 h. Yields of isolated products.

in high yields. Another two famous fire retardants, IPPP (**3e**) and BPDP (**3f**), were produced in excellent yields. Some electron-donating MeO, EtO, and BnO were investigated and afforded the corresponding products **3g–3i** in very high yields. [1,1'-Biphenyl]-4-ol and 4-cyclohexylphenol gave products **3j** and **3k** in 67% and 82% yields, respectively. 4-Fluorophenol produced **3l** in very low yield, accompanied by unidentified byproducts, and no P₄ was recovered. 4-Chlorophenol and 4-bromophenol were also examined. Unfortunately, no desired products were detected. In addition, substrates with *ortho*-, *meta*-, and multimethyl-substituted phenols were also tolerated (**3m–3t**). For example, *o*-cresol reacted with P₄ efficiently to give the famous fire retardant TOCP (**3m**) in 89% yield. Furthermore, aromatic thiols with *o*-MeO, *p*-F, and 2,4-dimethyl substituents all provided the corresponding products **3u–3w** in high yields. Aliphatic thiols were competent to do these transformations, affording products **3x–3z** in lower yields. When sulfur powder was used instead of hydrogen peroxide, thiophosphates such as triphenyl phosphorothioate (TPPT) were also efficiently prepared (**4a–4d**). Unfortunately, aliphatic alcohols were unreactive while white phosphorus disappeared completely.

The diphenyl diselenide-catalyzed coupling reaction of white phosphorus and phenols could be performed on a gram scale,

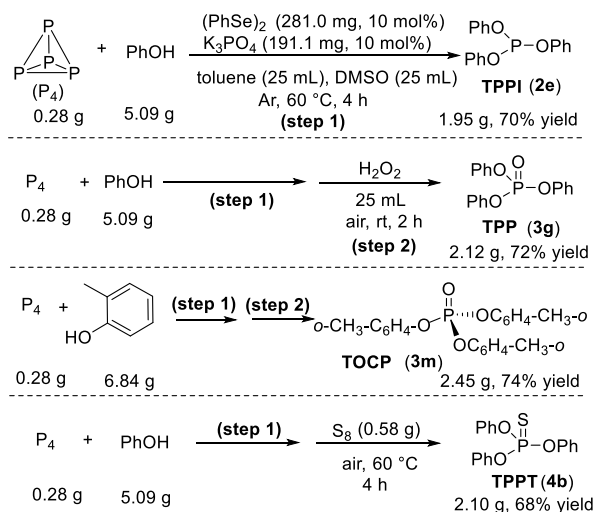
Scheme 3. Synthesis of Triaryl Phosphates [P(V)]^aStep 2)^c: sulfur powder instead of H₂O₂

^aConditions: (1) footnote a in Scheme 2; (2) 30% H₂O₂ (1 mL), 30 min, rt. ^bIn step 1, *t*-BuOK (0.045 mmol) instead of K₃PO₄, 8 h. ^cIn step 2, element sulfur (2 equiv, 0.36 mmol) instead of H₂O₂, 60 °C, 4 h.

producing TPPI (**2e**), TPP (**3g**), TOCP (**3m**), and TPPT (**4b**) in 70%, 72%, 74%, and 68% yields, respectively (Scheme 4).

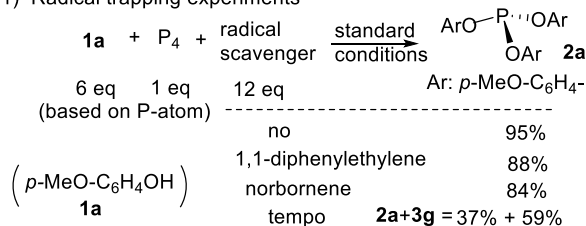
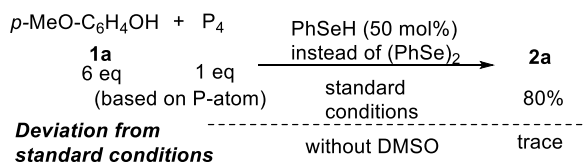
To probe the reaction mechanism of the novel diphenyl diselenide-catalyzed phosphorylation reaction, we first conducted the radical trapping experiments (Scheme 5). It was found that **2a** was obtained in slightly lower yield when 12

Scheme 4. Gram-Scale Preparation

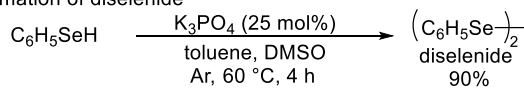


Scheme 5. Investigation of Reaction Mechanism

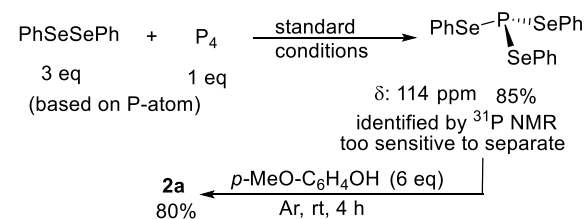
1) Radical trapping experiments

2) Synthesis of **2a** (P(III)) catalyzed by benzeneselenol

3) Formation of diselenide



4) Synthesis of triphenyl phosphorotriselenoite

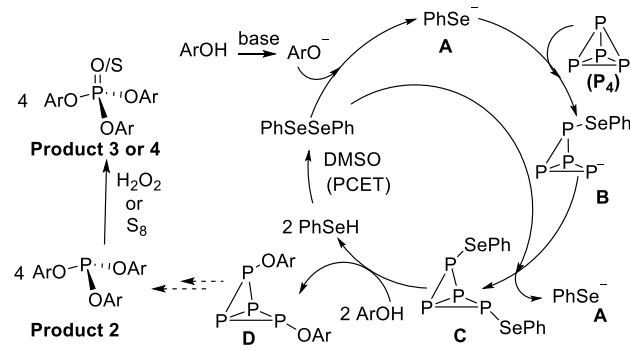


equiv of 1,1-diphenylethylene or norbornene was added, which suggested that radical reaction may not be involved (Scheme 5, 1). When 2,2,6,6-tetramethyl-1-piperidinyloxy (tempo) was used, both **2a** and $(\text{ArO})_3\text{P}(\text{O})$ **3g** were obtained in 37% and 59% yields, respectively, because tempo could act as an oxidant. Phenylselenol ($\text{C}_6\text{H}_5\text{SeH}$) as a catalyst also gave **2a** in good yield (Scheme 5, 2). Without DMSO, phenylselenol could not promote this transformation (Scheme 5, 2). Without the addition of P_4 , $\text{C}_6\text{H}_5\text{SeH}$ was converted into diphenyl diselenide in 90% yield under the standard conditions (Scheme 5, 3). These results suggested that DMSO was essential to this

transformation, and oxidation of phenylselenol to form diphenyl diselenide should be one of the key processes. Carrying out the reaction of diphenyl diselenide (3 equiv) and P_4 generated $(\text{C}_6\text{H}_5\text{Se})_3\text{P}$ in 85% yield, which was too sensitive to separate (Scheme 5, 4). *p*-Methoxyphenol (**1a**) was added to the reaction mixture mentioned above, and the desired product **2a** was obtained in high yield. These results suggested that reaction of the Se–P bond with phenol could efficiently produce the O–P bond.

On the basis of the mechanistic studies and our previous reports,¹² a possible mechanism for the coupling reaction of white phosphorus and phenols was proposed in Scheme 6.

Scheme 6. A Tentative Mechanistic Pathway



Initially, the anion of PhSe^- (**A**) is produced by the reaction of diphenyl diselenide with PhO^- or a base. Subsequent reaction with P_4 results in the formation of a phosphorus-based anion **B**. Intermediate **C** is subsequently generated from the reaction of **B** with diphenyl diselenide along with the regeneration of PhSe^- (**A**). The nucleophilic attack of ArOH to intermediate **C** takes place to form intermediate **D** with the release of benzeneselenol (PhSeH). Diphenyl diselenide can be formed from benzeneselenol by proton-coupled electron transfer (PCET). Further repetition of this catalytic cycle leads to cleavage of six P–P bonds and therefore formation of 12 P–O bonds, producing triaryl phosphite **2**. Final oxidation of triaryl phosphite **2** gives triaryl phosphate **3** or **4**.

In summary, we have successfully developed a diphenyl diselenide-catalyzed phosphorylation reaction involving phenols and white phosphorus for the synthesis of industrially important triaryl phosphites and triaryl phosphates such as TPPI, TPP, IPPP, BPDP, TOCP, and TPPT in good to excellent yields. The use of diphenyl diselenide as a catalyst along with a complete conversion of white phosphorus makes this transformation safe, practical, and green. Subsequent oxidation of triaryl phosphites produces triaryl phosphates and triaryl thiophosphates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c01695>.

Experimental procedures for the synthesis, spectral data, and copies of ^1H , ^{13}C , and ^{31}P NMR spectra of all of the products (PDF)

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Notes

The authors declare no competing financial interest.

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