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Tf_2O/DMSO-Promoted P−O and P−S Bond Formation: A Scalable Synthesis of Multifarious Organophosphinates and Thiophosphates

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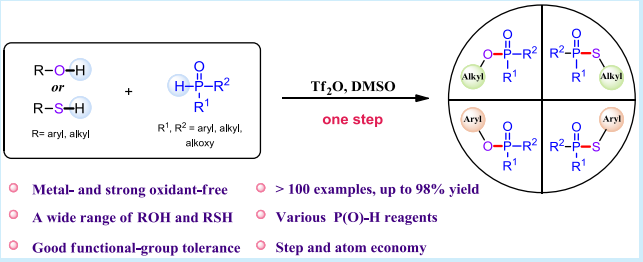
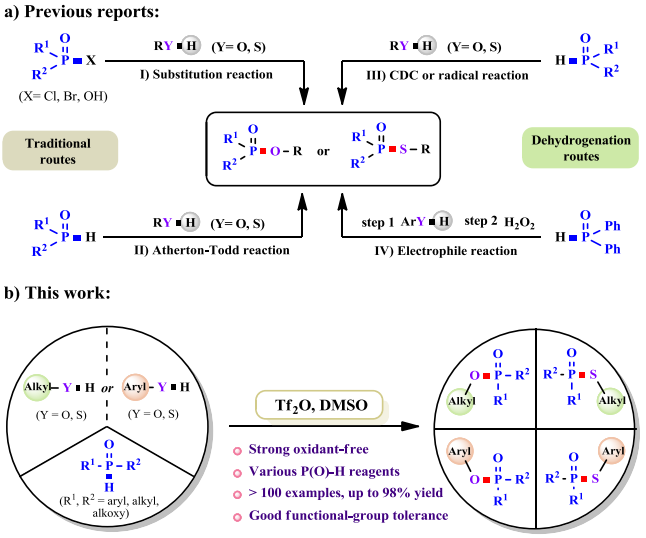
ABSTRACT: A Tf_2O/DMSO-based system for the dehydrogenative coupling of a wide range of alcohols, phenols, thiols, and thiophenols with diverse phosphorus reagents has been developed. This metal- and strong-oxidant-free strategy provides a facile approach to a great variety of organophosphinates and thiophosphates. The simple reaction system, good functional-group tolerance, and broad substrate scope enable the application of this method to the modification of natural products and the direct synthesis of bioactive molecules and flame retardants.



Chemical structures possessing a P−O or P−S bond are ubiquitous motifs that display remarkable chemical and biological properties,[1] which give them a broad utility in a range of diverse fields from the pharmaceutical chemistry[2] to agrochemistry,[3] organic synthesis,[4] and materials chemistry.[5] Accordingly, synthetic chemists have devoted considerable efforts to exploring efficient and convenient methods for the formation of P−O and P−S bonds, and remarkable progress has been made during recent years.[6−8] Among them, phosphinoylation of alcohols and thioalcohols continues to be a compelling and straightforward strategy (Scheme 1a), as chemicals containing an −OH or −SH group are abundant in nature and readily available.

The traditional routes for the phosphinoylation of R−OH and R−SH relies on their substitution with $R_2P(O)X$ reagents, including nucleophilic substitution with the toxic and moisture-sensitive phosphoryl halides[9] (Scheme 1a, path I), and the Atherton−Todd process[10] with toxic polyhaloalkanes as both the reagent and solvent (Scheme 1a, path II). The direct dehydrogenation phosphinoylation of P(O)−H reagents with R−OH and R−SH represents one of the most attractive strategies for P−O and P−S bond formation as it is a comparably etom-economical and efficient method for the synthesis of these compounds. In recent years, a variety of dehydrogenative methods, including CDC[11,12] (cross-dehydrogenative coupling) and P-radical-involved phosphinoylation reactions,[13] have been developed (Scheme 1a, path III). In 2017, Hirano and Miura pioneered an elegant metal-free strategy for dehydrogenative phosphinoylation[14] in which a P(III) intermediate was first generated. Following another oxidation step by H_2O_2, a P(V) product was produced. In 2018, Lu's group successfully applied this new strategy to the phosphinoylation of phenols and thiophenols (Scheme 1a, path IV);[15] however, aliphatic alcohols and thiols, as well as other phosphorus reagents, were not compatible in this Tf_2O/H_2O_2 system.

Scheme 1. Strategies for the Phosphinoylation of RO−H and RS−H



Although tremendous progress has been made in the field of the phosphinoylation of RO−H and RS−H, the existing

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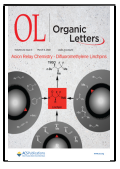

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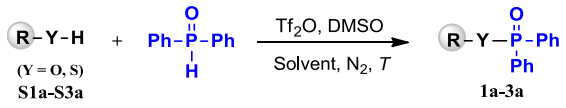
approaches still suffer from a number of limitations, such as the use of precious metal salts and strong oxidants, harsh conditions. Additionally, the reactions of RO−H and RS−H with arylphosphine oxide, phosphites, or other P(O)−H reagents are often incompatible in the same reaction. Therefore, developing new reaction systems that are more practical, environmentally friendly, and display an enhanced substrate compatibility would be highly desirable to the synthetic community. Due to our continued interest in discovering new organophosphorus transformations,[16] herein we describe a facile metal- and strong-oxidant-free system for the dehydrogenative coupling of a wide range of R−OH and R−SH compounds with diverse P(O)−H reagents (Scheme 1b). This one-step protocol exhibits a good functional-group tolerance and provides an extremely versatile approach to organophosphinates and thiophosphates.

In practice, we chose ethanol (**S1a**), phenol (**S2a**), and *p*-methylthiophenol (**S3a**) as substrates to screen the reaction parameters (see the Supporting Information for full optimization details). The optimized reaction conditions for each model substrate are shown in Table 1 (entries 1, 5, and 8). We also

Table 1. Reaction Optimization[a]



R−X−H	Entry	Tf_2O (eq.)	DMSO (eq.)	*T* (°C)	Yield (%)
EtOH S1a[b]	**1**	**2.0**	**2.0**	**RT**	**76**
	2	-	2.0	RT	n.r
	3	2.0	-	RT	10
	4[c]	**3.0**	**2.0**	**75**	**83**
OH S2a[d]	**5**	**3.0**	**2.0**	**90**	**77**
	6	-	2.0	90	n.r
	7	3.0	-	90	trace
SH S3a[e]	**8**	**2.0**	**2.0**	**RT**	**97**
	9	-	2.0	RT	n.r
	10	2.0	-	RT	33

[a]Stirred under N_2 overnight, isolated yield. [b]**S1a** (0.2 mmol, 9.2 mg)/P(O)−H/Tf_2O/DMSO 1:2.5:2:2, DMF (2.0 mL), RT. [c]P(O)−H (0.2 mmol, 40.4 mg)/Tf_2O/DMSO 1:3:2, **S1a** (1.0 mL), 75 °C, yields were calculated based on $HP(O)Ph_2$. [d]**S2a**/P(O)−H (0.2 mmol, 40.4 mg)/Tf_2O/DMSO 5:1:3:2, MeCN (2.0 mL), 90 °C, yields were calculated based on $HP(O)Ph_2$. [e]**S3a** (0.2 mmol, 24.8 mg)/P(O)−H/Tf_2O/DMSO 1:2:2:2, MeCN (2.0 mL), RT.

found that a higher yield was obtained when ethanol (**S1a**) was employed as both a reactant and a solvent (Table 1, entry 4). Control experiments revealed the requirement for Tf_2O, as when it was excluded from the system no product formation was detected (Table1, entries 2, 6, and 9). Additionally, the yield of the reaction dropped significantly in the absence of DMSO (Table 1, entries 3, 7, and 10).

With the optimized conditions in hand, we explored the scope of the reaction (Table 2). We were excited to find that a very broad range of RO−H and RS−H compounds efficiently underwent phosphinoylation to yield the corresponding products **1**−**5**. First, a variety of alcohols were tested (Table 2, first row). As shown, the yields of the primary alcohols (**1a**−**1g**) were higher than those of the secondary alcohols (**1h**−**1i**), whereas the phosphinoylation did not take place with a tertiary alcohol (**1j**). Moreover, alcohols with a variety of functional groups (**S1k**−**S1dd**) were found to be well tolerated. In addition, substrates containing *N*-heterocyclic moieties were also tolerated (**1ee**−**1ff**).

We then investigated the scope of phenol derivatives (Table 2, second row). It was shown that higher yields were obtained with electron-withdrawing groups (**2d**−**2k**) than with electron-donating groups (**2b** and **2c**). Moreover, multisubstituted substrates (**S2l** and **S2m**) and 2-naphthol (**S2n**) also reacted smoothly.

Subsequently, the substrate-scope study with regard to the RS−H compounds was explored (Table 2, third row). For thiophenol derivatives, both electron-rich and electron-deficient substrates gave the corresponding products **3a**−**3j** in excellent yields. It is interesting to note that the transformation occurred with complete chemoselectivity when 4-mercaptophenol (**S3k**) was used as a substrate, generating product **3k** in a good yield. For thiol derivatives, the phosphinoylation also proceeded well. Substrates bearing alkyl (**S3l**−**S3n**), ester (**S3o**), cycloalkyl (**S3p**), benzyl (**S3q**), and dithiol (**S3r**) substituents afforded the corresponding products **3l**−**3r** in moderate to good yields.

Furthermore, various natural products were directly used as substrates to evaluate the potential of this method in the modification of bioactive molecules (Table 2, fourth row). Natural products, including L-(−)-menthol (**S4a**), vitamin D3 (**S4b**), cholesterol (**S4c**), (−)-*β*-citronellol (**S4d**), and L-(−)-borneol (**S4e**), performed well in the reaction conditions.

We also examined the scope of the P(O)−H reagents (Table 2, last row). Pleasingly, a broad range of phosphorus reagents are compatible with this Tf_2O/DMSO system (**5a**−**5z**). As shown, various diarylphosphine oxides performed well with thiophenol (**5a**−**5d**). Gratifyingly, phosphites and other P(O)−H reagents could be successfully reacted with thiophenols to generate the corresponding products **5e**−**5m** in good yields. In addition, such P(O)−H reagents were also reactive with different thiols (**5n**−**5v**). When using alcohols and phenols, DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide) still exhibited a high reactivity (**5w** and **5x**, respectively), while butyl phenylphosphine oxide or ethyl phenylphosphinate performed relatively poorly (**5y** or **5z**, respectively). No reaction was observed when using diethyl phosphites with alcohols or phenols (**5aa** or **5bb**, respectively).

To demonstrate the practicality of this method, large-scale (4.0 mmol) reactions were carried out with a representative range of coupling partners (Scheme 2). Under the relevant standard conditions for each, compounds **1e**, **2d**, **3a**, and **5x** were synthesized in excellent yields.

Moreover, we also applied our method to the efficient synthesis of various bioactive molecules, flame retardants, and phosphorus-containing ligands (Scheme 3). A variety of bioactive molecules, including pesticide **6**, anticholinesterase **7**, antistatic agent **8**, curing accelerator **9**, and inezin 10 were synthesized with Tf_2O/DMSO conditions (Scheme 3A).[8c,o] The DOPO-type flame retardants **11**−**14**,[5e] which have excellent performance as flame retardants, were also smoothly synthesized (Scheme 3B). In addition, commonly used chiral auxiliaries diacetone-D-glucose **15** and (S)-BINOL **17** were successfully modified via our phosphinoylation process to produce the P−O ligand scaffolds **16** and **18**, respectively (Scheme 3C).[4d]

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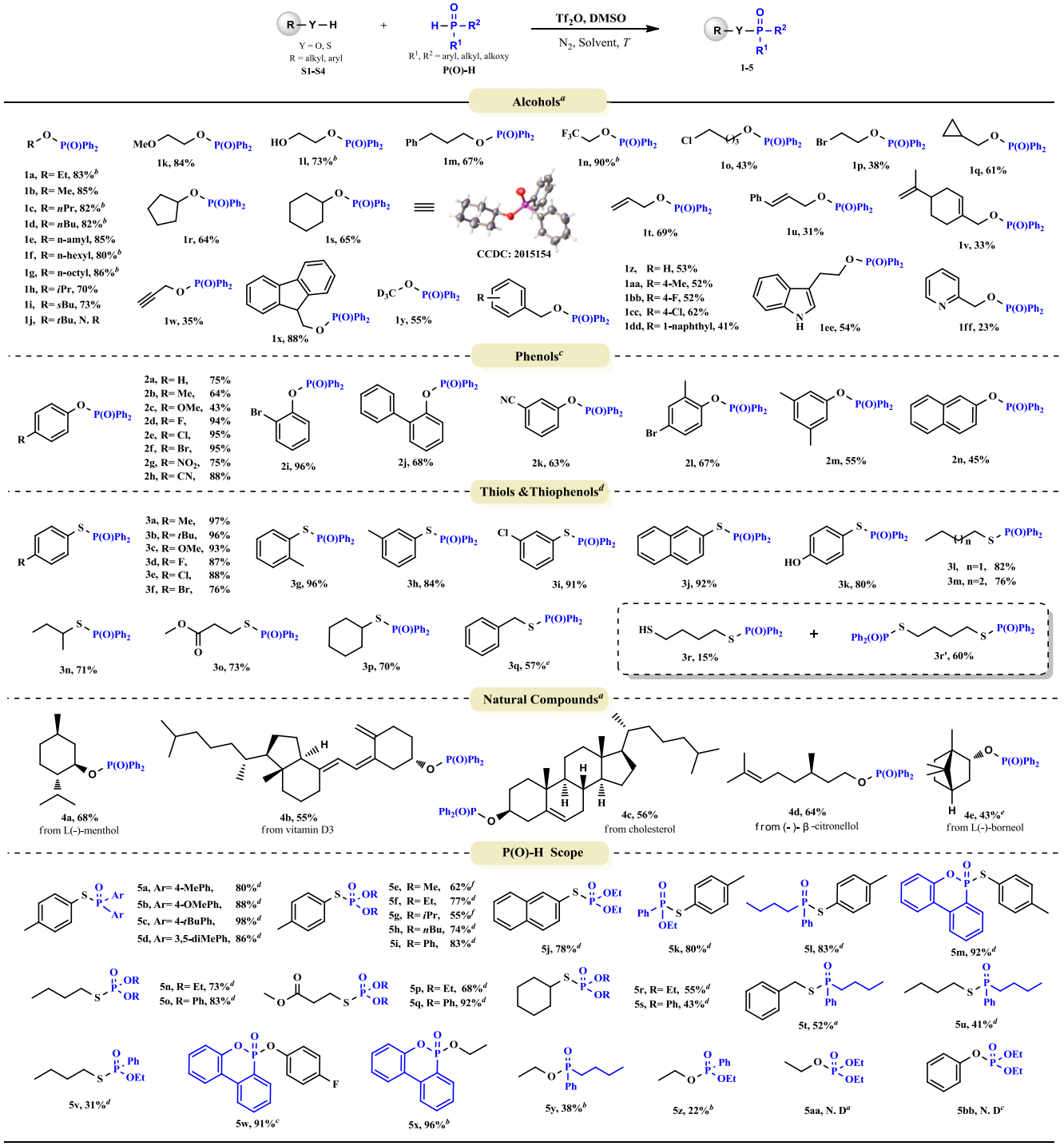
Table 2. Substrate Scope



[a]Conditions A: alcohols **S1**(0.2 mmol)/P(O)−H/Tf_2O/DMSO 1:2.5:2:2, DMF (2.0 mL), RT. [b]Conditions B: P(O)−H (0.2 mmol, 40.4 mg)/Tf_2O/DMSO 1:3:2, alcohols **S1** (1.0 mL), 75 °C, yields were calculated based on $HP(O)Ph_2$. [c]Conditions C: phenols **S2**/P(O)−H (0.2 mmol, 40.4 mg)/Tf_2O/DMSO 5:1:3:2, MeCN (2.0 mL), 90 °C, yields were calculated based on $HP(O)Ph_2$. [d]Conditions D: thiols or thiophenols **S3** (0.2 mmol)/P(O)−H/Tf_2O/DMSO 1:2:2:2, MeCN (2.0 mL), RT. [e]Performed under conditions A with P(O)−H (0.6 mmol) instead. [f]Performed under conditions D with P(O)−H (0.6 mmol) instead.

To deduce key information about the reaction mechanism and examine the actual role of Tf_2O and DMSO in this reaction, a series of control experiments were conducted (see the Supporting Information for more details). Some key results are listed in Scheme 4. First, when DMSO was replaced by DMSO[18], both **3a** and the O^{18} isotope-labeled product **3a′** were isolated as a mixture with a ratio of 3.8:1 (Scheme 4a). This indicates that some oxygen atom incorporation into the product come from DMSO. Moreover, the replacement of DMSO with butylsulfoxide led to the generation of dibutyl sulfide **19** (Scheme 4b). The alkanethiols, which were incompatible with the Tf_2O/H_2O_2 system,[15] could successfully react with HP(O)-

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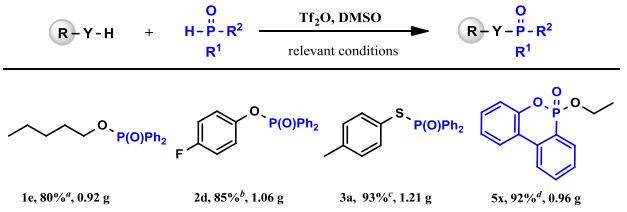
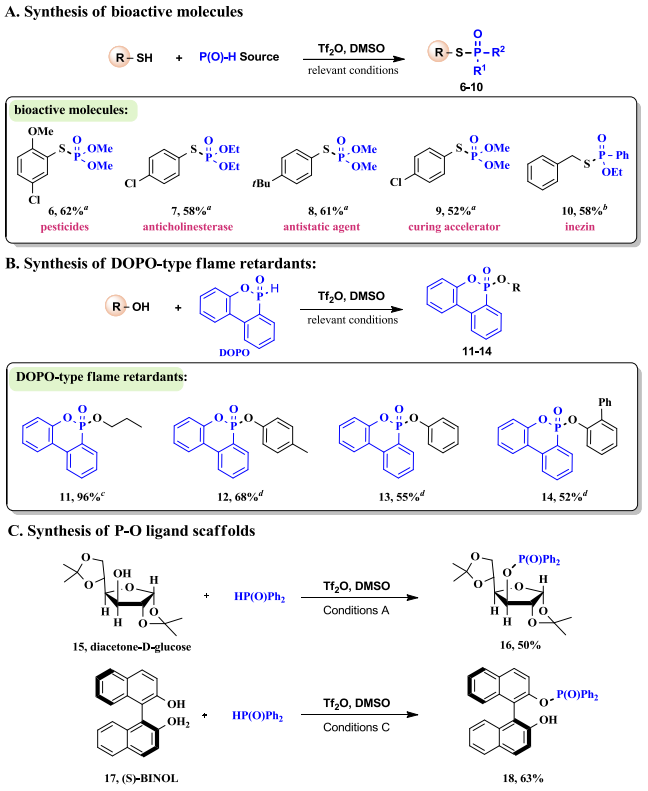
Scheme 2. Large-Scale Preparation



[a]Conditions A. [b]Conditions C. [c]Conditions D. [d]Conditions B.

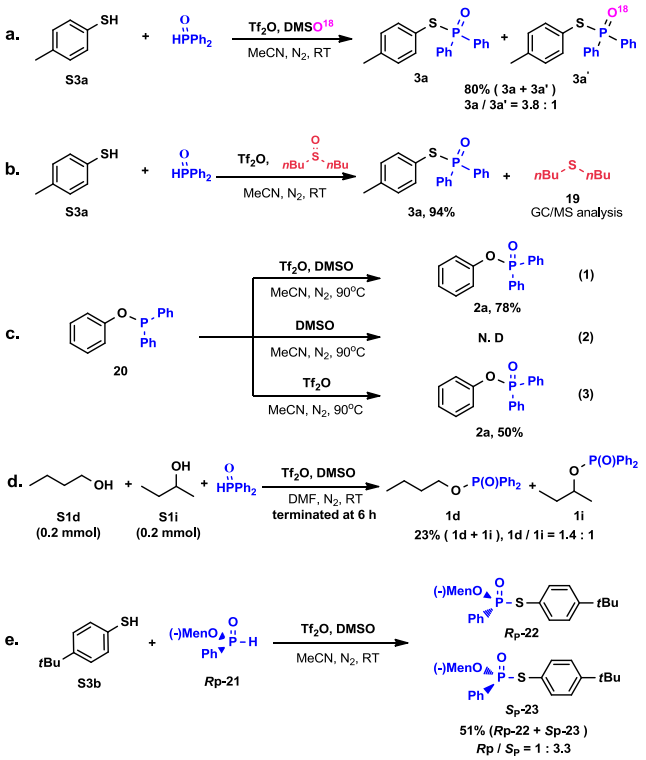
Scheme 3. Applications



[a]Performed under conditions D with P(O)–H (0.6 mmol) instead. [b]Performed under conditions A with P(O)–H (0.6 mmol), Tf_2O (0.6 mmol), and DMSO (0.6 mmol) instead. [c]Conditions B. [d]Conditions C.

Ph_2 to generate the corresponding products **3l**–**3r**. It is possible that DMSO may also act as a base to enhance the nucleophilicity of the R–SH substrates.[12d] Next, to verify our hypothesis that the P(V) product is formed by the oxidation of a P(III) intermediate, compound **20** was employed as a substrate (Scheme 4c). Indeed, the P(III) compound **20** could be smoothly converted to the desired P(V) product **2a** under the standard conditions (Scheme 4c, eq 1). Notably, the P(V) product was not detected in the absence of Tf_2O (Scheme 4c, eq 2). In contrast, product **2a** could be obtained in a 50% yield with only Tf_2O in the system (Scheme 4c, eq 3). By combining this with the above result in Scheme 4a, we believed that some oxygen atom incorporation into the product may come from Tf_2O. In the competition experiment between primary alcohol **S1d** and the secondary alcohol **S1i** with $HP(O)Ph_2$, the products **1d** and **1i**, respectively, were obtained with a ratio of 1.4:1, suggesting that an S_N2-type process might be involved in this reaction (Scheme 4d). Moreover, when a chiral phosphorus

Scheme 4. Control Experiments



reagent (R_P-**21**) was used in the phosphinoylation with thiophenol **S3b**, a mixture of the *R*-configuration product **22** and the *S*-configuration product **23** was obtained with a total yield of 51% and a ratio of 1:3.3 (Scheme 4e). It should be noted that in an S_N2-type Atherton–Todd reaction only the complete *stereo*-inversion product R_P-**22** was obtained.[10d,f] When compared with our experimental results, this suggests that the products were partially racemized during the reaction.

On the basis of the above mechanistic studies and previous literature,[14,15,17] a tentative mechanism was proposed (Scheme 5). First, the P(O)–H reagent undergoes tautomerization to the less-stable P(III) form, which then reacts with Tf_2O to generate an electrophilic phosphorus species **I**. Subsequently, the R–YH compound adds to species **I** via a nucleophilic pathway, generating the P(III) intermediates **A**. As shown by the control experiments, there are two sources of the oxygen atoms in the product. Accordingly, we propose two possible pathways to deliver the final P(V) products from **A** (Scheme 5, paths a and b). In path a, following the steps of a nucleophilic attack of the P(III) intermediate on Tf_2O, an intramolecular rearrangement of **B**,[17d] and further electron transfer, the P(III) intermediate captures an oxygen atom from Tf_2O to afford the desired P(V) product. In path b, an Albright–Goldman type process[17i] is involved. Tf_2O first reacts with DMSO to produce complex **D** and the triflate exchange complex **D′**, followed by the nucleophilic attack of **A** and the intermolecular attack by TfO^- at the phosphonium to generate **E** and **E′**, which undergo the intramolecular rearrangement to release dimethyl sulfide.[17e−g] The subsequent electron transfer of **F** and **F′** produces the desired P(V) products.

In summary, we have developed a mild and efficient Tf_2O/DMSO-based system for the dehydrogenative phosphinoylation of a wide range of R–OH or R–SH compounds with diverse phosphorus reagents to provide a simple and practical approach

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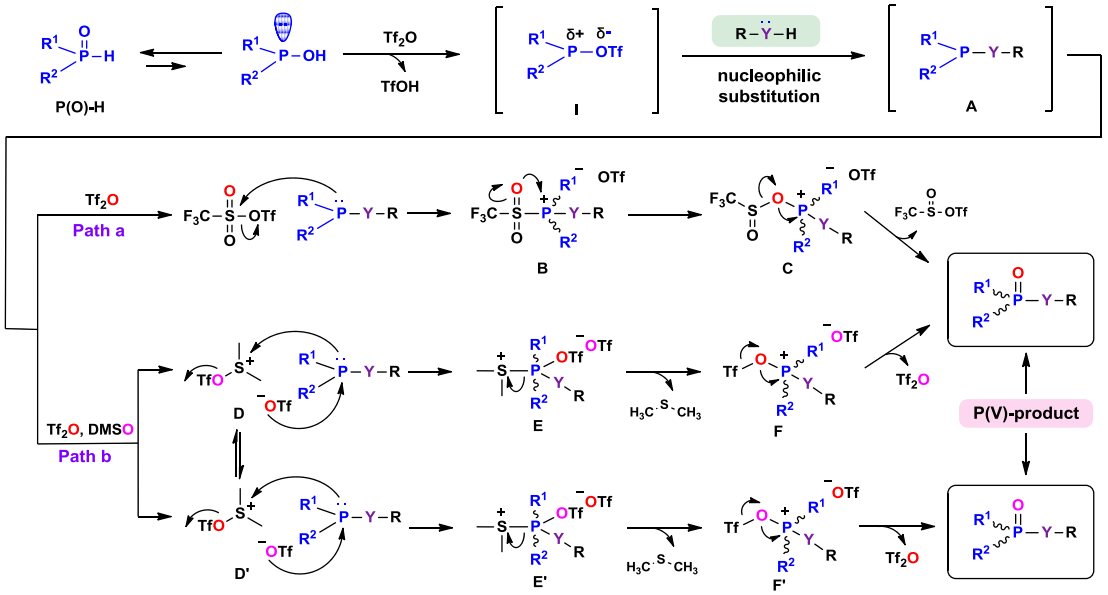
Scheme 5. Plausible Mechanistic Pathway



to various organophosphinates and thiophosphates. The broad substrate scope and the good functional-group tolerance enable the application of this method in the direct synthesis of bioactive molecules and phosphorus flame retardants. This one-step approach does not require strong oxidants, and a broad range of phosphorus reagents and R–YH (Y = O, S) compounds are compatible. Further investigations into the mechanism and more applications of this strategy are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04127.

Experimental procedures; characterization data; and ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR spectra (PDF)

FAIR data, including the primary NMR FID files, for compounds **1a–1ff**, **2a–2n**, **3a–3r′**, **4a–4e**, **5a–5z**, **6–14**, **16**, and **18** (ZIP)

Accession Codes

CCDC 2015154 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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