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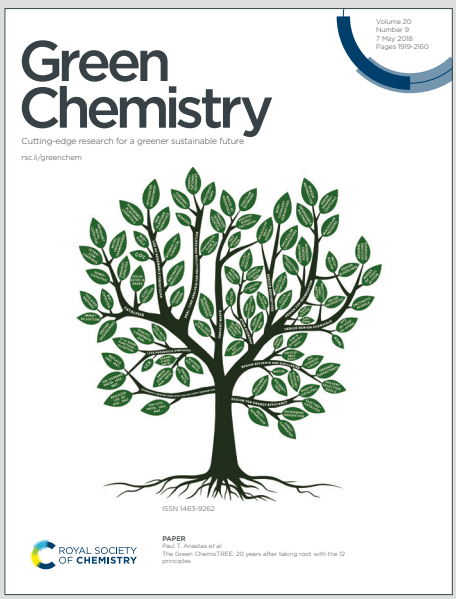

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ARTICLE

Synthesis of mixed phosphorotrithioates from white phosphorus

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The first general and high-yielding synthesis of mixed phosphorotrithioates $(R^1S)_2P(O)SR^2$ involving white phosphorus, disulfides, and alkyl halides is presented, which opens the shortest and environmentally benign way to these compounds of practical importance. Only one method for the formation of $(R^1S)_2P(O)SR^2$ from elemental phosphorus has been developed. Here, with the use of KOH as a base, DMSO-toluene as a solvent, various disulfides couple readily with white phosphorus to give *O*-potassium *S,S*-dialkylphosphorotrithioates $(R^1S)_2P(S)OK$ in almost quantitative yield, which react with alkyl halides to form $(R^1S)_2P(O)SR^2$ in high yields. The reaction is characterized by a complete conversion of white phosphorus. Moreover, this method can be easily adapted to large-scale preparation. Our mechanistic data suggest that the attack of RSK on *S,S,S*-trialkyl phosphorotrithioates and subsequent C−S bond cleavage, the Michaelis-Arbuzov-like dealkylation, are the key steps in the formation of $(R^1S)_2P(S)OK$.

Introduction

The importance of sulfur-containing organophosphorus molecules as pharmaceuticals, agrochemicals, and functional materials has fuelled an ever-increasing interest in developing efficient and sustainable C−S−P bond forming reactions in phosphorus chemistry.[1-5] In fact, more than 60 molecules containing at least one C−S−P bond are widely used as agricultural pesticides (Fig 1).[5] A wide array of phosphorothioate, phosphonothioate and phosphinothioate compounds may be readily prepared from $R_2P(O)H$ compounds and their derivatives.[6-11] However, multistep and environmentally toxic processes are usually involved to make $R_2P(O)H$ compounds from white phosphorus (P_4) via a chlorinated process followed by a nucleophilic substitution reaction.[12] Although the activation of P_4 by main group elements,[13-18] transition-metal complexes[19-24] and rare-earth-metals[25-28] started and is still being developed well, the synthesis of organophosphorus compounds (OPCs) from white phosphorus is still the main challenge in this area.[29-31]

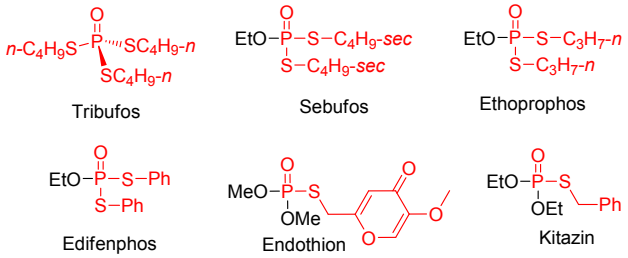

Figure 1. Selected agrochemicals.

In the past 70 years, only six methods for the preparation of C−S−P bonds from P_4 have been developed.[32-41] In 1951, Stevens treated P_4 with disulfides at very high temperatures to produce the corresponding trithiophosphites $[P(SR)_3]$.[32] Wu later demonstrated that this process could be conducted in dipolar aprotic solvents under much milder conditions in the presence of KOH.[33] In 1978, Hudson *et al.* investigated the sulfenylation of P_4 with sodium alkanethiolates in CCl_4 under a nitrogen atmosphere to produce trithiophosphites.[34,35] In 2005, Sinyashin and coworkers successfully prepared $P(O)(SPh)_3$ from thiophenol and P_4 in refluxing acetonitrile under air conditions.[36-38] In 2019, we discovered an efficient photochemical process for accessing phosphorotrithioates from arythiols and P_4 using visible light and Eosin Y as a photosensitizer. Addition of hydrogen peroxide can oxidize the trithiophosphites to the target phosphorotrithioates.[39] In 2020, we developed the first general synthesis of $P(SR)_3$ and $P(O)(SR)_3$ from P_4 and thiols. Both arythiols and alkylthiols are tolerant in this transformation.[40] These breakthroughs laid the foundation of the systematic use of white phosphorus for the synthesis of unavailable or unknown phosphorotrithioates which contain the same three RS groups.

Compared to $P(O)(SR)_3$, $(R^1S)_2P(O)OR^2$ and $(R^1O)_2P(O)SR^2$ as general structures in pesticide chemicals,[5] $(R^1S)_2P(O)SR^2$ is regarded as difficult structures to access, and only very limited methods have been developed thus far.[42-44] We speculated that replacing one OR group with SR group in these pesticide chemicals, would provide an opportunity to adjust their bioactivities. In 1977, Stec and coworkers described the synthesis of $R^1SP(O)(NHPh)_2$, (R^1S) $(R^2S)P(O)NHPh$, and (R^1S) $(R^2S)P(O)SR^3$ from $P(O)(NHPh)_3$, carbon disulfide and alkyl halides (Scheme 1A).[42] In 2009, Trofimov and colleagues synthesized *O*-potassium *S,S*-dialkyl trithiophosphates in 12–20% yields through the reaction of red phosphorus with alkanethiolate anions.[43,44] *O*-Potassium *S,S*-dialkyl trithiophosphates are readily alkylated with organic halides to form mixed *S,S,S*-trialkyl trithiophosphates $[(R^1S)_2P(O)SR^2$, Scheme

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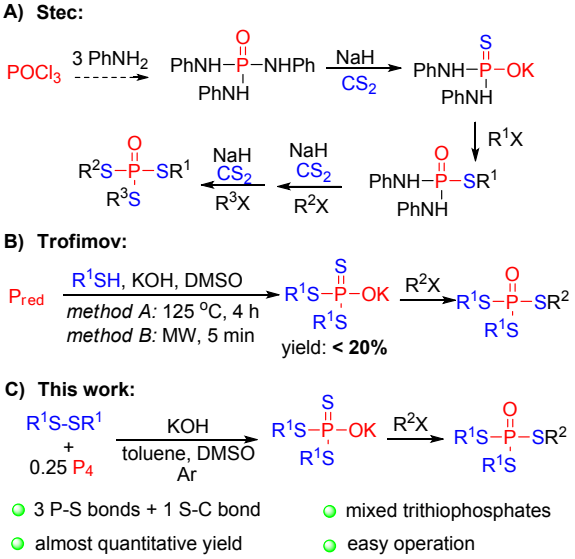
1B].[43,44] Inspired by the above results and our study on the construction C–S–P bond,[45-47] we envisioned that the base-promoted S-P coupling of $(RS)_2$ and P_4 might generate $P(SR)_5$ or $(RS)_4P^+SR^-$ species, which would undergo further dealkylated Michaelis-Arbuzov reaction, eventually leading to *O*-potassium *S,S*-dialkyl trithiophosphates [$(RS)_2P(S)OK$, Scheme 1C]. Herein, we report the successful high-yielding synthesis of $(R^1S)_2P(O)SR^2$ from $(RS)_2$, P_4 and alkyl halides through a base-promoted RS–P coupling followed by Michaelis-Arbuzov reaction and alkylation.

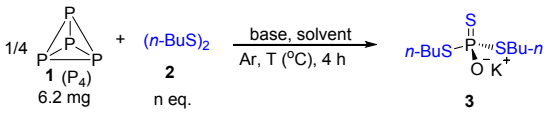


Scheme 1. Synthesis of $(R^1S)_2P(O)SR^2$.

Results and discussion

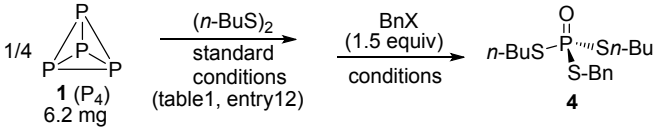
A preliminary optimization of the reaction conditions was carried out with P_4 (**1**) and $(n\text{-}C_4H_9S)_2$ (**2**) as reaction partners (Table 1). Inspired by our previous work, KOH was investigated in this reaction.[40] In the presence of KOH, DMSO, DMF and toluene afforded product *O*-potassium *S,S*-dibutylphosphorotrithioate [$(n\text{-}C_4H_9S)_2P(S)OK$] (**3**, ^{31}P NMR: s, 75 ppm) with very low yield under argon at 25 °C for 12 h (entries 1-3). Other mixed solvents such as toluene-CH_3CN, -THF, -1,4-dioxane were also ineffective (entries 4-6). Pleasingly, the targeted salt **3** was detected in 56% yield in the mixed solvent of toluene (0.5 mL) and DMF (0.5 mL) at room temperature for 12 h (entry 7). Furthermore, an 81% yield was achieved with the mixed solvent of toluene and DMSO application (entry 8). Other alkali-metal salts (K_2CO_3, Na_2CO_3) and organic bases (DBU and NEt_3) could not promote this process (entry 9). The reaction was carried out in air, in an open flask with a calcium chloride drying tube, leading to salt **3** and $(n\text{-}C_4H_9S)_3P(O)$ in 20% and 60% yields, respectively (entry 10). The reaction performed well at 80 °C for 4 h and gave salt **3** in almost quantitative yield (entry 12). The structure of **3** was confirmed by its ^1H and ^{13}C NMR spectra and mass spectrometry (see ESI). Indeed, no P_4 left within 30 min determined by ^{31}P NMR analysis of the crude reaction mixture. To ensure 100% conversion of white phosphorus, the reaction time was prolonged to 4 h. Trofimov synthesized salt **3** in 12% yield through the reaction of red phosphorus with 1-butanethiol.[43] In our method, using $(C_6H_5)_3P(O)$ (26 ppm) as an internal standard, a single pulse ^{31}P NMR experiment showed over 95% conversion to salt **3**. However, the yield of **3** decreased when the temperature was increased to 100 °C or decreased to 60 °C (entries 11 and 13). When the loading of KOH or $(n\text{-}C_4H_9S)_2$ (**2**) was decreased, the yield of **3** also decreased (entries 14 -16). The reactions of red phosphorus with $(n\text{-}C_4H_9S)_2$ under standard conditions gave a 32% conversion of red phosphorus, and produced $[(n\text{-}C_4H_9S)_2P(S)OK]$ (**3**) with a yield of 25% based on the starting red phosphorus (a yield of 78% based on the converted red phosphorus, entry 17).

Table 1. Synthesis of $(n\text{-}C_4H_9S)_2P(S)OK$ (**3**)[a]



Entry	n	Base(mol%)[b]	Solvent (1 mL)	T(°C)	Yield[c]
1	3.0	KOH (200)	DMSO	25	11%
2	3.0	KOH (200)	DMF	25	22%
3	3.0	KOH (200)	PhMe	25	0%
4	3.0	KOH (200)	PhMe+CH_3CN	25	0%
5	3.0	KOH (200)	PhMe+ THF	25	0%
6	3.0	KOH (200)	PhMe+1,4-dioxane	25	0%
7	3.0	KOH (200)	PhMe+DMF	25	56%
8	3.0	KOH (200)	PhMe+DMSO	25	81%
9	3.0	Base[d]	PhMe+DMSO	25	<5%
10[e]	3.0	KOH (200)	PhMe+DMSO	25	20%
11	3.0	KOH (200)	PhMe+DMSO	60	86%
12	3.0	KOH (200)	PhMe+DMSO	80	>95%
13	3.0	KOH (200)	PhMe+DMSO	100	92%
14	3.0	KOH (150)	PhMe+DMSO	80	80%
15	2.0	KOH (200)	PhMe+DMSO	80	38%
16	2.5	KOH (200)	PhMe+DMSO	80	84%
17[f]	3.0	KOH (200)	PhMe+DMSO	80	25%

[a] Reaction conditions: $(n\text{-}C_4H_9S)_2$ (n equivalents of disulfide per P-atom), P_4 (6.2 mg, a 0.10 M solution of P_4 in toluene, 0.5 mL), and base in solvent (1 mL) were stirred for 4 h in Ar. Mixed solvents: toluene (0.5 mL) + other solvent (0.5 mL). [b] mol% per P-atom. [c] Yield of **3**, determined by ^{31}P NMR analysis of the crude reaction mixture using $(C_6H_5)_3P(O)$ as an internal standard. [d] Base: K_2CO_3, Na_2CO_3, DBU or $(Et)_3N$ as a base. [e] Open to air. [f] Red phosphorus (6.2 mg) was used instead of P_4.

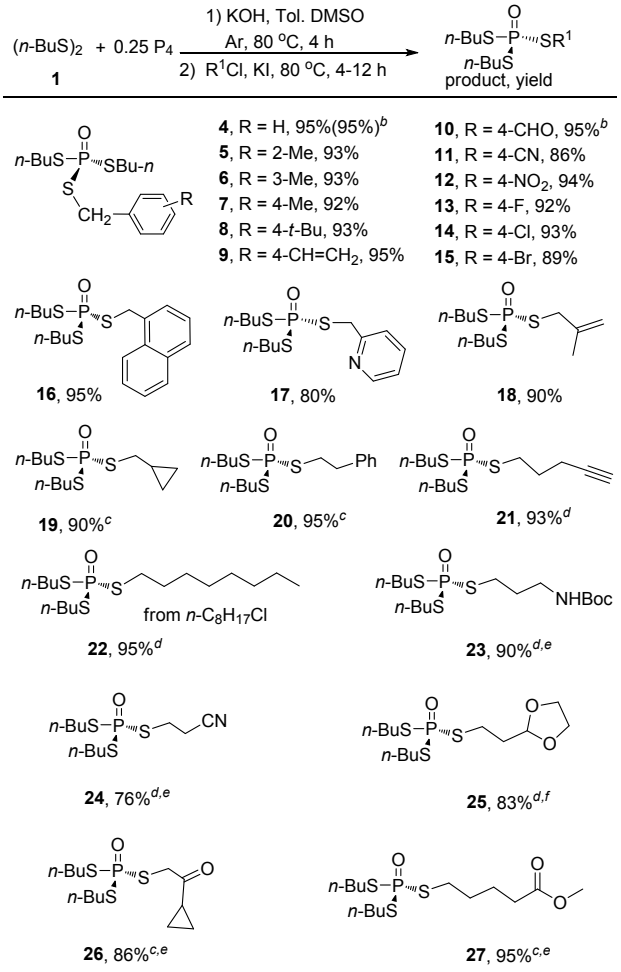


BnX	conditions	yield
BnCl	rt, 12 h	44%
BnCl	KI(0.2 equiv), rt, 12 h	87%
BnCl	80 °C, 12 h	90%
BnCl	KI(0.2 equiv), 80 °C, 4 h	95%
BnCl	NaI(0.2 equiv), 80 °C, 4 h	90%
BnBr	rt, 12 h	95%
BnBr	KI(0.2 equiv), rt, 4 h	95%

Scheme 2 Synthesis of $(n\text{-}C_4H_9S)_2P(O)SBn$ (**4**) in one-pot.

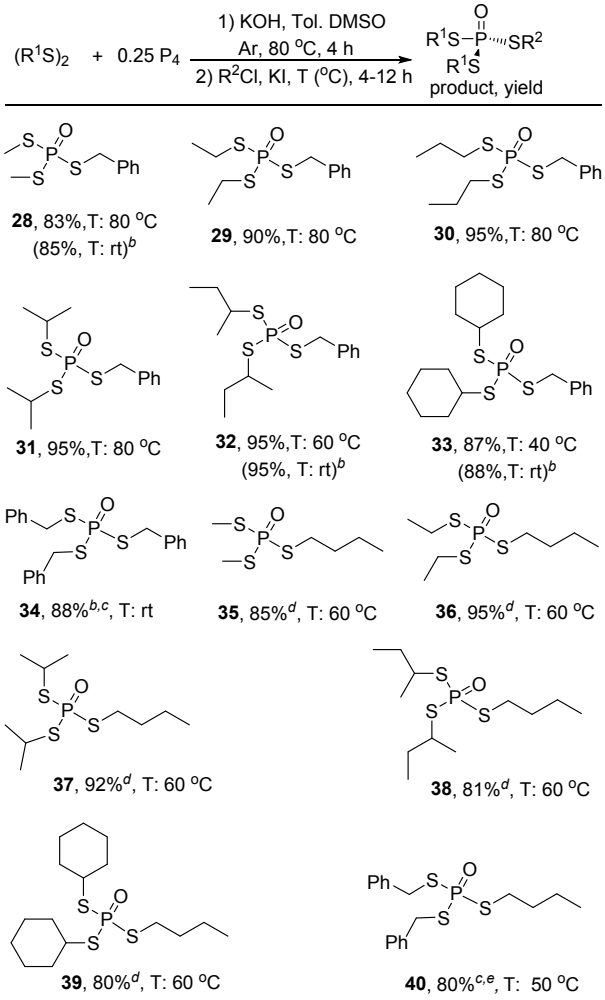
As high-yielding synthesis of *O*-potassium *S,S*-dibutylphosphorotrithioate (salt **3)** involving white phosphorus and disulfides was found, we investigated whether the synthesis of mixed phosphorotrithioates could be carried out in one-pot directly from white phosphorus without the isolation of intermediate **3** (Scheme 2). After stirring (*n*-$C_4H_9S)_2$ (**2**) and P_4 for 4 h at 80 °C in argon, we added benzyl chloride, and then the mixture was stirred at room temperature for another 12 h, giving product (*n*-$C_4H_9S)_2P(O)SBn$ (**4**) in 44% yield. When the reaction was heated at 80 °C, product **4** was obtained in 90% yield. The yield of **4** increased obviously (87%, rt; 95%, 80 °C) with the use of KI as an additive. The alkylation reaction was highly regiospecific, no *O*-alkylated product was detectable in ^{31}P NMR spectra of the crude reaction mixture. Sodium iodide was also a good additive. Benzyl bromide could react well with **3** to form product **4** in almost quantitative yield at room temperature.

Table 2. Scope of alkyl halides [a]



[a] Reaction conditions: 1) (*n*-$C_4H_9S)_2$ (0.6 mmol), P_4–toluene solution (P_4: 6.2 mg, a 0.10 M solution of P_4 in toluene, 0.5 mL), DMSO (0.5 mL), KOH (0.4 mmol, 22.4 mg), with stirring under argon at 80 °C for 4 h; 2) RCl (1.5 equiv), KI (0.2 equiv) with stirring at 80 °C for 4-12 h; Yields of isolated products. [b] RBr was used. [c] RX (2.0 equiv). [d] RX (3.0 equiv). [e] RBr, KI, rt, 12 h. [f] RBr, KI, 60 °C, 12 h.

Table 3. Scope of disulfides [a]



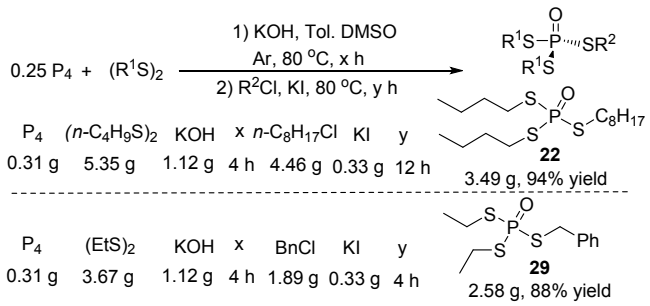
[a] Reaction conditions: 1) Disulfide (0.6 mmol), P_4–toluene solution (P_4: 6.2 mg, a 0.10 M solution of P_4 in toluene, 0.5 mL), DMSO (0.5 mL), KOH (0.4 mmol, 22.4 mg), with stirring under argon at 80 °C for 4 h; 2) RCl (1.5 equiv), KI (0.2 equiv) with stirring at 80 °C for 4-12 h; Yields of isolated products. [b] BnBr (1.5 equiv), 4 h. [c] Water (20 μL) was added in step 1, rt, 8 h. [d] *n*-C_4H_9Br (2.0 equiv), 12 h. [e] *n*-C_4H_9Br (3.0 equiv), 12 h.

Having the optimal conditions in hand, we next examined the reactions of alkyl halides with (*n*-$C_4H_9S)_2$ and P_4 to probe the scope of the reaction (Table 2). With alkyl and alkenyl substitution on benzene, these compounds reacted efficiently to give the desired products (**4**–**9**) in high yields, indicating that the position on the benzene ring exerted a small influence. Some electron-withdrawing CHO, CN and NO_2 groups were investigated and gave the corresponding products **10**–**12** in 86%–95% yields. Halogen atoms such as fluoro, chloro, and bromo on the aromatic ring were not affected under the present reaction conditions to afford the corresponding products **13**–**15** in 89%–93% yields. It was found that 1-(chloromethyl)naphthalene, 2-(chloromethyl)pyridine and 3-chloro-2-methylprop-1-ene reacted smoothly to give the corresponding products **16**–**18** in 80%–95% yields. Indeed, the substrates were not limited to the above-mentioned benzyl halide derivatives; other alkyl halides bearing terminal alkyne bond, amide, nitrile, acetal, keto and ester groups worked well in this process to

produce the corresponding $(n\text{-}C_4H_9S)_2P(O)SR$ **19**–**27** under slightly modified conditions. For benzyl halides, most reactions were complete within 4 hours; however, for alkyl halides, a longer time (12 hours) was required. The long-chain 1-chlorooctane gave the desired products **22** in almost quantitative yield. Alkyl bromide bearing acetal group could be tolerated at 60 °C to give the desired product **25** in 83% yield. For other alkyl bromides, the reactions were conducted at room temperature and gave the corresponding products with satisfied yields.

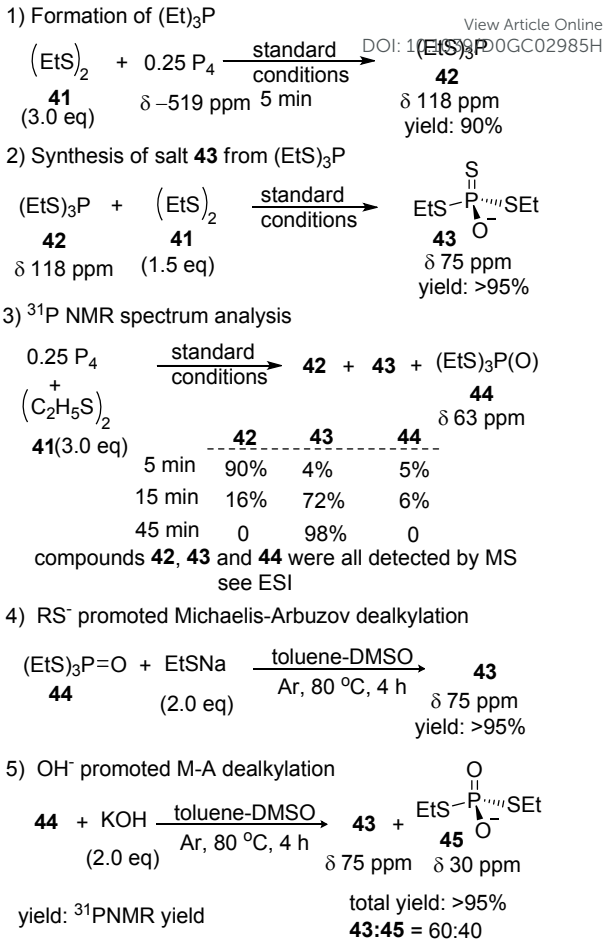
Encouraged by the findings described above, we continued to explore the reactivity of *O*-potassium *S,S*-dialkylphosphorotrithioates which were prepared from various dialkyldisulfides. In addition to *O*-potassium *S,S*-dibutylphosphorotrithioate, *S,S*-dimethylphosphorotrithioate, *S,S*-diethylphosphorotrithioate, *S,S*-dipropylphosphorotrithioate, *S,S*-di-isopropylphosphorotrithioate, *S,S*-di-sec-butylphosphorotrithioate, *S,S*-dicyclohexylphosphorotrithioate and *S,S*-dibenzylphosphorotrithioate all could be used as the substrates to react with benzyl halides, generating the corresponding mixed phosphorotrithioates (**28**–**34**) in 83–95% yields. *n*-Butyl bromide could react well with above-mentiond *O*-potassium *S,S*-dialkylphosphorotrithioates to form mixed phosphorotrithioates **35**–**40** in good to excellent yield. Diphenyldisulfide was also examined. Unfortunately, no desired *O*-potassium *S,S*-diphenylphosphorotrithioates was detected by ^{31}P NMR.

In order to demonstrate the practical application of this method, the gram-scale experiments were conducted by employing P_4 (2.5 mmol, 0.31 g) to deliver **22** and **29** in 94% and 88% yields, respectively (Scheme 3), indicating this reaction could be scaled up with a high efficiency.



Scheme 3. Gram-scale preparation of **22** and **29**.

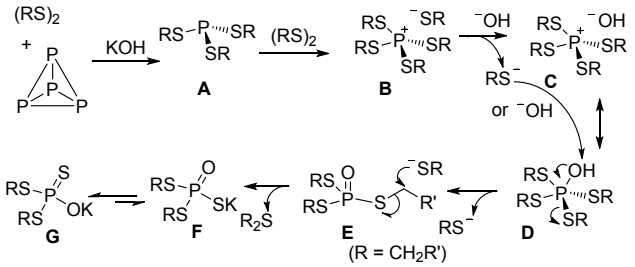
To understand the mechanism, further experiments were conducted (Scheme 4). Carrying out the reaction of $(C_2H_5S)_2$ (**41**, 3.0 equivalents of disulfide per P-atom) and P_4 in toluene-DMSO under argon at 80 °C for 5 min generated $(C_2H_5S)_3P$ (**42**, 118 ppm) in 90% yield (Scheme 4-1).[40] When 1.5 equivalents of $(C_2H_5S)_2$ reacted with $(C_2H_5S)_3P$ (**42**), *O*-potassium *S,S*-diethylphosphorotrithioate (salt **43**, 75 ppm) was obtained in almost quantitative yield (Scheme 4-2). To further investigate the mechanism, the formation of salt **43** was monitored by ^{31}P NMR spectroscopy (see ESI) and the data were shown in Scheme 4-3. The starting P_4 showed signal in the ^{31}P NMR spectrum at δ = -519 ppm. After $(C_2H_5S)_2$ (**41**, 3.0 equiv) and KOH were added to the solution of P_4, the reaction was conducted under standard conditions; the



Scheme 4. Investigation for reaction mechanism.

expected phosphorotrithioites [P(III), **42**] was produced (δ = 118 ppm) in 5 minutes and P_4 disappeared completely. In the meantime, there are two obvious peaks that appeared during the synthesis of **42**. The signals at δ = 75 and δ = 63 ppm belong to salt **43** and phosphorotrithioate [P(V), **44**],[40] respectively. Compounds **42**, **43** and **44** were all detected by MS (see ESI). As time progressed, the ^{31}P NMR signals of the phosphorotrithioites [P(III), **42**] and phosphorotrithioate [P(V), **44**] disappeared gradually and the signal of salt **43** (δ = 75 ppm) increased. The reaction was almost complete after 45 min according to the ^{31}P NMR spectra (see ESI). During the reaction course, two new weak peaks at 173 ppm and 180 ppm emerged; the peaks at 180 ppm disappeared after 30 min. These signals may belong to penta-coordinate ionic species **B** and **C** (Scheme 5). Although no spectroscopic data for intermediates **B** and **C** are available, 1,4,6,9-tetrathia-5-phosphoniaspiro[4.4]nonane tetrachloroborate has been previously studied by ^{31}P NMR, showing chemical shifts at 147 ppm,[48] similar to our proposed intermediates. Intermediates **B** and **C** were detected by HRMS (Scheme 5, see ESI). To classify the function of *S,S,S*-triethy phosphorothioate **44**, carrying out the reaction of sodium ethanethiolate (2.0 equiv) and **44** generated salt **43** in almost quantitative yield (Scheme 4-4). This result suggests that *S,S,S*-triethy phosphorothioate **44** was the key intermediate for the formation of salt **43**. To understand whether OH^- promotes Michaelis-Arbuzov dealkylation, KOH was examined. It

was found that the reaction gave both the normal dealkylated salt **43** and the saponification product **45** as a 60:40 mixture when KOH was used instead of EtSNa (Scheme 4-5). This result suggests that RS^- played a key role in Michaelis-Arbuzov dealkylation.



Scheme 5. Tentative mechanistic pathway.

Based on the above experiments and previous reports, a possible reaction mechanism is depicted in Scheme 5. Initially, the coupling of disulfide and P_4 affords phosphorotrithioites [P(III), **A**] in the presence of KOH under argon.[40] Reaction of phosphorotrithioites (P(III), **A**) with disulfide results in penta-coordinate ionic species **B**.[48,49] Ionic species **B** reacts with KOH to give intermediates **C** and **D** via an anion exchange. Phosphorotrithioate [P(V), **E**] is produced by elimination reaction of nonpolar penta-coordinate intermediate **D**. The attack of RSK to phosphorotrithioate **E** takes place and C−S bond breaks, the Michaelis-Arbuzov-like dealkylation, to form salt **F/G** along with the release of R_2S. A final alkylation of salt **F/G** gives mixed phosphorotrithioate.

Conclusions

In summary, we have successfully developed the first general and high yielding synthesis of $(R^1S)_2P(O)SR^2$ involving P_4, disulfides and alkyl halides. The use of KOH as a base, DMSO-toluene as a solvent, makes this transformation practical and green. The operationally simple reaction shows a broad scope of substrates and a good functional group tolerance. This method opens the shortest and environmentally benign way to these mixed phosphorotrithioates of practical importance. The reaction is characterized by a complete conversion of white phosphorus. Moreover, this method can be easily adapted to large-scale preparation. Our mechanistic data suggest that the nucleophilic attack of RSK on *S,S,S*-trialkyl phosphorotrithioates and subsequent C−S bond cleavage, the Michaelis-Arbuzov-like dealkylation, are the key steps in the formation of $(R^1S)_2P(S)OK$.

Experimental

Safety note for white phosphorus (P_4): White phosphorus is spontaneously flammable; it should be stored in water or glove box. On the other hand, white phosphorus is very soluble in toluene. White phosphorus-toluene solution should be sealed in argon and stored away from light.

Synthesis of (n-$C_4H_9S)_2P(O)SBn$ (4) from (n-$C_4H_9S)_2$, P_4 and benzyl chloride

An oven-dried Schlenk tube with a magnetic stir bar containing KOH (0.4 mmol, 22.4 mg) was evacuated and purged with argon three times. White phosphorus-toluene solution (6.2 mg total P_4, 0.5 mL, 0.1 mol/L) was added. Then (n-$C_4H_9S)_2$ (107.0 mg, 0.6 mmol), and DMSO (0.5 mL) were sequentially added to the system at room temperature. The reaction mixture was stirred for 4 hours at 80 °C. After completion, KI (0.02 mmol, 6.6 mg) and benzyl chloride (0.3 mmol, 37.8 mg) was added under air, and the mixture was stirred at 80 °C for another 4 hours. Saturated brine (3 mL) was added into the above reaction mixture. The mixture was extracted by EtOAc (3×2.0 mL). The combined organic layer concentrated by rotary evaporation. The crude reaction mixture was purified by flash chromatography using n-hexane−AcOEt [from 50:1 to 10:1 (v/v)] as the eluent to give the product **4** (66 mg, 95%).

Gram-scale synthesis of $(C_2H_5S)_2P(O)SBn$ (29) from $(C_2H_5S)_2$, white phosphorus (P_4) and benzylchloride

A 100 mL-round bottomed Schlenk flask with a magnetic stir bar containing KOH (1.12 g, 20.0 mmol) was evacuated and purged with argon three times. White phosphorus-toluene solution (0.31 g total P_4, 25.0 mL, 0.1 mol/L) was added. Then $(C_2H_5S)_2$ (3.67 g, 30.0 mmol), and DMSO (25.0 mL) were sequentially added to the system at room temperature. The reaction mixture was stirred for 4 hours at 80 °C. After completion, KI (0.33 g, 2.0 mmol) and benzylchloride (1.89 g, 15.0 mmol) was added under air, and the mixture was stirred at 80 °C for another 4 hours. Saturated brine (25.0 mL) was added into the above reaction mixture. The mixture was extracted by EtOAc (4×20.0 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash chromatography using n-hexane−AcOEt [from 50:1 to 10:1 (v/v)] as the eluent to give the product **29** (2.58 g, 88%).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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