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FULL PAPER

Reductive Rearrangement of Tetraphenyldiphosphine Disulfide to Trigger the Bisthiophosphinylation of Alkenes and Alkynes

Yuki Sato,[a] Misaki Nishimura,[a] Shin-ichi Kawaguchi,*[b] Akihiro Nomoto,[a] and Akiya Ogawa*[a]

Abstract: The facile synthesis of organophosphorus compounds is of great importance for the development of new synthetic methods using air-stable sources of phosphorus. In this respect, a synthetic method based on reductive rearrangement and capable of converting air-stable pentavalent phosphorus compounds into reactive trivalent phosphorus compounds is a powerful tool. In this study, we focused on tetraphenyldiphosphine disulfide, which is a shelf-stable solid, and revealed that it undergoes reductive rearrangement to trigger the bisthiophosphinylation of a variety of alkenes, such as terminal, cyclic, internal, branched alkenes, and 1,3-dienes, and terminal alkynes when exposed to light without any catalyst, base, or additive.

Introduction

Organophosphorus compounds are widely used as ligands for reactions catalyzed by transition metals, pharmaceuticals, and physiologically active compounds.[1] The synthesis of these compounds often requires the use of air- and moisture-sensitive sources of phosphorus. Therefore, the development of new synthetic methods involving air-stable sources of phosphorus, such as pentavalent phosphorus compounds,[2] is of great importance. Methods that employ the reductive rearrangement of pentavalent to trivalent phosphorus compounds therefore constitute a powerful tool, because they enable pentavalent phosphorus compounds to be used efficiently. For instance, it is known that (2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO, Scheme 1a), bearing a P(O)–C(O) single bond,[3] is transformed into a reactive trivalent phosphorus compound (Ph_2P–OC(O)Mes) when exposed to light.[4] We previously reported the application of this rearrangement to the synthesis of alkyl phosphines, which are trivalent phosphorus compounds.[5] In this reaction, alkyl radicals, generated in situ, efficiently react with the trivalent phosphorus atom of Ph_2P–OC(O)Mes to afford alkyl phosphines. In contrast, alkyl radicals are not captured by the pentavalent phosphorus atom of TMDPO at all because of its low radical capturing ability.

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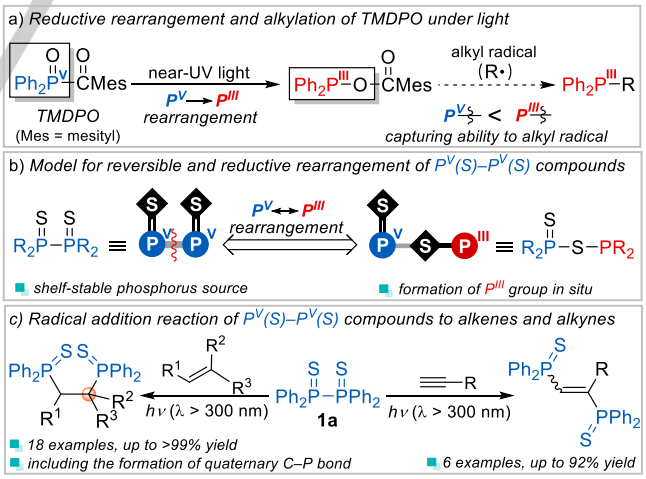
Inspired by the reductive rearrangement of TMDPO, we next focused on the reductive rearrangement of diphosphine disulfides, bearing $P^V(S)$–$P^V(S)$ single bonds (Scheme 1b). We expected a similar reductive rearrangement of several diphosphine disulfides to proceed under radical conditions to afford reactive trivalent phosphorus species in situ.

Diphosphines, bearing a P^{III}–P^{III} single bond, are important phosphorus sources for the *vic*-bisphosphination of carbon-carbon unsaturated bonds,[6],[7],[8] but they are difficult to handle because they are highly sensitive to air and moisture. In contrast, diphosphine disulfides[9],[10] are often sufficiently shelf-stable to be stored in the presence of air for several months. Therefore, diphosphine disulfides are attractive phosphorus sources for *vic*-bisthiophosphinylation, yet limited examples of their addition reactions to alkynes and alkenes[11] have been reported. The reported addition reactions using diphosphines and their analogues, which bear a P^V–P^{III} single bond,[12] require a trivalent phosphorus center because the ability to capture carbon radicals is the key factor in these reactions. Therefore, we hypothesized that the reductive rearrangements of diphosphine disulfides would generate reactive trivalent phosphorus species in situ and would enable the *vic*-bisthiophosphinylation of alkenes and alkynes.



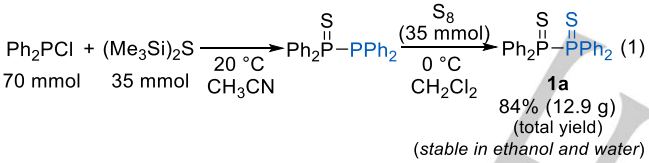
Scheme 1. Reductive rearrangement of TMDPO and diphosphine disulfide.

In this context, the reductive rearrangement of diphosphine disulfides and their addition reactions to alkenes and alkynes were investigated. As a result, we found that tetraphenyldiphosphine disulfide (**1a**) efficiently underwent reductive rearrangement to form tetraphenyldiphosphathiane monosulfide ($Ph_2P(S)$–$SPPh_2$) under light. This reductive

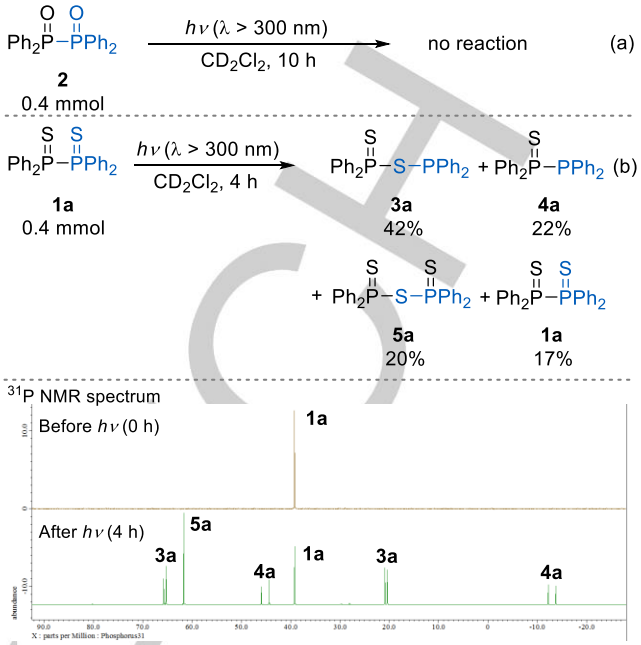
rearrangement triggered the 1,2-addition of diphosphine disulfide to a variety of alkenes and alkynes to afford bisthiophosphinylated alkanes and alkenes, respectively (Scheme 1c). The reason why not P^{III}-adducts but P^{V}-adducts are obtained selectively is described in detail in the text. Furthermore, bis(thiophosphinyl)alkanes can be easily reduced to afford bidentate bis(phosphino)alkane ligands,[8d, 12b] such as dppe (*vic*-bis(diphenylphosphino)ethane).[13] Therefore, we focused on the reductive rearrangement of diphosphine disulfides, and investigated this bisthiophosphinylation process in detail.

Results and Discussion

We initiated our study by developing the synthetic method to obtain diphosphine disulfide **1a**. Diphosphine disulfide **1a** is often synthesized via disulfurization of tetraphenyldiphosphine, prepared from diphenylphosphine and diphenylphosphine chloride, with a reported total yield of **1a** of 34%.[9d] We modified the existing method to synthesize diphosphine monosulfide, reported by Burford and Weigand et al.,[14] and successfully synthesized **1a** in 84% yield (12.9 g, Eq. 1) via a one-pot sequence from diphenylphosphine chloride (70 mmol) and bis(trimethylsilyl) sulfide (35 mmol). Diphosphine disulfide **1a** is shelf-stable solid, which does not undergo any noticeable decomposition in ethanol and water.

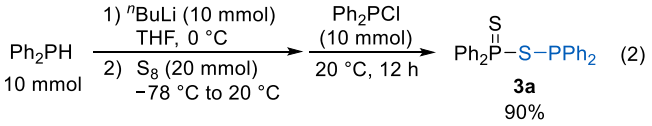


Next, we investigated the rearrangement of diphosphine dioxide **2** and diphosphine disulfide **1a**, both of which have a P^{V}–P^{V} single bond. Diphosphine dioxide **2** was irradiated with a xenon lamp (500 W) in a Pyrex NMR tube for 6 h (Scheme 2a), but the rearrangement of diphosphine dioxide **2** did not proceed at all. In the case of diphosphine disulfide **1a**, a pair of doublet peaks (δ_P = 20.6 ppm ($J_{P\text{-}P}$ = 78.0 Hz) and 65.4 ppm ($J_{P\text{-}P}$ = 78.0 Hz)) were observed by ^{31}P NMR spectroscopy of the mixture after irradiation (Scheme 2b). These peaks were assigned to diphosphathiane monosulfide **3a**, which has both pentavalent and trivalent phosphorus centers, and which was obtained in 42% yield. Additionally, diphosphine monosulfide **4a** (δ_P = −13.0 ppm ($J_{P\text{-}P}$ = 251.4 Hz) and 45.1 ppm ($J_{P\text{-}P}$ = 251.4 Hz)) and dithiophosphinoic anhydride **5a** (δ_P = 61.6 ppm) formed in yields of 22% and 20%, respectively. These results indicate that **1a** can undergo reductive rearrangement to generate trivalent phosphorus compounds **3a** accompanied with the formation of **4a** and **5a**.

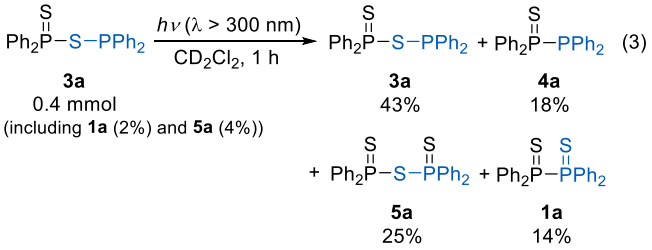


Scheme 2. Photoinduced rearrangements of diphosphine dioxide **2** and diphosphine disulfide **1a**.

We confirmed the reversibility of the rearrangement between **1a** and **3a** by developing a novel synthetic method for **3a** (Eq. 2). ^{n}BuLi (1.6 M in ^{n}hexane) was added to diphenylphosphine dissolved in THF followed by slow addition of two equivalents of elemental sulfur at −78 °C. This mixture was allowed to warm to room temperature slowly. Diphenylphosphine chloride was then added to the mixture, which was stirred for 12 h to give **3a** in 90% yield as a crude mixture containing **1a** (2%) and **5a** (4%).



After exposing **3a** to irradiation by a xenon lamp for 1 h, the conversion of **3a** to **1a** (14%), **4a** (18%), and **5a** (25%) was observed by ^{31}P NMR spectroscopy (Eq. 3). The ratio of the phosphorus compounds generated from **3a** was similar to the result shown in Scheme 2b.



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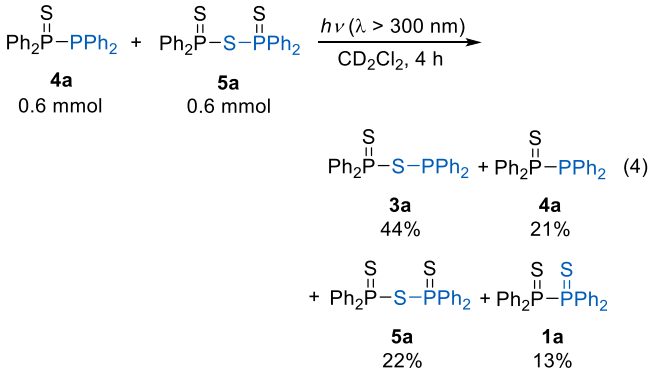
When the mixture containing equal amounts of **4a** and **5a** was also irradiated with a xenon lamp for 4 h, **4a** and **5a** were transformed into **1a** and **3a** (Eq. 4). The ratio of the phosphorus compounds generated from **4a** and **5a** was also similar to the results shown in Scheme 2b and Eq. 3.



These results revealed that **1a** and **3a**–**5a** were reversibly transformed to each other and they existed in the same molar ratio under light (Figure 1): Homolytic cleavage of the P(S)–P(S) single bond in **1a** is reversibly induced by photoirradiation to generate two diphenylthiophosphinyl radicals ($Ph_2P(S)\cdot$).[15] The unpaired electron of $Ph_2P(S)\cdot$ is delocalized on its phosphorus and sulfur atoms, as shown in a single occupied molecular orbital (SOMO) of $Ph_2P(S)\cdot$ calculated at UB3LYP/6-31G++(2d,p) level. Thus, $Ph_2P(S)\cdot$ partially coupled to form **3a**, bearing a P(S)–S–P structure, during the reversible homolytic cleavage of the P(S)–P(S) single bond. The transfer of a sulfur atom[16] from **1a** to **3a** also occurred to generate **4a** and **5a**, respectively.

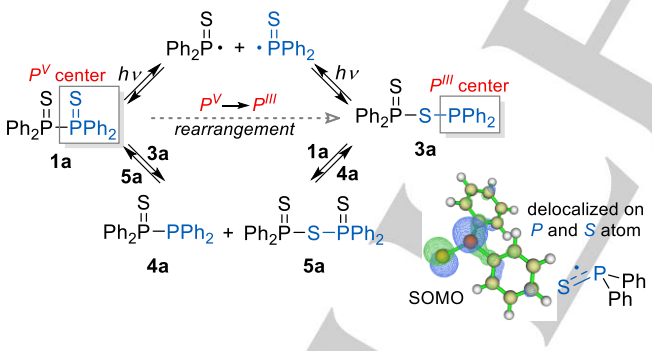
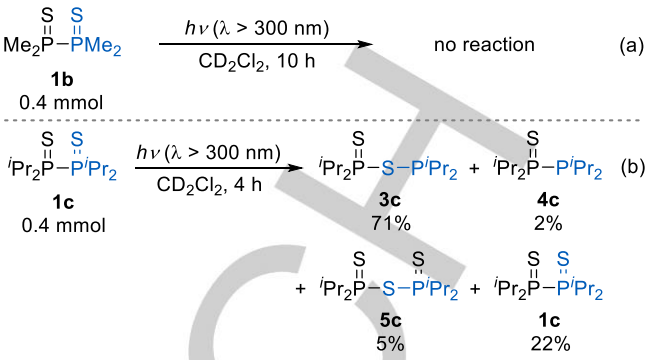


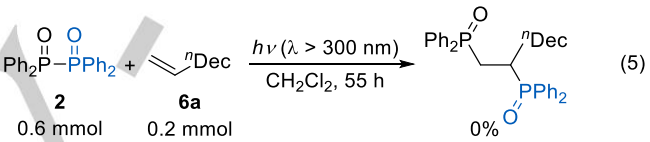
Figure 1. Reversible rearrangement between **1a** and **3a**–**5a**.

The influence of carbon substituents of diphosphine disulfides on their rearrangement was investigated by irradiating diphosphine disulfide **1b** and **1c** with a xenon lamp (Scheme 3). Although diphosphine disulfide **1b** was not consumed under light at all (Scheme 3a), **1c** was efficiently transformed to **3c** (71%), **4c** (2%), and **5c** (5%) (Scheme 3b).[17] These results indicated that the bulkiness of the carbon substituents influences the product ratio of **1** and **3**–**5** under light.



Scheme 3. Photoinduced rearrangements of diphosphine disulfides **1b** and **1c**.

Next, the radical addition reaction of diphosphine dioxide **2** and **1a** to 1-dodecene (**6a**) was examined. The addition reaction of **2** to **6a** did not proceed at all under light (Eq. 5).



In contrast, we previously reported that diphosphine monoxide **7**, bearing a $P^V(O)$–P^{III} single bond, adds to **6a** and affords the corresponding 1,2-adduct in 78% yield under the same conditions as in Eq. 5.[12a] The addition reaction proceeds in three steps (Figure 2): The photoinduced homolytic cleavage of the $P^V(O)$–P^{III} bond of **7** generates two phosphorus radicals, namely ***P(O)***· and ***P***·. The more electrophilic phosphorus radical (***P(O)***·) adds to an alkene and the generated alkyl radical is captured by the more electron-rich phosphorus group (***P***) of **7**. In this reaction, the diphenylphosphinyl group (***P(O)***) of **7** does not react with the alkyl radical because of its low capturing ability to alkyl radical.

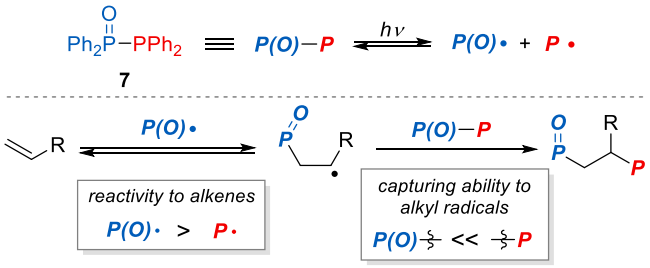


Figure 2. Model for radical addition of diphosphine monoxide **7** to alkenes under light.

In the case of diphosphine dioxide **2** (Figure 3, top), photoinduced homolytic cleavage of the $P^V(O)$–$P^V(O)$ bond of **2** can be achieved but the generated alkyl radical was not captured by the diphenylphosphinyl group (***P(O)***) of **2**. In contrast, diphosphine disulfide **1a** (***P(S)–P(S)***) generates the trivalent phosphorus species **3a** (***P(S)–SP***) and **4a** (***P(S)–P***), which are

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potentially good acceptors of alkyl radicals under exposure to UV light (Figure 3, bottom). Therefore, we hypothesized that the reductive rearrangement of **1a** enables the bisthiophosphinylation of alkenes.

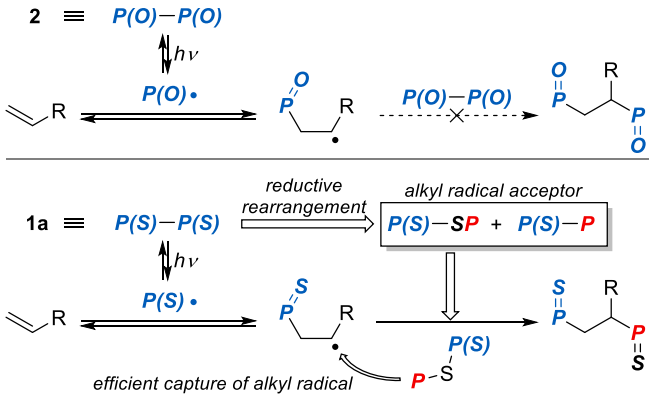
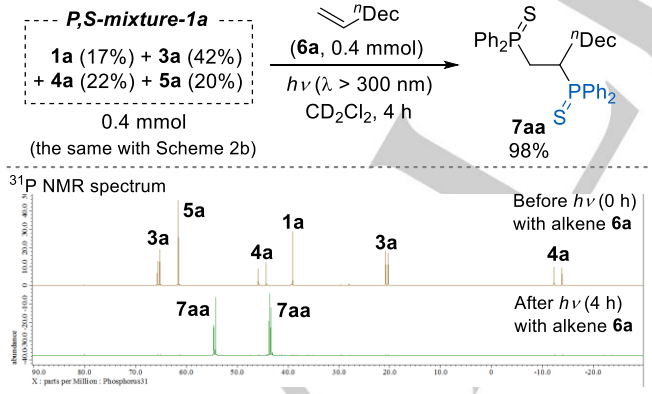


Figure 3. Model for radical addition of diphosphine dioxide **2** and diphosphine disulfide **1a** to alkenes under exposure to light.

Based on this hypothesis, the mixture of **1a** and **3a**–**5a**, generated by exposing **1a** to light (***P,S-mixture-1a***), was used as the phosphorus source for the bisthiophosphinylation of alkene **6a** (Scheme 4). After ***P,S-mixture-1a*** and **6a** was irradiated by light for 4 h, interestingly, **1a** and **3a**–**5a** were almost completely consumed and 1,2-bis(thiophosphinyl)alkane **7aa** was generated in 98% yield. In general, reactions consisting of four or more substrates usually afford complex mixtures of many products. In contrast, all components (**1a** and **3a**–**5a**) of ***P,S-mixture-1a*** converged to yield only one product **7aa**, almost quantitatively.



Scheme 4. Bisthiophosphinylation of alkene **6a** using the mixture of **1a** and **3a**–**5a**.

The bisthiophosphinylation of **6a** was investigated in detail by monitoring the conversion of **1a** and **3a**–**5a** to the 1,2-adduct **7aa** by ^{31}P NMR spectroscopy during the addition reaction, and the results are summarized in Figure 4. During the initial 1 h, **1a** was mainly converted to **3a**–**5a**. During the subsequent course of time, the conversion of **1a** and **3a**–**5a** and the bisthiophosphinylation of **6a** proceeded efficiently to generate the 1,2-adduct **7aa** in 98% yield. In particular, **1a** and **3a** were converted much faster than **4a** and **5a**. The addition of **4a** also occurred during the initial 1 h to 2 h but the 1,2-adduct of **4a** was converted to **7aa** after 2 h accompanied with the slow consumption of **1a** and **5a**.[18] These results indicate that **1a** and **3a** play a key role in this bisthiophosphinylation reaction and the 1,2-adduct of **4a** was sulfurized by the transfer of a sulfur atom from **1a** and **5a** to generate **7aa**.

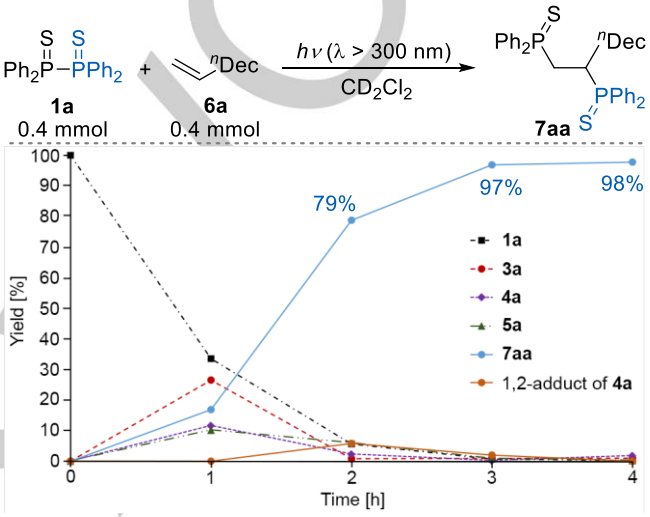


Figure 4. Yields during the addition reactions of diphosphine disulfide **1a** to alkene **6a** as a function of time, as monitored by ^{31}P NMR spectroscopy.

The reaction progress of bisthiophosphinylation of alkene **6a** using diphosphine disulfide **1a** or ***P,S-mixture-1a*** was monitored by ^{1}H NMR spectroscopy and compared (Figure 5). During the initial 1 h, we found that the bisthiophosphinylation of **6a** with ***P,S-mixture-1a*** (86% yield) proceeded approximately five times faster than the bisthiophosphinylation with **1a** (17% yield). The results summarized in Figures 4 and 5 strongly indicate that the formation of **3a**–**5a** is the induction step of the addition of **1a** and this step triggered the generation of 1,2-adduct **7aa**.

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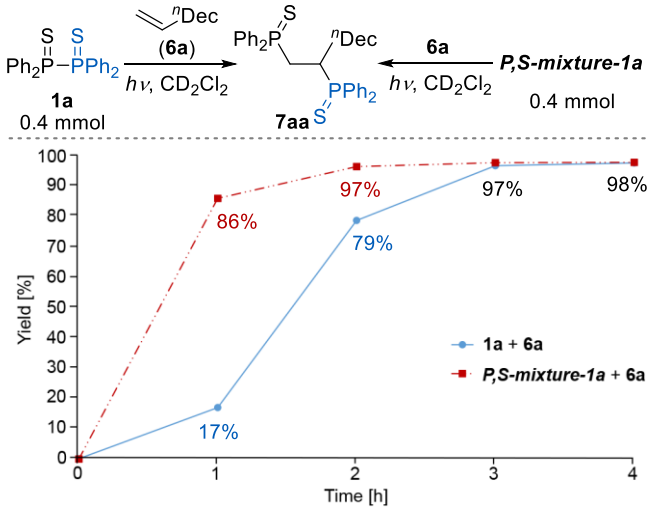
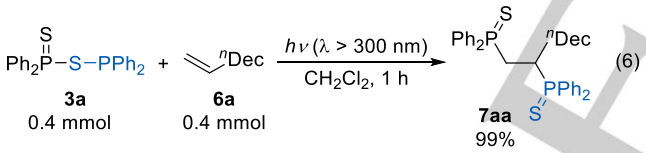


Figure 5. Yields during the bisthiophosphinylation of alkene **6a** using diphosphine disulfide **1a** or ***P,S-mixture-1a*** as a function of time, as monitored by ^{1}H NMR spectroscopy.

Notably, the addition of **3a** to **6a** efficiently proceeded to afford **7aa**, quantitatively, in an hour (Eq. 6). In our previous report, the addition of **4a** to **6a** while exposed to light for an hour provided the corresponding 1,2-adduct of **4a** in 62% yield.[12b] These results indicate that **3a** behaves as the main active species of the addition reaction to **6a**.



Plausible reaction pathways for the present reaction are illustrated in Figure 6. The bisthiophosphinylation proceeds via three steps: the $Ph_2P(S)$· attacks an alkene to afford the β-thiophosphinylated alkyl radical. The generated radical reacts with the diphenylphosphino group of **3a** and **4a** to afford the 1,2-bisthiophosphinylalkane **7a** and 1-thiophosphinyl-2-phosphinoalkane **8a**, respectively, accompanied with the release of $Ph_2P(S)$·. The sulfur atom was also transferred from **1a** and **5a** to **8a** to afford **7a** accompanied by the regeneration of **4a** and **3a**, respectively.

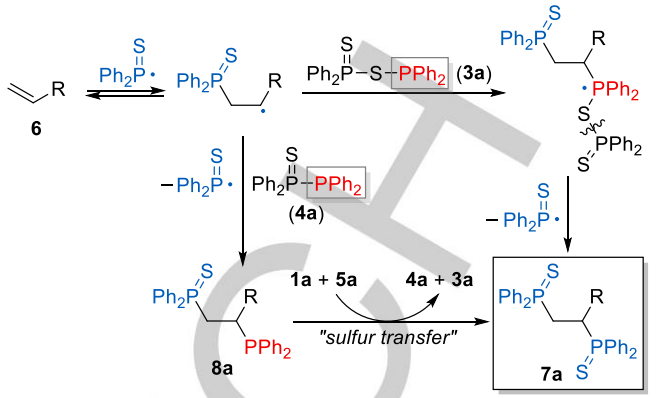
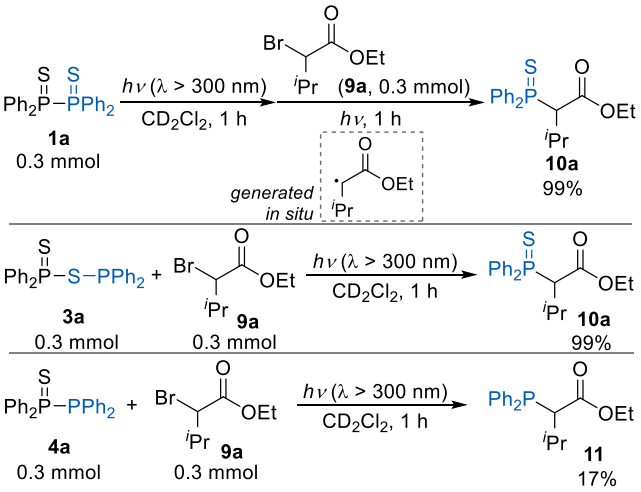


Figure 6. Plausible reaction pathways of bisthiophosphinylation of alkene **6** using the mixture of **1a** and **3a–5a**.

The capturing ability of alkyl radicals on **3a** or **4a** generated from **1a** was compared by conducting several experiments using the secondary alkyl radical generated from bromoacetate **9a** under light (Scheme 5). Diphosphine disulfide **1a** was irradiated with a xenon lamp for 1 h followed by the addition of **9a**. The mixture was irradiated for 1 h. In this reaction, **3a–5a** were generated from **1a** in situ by cleaving the P(S)–P(S) bond of **1a** under near-UV light in the first step, and the secondary alkyl radical was then also formed by the cleavage of the carbon–bromine bond in **9a** in the second step. The generated alkyl radical underwent homolytic substitution at the trivalent phosphorus group of **3a** and **4a** to afford alkylphosphine sulfide **10a** in 99% yield. Diphosphathiane monosulfide **3a** also reacted with **9a**, quantitatively. In contrast to **3a**, the reaction of **4a** was inefficient and alkylphosphine **11** was obtained in only 17% yield. These results indicate that the capturing ability of **3a** to the secondary alkyl radical (involving the 3-methyl-2-butanoate radicals) is higher than that of **4a**.



Scheme 5. Homolytic substitution reactions of **3a** and **4a** with the secondary alkyl radical generated from bromoacetate **9a** under light.

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FULL PAPER

The difference between the ability of **3a** and **4a** to capture alkyl radicals can be attributed to the weakness of the phosphorus–sulfur bond and the lower steric hindrance around the trivalent phosphorus center of **3a**. The capture of **3a** to alkyl radicals can proceed via an Arbuzov-type pathway: the alkyl radical undergoes a nucleophilic attack by the lone pair of the trivalent phosphorus atom of **3a** accompanied with homolytic cleavage of the P(S)–SP bond and formation of the P=S bond, as shown in Figure 7. In contrast, **4a** captures alkyl radicals via homolytic cleavage of the relatively strong P(S)–P bond. In general, the bond dissociation energy of the phosphorus–sulfur bond (442 ± 10 kJmol^{-1})[19] is lower than that of the phosphorus–phosphorus bond (489 ± 10 kJmol^{-1}).[19] In addition, the trivalent phosphorus center of **3a** is less sterically hindered than that of **4a** because of the greater distance maintained between the bulky thiophosphinyl group and the trivalent phosphorus center of **3a** by its sulfur bridge.

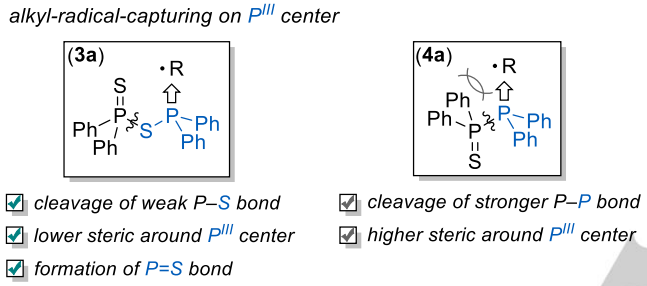
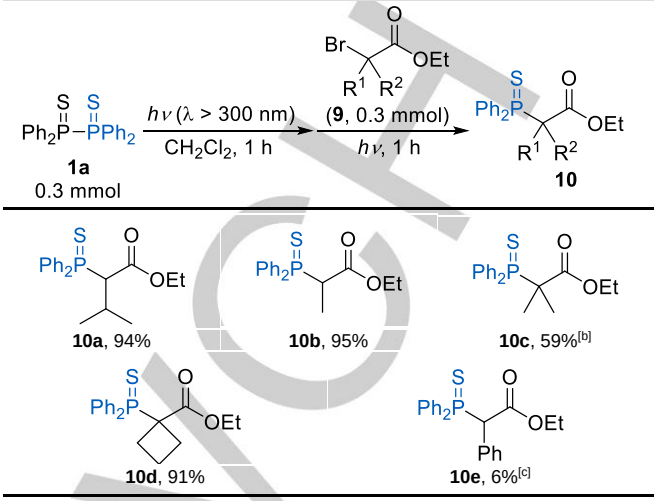


Figure 7. Model for the difference between the ability of **3a** and **4a** to capture alkyl radicals.

Homolytic substitution reactions of **3a** and **4a**, generated from **1a**, with several bromoacetates **9** were examined to reveal the scope of their ability to capture alkyl radicals (Table 1). Diphosphine disulfide **1a** efficiently reacts with aliphatic secondary bromoacetates **9a** and **9b** to afford alkylphosphine sulfides **10a** and **10b**, respectively, in excellent yields. The reaction with tertiary bromoacetate **9c** provided **10c**, bearing a quaternary carbon–phosphorus bond, in 59% yield. The alkyl radical generated from **9d**, bearing a cyclobutyl group, was also captured by **3a** and **4a** efficiently, to give **10d** in 94% yield. In contrast, the benzyl radical generated from **9e** could not be captured by **3a** and **4a**. Considering the electron-withdrawing from the ester groups of the acetate radicals generated from **9**, these results indicate that aliphatic and electron-rich alkyl radicals are efficiently captured by **3a** and **4a**.

Next, we investigated the ability of **1a** to undergo an addition reaction with alkenes under several radical conditions. The bisthiophosphinylation reaction of alkene **6a** proceeded efficiently even under weak irradiation and radical initiators (Table 2). Under 400 nm LED light (4.5 W), **1a** added to **6a** in 95% yield (entry 2). This reaction also proceeded under a 20 W fluorescent lamp to give the 1,2-adduct **7aa** in 51% yield (entry 3). The addition of **1a** was promoted by heating (80 °C) and the 1,2-adduct **7aa** was afforded in 95% yield under the 20 W fluorescent lamp (entry 4).

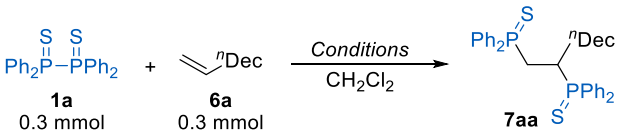
Table 1. Thiophosphinylation of several bromoacetates **9** with **1a**.[a]



Isolated yields. [a] Reaction conditions: **1a** (0.3 mmol), **9** (0.3 mmol), CH_2Cl_2 (0.3 mL), 20 °C, xenon lamp (500 W), Pyrex, and 1 h. [b] Irradiation for 10 h. [c] The yield was determined by ^{1}H NMR.

Photoredox reaction conditions were also available for this reaction: under blue LED light (6.5 W), 0.5 mol% of *fac*-Ir(ppy)$_3$ catalyzed the bisthiophosphinylation of **6a** to generate 1,2-adduct **7aa** in 91% yield (entry 5). In the presence of a catalytic amount of the radical initiator V-40 (1,1'-azobis(cyclohexane-1-carbonitrile)), **1a** added to **6a**, efficiently, and 1,2-adduct **7aa** was obtained in 95% yield (entry 6). In the absence of either light or the radical initiator, **7aa** was not observed by ^{1}H NMR spectroscopy under the same reaction conditions and **1a** was recovered quantitatively (entry 7).

Table 2. Bisthiophosphinylation of **6a** with **1a** under various reaction conditions conducive for generating radicals.[a]



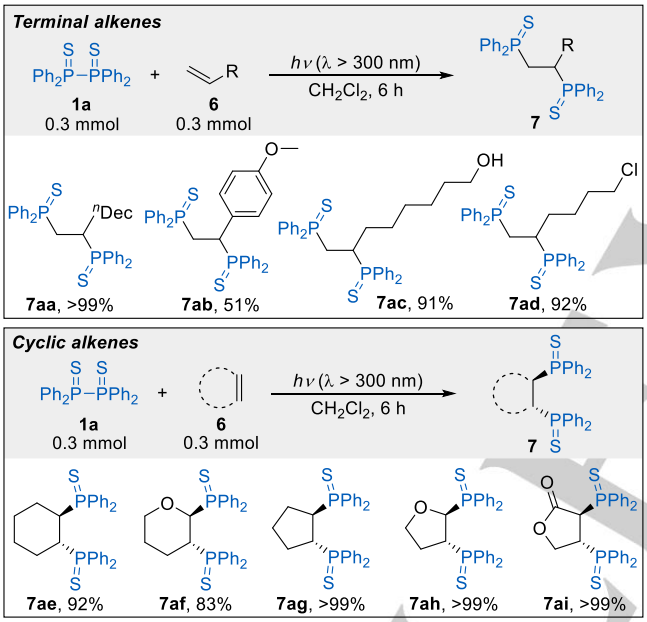
Entry	Conditions	Yield
1	Xenon lamp (λ > 300 nm, 500 W), rt, 6 h	>99%
2	400 nm LED (4.5 W), rt, 20 h	95%
3	20 W Fluorescent lamp, rt, 20 h	51%
4[b]	20 W Fluorescent lamp, 80 °C, 20 h	95%
5	Blue LED (6.5 W), *fac*-Ir(ppy)$_3$ (0.5 mol%), rt, 20 h	91%
6[b]	Dark, V-40 (10 mol%), 80 °C, 20 h	95%
7[b]	Dark, 80 °C, 20 h	0%

Yields were determined by ^{1}H NMR. [a] Reaction conditions: **1a** (0.3 mmol), **6a** (0.3 mmol), and CH_2Cl_2 (0.3 mL). [b] Benzene (0.45 mL) was used instead of CH_2Cl_2.

10.1002/chem.201900073

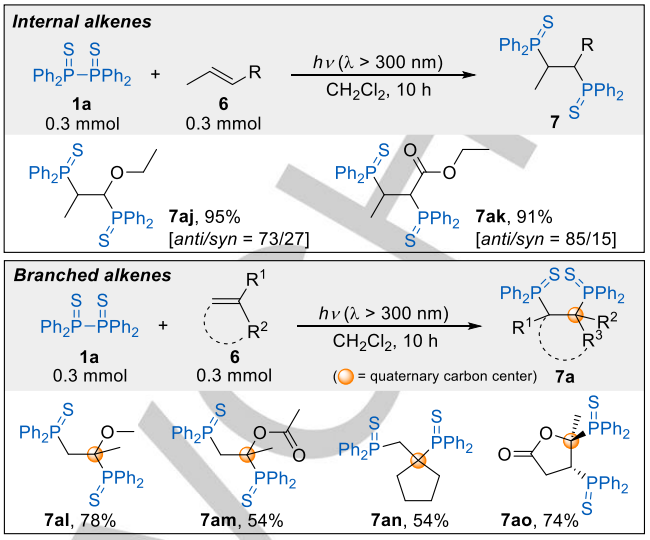
FULL PAPER

The addition reactions of **1a** to a variety of alkenes were performed under light. This bisthiophosphinylation reaction was effective for terminal and cyclic aliphatic alkenes **6a** and **6c–6i** as well as the aromatic alkene **6b** (Scheme 6). Diphosphine disulfide **1a** was tolerated by the hydroxy- (**6c**) and chloro- (**6d**) group under light and gave the desired product **7ac** and **7ad**, respectively, in excellent yields. Diphosphines with a trivalent phosphorus center, such as tetraphenyldisphosphine, immediately decompose in the presence of alchohol, such as **6c**. In contrast, **1a** is stable in the presence of alchohols, such as ethanol and water solvent, and therefore it can efficiently add to **6c** without decomposition. 4-Methoxystyrene (**6b**) was transformed into the 1,2-adduct in 55% yield. The addition to cyclic alkenes **6c–6h** afforded the corresponding 1,2-adducts **7ae–7ai** in excellent yields with excellent diastereoselectivities. In particular, sufficiently pure 1,2-adducts **7aa** and **7ag–7ai** were directly obtained, quantitatively, without any need for purification.



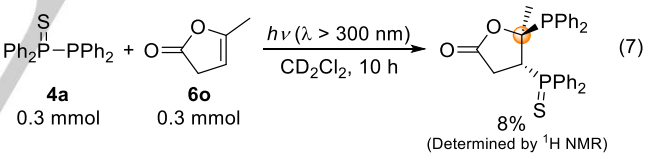
Scheme 6. Bisthiophosphinylation of several terminal and cyclic alkenes **6** with **1a**.

The higher capturing ability of **3a** to bulky alkyl radicals enabled efficient 1,2-additions to internal and branched alkenes. Therefore, the scope of internal and branched alkenes was also investigated (Scheme 7). For internal alkenes, such as vinyl ether **6j** and acrylate **6k**, the desired products **7aj** and **7ak** were generated in 95% and 91% yield, respectively, with good stereoselectivities. In general, 1,2-addition of diphosphines and their analogues, bearing a phosphorus–phosphorus single bond, to branched alkenes is difficult because of the bulkiness of their phosphorus groups. However, **1a** successfully added to branched alkenes **6l–6o** to afford the corresponding 1,2-adducts **7al–7ao**, bearing a quaternary carbon center, in good yields. These results demonstrate the high substrate generality of this reaction.



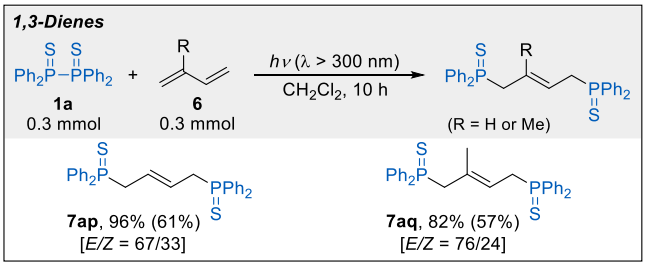
Scheme 7. Bisthiophosphinylation of several internal and branched alkenes **6** with **1a**.

As summarized in Schemes 6 and 7, this bisthiophosphinylation reaction is effective for relatively bulky alkenes, such as branched alkene **6l–6o**. In the case of diphosphine monosulfide **4a**, the attempted addition to **6o** did not proceed efficiently and gave the 1,2-adduct of **4a** in 8% yield (Eq. 7). The difference in the reactivity between **1a** and **4a** supported that **4a** does not play a key role in the addition reaction of **1a** to alkenes.



Therefore, the 1,2-addition reaction of diphosphine disulfide **1a** is a general synthetic method of 1,2-bis(thiophosphinyl)alkanes which are the synthetic precursors of 1,2-bis(phosphino)alkane ligands. This reaction was also effective for the synthesis of 1,4-bis(thiophosphinyl)alkanes which are the synthetic precursor of 1,4-bis(phosphino)alkane ligands, such as dppb (1,4-bis(phosphino)butane): the bisthiophosphinylation of 1,3-dienes **6p** and **6q** with **1a** gave the corresponding 1,4-adducts **7ap** and **7aq**, respectively, in good yields with good stereoselectivities (Scheme 8).

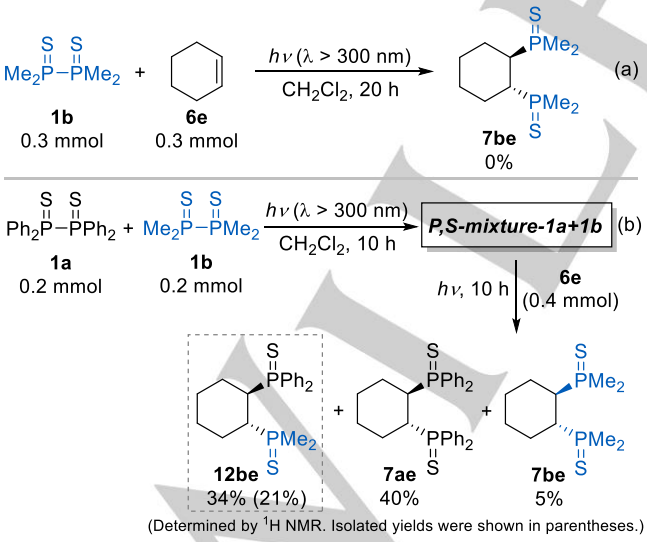
10.1002/chem.201900073



NMR yield of *E/Z* mixture (Isolated yield of *E*-isomer).
The NMR yields and the *E/Z* ratios was determined by ^{31}P NMR of the crude mixture.

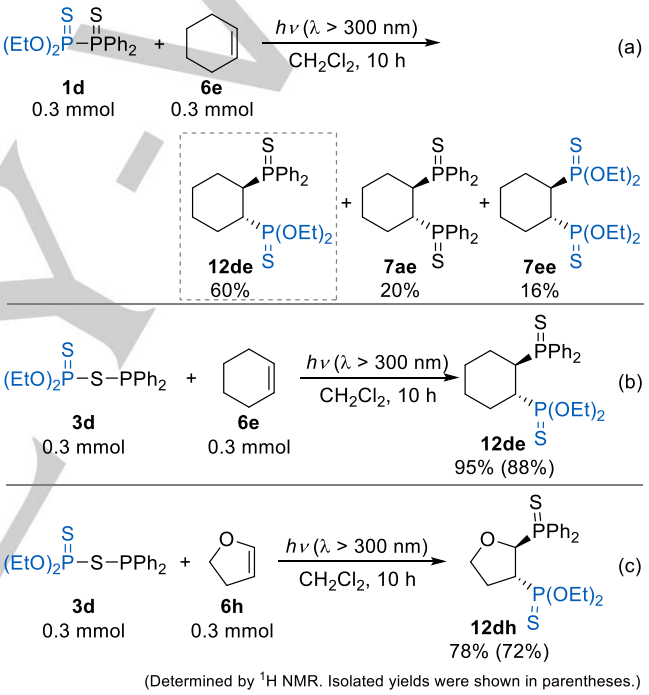
Scheme 8. Bisthiophosphinylation of several 1,3-dienes **6** with **1a**.

The influence of the substituents at phosphorus atoms of diphosphine disulfides on their addition to alkenes was investigated by irradiating a mixture of diphosphine disulfide **1b** and **6e** under light for 20 h but the addition reaction did not proceed at all (Scheme 9a). Diphosphine disulfide **1b** did not undergo the reductive rearrangement under light as shown in Scheme 3a. Thus, we hypothesized that **1b** could be activated by other trivalent phosphorus species, such as **3a** and **4a**, followed by the generation of the unsymmetrical coupled products, such as $Me_2P(S)–P(S)Ph_2$, and they could react with alkenes. When the mixture of **1a** and **1b** was irradiated under light for 10 h (Scheme 9b), the conversion of **1a** and **1b** to more than 11 phosphorus species (***P,S-mixture-1a+1b***), including $Me_2P(S)–P(S)Ph_2$ (56%), $Me_2P(S)–SPPh_2$ (11%), $Me_2P(S)–PPh_2$ (2%), and $Me_2P(S)–SP(S)Ph_2$ (25%), was observed by ^{31}P NMR spectroscopy. After addition of alkene **6e** and irradiation under light for 10 h, unsymmetrical 1,2-adduct **12be** was obtained in 34% yield accompanied with the generation of **7ae** (40%) and **7be** (5%).



Scheme 9. Radical addition of diphosphine disulfide **1b** to alkene **6e** with/without **1a**.

In the case of unsymmetrical diphosphine disulfide **1d**, 1,2-adduct **12de** was obtained in 60% yield (Scheme 10a). In this reaction, symmetrical 1,2-adducts **7ae** (20% yield) and **7ee** (16% yield) were also generated because of the presence of the two competing phosphorus radicals, $Ph_2P(S)$· and $(EtO)_2P(S)$·. In contrast, the addition of **3d** selectively afforded **12de** in 88% yield (Scheme 10b). Interestingly, **3d** added to alkene **6h** regioselectively, and the 1,2-adduct **12dh** was obtained in 72% yield (Scheme 10c). In these reactions, **1d** was efficiently converted to **3d**–**5d** (Scheme 10a) but the conversion of **3d** was relatively slower than **1d** (Scheme 10b and 10c). We concluded that the slow release of the thiophosphoryl radical from **3d** and its relatively fast ability to capture carbon radicals prevented the scramble for the two phosphorus radicals $(EtO)_2P(S)$· and $Ph_2P(S)$· (Figure 8).



Scheme 10. Selectivity in bisthiophosphinylation reaction of **6e** and **6h** using unsymmetrical diphosphine disulfide **1d** and diphosphathiane monosulfide **3d**.

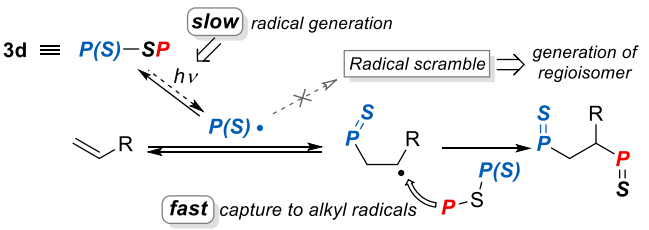
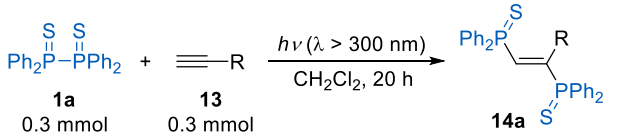


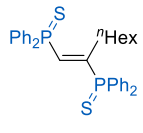
Figure 8. Model for regioselective 1,2-addition of diphosphathiane monosulfide **3d** to alkenes.

10.1002/chem.201900073

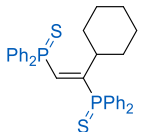
The bisthiophosphinylation reaction of a variety of alkynes **13** also proceeded efficiently to afford (*E*)-1,2-bisthiophosphinylated alkenes **14** with good stereoselectivities (Table 3). Diphosphine disulfide **1a** efficiently added to aliphatic alkynes with a long carbon chain (**13a**), cyclohexyl (**13b**), and trimethylsilyl groups (**13c**), and the desired products **14a–14c** were obtained in good yield with good stereoselectivities. The addition to phenylacetylene (**13d**) gave the 1,2-adduct **14ad** in 85% yield with good stereoselectivity. Both alkynes with an electron-donating group (**13e**) and electron-withdrawing group (**13f**) were available for this reaction and the corresponding 1,2-adducts **14ae** and **14af** were obtained in good yield with good stereoselectivities, respectively.

Table 3. Bisthiophosphinylation of several alkynes **13** with **1a**.[a]

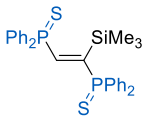




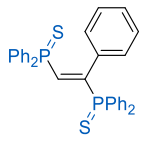
14aa, 92% (71%)
[*E*/*Z* = 82/18]



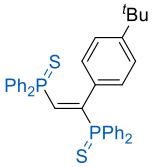
14ab, 86% (65%)
[*E*/*Z* = 80/20]



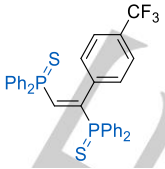
14ac, 82% (64%)
[*E*/*Z* = 82/18]



14ad, 85% (62%)
[*E*/*Z* = 75/25]



14ae, 93% (68%)
[*E*/*Z* = 76/24]



14af, 80% (54%)
[*E*/*Z* = 75/25][b]

NMR yield of *E*/*Z* mixture (Isolated yield of *E*-isomer). The NMR yields were determined by ^{31}P NMR. The *E*/*Z* ratios were determined by ^{31}P NMR of the crude mixture. [a] Reaction conditions: **1a** (0.3 mmol), **13** (0.3 mmol), CH_2Cl_2 (0.3 mL), 20 °C, xenon lamp (500 W), and 20 h. [b] Irradiation for 30 h.

Conclusions

In conclusion, we developed a simple and facile synthetic method for the preparation of bis(thiophosphinyl)alkanes and bis(thiophosphinyl)alkenes. Diphosphine disulfides are promising sources of phosphorus because of their facile preparation and because they are shelf-stable solids. However, previous examples of addition reactions involving diphosphine disulfides were limited. Our results showed that diphosphine disulfides underwent reductive rearrangement to reactive trivalent phosphorus species, such as diphosphathiane monosulfide, which has a P(S)–SP single bond, when exposed to light. In addition, this rearrangement triggered the efficient radical chain for the bisthiophosphinylation reaction of a variety of alkenes and alkynes. This reaction readily affords a variety of bis(thiophosphinyl)alkanes without the need for a catalyst, base, or additive. We believe this work provides a powerful tool for the synthesis of bis(phosphino)alkane ligands, such as dppe, which can easily be obtained by the desulfurization of bis(thiophosphinyl)alkanes.

Experimental Section

The general procedures for the bisthiophosphinylations of alkenes and alkynes with diphosphine disulfides were as follows. Diphosphine disulfide **1a** (0.3 mmol) and alkene **6** or alkyne **13** (0.3 mmol) in degassed dry CH_2Cl_2 (0.3 mL) were placed in a sealed Pyrex NMR tube under argon atmosphere and the mixture was irradiated with a xenon short arc lamp for the specified time at room temperature. The desired product was obtained after isolation by silica gel chromatography (*n*-hexane/AcOEt/$CHCl_3$). Further details of the experimental procedures and characterization data for the new compounds are included as supporting information.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Phosphanes • Phosphorylation • Radical reactions • Rearrangements

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[17] When the solution of **1b** (0.4 mmol) dissolved in CD_2Cl_2 (0.4 mL) was irradiated with a xenon lamp (500 W) in a quartz NMR tube for 10 h, **1b** (89%), $Me_2P(S)–SPMe_2$ (1%), $Me_2P(S)–PMe_2$ (3%), $Me_2P(S)–S–P(S)Me_2$ (3%), and three unidentified products were observed by ^{31}P NMR spectroscopy.

[18] Diphosphine disulfide **1a** (0.3 mmol) and 1,2-adduct of **4a** to **6a** ((1-diphenylthiophosphinyl-2-diphenylphosphino)dodecane) dissolved in CD_2Cl_2 (0.3 mL) were exposed to photoirradiation conditions for 6 h. Most of the 1,2-adduct of **4a** was sulfurized to afford **7aa**, quantitatively.

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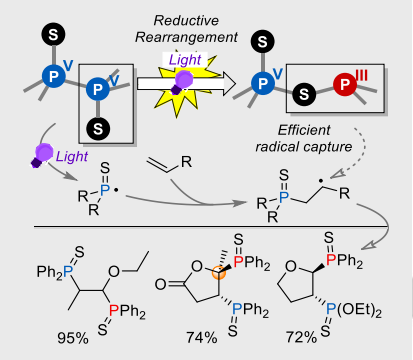
Entry for the Table of Contents

FULL PAPER

Synthetic methods involving reductive rearrangement to convert air-stable pentavalent phosphorus compounds to reactive trivalent phosphorus compounds constitute a powerful tool. We focused on tetraphenyldiphosphine disulfide, which is a shelf-stable solid, and revealed that its reductive rearrangement triggers *vic*-bisthiophosphinylation of a variety of alkenes and alkynes when exposed to light without requiring any catalyst, base, or additive.



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Page No. – Page No.

Title
Reductive Rearrangement of Tetraphenyldiphosphine Disulfide to Trigger the Bisthiophosphinylation of Alkenes and Alkynes