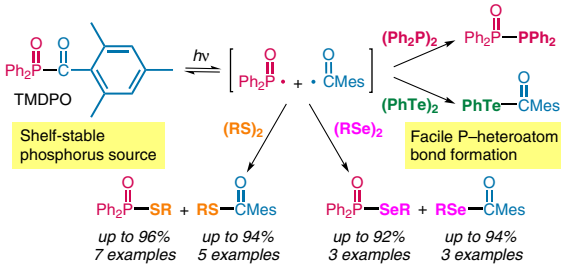
Synthesis Y. Sato et al. Feature

Photoinduced Coupling Reaction of Diphenyl(2,4,6-trimethylbenzoyl)phosphine Oxide with Interelement Compounds: Application to the Synthesis of Thio- or Selenophosphinates

Yuki Sato[a]
Shin-ichi Kawaguchi*[b]
Akihiro Nomoto[a]
Akiya Ogawa*[a]

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan
ogawa@chem.osakafu-u.ac.jp
[b] Center for Education and Research in Agricultural Innovation, Faculty of Agriculture, Saga University, 152-1 Shonan-cho, Karatsu, Saga 847-0021, Japan
skawa@cc.saga-u.ac.jp



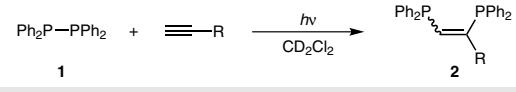
Received: 13.04.2017
Accepted after revision: 11.05.2017
Published online: 04.07.2017
DOI: 10.1055/s-0036-1588867; Art ID: ss-2017-z0251-fa

Abstract Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO) is a radical initiator widely used in the field of macromolecular chemistry, but not often applied in synthetic organic chemistry. We have focused on the use of TMDPO as a phosphorus source in reactions with different ***E–E*** compounds, where ***E–E*** represents a heteroatom–heteroatom bond, under photoirradiation. Interestingly, the cross-coupling reaction between TMDPO and disulfides or diselenides successfully affords thio- or selenophosphinates and thio- or selenoesters, respectively. The synthesis of series of thio- and selenophosphinates by this photoinduced cross-coupling reaction is demonstrated.

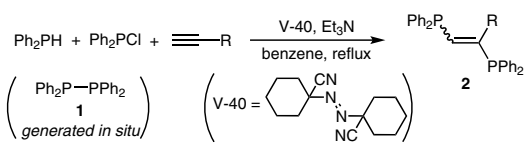
Key words cross-coupling, radical reaction, phosphorus, sulfur, selenium

Organophosphorus compounds have been widely used in various applications such as pharmaceuticals, agrochemicals, heat-resistant polymers, ligands for metal catalysts, and synthetic intermediates.[1] Thus, highly efficient and selective synthetic methods for these phosphorus-containing materials are highly desirable. However, in some cases, the characteristic features of phosphorus, i.e., high oxygen affinity resulting in air and moisture sensitivity, hinder the preparation of organophosphorus compounds. Recently, our group has been interested in 'phosphorus-centered radicals' as key intermediates in the practical synthesis of organophosphorus compounds, because of the appropriate reactivity of these radical species toward unsaturated bonds and the possibility to develop metal-free processes.

During our study on the photoinduced radical addition of interelement compounds such as $(PhS)_2$, $(PhSe)_2$, and $(PhTe)_2$ to a variety of carbon–carbon unsaturated compounds,[2] we started to investigate the photoinduced radical addition of tetraphenyldiphosphine (**1**) to alkynes, which afforded *vic*-bis(diphenylphosphino)alkenes **2** with high *Z*-selectivity (Scheme 1).[3] However, $(Ph_2P)_2$ is air- and moisture-sensitive, and requires careful handling. Yorimitsu and Oshima reported a practical radical addition of **1**, generated in situ from Ph_2PH and Ph_2PCl, to alkynes in the presence of a radical initiator, which afforded the *E*-isomer of **2** selectively (Scheme 2).[4]



Scheme 1 Photoinduced *Z*-selective radical addition of tetraphenyldiphosphine (**1**) to alkynes



Scheme 2 *E*-Selective radical addition of **1**, generated in situ from Ph_2PH and Ph_2PCl, to alkynes using the radical initiator V-40 [1,1′-azobis(cyclohexanecarbonitrile)]

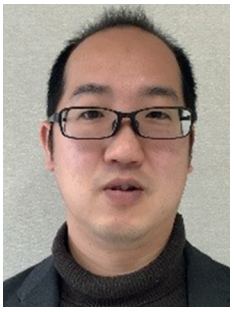
Very recently, we have focused on diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO) (**3**)[5] as a potentially attractive phosphorus radical source because of its air stability and easy handling. Upon photoirradiation, TMDPO generates a diphenylphosphinyl radical [$Ph_2P(O)^•$] along with a 2,4,6-trimethylbenzoyl radical [2,4,6-$Me_3C_6H_2C(O)^•$] by homolytic cleavage of the P–C bond.[1,6,7] TMDPO is a commercially available radical initiator for polymerization, and is widely used in macromolecular chemistry, not only for surface processing, such as coating[8] and adhesive materials,[9] but also for photonic crystals[10] and

mechanical devices.[11,12] However, there are only very limited examples of synthetic reactions of organophosphorus compounds using TMDPO as a phosphorus source.[13]

Recently, we reported that TMDPO efficiently reacts with perfluoroalkyl iodides under photoirradiation to afford the corresponding *P*-perfluoroalkylated diphenylphosphines (*P*-fluorous phosphine) (Scheme 3).[14] In this reaction, the selective formation of trivalent phosphines such as Ph_2PR_f is noteworthy, considering that the pentavalent phosphorus radical $Ph_2P(O)^{\bullet}$ is generated from TMDPO at the initial stage. The spin density of $Ph_2P(O)^{\bullet}$ is located on both the phosphorus and oxygen atoms. This feature enables the reductive transformation of TMDPO to $Ph_2P^{III}O\text{-}P^{V}(O)Ph_2$ and $Ph_2P^{III}O\text{-}C(O)Mes$ in situ,[15] which undergo substitution by the photogenerated $R_f^{\bullet}$.

Biographical Sketches

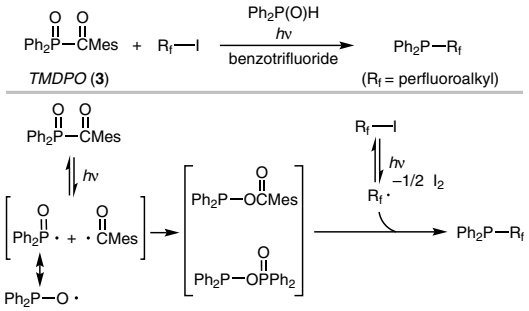
Yuki Sato was born in Hiroshima (Japan) in 1991. He graduated in 2010 and obtained his master's degree in synthetic organic chemistry under the direction of Professor Akiya Ogawa at Osaka Prefecture University. His Ph.D. research focused on the development of efficient synthetic methods toward organophosphorus compounds.



Shin-ichi Kawaguchi is a Specially Appointed Assistant Professor at Saga University, Japan (2016 to present). He received his doctorate of engineering degree in 2012 from Osaka Prefecture University, Japan, under the supervision of Professor Akiya Ogawa. He was a Research Fellow of the Japan Society for the Promotion of Science (DC1, 2009–2012). In 2010, he was a visiting researcher (JSPS Excellent Young Researcher Overseas Visit Program) at Uppsala University, Sweden, with Professor Lars Engman. He was a Postdoctoral Research Fellow of the Japan Society for the Promotion of Science (2012–2015) at Tohoku University, Japan, with Professor Toshio Miyata. His research interests include heteroatom chemistry, medicinal chemistry, and cosmetic science.

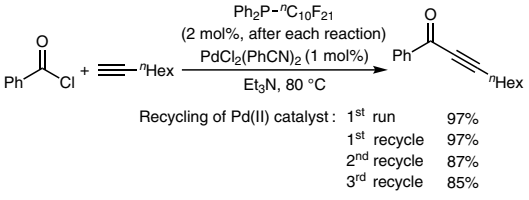
Akihiro Nomoto was born in Osaka (Japan) in 1969 and earned his B.S. and Ph.D. from Osaka University under the supervision of Professor Toshikazu Hirao. He held postdoctoral fellowships with Professor Yoshiaki Kobuke at Nara Institute of Science and Technology, Professor Yoshito Tobe at Osaka University, and Professor Minoru Inaba at Doshisha University. He joined Professor Akiya Ogawa's group as an Assistant Professor in 2005, Lecturer in 2014, and Associate Professor in 2016 at Osaka Prefecture University. His research interests include metal-complex catalysts, bioactive complexes, and heteroatom-containing conjugated chemistry.

Akiya Ogawa was born in Osaka (Japan) in 1957 and received his Ph.D. from Osaka University (1985) under the supervision of Professor Noboru Sonoda. He worked as a Postdoctoral Researcher of the Japan Society for the Promotion of Science (1985–1987), an Assistant Professor at Osaka University (1987–1995, Professor Noboru Sonoda's group), an Associate Professor at Osaka University (1995–2000, Professor Toshikazu Hirao's group), and a visiting professor at the University of Pittsburgh (1996, Professor Dennis P. Curran's group). In 2000, he joined the Department of Chemistry at Nara Women's University as Full Professor. In 2004, he moved to the Department of Applied Chemistry at Osaka Prefecture University as Full Professor. His research interests include organic synthesis, heteroatom chemistry,



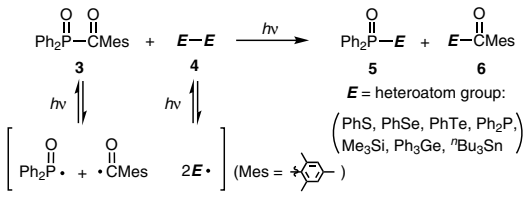
Scheme 3 Photoinduced reductive transformation of TMDPO and perfluoroalkyl iodide (R_f–I) into *P*-fluorous phosphine (Ph_2PR_f)

Despite their electron-poor nature, the synthesized *P*-fluorous phosphines can coordinate a variety of transition-metal catalysts.[16] Thus, we further investigated cross-coupling and related reactions using transition-metal catalysts bearing *P*-fluorous phosphine ligands, and examined the recyclability of the catalytic systems (Scheme 4).[17]



Scheme 4 Copper-free Sonogashira cross-coupling reaction of benzoyl chloride with 1-octyne using *P*-fluorous phosphine ($Ph_2P^nC_{10}F_{21}$) and the palladium precatalyst [$PdCl_2(PhCN)_2$]

Organic heteroatom compounds having interelement linkages (***E*–*E***), such as disulfide (S–S),[18] diselenide (Se–Se),[18] ditelluride (Te–Te),[19] diphosphine (P–P),[20] disilane (Si–Si),[21] digermane (Ge–Ge),[22] and distannane (Sn–Sn)[23] bonds, are attractive heteroatom sources because they undergo homolytic cleavage of the ***E*–*E*** bond upon photoirradiation or by radical initiators to generate the corresponding heteroatom-centered radicals. Thus, many radical addition reactions of these ***E*–*E*** compounds to unsaturated bonds have been reported.[2] These ***E*–*E*** compounds have also been used in transition-metal-catalyzed addition reactions via oxidative addition to metal catalysts.[24] Moreover, unsymmetrical ***E*–*E′*** compounds are interesting and promising substrates from a synthetic point of view. Thus, we have investigated a series of cross-coupling reactions between TMDPO and ***E*–*E*** compounds **4** under light irradiation, which would afford phosphorus-containing unsymmetrical ***E*–*E′*** compounds **5**, along with aroyl compounds **6** (Scheme 5).



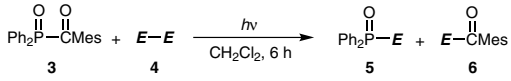
Scheme 5 Photoinduced coupling reaction between TMDPO and ***E*–*E*** compounds

In this paper, we describe the photoinduced coupling reactions between TMDPO and ***E*–*E*** compounds, especially for the synthesis of thio- and selenophosphinates.

First, we investigated the reactions of TMDPO with different ***E*–*E*** compounds containing a heteroatom–heteroatom single bond of group 13–16 elements,[25] under light irradiation (Table 1). When a mixture of TMDPO (**3**) and diphenyl disulfide (**4aa**) was irradiated with a xenon lamp through Pyrex, the photoinduced cross-coupling reaction between TMDPO and **4aa** successfully proceeded to afford *S*-phenyl diphenylthiophosphinate (**5aa**) and *S*-phenyl 2,4,6-trimethylthiobenzoate (**6aa**) in good yields (Table 1, entry 1). The reaction did not proceed at all in the dark (Table 1, entry 2). Using diphenyl diselenide (**4ba**) instead of **4aa** afforded *Se*-phenyl diphenylselenophosphinate (**5ba**) and *Se*-phenyl 2,4,6-trimethylselenobenzoate (**6ba**) in excellent yields (Table 1, entry 3). Upon irradiation of a mixture of TMDPO and diphenyl ditelluride (**4ca**), *Te*-phenyl 2,4,6-trimethyltellurobenzoate (**6ca**) was obtained in good yield. However, *Te*-phenyl diphenyltellurophosphinate (**5ca**) was not detected, most probably because of its instability under photoirradiation (Table 1, entry 4).[26] In the case of tetraphenyldiphosphine (**4da**), tetraphenyldiphosphine monoxide **5da** was obtained quantitatively, and diphenyl(2,4,6-trimethylbenzoyl)phosphine (**6da**) was generated in only 9% yield along with the formation of a complex mixture derived from the 2,4,6-trimethylbenzoyl unit (Table 1, entry 5). In contrast, hexamethyldisilane (**4ea**), hexaphenyldigermane (**4fa**), hexabutyldistannane (**4ga**), and bis(pinacolato)diboron (**4ha**)[27] did not afford the corresponding coupling products (Table 1, entries 6–9). In these reactions, large amounts of ***E*–*E*** compounds remained unreacted, and many by-products derived from the photolysis of TMDPO were generated, such as $Ph_2P(O)OP(O)Ph_2$ and $Ph_2P(O)P(O)Ph_2$.

To gain insight into the pathway of this transformation, two experiments were performed. When a mixture of TMDPO and PhSH (**7**) was stirred in the presence of the radical initiator V-70 [2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)] at 40 °C for 20 hours, thiophosphinate **5aa** was not obtained, and unreacted TMDPO was fully recovered (Scheme 6). V-70 can abstract a hydrogen atom from

Table 1 Photoinduced Reactions of TMDPO with Different ***E*–*E*** Compounds[a]

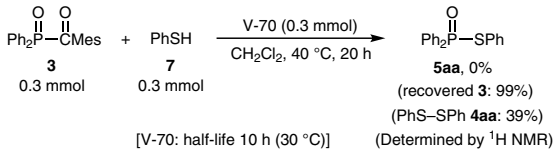


3 4 5 6

Entry	*E*–*E*	Yield[b] 5	6
1	PhS–SPh (**4aa**)	99% (95%)	84% (78%)
2[c]	PhS–SPh (**4aa**)	0%	0%
3	PhSe–SePh (**4ba**)	99% (92%)	95% (88%)
4	PhTe–TePh (**4ca**)	0%	86% (54%)
5	Ph_2P–PPh_2 (**4da**)	>99%	9%
6	Me_3Si–$SiMe_3$ (**4ea**)	0%	0%
7	Ph_3Ge–$GePh_3$ (**4fa**)	0%	0%
8	$^nBu_3Sn$–Sn^nBu_3 (**4ga**)	0%	0%
9	pinB–Bpin (**4ha**)	0%	0%

[a] Reaction conditions: TMDPO (**3**) (0.3 mmol), interelement compound **4** (0.3 mmol) and CH_2Cl_2 (0.6 mL) were added into a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp.
[b] Determined by ^{31}P and ^1H NMR spectroscopy. Yields of isolated products are shown in parentheses.
[c] The reaction was carried out in the dark.

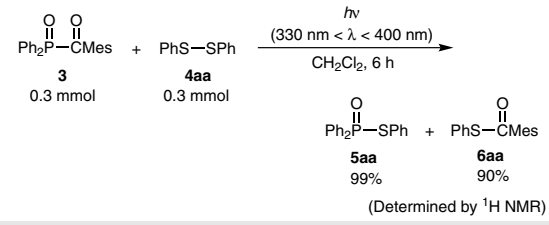
PhSH to generate a thiyl radical but it cannot cleave the C–P bond of TMDPO. As a result, PhS–SPh was obtained from homocoupling of PhS•.



Scheme 6 The reaction of TMDPO with thiol **7** in the presence of an equimolar amount of radical initiator V-70 [2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)]

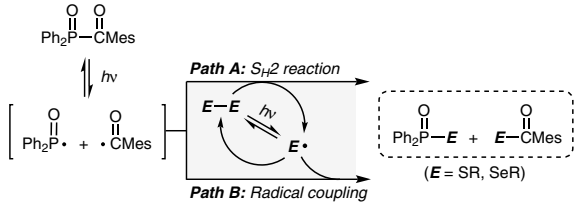
TMDPO shows an absorption maximum at λ = 380 nm,[7b] whereas PhS–SPh exhibits an absorption up to about λ = 320 nm.[18] Thus, a mixture of TMDPO and PhS–SPh was irradiated with a xenon lamp through a filter (330 nm < λ < 400 nm), and thiophosphinate **5aa** and thioester **6aa** were obtained in high yields (Scheme 7). Clearly, under these conditions, only TMDPO can undergo homolytic cleavage to give the phosphinoyl radical, which can be captured by the disulfide.

On the basis of these results, plausible pathways for the photoinduced cross-coupling reaction of TMDPO with ***E*–*E*** compounds are illustrated in Scheme 8. In the case of ***E*** = PhS, the phosphinoyl radical [$Ph_2P(O)^•$] formed from TMDPO by photoirradiation undergoes an S_H2 reaction on the sulfur atom of the disulfide to give thiophosphinate **5aa**



Scheme 7 Photoinduced reaction of TMDPO with disulfide **4aa** through a filter (330 nm < λ < 400 nm)

and a thiyl radical. The S_H2 reaction of the carbonyl radical [MesC(O)•] with the disulfide also proceeds efficiently to give thioester **6aa** (Path A). In another pathway, $Ph_2P(O)^•$ and MesC(O)• couple with the thiyl radical to afford thiophosphinate **5aa** and thioester **6aa**, respectively (Path B). Moreover, the thiyl radicals can react with each other to regenerate the disulfide. In the case of ***E*** = PhSe, the generated $Ph_2P(O)^•$ attacks the diselenide to give the corresponding selenophosphinate **5ba** as in the case of $(PhS)_2$. On the other hand, when diphenyl ditelluride is used, MesC(O)• can attack the ditelluride to give the telluroester (Path A), but the desired $Ph_2P(O)TePh$, generated from the reaction of $Ph_2P(O)^•$ with the ditelluride, is quite unstable.[28] In addition, tetraphenyldiphosphine (***E*** = Ph_2P) can be attacked by $Ph_2P(O)^•$ efficiently to give diphosphine monoxide, whereas the reaction with MesC(O)• is not efficient. In the case of ***E*** = Me_3Si, Ph_3Ge, $^nBu_3Sn$, or (pin)B, $Ph_2P(O)^•$ and MesC(O)• do not undergo the S_H2 reaction with ***E*–*E***.

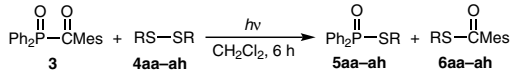


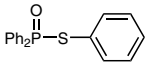
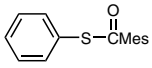
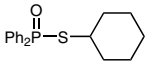
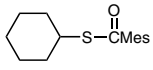
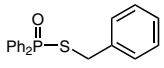
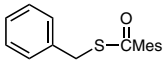
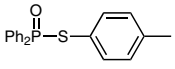
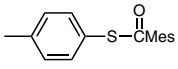
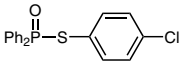
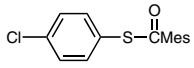
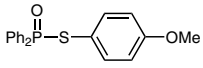
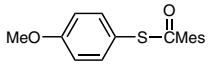
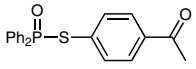
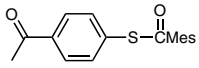
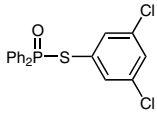
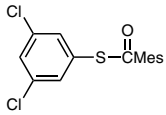
Scheme 8 Plausible pathways for the photoinduced cross-coupling reaction of TMDPO with ***E*–*E*** compounds

Our findings show that the cross-coupling reaction between TMDPO and PhS–SPh or PhSe–SePh can be useful for the synthesis of *S*- or *Se*-substituted thio- or selenophosphinates, respectively. Thiophosphinates are important building blocks used not only as synthetic intermediates, but also for the synthesis of biologically active molecules.[1,29] Thus, several synthetic methods for thiophosphinates have been reported recently,[30] and a number of synthetic routes to selenophosphinates have also been developed.[31] Nevertheless, the present reaction is considered advantageous in terms of easy operation. Next, we investigated the scope of disulfides for the synthesis of thiophosphinates using TMDPO as a phosphorus source (Table 2). As mentioned above, the cross-coupling reaction between TMDPO and di-

phenyl disulfide (**4aa**) afforded *S*-phenyl diphenylthiophosphinate (**5aa**) and *S*-phenyl 2,4,6-trimethylthiobenzoate in good yields (Table 2, entry 1). Aliphatic disulfides **4ab** and **4ac** also afforded the corresponding thiophosphinates in excellent yields along with moderate amounts of the corresponding thioesters (Table 2, entries 2 and 3). When aromatic disulfides such as bis(4-methylphenyl) disulfide (**4ad**), bis(4-chlorophenyl) disulfide (**4ae**), bis(4-methoxyphenyl) disulfide (**4af**), bis(4-acetylphenyl) disulfide (**4ag**), and bis(3,5-dichlorophenyl) disulfide (**4ah**) were employed, the corresponding *S*-aryl diphenylthiophosphinates (**5ad–af** and **5ah**) were obtained in good yields (Table 2, entries 4–6 and 8), whereas the reaction of bis(4-acetylphenyl) disulfide (**4ag**) was not efficient (Table 2, entry 7).

Table 2 Scope of Disulfides in the Photoinduced Cross-Coupling Reaction with TMDPO[a]

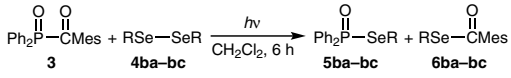


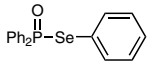
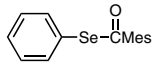
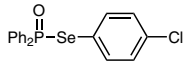
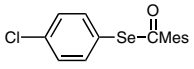
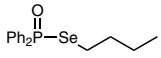
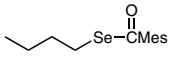
Entry	Yield[b]	
	5a	**6a**
1	 **5aa**, >99% (95%)	 **6aa**, 84% (78%)
2	 **5ab**, 99% (87%)	 **6ab**, 43%
3	 **5ac**, 98% (91%)	 **6ac**, 40%
4	 **5ad**, >99% (93%)	 **6ad**, >99% (94%)
5	 **5ae**, 98% (87%)	 **6ae**, 72% (64%)
6	 **5af**, 99% (96%)	 **6af**, 96% (87%)
7	 **5ag**, 0%	 **6ag**, 0%
8	 **5ah**, 98% (87%)	 **6ah**, 95% (87%)

[a] Reaction conditions: TMDPO (**3**) (0.3 mmol), disulfide (**4a**) (0.3 mmol), and CH_2Cl_2 (0.6 mL) were added into a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp for 6 h.
[b] Determined by ^{31}P and ^{1}H NMR spectroscopy. Yields of isolated products are shown in parentheses.

Next, we conducted the photoinduced cross-coupling reaction of TMDPO with different diselenides (Table 3). The reaction of TMDPO with aromatic bis(4-chlorophenyl) diselenide (**4bb**) successfully afforded the corresponding *Se*-(4-chlorophenyl) diphenylselenophosphinate (**5bb**) in good yield (Table 3, entry 2). Gratifyingly, the reaction of aliphatic di-*n*-butyl diselenide (**4bc**) also proceeded smoothly to give *Se*-*n*-butyl diphenylselenophosphinate (**5bc**) in excellent yield (Table 3, entry 3).

Table 3 Scope of Diselenides in the Photoinduced Cross-Coupling Reaction with TMDPO[a]

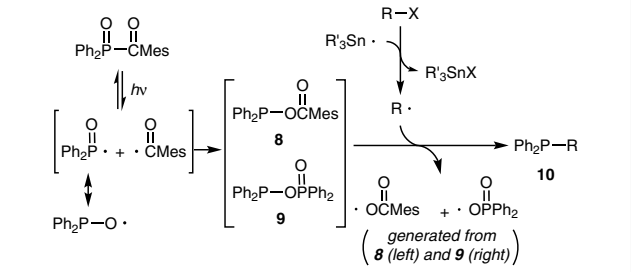


Entry	Yield[b]	
	5b	**6b**
1	 **5ba**, >99% (92%)	 **6ba**, 95% (88%)
2	 **5bb**, >99% (92%)	 **6bb**, 99% (94%)
3	 **5bc**, >99% (91%)	 **6bc**, >99% (94%)

[a] Reaction conditions: TMDPO (**3**) (0.3 mmol), diselenide (**4b**) (0.3 mmol), and CH_2Cl_2 (0.6 mL) were added into a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp for 6 h.
[b] Determined by ^{31}P and ^{1}H NMR spectroscopy. Yields of isolated products are shown in parentheses.

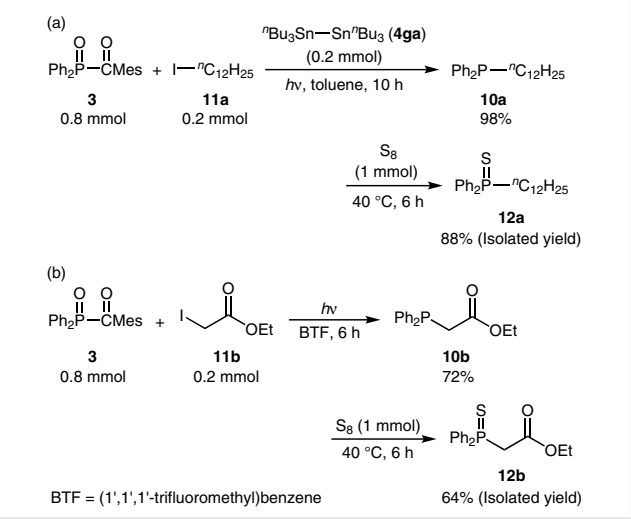
Moreover, the unsuccessful cross-coupling reaction between TMDPO and hexabutyldistannane (**4ga**) under light irradiation prompted us to investigate the possibility to use this substrate in a novel synthetic method. In particular, we envisioned that hexabutyldistannane could be used as a radical mediator of alkyl radicals in the presence of TMDPO, as summarized in Scheme 9. The formation of trivalent phosphorus species **8** and **9** in a solvent cage from TMDPO under photoirradiation was supported by the reports of

Wirz[15b] and George.[15f] The stannyl radical formed upon photoirradiation of distannane could abstract a halide atom from the alkyl halide to form an alkyl radical. Intermediates **8** and **9** could then react with the alkyl radical on the phosphorus atom to provide alkylphosphines **10**.



Scheme 9 A proposed pathway for synthesis of alkylphosphines from TMDPO, alkyl halides, and distannanes

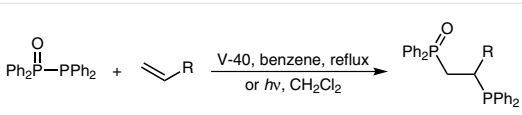
On the basis of this hypothesis, a mixture of TMDPO, hexabutyldistannane (**4ga**), and 1-iodododecane (**11a**) in toluene was irradiated with a xenon lamp through Pyrex. The ^{31}P NMR spectrum indicated the generation of dodecylphosphine **10a** (δ = –16 ppm). Treatment of the resulting mixture with sulfur gave dodecyldiphenylphosphine sulfide (**12a**) in moderate yield (Scheme 10, a). Ethyl iodoacetate (**11b**) (Scheme 10, b) also successfully provided the corresponding alkylphosphine **10b**, but in this case the alkyl radical was formed under light irradiation without the aid of a distannane.



Scheme 10 (a) Photoinduced reaction of TMDPO with alkyl iodide **11a** using distannane **4ga** as a radical mediator. (b) Synthesis of alkyl phosphine **10b** without **4ga**.

In summary, the photoinduced coupling reactions between TMDPO and a series of ***E*–*E*** compounds have been investigated in detail, and novel synthetic methods for the formation of *S*- or *Se*-substituted thio- or selenophosphinates, respectively, and diphosphine monoxide have been successfully developed. The interelement compounds served as heteroatom sources in the radical addition reaction with unsaturated compounds. For example, thio- and selenophosphination of alkynes have been reported to proceed with high selectivity under radical conditions.[32]

Moreover, we have reported the first example of the addition of tetraphenyldiphosphine monoxide to alkenes (Scheme 11).[33,34]



Scheme 11 Addition of tetraphenyldiphosphine monoxide to alkenes

In addition, after a thorough study of the characteristic features of the reaction of each interelement compound with TMDPO under light irradiation, a novel synthesis of alkylphosphines was successfully demonstrated. We believe that this study of the reactivity of TMDPO under light irradiation will be useful for the development of new reactions using TMDPO as a phosphorus source.

All reactions were carried out in a sealed Pyrex NMR tube under an argon atmosphere. TMDPO (**3**) was obtained from Tokyo Chemical Industry Co., Ltd. All diaryl disulfides and diphenyl diselenide were obtained from commercial suppliers. The other diaryl diselenides were synthesized according to literature procedures.[35] Di-*n*-butyl diselenide (**4bc**) was prepared according to the literature.[36] All solvents were distilled, dried, and degassed with argon before use. All products were isolated by a JAIGEL-HH (GPC) column (2HH; 20 x 600 mm, Japan Analytical Industry Co., Ltd.) with a recycling preparative HPLC system (LC-908; Japan Analytical Industry Co., Ltd.). All melting points were determined on a Yanagimoto micro melting point apparatus. IR spectra were recorded on a Perkin Elmer Model 1600 spectrometer. NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) or a JEOL JNM-ECX400 (400 MHz) FT NMR system. ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were measured at 100 MHz in $CDCl_3$. ^{31}P NMR spectra were recorded at 162 MHz in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. ^{77}Se NMR spectra were recorded at 75 MHz $CDCl_3$ with Me_2Se as an external standard. ^{123}Te NMR spectra were measured at 104 MHz in $CDCl_3$ with Me_2Te as an external standard. High-resolution mass spectra were obtained on a JEOL-JMS-DX303 spectrometer at Kyoto-Nara Advanced Nanotechnology Network or on an Agilent-6624-TOF-LC/MS spectrometer at Saga University.

Photoinduced Reaction between TMDPO and Interelement Compounds 4; General Procedure

TMDPO (**3**) (104.5 mg, 0.3 mmol), interelement compound **4** (0.3 mmol), and dry, degassed CH_2Cl_2 (0.6 mL) were placed in a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp (500 W) for 6 h at r.t. The reaction mixture

was then concentrated under reduced pressure, and the nature of the product was determined by ^{1}H, ^{31}P, and appropriate multinuclear NMR analysis.

Chalcogenophosphinates 5 and Chalcogenocarboxylates 6; General Procedure

TMDPO (**3**) (104.5 mg, 0.3 mmol), dichalcogenide **4** (0.3 mmol), and dry, degassed CH_2Cl_2 (0.6 mL) were placed in a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp (500 W) for 6 h at r.t. The reaction mixture was then concentrated under reduced pressure, and the crude mixture was purified by gel permeation chromatography (eluent: $CHCl_3$) to give the desired products.

***S*-Phenyl Diphenylthiophosphinate (5aa)**[30e]

[CAS Registry No. 5510-78-1]

Yield: 88.5 mg (95%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (ddd, J_{H-H} = 12.8 Hz, 1.4 Hz, J_{H-P} = 6.9 Hz, 4 H), 7.26–7.15 (m, 3 H), 7.52–7.38 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.3 (d, J_{C-P} = 3.8 Hz), 132.5 (d, J_{C-P} = 107.4 Hz), 132.2 (d, J_{C-P} = 2.9 Hz), 131.5 (d, J_{C-P} = 10.5 Hz), 129.0, 128.8, 128.4 (d, J_{C-P} = 13.4 Hz), 126.1 (d, J_{C-P} = 4.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.0.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}OPS$: 311.0654; found: 311.0656.

***S*-Cyclohexyl Diphenylthiophosphinate (5ab)**[30f]

[CAS Registry No. 157949-54-7]

Yield: 82.6 mg (87%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.82 (m, 4 H), 7.54–7.41 (m, 6 H), 3.38–3.24 (m, 1 H), 2.00–1.89 (m, 2 H), 1.72–1.60 (m, 2 H), 1.58–1.43 (m, 3 H), 1.33–1.18 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.1 (d, J_{C-P}= 109.3 Hz), 131.9, 131.3 (d, J_{C-P}= 10.5 Hz), 128.4 (d, J_{C-P}= 13.4 Hz), 44.3, 35.4, 25.6, 25.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.5.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{22}OPS$: 317.1123; found: 317.1104.

***S*-Benzyl Diphenylthiophosphinate (5ac)**[30f]

[CAS Registry No. 3096-05-7]

Yield: 88.6 mg (91%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (ddd, J_{H-H} = 13.3 Hz, 1.4 Hz, J_{H-P} = 6.9 Hz, 4 H), 7.55–7.49 (m, 2 H), 7.48–7.42 (m, 4 H), 7.22–7.15 (m, 5 H), 4.02 (d, J_{H-H} = 9.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8 (d, J_{C-P} = 5.8 Hz), 133.0 (d, J_{C-P} = 106.4 Hz), 132.2 (d, J_{C-P} = 2.9 Hz), 131.5 (d, J_{C-P} = 10.5 Hz), 129.0, 128.6 (d, J_{C-P} = 13.4 Hz), 128.5, 127.4, 33.1 (d, J_{C-P} = 1.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 43.4.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}OPS$: 325.0810; found: 325.0805.

***S*-(4-Methylphenyl) Diphenylthiophosphinate (5ad)**[37]

[CAS Registry No. 5510-81-6]

Yield: 91.4 mg (94%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (ddd, J_{H-H} = 12.8 Hz, 1.4 Hz, J_{H-P} = 6.9 Hz, 4 H), 7.49 (dt, J_{H-H} = 7.3 Hz, 1.8 Hz, 2 H), 7.46–7.39 (m, 4 H), 7.32 (dd, J_{H-H} = 8.2 Hz, J_{H-P} = 1.8 Hz, 2 H), 7.00 (d, J_{H-H} = 8.2 Hz, 2 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 135.3 (d, J_{C-P} = 3.8 Hz), 132.6 (d, J_{C-P} = 106.4 Hz), 132.1 (d, J_{C-P} = 2.9 Hz), 131.5 (d, J_{C-P} = 9.6 Hz), 129.9, 128.4 (d, J_{C-P} = 13.4 Hz), 122.2 (d, J_{C-P} = 4.8 Hz), 21.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.8.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}OPS$: 325.0810; found: 325.0830.

***S*-(4-Chlorophenyl) Diphenylthiophosphinate (5ae)**[37]

[CAS Registry No. 21081-94-7]

Yield: 88.6 mg (87%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.78 (m, 4 H), 7.54–7.34 (m, 8 H), 7.16 (d, J_{H-H} = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4 (d, J_{C-P} = 3.9 Hz), 135.4, 132.4 (d, J_{C-P} = 2.9 Hz), 132.2 (d, J_{C-P} = 107.4 Hz), 131.5 (d, J_{C-P} = 10.5 Hz), 129.2, 128.5 (d, J_{C-P} = 12.5 Hz), 124.7 (d, J_{C-P} = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.0.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}ClOPS$: 345.0264; found: 345.0261.

***S*-(4-Methoxyphenyl) Diphenylthiophosphinate (5af)**[37]

[CAS Registry No. 99234-85-2]

Yield: 98.0 mg (96%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (dd, J_{H-H} = 11.8 Hz, J_{H-P} = 7.8 Hz, 4 H), 7.53–7.39 (m, 6 H), 7.33 (d, J_{H-H} = 8.2 Hz, 2 H), 6.72 (d, J_{H-H} = 8.2 Hz, 2 H), 3.71 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (*ipso*-carbon of diphenylphosphine oxide overlapped with the *ortho*-carbon of the thiophenyl ring), 136.9, 132.1, 131.5 (d, J_{C-P} = 9.5 Hz), 128.4 (d, J_{C-P} = 12.4 Hz), 115.9, 114.7, 55.2.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.9.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}O_2PS$: 341.0760; found: 341.0760.

***S*-(3,5-Dichlorophenyl) Diphenylthiophosphinate (5ah)**

Yield: 99.0 mg (87%); white solid; mp 121–122 °C.

IR (KBr): 3051, 2360, 1558, 1436, 1201, 1112, 1101, 850, 724, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (ddd, J_{H-H} = 12.4 Hz, 1.4 Hz, J_{H-P} = 8.2 Hz, 4 H), 7.56 (dt, J_{H-H} = 7.3 Hz, 1.4 Hz, 2 H), 7.52–7.45 (m, 4 H), 7.33 (dd, J_{H-H} = 1.8 Hz, 1.8 Hz, 2 H), 7.25–7.23 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.0 (d, J_{C-P} = 1.9 Hz), 133.0 (d, J_{C-P} = 3.8 Hz), 132.7 (d, J_{C-P} = 2.9 Hz), 131.7 (d, J_{C-P} = 108.3 Hz), 131.6 (d, J_{C-P} = 10.5 Hz), 129.6 (d, J_{C-P} = 5.8 Hz), 129.2, 128.7 (d, J_{C-P} = 13.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.4.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{13}Cl_2OPS$: 378.9875; found: 378.9875.

***Se*-Phenyl Diphenylselenophosphinate (5ba)**[31b]

[CAS Registry No. 2049-62-9]

Yield: 98.6 mg (92%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, J_{H-H} = 13.1 Hz, J_{H-P} = 7.7 Hz, 4 H), 7.53–7.47 (m, 4 H), 7.46–7.39 (m, 4 H), 7.24 (t, J_{H-H} = 7.3 Hz, 1 H), 7.16 (t, J_{H-H} = 7.7 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.5 (d, J_{C-P} = 97.3 Hz), 132.2 (d, J_{C-P} = 2.9 Hz), 131.3 (d, J_{C-P} = 10.5 Hz), 129.2, 128.7, 128.5 (d, J_{C-P} = 13.4 Hz), 123.8 (d, J_{C-P} = 4.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.4 (d, J_{P-Se} = 382.5 Hz).

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 381.3 (d, J_{Se-P} = 381.5 Hz).

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{16}OPSe$: 359.0098; found: 359.0105.

Se-(4-Chlorophenyl) Diphenylselenophosphinate (5bb)

Yield: 108.1 mg (92%); white solid; mp 85–86 °C.

IR (KBr): 3056, 2360, 1437, 1198, 1114, 1089, 815, 747, 723 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.77 (m, 4 H), 7.54–7.48 (m, 2 H), 7.47–7.38 (m, 6 H), 7.13 (d, J_{H-H} = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2 (d, J_{C-P} = 2.9 Hz), 135.1 (d, J_{C-P} = 1.9 Hz),, 132.9 (d, J_{C-P} = 97.8 Hz), 132.2 (d, J_{C-P} = 2.9 Hz), 131.0 (d, J_{C-P} = 10.5 Hz), 129.2, 128.4 (d, J_{C-P} = 13.4 Hz), 121.7 (d, J_{C-P} = 5.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.6 (d, J_{P-Se} = 377.1 Hz).

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 377.8 (d, J_{Se-P} = 372.7 Hz).

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}ClOPSe$: 392.9709; found: 392.9723.

Se-*n*-Butyl Diphenylselenophosphinate (5bc)[31a]

[CAS Registry No. 882000-56-8]

Yield: 92.1 mg (91%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dddd, J_{H-H} = 13.1 Hz, 1.8 Hz, 1.4 Hz, J_{H-P} = 6.8 Hz, 4 H), 7.54–7.44 (m, 6 H), 2.83 (dt, J_{H-H} = 7.3 Hz, J_{H-P} = 9.5 Hz, 2 H), 1.64 (quin, J_{H-H} = 7.3 Hz, 2 H), 1.31 (sext, J_{H-H} = 7.3 Hz, 2 H), 0.81 (t, J_{H-H} = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4 (d, J_{C-P} = 97.3 Hz), 132.1 (d, J_{C-P} = 2.9 Hz), 131.1 (d, J_{C-P} = 10.5 Hz), 128.5 (d, J_{C-P} = 13.4 Hz), 32.7 (d, J_{C-P} = 3.8 Hz), 25.1 (d, J_{C-P} = 2.9 Hz), 22.7, 13.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.2 (d, J_{P-Se} = 391.1 Hz).

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 215.8 (d, J_{Se-P} = 393.0 Hz).

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{20}OPSe$: 339.0411; found: 339.0416.

S-Phenyl 2,4,6-Trimethylthiobenzoate (6aa)[38]

[CAS Registry No. 50404-53-0]

Yield: 60.0 mg (78%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.49 (m, 2 H), 7.48–7.39 (m, 3 H), 6.86 (s, 2 H), 2.38 (s, 6 H), 2.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 139.5, 137.2, 134.3, 133.7, 129.5, 129.3, 128.4, 128.0, 21.1, 19.0.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}OS$: 257.0995; found: 257.1008.

S-(4-Methylphenyl) 2,4,6-Trimethylthiobenzoate (6ad)

Yield: 55.8 mg (94%); white solid; mp 67–68 °C.

IR (KBr): 2918, 2359, 1690, 1450, 1202, 1141, 1017, 870, 842, 810 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J_{H-H} = 7.8 Hz, 2 H), 7.26 (d, J_{H-H} = 7.8 Hz, 2 H), 6.86 (s, 2 H), 2.39 (s, 3 H), 2.37 (s, 6 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 139.8, 139.4, 137.3, 134.3, 133.7, 130.1, 128.4, 124.4, 21.3, 21.1, 19.0.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{18}OS$: 271.1151; found: 271.1150.

S-(4-Chlorophenyl) 2,4,6-Trimethylthiobenzoate (6ae)

Yield: 55.8 mg (64%); colorless oil.

IR (NaCl): 2920, 1681, 1476, 1206, 1094, 1014, 869, 848, 818 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J_{H-H} = 8.7 Hz, 2 H), 7.42 (d, J_{H-H} = 8.7 Hz, 2 H), 6.87 (s, 2 H), 2.36 (s, 6 H), 2.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.4, 139.7, 136.9, 135.9, 135.5, 133.7, 129.5, 128.4, 126.5, 21.1, 19.0.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}ClOS$: 290.0532; found: 290.0532.

S-(4-Methoxyphenyl) 2,4,6-Trimethylthiobenzoate (6af)

Yield: 55.8 mg (87%); white solid; mp 68–69 °C.

IR (KBr): 2937, 1684, 1492, 1251, 1175, 1031, 874, 855, 827 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J_{H-H} = 8.6 Hz, 2 H), 6.97 (d, J_{H-H} = 8.6 Hz, 2 H), 6.85 (s, 2 H), 3.81 (s, 3 H), 2.37 (s, 6 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.0, 160.7, 139.4, 137.2, 135.9, 133.6, 128.3, 118.6, 114.9, 55.3, 21.1, 19.0.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}O_2S$: 287.1100; found: 287.1101.

S-(3,5-Dichlorophenyl) 2,4,6-Trimethylthiobenzoate (6ah)

Yield: 84.9 mg (87%); white solid; mp 111–112 °C.

IR (KBr): 1693, 1558, 1404, 1203, 1143, 862, 841, 796 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 3 H), 6.88 (s, 2 H), 2.36 (s, 6 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.2, 140.1, 136.5, 135.4, 133.8, 132.2, 131.1, 129.7, 128.5, 21.2, 19.1.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}Cl_2OS$: 325.0215; found: 325.0215.

Se-Phenyl 2,4,6-Trimethylselenobenzoate (6ba)

Yield: 80.0 mg (88%); colorless oil.

IR (NaCl): 2918, 1716, 1438, 1203, 1141, 1022, 833, 740, 726 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.55 (m, 2 H), 7.42–7.36 (m, 3 H), 6.83 (s, 2 H), 2.37 (s, 6 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.0, 140.0, 138.9, 135.6, 132.7, 129.4, 128.9, 128.5, 127.1, 21.1, 19.0.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 693.9.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}OSe$: 305.0439; found: 305.0447.

Se-(4-Chlorophenyl) 2,4,6-Trimethylselenobenzoate (6bb)

Yield: 95.2 mg (94%); colorless oil.

IR (NaCl): 2920, 1716, 1474, 1203, 1140, 1089, 1012, 833, 812 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J_{H-H} = 8.7 Hz, 2 H), 7.35 (d, J_{H-H} = 8.7 Hz, 2 H), 6.83 (s, 2 H), 2.35 (s, 6 H), 2.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 139.7, 138.6, 136.8, 135.3, 132.6, 129.6, 128.5, 125.2, 21.1, 18.9.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 689.1.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}ClOSe$: 339.0049; found: 339.0035.

Se-*n*-Butyl 2,4,6-Trimethylselenobenzoate (6bc)

Yield: 79.9 mg (94%); colorless oil.

IR (NaCl): 2958, 2929, 2860, 1674, 1461, 1204, 1143, 859, 843 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 2 H), 3.07 (t, J_{H-H} = 7.3 Hz, 2 H), 2.29 (s, 6 H), 2.27 (s, 3 H), 1.75 (quin, J_{H-H} = 7.3 Hz, 2 H), 1.44 (sext, J_{H-H} = 7.3 Hz, 2 H), 0.95 (t, J_{H-H} = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.6, 139.9, 139.1, 132.5, 128.4, 32.6, 26.1, 23.1, 21.1, 18.9, 13.6.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 587.0.

HRMS (FAB+): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{21}OSe$: 285.0752; found: 285.0746.

Te-Phenyl 2,4,6-Trimethyltellurobenzoate (6ca)

Following gel permeation chromatography (eluent: $CHCl_3$) the product was extracted with *n*-hexane.

Telluroester **6ca** was decomposed by the EtOH contained in $CHCl_3$ and was obtained in 81 wt% purity [including ethyl 2,4,6-trimethylbenzoate (12 wt%) and diphenyl ditelluride (**4ca**) (6 wt%)].

Yield: 54.6 mg (54%); reddish-yellow oil.

IR (NaCl): 2917, 1696, 1434, 1198, 1136, 1017, 812, 733, 720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, J_{H-H} = 8.2 Hz, 1.4 Hz, 2 H), 7.38–7.32 (m, 1 H), 7.31–7.26 (m, 2 H), 6.76 (s, 2 H), 2.33 (s, 6 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.1, 143.0, 140.7, 139.6, 139.4, 130.9, 129.5, 128.6, 115.4, 21.1, 18.8.

^{123}Te NMR (104 MHz, $CDCl_3$): δ = 1041.

Alkyldiphenylphosphine Sulfides 12

TMDPO (**3**) (278.7 mg, 0.8 mmol), alkyl iodide **11** (0.2 mmol), 1,1,1,2,2,2-hexabutyldistannane (**4ga**) (0.2 mmol, only for Scheme 10 a), and dry, degassed toluene (0.6 mL, Scheme 10 a) or BTF [(1′,1′,1′-trifluoromethyl)benzene] (0.6 mL, Scheme 10 b] were placed in a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp (500 W) for 6 h at r.t. Elemental sulfur (S_8) (1 mmol) was added under an inert atmosphere, and the mixture was stirred for 6 h at 40 °C. The reaction mixture was concentrated, and product **12** was isolated by gel permeation chromatography.

Dodecyldiphenylphosphine Sulfide (12a)

Yield: 68.0 mg (88%); colorless oil.

IR (NaCl): 2925, 2853, 1437, 1104, 755, 710, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (ddd, J_{H-H} = 12.4 Hz, 0.9 Hz, J_{H-P} = 7.3 Hz, 4 H), 7.50–7.39 (m, 6 H), 2.49–2.39 (m, 2 H), 1.68–1.56 (m, 2 H), 1.42–1.33 (m, 2 H), 1.32–1.16 (m, 16 H), 0.87 (t, J_{H-H} = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.9 (d, J_{C-P} = 79.6 Hz), 131.2 (d, J_{C-P} = 2.9 Hz), 130.9 (d, J_{C-P} = 9.6 Hz), 128.4 (d, J_{C-P} = 11.5 Hz), 32.4 (d, J_{C-P} = 56.6 Hz), 31.7, 30.5 (d, J_{C-P} = 16.3 Hz), 29.44 (two overlapping carbons of the alkyl chain), 29.38, 29.23, 29.16, 29.0, 22.5, 22.0, 14.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 43.3.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{35}NaPS$: 409.2095; found: 409.2097.

Ethyl 2-(Diphenylthiophosphinyl)acetate (12b)

Yield: 39.0 mg (64%); colorless oil.

IR (NaCl): 2981, 2928, 1731, 1437, 1263, 1115, 1103, 708, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (ddd, J_{H-H} = 13.6 Hz, 1.8 Hz, J_{H-P} = 6.8 Hz, 4 H), 7.56–7.44 (m, 6 H), 4.02 (q, J_{H-H} = 7.3 Hz, 2 H), 3.65 (d, J_{H-P} = 14.5 Hz, 2 H), 1.10 (t, J_{H-H} = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7 (d, J_{C-P}= 5.8 Hz), 132.0 (d, J_{C-P}= 84.4 Hz), 131.8 (d, J_{C-P}= 2.9 Hz), 131.3 (d, J_{C-P}= 10.5 Hz), 128.5 (d, J_{C-P}= 12.5 Hz), 61.5, 42.4 (d, J_{C-P}= 47.9 Hz), 13.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 38.4.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{17}NaO_2PS$: 327.0585; found: 327.0583.

Funding Information

This research was supported by a Grant-in-Aid for Exploratory Research (26620149, A.O., 26860168, S.K.) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Acknowledgment

We thank Dr. Yuta Kimura for the measurement of high-resolution mass spectra.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588867.

References

(1) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley Interscience: New York, **2000**.
(2) (a) Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Sekiguchi, M.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1990**, *31*, 5931. (b) Ogawa, A.; Yokoyama, K.; Yokoyama, H.; Obayashi, R.; Kambe, N.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1748. (c) Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 111. (d) Ogawa, A.; Obayashi, R.; Doi, M.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 4277. (e) Ogawa, A.; Obayashi, R.; Ine, H.; Tsuboi, Y.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 881. (f) Tsuchii, K.; Tsuboi, Y.; Kawaguchi, S.-i.; Takahashi, J.; Sonoda, N.; Nomoto, A.; Ogawa, A. *J. Org. Chem.* **2007**, *72*, 415.
(3) Kawaguchi, S.-i.; Nagata, S.; Shirai, T.; Tsuchii, K.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2006**, *47*, 3919.
(4) Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1694.
(5) (a) Lechtken, P.; Buethe, I.; Hesse, A. US4324744, **1982**. (b) Lechtken, P.; Buethe, I.; Jacobi, M.; Trimborn, W. US4710523, **1987**.
(6) The absorption maximum of TMDPO is 380 nm (S_0 to S_1) and 295 nm (S_0 to S_2). The quantum yield of radical formation is Φ 0.5 to 0.7.
(7) (a) Sumiyoshi, T.; Katayama, M.; Schnabel, W. *Chem. Lett.* **1985**, *14*, 1647. (b) Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P. *Polymer* **1985**, *26*, 141.

(8) (a) Decker, C.; Bendaikha, T. *J. Appl. Polym. Sci.* **1998**, *70*, 2269. (b) Decker, C.; Zahouily, K.; Decker, D.; Nguyen, T.; Viet, T. *Polymer* **2001**, *42*, 7551.
(9) (a) Ikemura, K.; Ichizawa, K.; Yoshida, M.; Ito, S.; Endo, T. *Dent. Mater. J.* **2008**, *27*, 765. (b) Ikemura, K.; Ichizawa, K.; Jogetsu, Y.; Endo, T. *Dent. Mater. J.* **2010**, *29*, 122. (c) Ikemura, K.; Kadoma, Y.; Endo, T. *Dent. Mater. J.* **2011**, *30*, 769. (d) Miletic, V.; Santini, A. *Dent. Mater. J.* **2012**, *31*, 717.
(10) (a) Radke, A.; Gissibl, T.; Klotzbücher, T.; Braun, P. V.; Giessen, H. *Adv. Mater.* **2011**, *23*, 3018. (b) Vasilantonakis, N.; Terzaki, K.; Sakellari, I.; Purlys, V.; Gray, D.; Soukoulis, C. M.; Vamvakaki, M.; Kafesaki, M.; Farsari, M. *Adv. Mater.* **2012**, *24*, 1101.
(11) Tian, Y.; Zhang, Y.-L.; Ku, J.-F.; He, Y.; Xu, B.-B.; Chen, Q.-D.; Xia, H.; Sun, H.-B. *Lab Chip* **2010**, *10*, 2902.
(12) Gansel, J. K.; Thiel, M.; Rill, M. S.; Decker, M.; Bade, K.; Saile, V.; von Freymann, G.; Linden, S.; Wegener, M. *Science* **2009**, *325*, 1513.
(13) (a) Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 1456. (b) Frey, G.; Lesiecki, H.; Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 763. (c) Lesiecki, H.; Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 793. (d) Lindner, E.; Kern, H. *Chem. Ber.* **1984**, *117*, 355. (e) Cho, C. H.; Kim, S.; Yamane, M.; Miyauchi, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1665. (f) Said, N.; Touil, S.; Akacha, A. B.; Efrit, M. L. *Phosphorus, Sulfur Silicon Relat. Elem.* **2008**, *183*, 2726.
(14) Sato, Y.; Kawaguchi, S.-i.; Ogawa, A. *Chem. Commun.* **2015**, *51*, 10385.
(15) (a) Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148. (b) Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. *J. Am. Chem. Soc.* **1996**, *118*, 6477. (c) Sluggett, G. W.; McGarry, P. F.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 7367. (d) Jockusch, S.; Koptyug, I. V.; McGarry, P. F.; Sluggett, G. W.; Turro, N. J.; Watkins, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11495. (e) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 11773. (f) Colley, C. S.; Grills, D. C.; Besley, N. A.; Jockusch, S.; Matousek, P.; Parker, A. W.; Towrie, M.; Turro, N. J.; Gill, P. M. W.; George, M. W. *J. Am. Chem. Soc.* **2002**, *124*, 14952.
(16) (a) Kawaguchi, S.-i.; Saga, Y.; Sato, Y.; Minamida, Y.; Nomoto, A.; Ogawa, A. *Inorganics* **2017**, *5*, 5. (b) Kawaguchi, S.-i.; Minamida, Y.; Ohe, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 1748.
(17) Kawaguchi, S.-i.; Minamida, Y.; Okuda, T.; Sato, Y.; Saeki, T.; Yoshimura, A.; Nomoto, A.; Ogawa, A. *Adv. Synth. Catal.* **2015**, *357*, 2509.
(18) Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405.
(19) Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L.-B.; Kambe, N.; Sonoda, N. *Tetrahedron* **1993**, *49*, 1177.
(20) Troy, D.; Turpin, R.; Voigt, D. *Bull. Soc. Chim. Fr. I-Phys.* **1979**, 241.
(21) Craw, M. T.; Alberti, A.; Depew, M. C.; Wan, J. K. S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3675.
(22) Saiful, I. S. M.; Ohba, Y.; Mochida, K.; Yamauchi, S. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1011.
(23) Chambers, R. D. C.; Clark, H. C.; Willis, C. J. *Chem. Ind. (London)* **1960**, 76.
(24) (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (b) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796. (c) Ogawa, A.; Kuniyasu, H.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1997**, *62*, 8361. (d) Kamiya, I.; Nishinaka, E.; Ogawa, A. *Tetrahedron Lett.* **2005**, *46*, 3649. (e) Kodama, S.; Nishinaka, E.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Tetrahedron Lett.* **2007**, *48*, 6312. (f) Higashimae, S.; Tamai, T.; Nomoto, A.; Ogawa, A. *J. Org. Chem.* **2015**, *80*, 7126.
(25) ***E*–*E*** compounds containing the most commonly used elements were selected for the photoinduced reaction.
(26) The bond-dissociation energy (BDE) of the P–Te single bond (297.9 ± 10.0 kJ mol^{-1}) is much weaker than that of P–S (442.0 ± 10.0 kJ mol^{-1}) and P–Se (363.7 ± 10.0 kJ mol^{-1}), as referred to in: Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, **2007**.
(27) (a) Yoshimura, A.; Takamachi, Y.; Han, L.-B.; Ogawa, A. *Chem. Eur. J.* **2015**, *21*, 13930. (b) Yoshimura, A.; Takamachi, Y.; Mihara, K.; Saeki, T.; Kawaguchi, S.-i.; Han, L.-B.; Nomoto, A.; Ogawa, A. *Tetrahedron* **2016**, *72*, 7832.
(28) To date, $R^1R^2P(O)TeR^3$ species have not been reported.
(29) Loranger, M. W.; Beaton, S. A.; Lines, K. L.; Jakeman, D. L. *Carbohydr. Res.* **2013**, *379*, 43.
(30) (a) Grayson, M.; Farley, C. E.; Streuli, C. A. *Tetrahedron* **1967**, *23*, 1065. (b) Arisawa, M.; Ono, T.; Yamaguchi, M. *Tetrahedron Lett.* **2005**, *46*, 5669. (c) Wang, J.; Huang, X.; Ni, Z.; Wang, S.; Wu, J.; Pan, Y. *Green Chem.* **2015**, *17*, 314. (d) Li, S.; Chen, T.; Saga, Y.; Han, L.-B. *RSC Adv.* **2015**, *5*, 71544. (e) Zhang, L.; Zhang, P.; Li, X.; Xu, J.; Tang, G.; Zhao, Y. *J. Org. Chem.* **2016**, *81*, 5588. (f) Renard, P.-Y.; Schwebel, H.; Vayron, P.; Josien, L.; Valleix, A.; Mioskowski, C. *Chem. Eur. J.* **2002**, *8*, 2910.
(31) (a) Kimura, T.; Murai, T.; Mizuhata, N. *Heteroat. Chem.* **2005**, *16*, 185. (b) Kawaguchi, S.-i.; Kotani, M.; Atobe, S.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Organometallics* **2011**, *30*, 6766. (c) Kobiki, Y.; Kawaguchi, S.-i.; Ogawa, A. *Tetrahedron Lett.* **2013**, *54*, 5453.
(32) (a) Wada, T.; Kondoh, A.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 1155. (b) Shirai, T.; Kawaguchi, S.-i.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2008**, *49*, 4043. (c) Kawaguchi, S.-i.; Shirai, T.; Ohe, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. *J. Org. Chem.* **2009**, *74*, 1751.
(33) Sato, Y.; Kawaguchi, S.-i.; Nomoto, A.; Ogawa, A. *Angew. Chem. Int. Ed.* **2016**, *55*, 9700.
(34) Very recently, copper/*N*-heterocyclic carbene catalyzed vicinal diphosphination of styrenes with (trimethylsilyl)phosphine was reported, see: Okugawa, Y.; Hirano, K.; Miura, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 13558.
(35) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(36) Krief, A.; Van Wemmel, T.; Redon, M.; Dumont, W.; Delmotte, C. *Angew. Chem. Int. Ed.* **1999**, *38*, 2245.
(37) Wang, D.; Zhao, J.; Xu, W.; Shao, C.; Shi, Z.; Li, L.; Zhang, X. *Org. Biomol. Chem.* **2017**, *15*, 545.
(38) Imamoto, T.; Kodera, M.; Yokoyama, M. *Synthesis* **1982**, 134.