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Reactions of selenothioic acid *S*-esters with trivalent phosphorus compounds: new synthetic methods for α-phosphoryl alkyl sulfides and alkyl selenides

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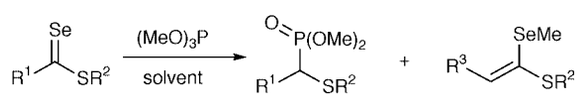
The reaction of selenothioic acid *S*-esters **1** with trialkyl phosphites proceeds smoothly with the extrusion of selenium atoms to afford α-phosphoryl sulfides **2** in good to high yields. A similar reaction takes place more easily with dimethyl phenylphosphonite and methyl diphenylphosphinite, although the ketene selenothioacetals **3** are also formed as by-products in increased yields. The use of diselenoic acid esters **1f** and **1g** gives α-phosphoryl selenides **2m** and **2n**. The products exhibit characteristic chemical shifts and coupling constants in their ^{31}P NMR spectra. The structure of α-phosphoryl selenide **2n** is confirmed by X-ray molecular structure analysis. The reaction with triphenylphosphine leads to oxidative dimerization of ester **1d** to give divinyl diselenide **4** in good yield. A catalytic amount of triphenylphosphine is also effective to form divinyl diselenide **4**. The reaction may begin with the nucleophilic attack of triphenylphosphine on the carbon atom of the selenocarbonyl group of ester **1d**. Details of the reaction pathway leading to α-phosphoryl sulfides **2** are also discussed. The reaction with menthyl diphenylphosphinite **12** has suggested that the reaction may proceed *via* initial nucleophilic attack of trivalent phosphorus compounds bearing alkoxy groups on the selenium atom of esters **1**. The intermediacy of phosphonium ylide **14** has also been supported by the reaction of the ester **1h** which gives 1,4-oxathiane **15**.

Introduction

It is of current interest to study the syntheses and reactions of selenocarbonyl compounds.[1] Much attention has been paid to the higher reactivity of the selenocarbonyl group compared to the reactivity of ordinary carbonyl and thiocarbonyl compounds. The patterns of the reactions of selenocarbonyl compounds are moderately affected by the substituents attached to the carbon atom of the selenocarbonyl group. For example, the reaction of triseleno- and dithioselenocarbonates with trialkyl phosphites has been used as a synthetic method for fulvalene derivatives.[2] The treatment of selenoic acid *O*-alkyl esters (RC(Se)OR′) with triethylphosphine has also been reported to generate purple intermediates which were converted to ordinary esters by reaction with oxygen.[3] Very recently, convenient methods for the synthesis of selenothioic acid *S*-esters (RC(Se)SR′)[4] and diselenoic acid esters (RC(Se)SeR′)[5] **1** have been



1a: R^1 = Me, R^2 = Bu **2a**: R^1 = Me, R^2 = Bu **3a**: R^2 = Bu, R^3 = H

Scheme 1

established. During the course of our studies on the reactivity of esters **1** we found that treatment of esters **1** with trialkyl phosphites provided a new synthetic method for α-phosphoryl sulfides.[6] α-Phosphoryl and α-phosphinoyl alkyl sulfides play an important role in organic chemistry.[7,8] They have been used as key intermediates of syntheses of olefins involving Wittig-type reactions.[9] They have also been employed as precursors of phosphorylalkyl radicals.[10] In this paper, we report in detail on the reactions of esters **1** and trivalent phosphorus compounds and their reaction pathways.

Results and discussion

The reaction of selenothioic acid *S*-butyl ester **1a** with trimethyl phosphite was carried out (Scheme 1). The results are summarised in Table 1. The use of MeOH, CH_3CN, toluene and hexane as a solvent gave α-phosphoryl sulfide **2a** and ketene selenothioacetal **3a** as the products. In the reaction with 1 equiv. of trimethyl phosphite in toluene, the ratio of **3a** increased along with the recovery of starting ester **1a** (entry 4), whereas in other cases the ratio of products **2a** and **3a** was about 2:1. The reaction of ester **1a** with trimethyl phosphite for 10 min at 85 °C in toluene afforded the products **2a** and **3a** in 57% and 31% isolated yields, respectively, along with 31% of trimethyl selenophosphate (entry 5). These results are in marked contrast to the reaction of dithioic acid esters with trimethyl phosphite where the condensation reaction of the esters took place and α,β-unsaturated dithioic acid esters were obtained only in low yields after 8 h.[11]

Second, the reactions with other trialkyl phosphites, dimethyl phenylphosphonite [$PhP(OMe)_2$], methyl diphenylphosphinite [Ph_2POMe] and triphenylphosphine [PPh_3] were carried out (Table 2). The use of triethyl phosphite and triisopropyl phosphite gave products **2** along with ketene selenothioacetals **3** (entries 1 and 2) under identical reaction conditions to the reaction with trimethyl phosphite (Table 1, entry 6). However, the reaction with triphenyl phosphite [$(PhO)_3P$] did not proceed, and the starting ester **1a** was recovered. The reaction of ester **1a** with $PhP(OMe)_2$, Ph_2POMe and PPh_3 was complete within 30 min. When one or two alkoxy groups were attached to the phosphorus atom, a similar transformation proceeded to afford α-phosphoryl and α-phosphinoyl sulfides (entries 3–5). On the contrary, the use of PPh_3 gave a complex mixture. In the reaction with $PhP(OMe)_2$ two diastereomers were formed in a nearly equal ratio (entry 3). To improve the diastereoselectivity of product **2d**, MeOH, Et_2O, CH_3CN, hexane and THF were

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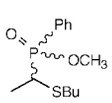
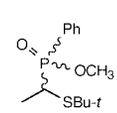
Table 1 Reactions of selenothioic acid *S*-butyl ester **1a** with trimethyl phosphite[a]

Entry	Solvent	$(MeO)_3P$ (equiv.)	Temp./°C	Time	Yield (%)[b,c] **2a**	**3a**
1	MeOH	3	rt	6 h	71	29
2	CH_3CN	3	rt	6 h	67	33
3	toluene	3	rt	6 h	60	23
4	toluene	1	85	40 min	51	42
5	toluene	3	85	10 min	68 (57)	32 (31)
6	toluene	5	65	40 min	66	34
7	hexane	3	rt	6 h	55	11
8	hexane	3	69	1 h	62	38

[a] The ester **1a** (0.5 mmol) was stirred with trimethyl phosphite in a solvent (2.5 mL). [b] Yield was determined on the basis of ^{1}H NMR spectra of the reaction mixture. [c] Isolated yields are shown in parentheses.

Table 2 Reaction of selenothioic acid *S*-butyl ester **1a** with phosphorus compounds[a]

Entry	Reaction conditions	Product yield (%)[b]	
1	$(EtO)_3P$ toluene 85 °C, 10 min	 **2b** (53%)	 **3b** (42%)
2	$(Pr^iO)_3P$ toluene 85 °C, 30 min	 **2c** (46%)	 **3c** (33%)
3	$PhP(OMe)_2$ toluene rt, 30 min	 **2d** (49%, 57:43)	 **3a** (25%)
4[d]	$PhP(OMe)_2$ Et_2O rt, 1 h	 **2e** (27%, 67:33)	 **3d** (9%)
5	Ph_2POCH_3 toluene rt, 5 min	 **2f** (25%)	 **3a** (32%)

[a] The ester **1a** (0.5 or 1 mmol) was stirred with phosphorus compounds (2 or 3 equiv.) in a solvent (2.5 or 5 mL). [b] Isolated yield. [c] The ratio of the stereoisomers was determined on the basis of ^{13}C NMR spectra of the reaction mixture. [d] Ethaneselenothioic acid *S*-*tert*-butyl ester was used as the ester.

used as solvent, but the ratio of the stereoisomers did not change. The use of selenothioacetic acid *S*-*tert*-butyl ester gave product **2e** with better selectivity, although the yield of product **2e** decreased (entry 4).

Next, α-substituted esters **1** were used as a starting material. The results are summarised in Table 3. The reaction of α-mono- **1b** and α-disubstituted esters **1d** and **1e** with trimethyl phosphite successfully proceeded to give the corresponding α-phosphoryl sulfides in good yields, although the reaction time was strongly affected by the substituents next to the selenocarbonyl group (entries 1, 3 and 6). In these reactions the formation of ketene selenothioacetals **3** was suppressed. On the contrary, the reaction with esters **1c**, in which a hydroxy group was attached to the carbon atom β to the selenocarbonyl group,

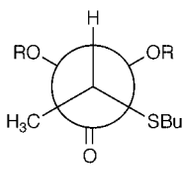


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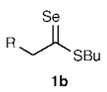
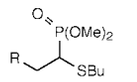
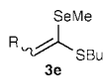
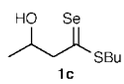
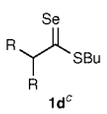
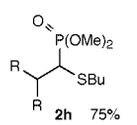
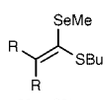
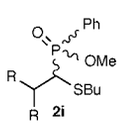
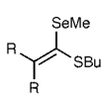
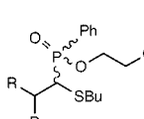
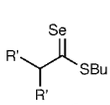
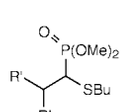
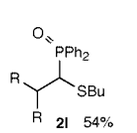
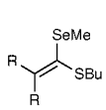
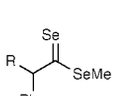
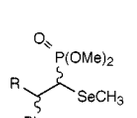
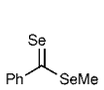
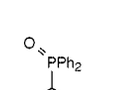
Fig. 1 Stable conformation of compound **2**.

gave a complex mixture (entry 2). $PhP(OMe)_2$ and Ph_2POMe also reacted smoothly with α-disubstituted ester **1d** (entries 4 and 7). In the former case one of the diastereomers was formed predominantly, although the stereochemistry of the product was not determined. The reaction of dioxaphospholane took place accompanied by the ring opening of the dioxaphospholane to afford product **2j** in 70% yield (entry 5). Finally, diselenoic acid esters **1f** and **1g** were reacted with Ph_2POMe to give α-phosphoryl selenides **2m** and **2n** in 84 and 47% yields, respectively (entries 8 and 9).

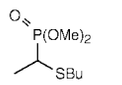
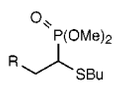
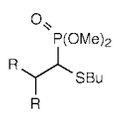
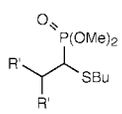
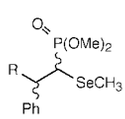
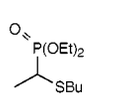
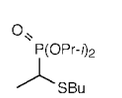
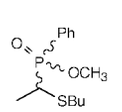
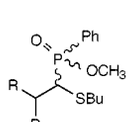
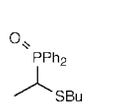
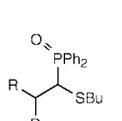
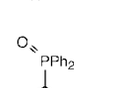
The α-phosphoryl sulfides obtained showed characteristic ^{31}P NMR spectra (Table 4). The signals of α-phosphoryl sulfides **2a**, **2g**, **2h** and **2k** were observed at about δ 29 (entries 1–4). The replacement of a methoxy group with a phenyl group shifted the signals to lower fields by about 15 ppm (entries 8 and 9). Interestingly, further replacement of a methoxy group with a phenyl group, namely, α-diphenylphosphoryl sulfides **2f** and **2l** showed the signals higher than those of α-methoxy(phenyl)-phosphoryl sulfides **2d** and **2i** (entries 10 and 11). In contrast, the coupling constants between the phosphorus atom and the carbon atom ($^1J_{P\text{-}C}$) became larger as the number of alkoxy groups increased. This may be understood as follows. The conformer of **2** shown in Fig. 1 appears to be the most stable among several possible conformers. Then, stereoelectronic effects may be present between an O–P bond and the C–S bond. In other words, delocalization of the electrons from the C–S σ orbital to the P–O σ* orbital may occur, and this enhances the strength of the bond between the phosphorus and carbon atoms. As a matter of fact, ^1J value of **2b** is larger than that of Bu-P(O)$(OEt)_2$ ($^1J_{P\text{-}C}$ = 140.9 Hz) by about 10 Hz.[12] Finally, no substantial difference was observed between the sulfides and selenide (entries 10–12), although in the latter case, a $^2J_{P\text{-}Se}$ coupling was observed (36.6 Hz). The structure of α-phosphoryl selenide **2n** was further confirmed by X-ray analysis. Fig. 2 shows an ORTEP drawing of **2n**, and selected bond lengths and bond angles are listed in Table 5. The bond length of Se1–C1 is 1.981(3) Å, which is close to the value of the carbon–selenium single bond of *trans*-2-dimethoxyphosphoryl-1,3-diselenane (C–Se: 1.97 Å).[13] The torsion angle of Se1–C1–P1–O1 of **2n** is 56.9(2)°. The α-phosphoryl selenide exists in a bisecting conformation in the solid state. A substantial non-bonded interaction, which has recently been discussed in compounds containing selenium and oxygen atoms,[14] was not observed.

Table 3 Reaction of selenothioic acid *S*-butyl esters **1** with trivalent phosphorus compounds[a]

Entry	Ester	Reaction conditions	Product yield (%)[b]
1	 **1b**	$(MeO)_3P$ 85 °C 1.5 h	 **2g** 56%  **3e** 16% (75 : 25)
2	 **1c**	$(MeO)_3P$ 85 °C 1 h	Complex mixture
3	 **1d**[c]	$(MeO)_3P$ 110 °C 6 h	 **2h** 75%  **3f** 3%
4	**1d**	$PhP(OMe)_2$ 110 °C 20 min	 **2i** 90% (62 : 38)[d]  **3f** 4%
5	**1d**	 110 °C 5 h	 **2j** 70% (68 : 32)[d]
6	 **1e**[e]	$(MeO)_3P$ 110 °C 6 h	 **2k** 84%
7	**1d**	Ph_2POMe 110 °C 10 min	 **2l** 54%  **3f** 30%
8	 **1f**	$(MeO)_3P$ 110 °C 4 h	 **2m** 84% (60 : 40)[d]
9	 **1g**	Ph_2POMe rt 15 min	 **2n** 47%

[a] The ester **1** (0.5, 0.8 or 1 mmol) was stirred with trimethyl phosphite (3 equiv.) in toluene (2.5 or 5 mL). [b] Isolated yield. [c] R represents $CH_2CH{=}CH_2$. [d] The ratio of diastereomers is shown in parentheses. [e] R′ represents $CH_2CBr{=}CH_2$.

Table 4 Spectroscopic data of **2**[a]

Entry	Compound[b,c]		^{31}P NMR δ (ppm)	$^1J_{P\text{-}C}$[d]/ Hz
1		**2a**	29.9	150.2
2		**2g**	29.3	151.1
3		**2h**	29.5	149.2
4		**2k**	28.1	149.2
5		**2m**	28.8 28.5	149.2 144.7
6		**2b**	27.6	151.1
7		**2c**	25.5	152.1
8		**2d**	44.3 44.4	103.4 104.3
9		**2i**	44.0 43.4	102.9 104.8
10		**2f**	33.8	71.2
11		**2l**	31.3	72.2
12		**2n**	30.7	68.3

[a] $CDCl_3$ was used as a solvent. [b] R represents $CH_2CH{=}CH_2$. [c] R′ represents $CH_2CBr{=}CH_2$. [d] Coupling constant was determined on the basis of ^{13}C NMR spectra.

Finally, the reaction of α-disubstituted ester **1d** with PPh_3 was carried out (Scheme 2). The use of 1 equiv. of PPh_3 in CH_3CN gave diselenide **4** in 68% yield. Interestingly, a catalytic amount of PPh_3 was effective for the conversion of **1d** to **4**. A plausible reaction pathway leading to **4** is outlined in Scheme 3. Nucleophilic attack of PPh_3 on the carbon atom of the selenocarbonyl group of **1d** initially may take place to form **5**. Then, migration to the selenium atom of the proton α to the selenocarbonyl group proceeds to generate eneselenol **6**, followed by air oxidation to give **4**. In general, it is known that diselenides are easily reduced to the corresponding selenols with sodium borohydride in MeOH at room temperature,[15] but in this case the reaction gave ester **1d** rather than eneselenol **6** in 83% yield.

The reaction pathway using trialkyl phosphites is outlined in Scheme 4 on the basis of the proposed mechanism of the reactions of thiocarbonyl compounds with trialkyl phosphites.[16–18] In the first step, trialkyl phosphites may nucleophilically

Table 5 Selected bond lengths and angles for compound **2n** with estimated standard deviation in parentheses

Bond length/Å		Bond angle (°)	
Se(1)–C(1)	1.981(3)	Se(1)–C(1)–P(1)	106.3(1)
P(1)–O(1)	1.490(2)	C(1)–Se(1)–C(2)	98.0(1)
P(1)–C(1)	1.819(3)	C(1)–P(1)–O(1)	114.2(1)
Se(1)–C(2)	1.936(3)	C(1)–P(1)–C(9)	106.0(1)
P(1)–C(9)	1.808(3)	C(1)–P(1)–C(15)	107.5(1)
P(1)–C(15)	1.805(3)	P(1)–C(1)–C(3)	114.1(2)

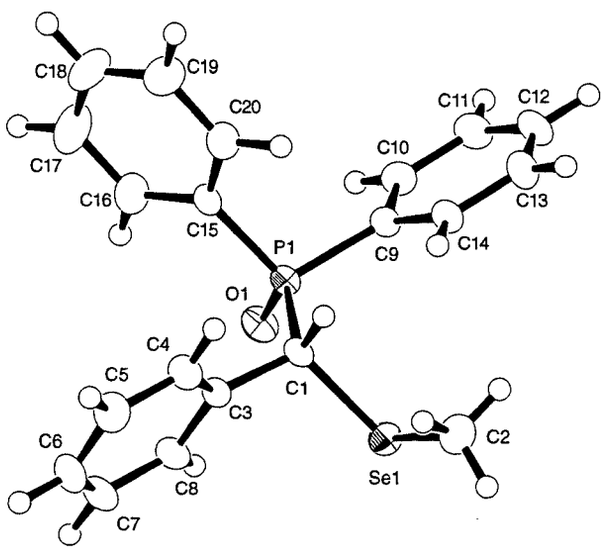
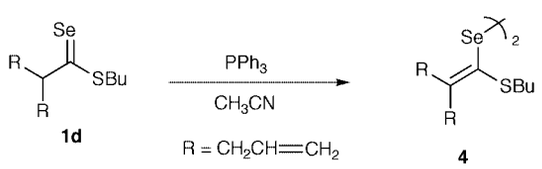
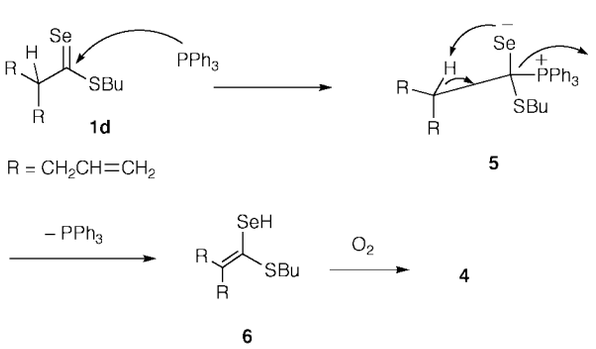


Fig. 2 ORTEP drawing of compound **2n** with atomic numbering scheme.



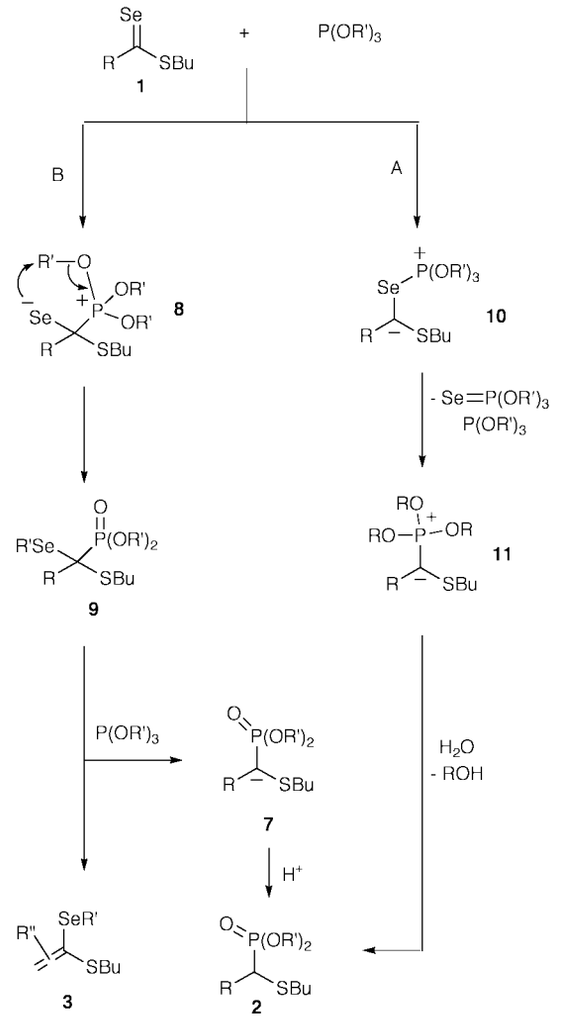
PPh_3 1.2 equiv	rt, 20 h	68%
PPh_3 0.25 equiv	rt, 20 h	83%
PPh_3 0.1 equiv	rt, 41 h	70%
PPh_3 0 equiv	rt, 20 h	0%

Scheme 2



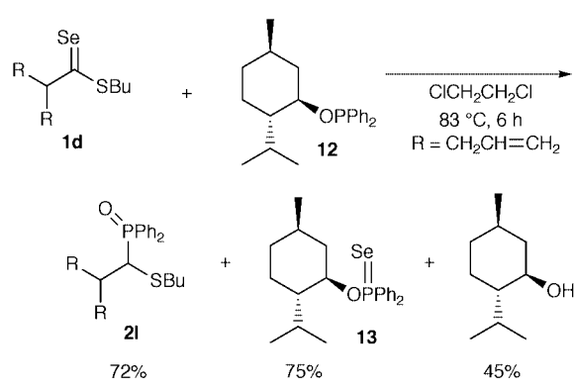
Scheme 3

attack the carbon atom of esters **1** (path B) similarly to the reaction with PPh_3 shown in Scheme 3. Then, intramolecular rearrangement of the alkyl group on the phosphoryl group of **8** may occur to form **9**. A similar rearrangement has been postulated for the reactions of cycloalkanethiones with trialkyl phosphites.[17] The formation of products **3** may be explained by



Scheme 4

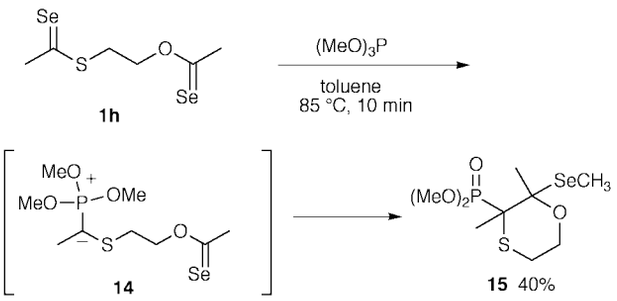
the β-elimination of dialkyl phosphites from **9**. On the other hand, two reaction pathways can be proposed for the formation of the products **2**. One involves the intermediate **9** (Path B). Alternatively, the process involving the initial attack of trialkyl phosphites on the selenium atom of the esters **1** is possible (path A). Then, the elimination of $Se{=}P(OR)_3$ from **10** gives phosphonuim salt **11**, followed by hydrolysis to give the product **2**. To confirm the validity of the proposed reaction pathway menthyl phosphinite **12** was reacted with ester **1d** (Scheme 5).



Scheme 5

The reaction proceeded smoothly in 1,2-dichloroethane at 83 °C to afford α-phosphoryl sulfide **2l** in better yield than the reaction with Ph_2POMe (Table 3, entry 7) along with 75% yield of selenophosphinite **13**. No product having a menthylselanyl

group, which should be formed when the migration of the menthyl group (analogous to the process from **8** to **9**) occurred, was observed. The formation of menthol as a by-product has suggested hydrolysis of an intermediate similar to **11**. Finally, the reaction of ester **1h** with trimethyl phosphite was carried out. The reaction was complete within 10 min at 85 °C to give 1,4-oxathiane **15** in 40% yield (Scheme 6). The initial reaction



Scheme 6

selectively takes place on the selenocarbonyl group attached to the alkylthio group, and phosphonium salt **14** may be formed as an intermediate, followed by the intramolecular cyclisation to give product **15**.

In conclusion, reactions of selenothioic acid *S*-esters and diselenoic acid esters with trivalent phosphorus compounds have been demonstrated. The reactions provide a new and efficient synthetic method for α-phosphoryl sulfides and selenides. The reaction may involve nucleophilic attack of trivalent phosphorus compounds on the selenium atom of the esters, and phosphonium salts may be formed as intermediates.

Experimental

General

The IR spectra were obtained on a Perkin Elmer FT-IR 1640 spectrophotometer. The ^{1}H NMR spectra were measured on a JEOL α-400 (399.7 MHz) in $CDCl_3$. Chemical shifts of protons are reported in δ values referenced to tetramethylsilane as an internal standard, and the following abbreviations were used; s: singlet, d: doublet, t: triplet, q: quartet, qui: quintet, sex: sextet, hep: heptet, m: multiplet. The ^{13}C NMR spectra were measured on a JEOL α-400 (100.4 MHz). The ^{31}P NMR (161.7 Hz) and ^{77}Se NMR (76.2 MHz) spectra were obtained from a JEOL α-400 spectrometer, and their chemical shifts are expressed in δ values deshielded with respect to neat PPh_3 and Me_2Se, respectively as an external standard. All spectra were acquired in the proton-decoupled mode; generally 0.05–0.3 mmol solutions in $CDCl_3$ (0.4 mL) were used. The mass spectra (MS) were taken on Shimadzu GCMS QP1000 (EI mode) or GCMS 9020DF high resolution mass spectrometers. The high resolution mass spectroscopy was taken on a Shimadzu GCMS 9020DF high resolution mass spectrometer. Elemental analyses were carried out by the Elemental Analysis Center of Kyoto University. High performance liquid chromatography (HPLC) was performed using a Japan Analytical Industry LC-908 recycling preparative HPLC coupled to an RI indicator and UV detector (256 nm). Melting points were determined using a Yanaco micromelting point apparatus and are uncorrected. 2-Phenyl-1,3,2-dioxaphospholane[19] and menthyl diphenylphosphinate[20] were prepared according to the literature. All the starting esters **1** were prepared by the literature method.[4] Other substrates were commercially received.

General procedure for reactions of selenothioic acid *S*-esters with trivalent phosphorus compounds

To a solution of ethaneselenothioic acid *S*-butyl ester **1a** (0.098 g, 0.5 mmol) in toluene (2.5 mL) was added trimethyl phosphite (0.18 mL, 1.5 mmol) at room temperature. After being stirred at 85 °C (temperature of oil bath) for 10 min under nitrogen, the resulting mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane–Et_2O (100:0 to 80:20) as the solvent to elute α-phosphoryl sulfide **2a** (0.065 g, 57%) and ketene selenothioacetal **3a** (0.032 g, 31%).

2-(Dimethoxyphosphoryl)-3-thiaheptane 2a. A colourless oil (Found: C, 42.37; H, 8.73. $C_8H_{19}O_3PS$ requires C, 42.47; H, 8.46%); ν_{max}/cm^{-1} 3476, 2957, 2873, 2361, 2343, 1458, 1377, 1238, 1184, 1028, 827, 808, 734, 669, 533; δ_H (400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.3, CH_3), 1.42 (2 H, sex, *J* 7.4, CH_2), 1.49 (3 H, dd, *J* 7.4, $^{3}J_{P\text{-}H}$ 17.2, CH_3), 1.54–1.62 (2 H, m, CH_2), 2.70–2.83 (2 H, m, SCH_2), 2.85 (1 H, qui, *J* 7.3, $^{2}J_{P\text{-}H}$ 7.3, PCHS), 3.82 (3 H, d, $^{3}J_{P\text{-}H}$ 10.7, OCH_3), 3.84 (3 H, d, $^{3}J_{P\text{-}H}$ 10.5, OCH_3); δ_C (100 MHz, $CDCl_3$) 13.6, 16.1, 21.9, 31.3, 31.8, 33.9, 53.4, 53.7; *m*/*z* (EI) 226 (M^+), 169 (M^+ − Bu).

2-(Diethoxyphosphoryl)-3-thiaheptane 2b. A colourless oil (Found: C, 46.95; H, 9.03. $C_{10}H_{23}O_3PS$ requires C, 47.23; H, 9.12%); ν_{max}/cm^{-1} 3475, 2933, 2874, 1654, 1456, 1392, 1236, 1164, 1024, 959, 789, 731, 666, 538; δ_H (400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.2, CH_2CH_3), 1.34 (3 H, t, *J* 7.1, OCH_2CH_3), 1.35 (3 H, t, *J* 7.1, OCH_2CH_3), 1.39–1.46 (2 H, m, CH_2CH_3), 1.48 (3 H, dd, *J* 7.6, $^{3}J_{P\text{-}H}$ 17.1, $PCHCH_3$), 1.54–1.62 (2 H, m, SCH_2CH_2), 2.70–2.86 (3 H, m, SCH_2, PCHS), 4.14–4.24 (4 H, m, OCH_2); δ_C (100 MHz, $CDCl_3$) 13.6, 16.2, 16.4, 16.5, 21.9, 31.3, 31.7, 34.1, 62.5, 62.9; *m*/*z* (EI) 254 (M^+).

2-(Diisopropoxyphosphoryl)-3-thiaheptane 2c. A colourless oil (Found: C, 50.84; H, 9.54. $C_{12}H_{27}O_3PS$ requires C, 51.04; H, 9.64%); ν_{max}/cm^{-1} 3476, 2978, 2874, 2366, 2345, 1718, 1654, 1456, 1385, 1236, 1178, 1142, 1108, 985, 886, 788, 734, 669, 547, 486; δ_H (400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.3, CH_2CH_3), 1.33–1.36 (12 H, m, $OCH(CH_3)CH_3$), 1.39–1.44 (2 H, m, CH_2CH_3), 1.45 (3 H, dd, *J* 7.3, $^{3}J_{P\text{-}H}$ 16.8, $PCHCH_3$), 1.53–1.61 (2 H, m, SCH_2CH_2), 2.70–2.84 (3 H, m, SCH_2, PCHS), 4.70–4.83 (2 H, m, OCH); δ_C (100 MHz, $CDCl_3$) 13.6, 16.4, 21.9, 23.86, 23.9, 24.1, 24.2, 31.4, 31.8, 34.7, 70.8, 71.3; *m*/*z* (EI) 282 (M^+).

2-[Methoxy(phenyl)phosphoryl]-3-thiaheptane 2d. A colourless oil; ν_{max}/cm^{-1} 3454, 3058, 2958, 2872, 2366, 2346, 1592, 1439, 1376, 1222, 1181, 1122, 1039, 793, 747, 697, 654, 542, 509; δ_H (400 MHz, $CDCl_3$) (Major) 0.89 (3 H, t, *J* 7.3, CH_2CH_3), 1.27–1.43 (2 H, m, CH_2CH_3), 1.39 (3 H, dd, *J* 7.4, $^{3}J_{P\text{-}H}$ 16.5, $PCHCH_3$), 1.45–1.56 (2 H, m, SCH_2CH_2), 2.58–2.76 (2 H, m, SCH_2), 2.86–2.95 (1 H, m, PCHS), 3.74 (3 H, d, $^{3}J_{P\text{-}H}$ 10.7, CH_3), 7.47–7.60 (3 H, m, Ar), 7.81–7.87 (2 H, m, Ar); (Minor) 0.86 (3 H, t, *J* 7.2, CH_2CH_3), 1.27–1.43 (2 H, m, CH_2CH_3), 1.45–1.56 (2 H, m, SCH_2CH_2), 1.49 (3 H, dd, *J* 7.4, $^{3}J_{P\text{-}H}$ 16.0, $PCHCH_3$), 2.48–2.62 (2 H, m, SCH_2), 2.86–2.95 (1 H, m, PCHS), 3.72 (3 H, d, $^{3}J_{P\text{-}H}$ 10.7, CH_3), 7.47–7.60 (3 H, m, Ar), 7.81–7.87 (2 H, m, Ar); δ_C (100 MHz, $CDCl_3$) (Major) 13.61, 15.8, 21.9, 31.4, 32.1, 37.1, 51.9, 128.1, 128.371, 132.5, 132.7, 132.8, 132.9; (Minor) 13.58, 15.3, 21.8, 31.3, 31.5, 36.7, 51.9, 128.371, 128.372, 132.5, 132.7, 132.8, 132.9; *m*/*z* (EI HRMS) 272.10093 (M^+, $C_{13}H_{21}P_2S$ requires 272.1016728); *m*/*z* (EI LRMS) 272 (M^+).

4,4-Dimethyl-2-[methoxy(phenyl)phosphoryl]-3-thiapentane 2e. A colourless solid, mp 53–55 °C; ν_{max}/cm^{-1} 3502, 2960, 1774, 1654, 1463, 1439, 1366, 1252, 1224, 1176, 1160, 1116, 1037, 805, 766, 752, 700, 660, 590, 546, 509; δ_H (400 MHz, $CDCl_3$) (Major) 1.16 (9 H, s, $SC(CH_3)_3$), 1.51–1.60 (3 H, m, $PCHCH_3$), 2.73–2.86 (1 H, m, PCHS), 3.74 (3 H, d, $^{3}J_{P\text{-}H}$ 10.9, OCH_3), 7.44–7.58 (3 H, m, Ar), 7.82–7.90 (2 H, m, Ar); (Minor) 1.13 (9 H, s, $SC(CH_3)_3$), 1.51–1.60 (3 H, m, $PCHCH_3$), 2.73–2.86 (1 H, m, PCHS), 3.71 (3 H, d, $^{3}J_{P\text{-}H}$ 11.2, OCH_3), 7.44–7.58 (3 H, m, Ar), 7.82–7.90 (2 H, m, Ar); δ_C (100 MHz, $CDCl_3$) (Major) 18.6,

30.5, 35.1, 44.2, 51.9, 128.1, 128.3, 132.3, 132.9, 133.0, 133.1; (Minor) 18.4, 30.5, 34.8, 44.1, 51.9, 128.2, 128.4, 132.3, 132.9, 133.0, 133.1; *m*/*z* (EI HRMS) 272.09912 (M^+, $C_{13}H_{21}O_2PS$ requires 272.1016728); *m*/*z* (EI LRMS) 272 (M^+).

2-(Diphenylphosphoryl)-3-thiaheptane 2f. A colourless solid, mp 85.3–87.3 °C (Found: C, 67.74; H, 7.25. $C_{18}H_{23}OPS$ requires C, 67.90; H, 7.28%); ν_{max}/cm^{-1} 3056, 2959, 2924, 2362, 1508, 1487, 1438, 1182, 1119, 1072, 1026, 998, 741, 722, 701, 692, 546, 532; δ_H (400 MHz, $CDCl_3$) 0.83 (3 H, t, *J* 7.3, CH_2CH_3), 1.28 (2 H, sex, *J* 7.3, CH_2CH_3), 1.44 (2 H, qui, *J* 7.4, SCH_2CH_2), 1.55 (3 H, dd, *J* 7.4, $^3J_{P-H}$ 15.0, PCHCH_3), 2.40–2.47 (1 H, m, SC*H*HCH$_2$), 2.50–2.57 (1 H, m, SCH*H*CH$_2$), 3.30 (1 H, dq, *J* 7.3, $^2J_{P-H}$ 9.5, PC*H*S), 7.45–7.54 (6 H, m, Ar), 7.84–7.94 (4 H, m, Ar); δ_C (100 MHz, $CDCl_3$) 13.5, 15.8, 21.6, 31.2, 31.6, 37.3, 128.3, 128.4, 131.4, 131.7, 131.8, 132.0; *m*/*z* (EI LRMS) 318 (M^+).

5-(Dimethoxyphosphoryl)-6-thiadec-1-ene 2g. A colourless oil (Found: C, 49.34; H, 8.93. $C_{11}H_{23}O_3PS$ requires C, 49.61; H, 8.70%); ν_{max}/cm^{-1} 3484, 3078, 2956, 2852, 2367, 2345, 1846, 1641, 1560, 1458, 1380, 1252, 1183, 1032, 915, 821, 752, 637, 550, 479; δ_H (400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.3, CH_2CH_3), 1.37–1.49 (2 H, m, CH_2CH_3), 1.53–1.61 (2 H, m, SCH_2CH_2), 1.62–1.72 (1 H, m, PCHC*H*H), 1.96–2.07 (1 H, m, PCHCH*H*), 2.22–2.31 (1 H, m, C*H*HCH=CH$_2$), 2.38–2.46 (1 H, m, CH*H*-CH=CH$_2$), 2.63–2.71 (2 H, m, SCH_2), 2.74–2.81 (1 H, m, PC*H*S), 3.83 (6 H, d, $^3J_{P-H}$ 10.5, OCH_3), 5.01–5.11 (2 H, m, CH=CH_2), 5.72–5.83 (1 H, m, C*H*=CH$_2$); δ_C (100 MHz, $CDCl_3$) 13.6, 21.9, 28.2, 30.6, 31.3, 32.0, 38.8, 53.5, 53.6, 115.9, 137.1; *m*/*z* (EI LRMS) 266 (M^+).

5-(Dimethoxyphosphoryl)-4-prop-2-enyl-6-thiadec-1-ene 2h. A colourless oil (Found: C, 54.62; H, 8.86. $C_{14}H_{27}O_3PS$ requires C, 54.88; H, 8.88%); ν_{max}/cm^{-1} 3484, 3077, 2957, 2367, 1838, 1641, 1442, 1380, 1346, 1256, 1182, 1057, 915, 820, 749, 651, 564, 484; δ_H (400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.3, CH_2CH_3), 1.42 (2 H, sex, *J* 7.3, CH_2CH_3), 1.56 (2 H, qui, *J* 7.3, SCH_2CH_2), 1.95–2.03 (1 H, m, C*H*HCH=CH$_2$), 2.08–2.15 (1 H, m, C*H*-CH$_2$CH=CH$_2$), 2.27–2.31 (2 H, m, CH_2CH=CH$_2$), 2.49–2.55 (1 H, m, CH*H*CH=CH$_2$), 2.65–2.74 (2 H, m, SCH_2), 2.91 (1 H, dd, *J* 2.3, $^2J_{P-H}$ 17.7, PC*H*S), 3.82 (3 H, d, $^3J_{P-H}$ 10.5, OCH_3), 3.84 (3 H, d, $^3J_{P-H}$ 10.5, OCH_3), 5.02–5.11 (4 H, m, CH=CH_2), 5.66–5.80 (2 H, m, C*H*=CH$_2$); δ_C (100 MHz, $CDCl_3$) 13.6, 21.8, 31.3, 33.9, 34.7, 35.1, 38.6, 42.7, 53.2, 53.7, 116.8, 117.3, 136.7, 137.1; *m*/*z* (EI LRMS) 306 (M^+).

5-[Methoxy(phenyl)phosphoryl]-4-prop-2-enyl-6-thiadec-1-ene 2i. A colourless oil; ν_{max}/cm^{-1} 3076, 2957, 2930, 2873, 2368, 2346, 1654, 1639, 1591, 1438, 1276, 1236, 1119, 1036, 998, 914, 782, 751, 697, 561, 541, 498; δ_H (400 MHz, $CDCl_3$) 0.86 (3 H, t, *J* 7.1, CH_2CH_3), 1.13–1.49 (4 H, m, CH_2CH_3, SCH_2CH_2), 1.94–2.16 (2 H, m, CH_2CH=CH$_2$), 2.19–2.36 (3 H, m, C*H*CH$_2$CH=CH$_2$, CH_2CH=CH$_2$), 2.43–2.58 (2 H, m, SCH_2), 2.90 (1 H, dd, *J* 1.5, $^2J_{P-H}$ 13.2, PC*H*S), 3.72 (3 H, d, $^3J_{P-H}$ 11.2, OCH_3), 4.96–5.09 (4 H, m, CH=CH_2), 5.49–5.79 (2 H, m, C*H*=CH$_2$), 7.47–7.60 (3 H, m, Ar), 7.81–7.88 (2 H, m, Ar); (Minor) 0.77 (3 H, t, *J* 7.1, CH_2CH_3), 1.13–1.49 (4 H, m, CH_2CH_3, SCH_2CH_2), 1.94–2.16 (2 H, m, CH_2CH=CH$_2$), 2.19–2.36 (3 H, m, C*H*CH$_2$CH=CH$_2$, CH_2CH=CH$_2$), 2.43–2.58 (2 H, m, SCH_2), 2.89 (1 H, dd, *J* 1.5, $^2J_{P-H}$ 13.7, PC*H*S), 3.70 (3 H, d, $^3J_{P-H}$ 10.7, OCH_3), 4.96–5.09 (4 H, m, CH=CH_2), 5.49–5.79 (2 H, m, C*H*=CH$_2$), 7.47–7.60 (3 H, m, Ar), 7.81–7.88 (2 H, m, Ar); δ_C (100 MHz, $CDCl_3$) (Major) 13.6, 21.8, 31.4, 34.3, 35.1, 35.3, 37.6, 46.0, 51.5, 116.6, 117.3, 128.5, 129.7, 132.4, 132.5, 132.7, 132.8, 136.8, 137.1; (Minor) 13.5, 21.7, 31.2, 34.1 (S*C*H$_2$), 34.96, 34.97, 38.0, 45.9, 51.9, 116.6, 117.2, 128.4, 129.9, 132.4, 132.5, 132.7, 132.8, 136.9, 137.3; *m*/*z* (EI HRMS) 352.16682 (M^+, $C_{19}H_{29}O_2PS$ requires 352.16427); *m*/*z* (EI LRMS) 352 (M^+).

5-[(2-Hydroxyethoxy)phenylphosphoryl]-4-prop-2-enyl-6-thiadec-1-ene 2j. Colourless oil; ν_{max}/cm^{-1} 3374, 3076, 2958, 2930, 2873, 2346, 1831, 1639, 1592, 1439, 1379, 1276, 1208, 1120, 1098, 1035, 950, 916, 884, 751, 697, 563; δ_H (400 MHz, $CDCl_3$) (Major) 0.87 (3 H, t, *J* 7.3, CH_2CH_3), 1.13–1.51 (4 H, m, CH_2CH_3, SCH_2CH_2), 1.91–2.18 (2 H, m, CH_2CH=CH$_2$), 2.24–2.38 (3 H, m, C*H*CH$_2$CH=CH$_2$, CH_2CH=CH$_2$), 2.47–2.61 (2 H, m, SCH_2), 2.94 (1 H, dd, *J* 1.0, $^2J_{P-H}$ 4.9, PC*H*S), 3.71–3.76 (1 H, m, OC*H*H), 3.84–3.90 (2 H, m, OCH*H*, O*H*), 4.09–4.16 (2 H, m, OCH_2), 4.96–5.11 (4 H, m, CH=CH_2), 5.48–5.79 (2 H, m, C*H*=CH$_2$), 7.48–7.61 (3 H, m, Ar), 7.83–7.90 (2 H, m, Ar); (Minor) 0.77 (3 H, t, *J* 7.3, CH_2CH_3), 1.13–1.51 (4 H, m, CH_2CH_3, SCH_2CH_2), 1.91–2.18 (2 H, m, CH_2CH=CH$_2$), 2.24–2.38 (3 H, m, C*H*CH$_2$CH=CH$_2$, CH_2CH=CH$_2$), 2.47–2.61 (2 H, m, SCH_2), 2.97 (1 H, dd, *J* 1.5, $^2J_{P-H}$ 4.4, PC*H*S), 3.71–3.76 (1 H, m, OC*H*H), 3.84–3.90 (2 H, m, OCH*H*, O*H*), 4.09–4.16 (2 H, m, OCH_2), 4.96–5.11 (4 H, m, CH=CH_2), 5.48–5.79 (2 H, m, C*H*=CH$_2$), 7.48–7.61 (3 H, m, Ar), 7.83–7.90 (2 H, m, Ar); δ_C (100 MHz, $CDCl_3$) (Major) 13.5, 21.6, 31.1, 34.1, 35.0, 35.1, 37.6, 45.71, 62.3, 69.3, 116.8, 117.4, 128.5, 129.8, 132.67, 132.72, 136.7, 137.1; (Minor) 13.6, 21.8, 31.4, 34.4, 34.9, 35.4, 38.1, 45.69, 62.3, 69.0, 116.8, 117.5, 128.6, 129.8, 132.5, 132.67, 136.6, 137.0; *m*/*z* (EI HRMS) 382.16738 (M^+, $C_{20}H_{31}O_3PS$ requires 382.174833); *m*/*z* (EI LRMS) 382 (M^+).

2-Bromo-4-(2-bromoprop-2-enyl)-5-(dimethoxyphosphoryl)-6-thiadec-1-ene 2k. A colourless oil (Found: C, 35.96; H, 5.31. $C_{14}H_{25}Br_2O_3PS$ requires C, 36.23; H, 5.43%); ν_{max}/cm^{-1} 3752, 3484, 2955, 2851, 2346, 1794, 1628, 1508, 1465, 1380, 1298, 1257, 1182, 1136, 1032, 892, 854, 822, 751, 620, 564, 538, 517, 485; δ_H (400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.3, CH_2CH_3), 1.42 (2 H, sex, *J* 7.4, CH_2CH_3), 1.55–1.62 (2 H, m, SCH_2CH_2), 2.34–2.40 (1 H, m, C*H*HCHCH$_2$), 2.53–2.58 (1 H, m, CH*H*CHCH$_2$), 2.65–2.72 (1 H, m, C*H*CH$_2$CBr), 2.74–2.90 (3 H, m, SCH_2, PC*H*S), 2.93–3.00 (2 H, m, CH*H*CHCH*H*), 3.83 (3 H, d, $^3J_{P-H}$ 10.7, OCH_3), 3.87 (3 H, d, $^3J_{P-H}$ 10.7, OCH_3), 5.51 (1 H, d, $^6J_{P-H}$ 1.0, CBr=C*H*H), 5.55 (1 H, d, $^6J_{P-H}$ 1.0, CBr=CH*H*), 5.67 (1 H, d, $^6J_{P-H}$ 0.7, CBr=C*H*H), 5.69 (1 H, s, CBr=CH*H*); δ_C (100 MHz, $CDCl_3$) 13.6, 21.9, 31.3, 33.9, 36.1, 41.3, 41.4, 41.8, 53.3, 54.1, 119.5, 132.1, 132.4; *m*/*z* (EI LRMS) 464 (M^+).

5-(Diphenylphosphoryl)-4-prop-2-enyl-6-thiadec-1-ene 2l. A colourless solid; mp 78.5–81.5 °C (Found: C, 72.04; H, 7.91. $C_{24}H_{31}OPS$ requires C, 72.33; H, 7.84%); ν_{max}/cm^{-1} 3057, 2958, 2928, 2872, 1638, 1437, 1179, 1118, 1072, 995, 910, 785, 750, 720, 700, 538, 524; δ_H (400 MHz, $CDCl_3$) 0.74 (3 H, t, *J* 7.3, CH_2CH_3), 1.08–1.29 (4 H, m, CH_2CH_3, SCH_2CH_2), 1.87–2.01 (2 H, m, CH_2CH=CH$_2$), 2.08–2.15 (1 H, m, C*H*CH$_2$CH=CH$_2$), 2.21–2.37 (3 H, m, CH_2CH=CH$_2$, SC*H*H), 2.60–2.66 (1 H, m, SCH*H*), 3.29 (1 H, dd, *J* 1.8, $^2J_{P-H}$ 8.4, PC*H*S), 4.88–4.93 (2 H, m, CH=CH_2), 5.04–5.17 (2 H, m, CH=CH_2), 5.52–5.73 (2 H, m, C*H*=CH$_2$), 7.43–7.55 (6 H, m, Ar), 7.85–8.02 (4 H, m, Ar); δ_C (100 MHz, $CDCl_3$) 13.4, 21.6, 31.2, 34.8, 35.4, 35.5, 38.4, 46.7, 116.5, 117.6, 128.2, 128.6, 131.3, 131.6, 131.7, 131.8, 132.80, 132.84, 136.8, 137.4; *m*/*z* (EI LRMS) 398 (M^+).

5-(Dimethoxyphosphoryl)-4-phenyl-6-selenahept-1-ene 2m. A colourless oil (Found: C, 48.64; H, 6.01. $C_{14}H_{21}O_3PSe$ requires C, 48.42; H, 6.10%); ν_{max}/cm^{-1} 3462, 3063, 3029, 3004, 2977, 2952, 2928, 2850, 1640, 1603, 1496, 1455, 1419, 1277, 1244, 1183, 1060, 1032, 914, 846, 818, 775, 758, 742, 702, 664, 594, 539; δ_H (400 MHz, $CDCl_3$) (Major) 2.12 (3 H, s, $^2J_{Se-H}$ 12.0, SeCH_3), 2.56–2.64 (1 H, m, C*H*HCH=CH$_2$), 2.78–2.86 (1 H, m, CH*H*CH=CH$_2$), 3.03 (1 H, dd, *J* 4.2, $^2J_{P-H}$ 16.3, PC*H*Se), 3.33–3.40 (1 H, m, PCHC*H*), 3.57 (3 H, d, $^3J_{P-H}$ 10.7, OCH_3), 3.65 (3 H, d, $^3J_{P-H}$ 10.7, OCH_3), 4.89–5.14 (2 H, m, CH=CH_2), 5.54–5.73 (1 H, m, C*H*=CH$_2$), 7.20–7.37 (5 H, m, Ar); (Minor) 1.81 (3 H, s, $^2J_{Se-H}$ 12.0, SeCH_3), 2.66–2.72 (1 H, m, C*H*HCH=CH$_2$), 2.78–2.86 (1 H, m, CH*H*CH=CH$_2$), 2.86 (1 H, dd, *J* 4.3, $^2J_{P-H}$ 17.4, PC*H*Se), 3.33–3.40 (1 H, m, PCHC*H*), 3.72 (3 H, d, $^3J_{P-H}$

10.7, OCH_3), 3.79 (3 H, d, $^3J_{P\text{-}H}$ 10.7, OCH_3), 4.89–5.14 (2 H, m, CH=CH_2), 5.54–5.73 (1 H, m, CH=CH_2), 7.20–7.37 (5 H, m, Ar); δ_C (100 MHz, $CDCl_3$) (Major) 7.5, 38.8, 39.7, 44.5, 53.2, 53.4, 117.5, 127.0, 127.8, 128.7, 136.3, 140.9; (Minor) 7.2, 35.6, 42.8, 44.4, 53.4, 53.8, 116.6, 126.8, 128.2, 128.5, 136.1, 141.5; δ_{Se} (76.2 MHz, $CDCl_3$) (Major) 74.9 (d, $^2J_{Se\text{-}P}$ 12.2); (Minor) 77.8 (d, $^2J_{Se\text{-}P}$ 18.3); *m*/*z* (EI LRMS) 348 (M^+).

1-(Diphenylphosphoryl)-1-phenyl-2-selenapropane 2n. A colourless solid; mp 221.5–223.5 °C (Found: C, 62.32; H, 4.98. $C_{20}H_{19}OPSe$ requires C, 62.35; H, 4.97%); ν_{max}/cm^{-1} 3057, 2934, 1654, 1560, 1492, 1438, 1262, 1184, 1174, 1120, 1107, 1071, 1027, 796, 718, 698, 600, 533, 519; δ_H (400 MHz, $CDCl_3$) 1.93 (3 H, s, $^2J_{Se\text{-}H}$ 12.0, SeCH_3), 4.47 (1 H, d, $^2J_{P\text{-}H}$ 5.9, PCHSe), 7.14–7.60 (13 H, m, Ar), 7.90–7.95 (2 H, m, Ar); δ_C (100 MHz, $CDCl_3$) 6.2, 40.9, 127.4, 128.1, 128.2, 128.4, 128.5, 129.85, 129.91, 131.2, 131.3, 131.4, 131.5, 131.88, 131.91, 135.8; δ_{Se} (76.2 MHz, $CDCl_3$) 238.2 (d, $^2J_{Se\text{-}P}$ 36.6); *m*/*z* (EI LRMS) 292 ($M^+ - SeCH_3$).

A procedure for the reaction of 2-prop-2-enylpent-4-eneselenothioic acid *S*-butyl ester 1d with triphenylphosphine

To a solution of 2-prop-2-enylpent-4-eneselenothioic acid *S*-butyl ester **1d** (0.275 g, 1.0 mmol) in CH_3CN (5 mL) was added triphenylphosphine (0.066 g, 0.25 mmol) at room temperature. After being stirred at this temperature for 20 h, the resulting mixture was concentrated *in vacuo*. To the residue was added hexane, and the mixture was filtered. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel using hexane to elute **5** (0.228 g, 83% as a yellow oil).

A procedure for the reduction of bis[1-(butylthio)-2-prop-2-enylpenta-1,4-dienyl] diselenide 4

To a solution of bis[1-(butylthio)-2-prop-2-enylpenta-1,4-dienyl] diselenide **5** (1.646 g, 3.0 mmol) in MeOH (30 mL) was added sodium borohydride (0.340 g, 9.0 mmol) at room temperature. After being stirred at this temperature for 5 min under nitrogen, the resulting mixture was poured into water, and extracted with Et_2O three times. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane to elute **1d** (1.364 g, 83% as a red violet oil).

2,3-Dimethyl-2-methylselanyl-3-(dimethoxyphosphoryl)-1,4-oxathiane 15. To a solution of ethaneselenothioic acid *S*-selenoacetoxyethyl ester **1h** (0.191 g, 0.66 mmol) in toluene (15 mL) was added trimethyl phosphite (0.47 mL, 3.96 mmol) at room temperature. After being stirred at 85 °C for 10 min, the resulting mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane and Et_2O to elute **15** (0.089 g, 40% as a yellow oil). A colourless liquid (Found: C, 32.30; H, 5.59. $C_9H_{19}O_4PSSe$ requires C, 32.44; H, 5.75%); ν_{max}/cm^{-1} 3483, 2954, 2852, 1736, 1654, 1589, 1449, 1370, 1281, 1187, 1040, 850, 803, 734, 664, 510, 468, 460; δ_H (400 MHz, $CDCl_3$) 2.16 (3 H, s, SCCH_3), 2.17 (3 H, q, *J* 1.5, OCCH_3), 2.31 (3 H, q, *J* 1.5, SeCH_3), 2.95 (2 H, t, *J* 7.2, SCH_2), 3.78 (6 H, d, $^3J_{P\text{-}H}$ 11.2, OCH_3), 4.08 (2 H, q, *J* 7.3, OCH_2); δ_C (100 MHz, $CDCl_3$) 5.9, 21.9, 22.9, 31.9, 54.3, 66.4, 123.3, 130.8; δ_P (161.7 MHz, $CDCl_3$) 1.5; δ_{Se} (76.2 MHz, $CDCl_3$) 230.5; *m*/*z* (EI LRMS) 334 (M^+).

X-Ray structure analysis †

The measurement was carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). An X-ray quality crystal of **2n** was obtained by recrystallization from MeOH. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least-square cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom. Other parameters are summarised in Table 6.

† CCDC reference number 207/393. See http://www.rsc.org/suppdata/p1/a9/a909469e/ for crystallographic files in .cif format.

Table 6 Crystal data for **2n**

Chemical formula	$C_{20}H_{19}OPS$
Formula weight	385.30
Crystal system	Triclinic
μ(Mo-Kα)	22.84 cm^{-1}
Unit-cell dimensions	0.17 × 0.17 × 0.14
Space group	$P\bar{1}$ (#2)
Z	2
a	9.404(3) Å
b	16.703(4) Å
c	5.777(1) Å
α	96.67(2)
β	107.37(2)
γ	83.96(2)
V	857.9(4) Å^3
Radiation	Mo-Kα
T/°C	−80.0
R	0.034
R_w	0.036
Observed reflections	4194
Unique reflections	3951
R_{int}	0.026

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