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Oxidative Metal-Free Cross-Coupling of Secondary Phosphine Chalcogenides and Benzenediols: Synthesis of Phosphinochalcogenoic *O*-Diesters

Nina K. Gusarova, Pavel A. Volkov, Nina I. Ivanova, Ludmila I. Larina, and Boris A. Trofimov

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation

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ABSTRACT: *Benzenediols react with 2 equiv of secondary phosphine chalcogenides in the CCl_4–Et_3N system under mild conditions (50–52°C, 1.5–13 h) to give phosphinochalcogenoic O-diesters in 62–91% isolated yields.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 00:1–7, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21020

INTRODUCTION

Transition metal-catalyzed cross-coupling reactions have been established as one of the powerful tools for the formation of the C—C and C—X bonds [1]. However, transition metal–based protocols usually have some inherent limitations, such as costly metal catalysts, environmental toxicity, and moisture sensitivity [2]. With the prevalence of "green chemistry," the cross-coupling reactions without any metal catalysts have attracted great interest [3]. Now these reactions are successfully used to form new C—C [3a–g,i] and C-heteroatom [2,3h,j] bonds. For instance, an efficient metal-free Sonogashira coupling between phenylacetylene and different electron-deficient aryl halides catalyzed by 1, 4-diazabicyclo[2.2.2]octane (DABCO) has been realized [3i]. Microwave-promoted Suzuki-type coupling of 4-bromoacetophenone and phenylboronic acid in water has been developed [3b]. Recently, original and effective transition-metal-free cross-coupling between halogenoacetylenes and pyrroles or indoles on Al_2O_3, BaO, and K_2CO_3 has been proposed [4]. It has been reported as a metal-free coupling reaction of 1,3-diarylpropenes or 1,3-diarylpropynes with alcohols promoted by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to form the C—O bonds [2,3h].

Most recently, we have published results on oxidative transition-metal-free cross-coupling between secondary phosphine chalcogenides and amines [5], alcohols and phenols [6] to furnish the P—N and P—O bonds, correspondingly. These reactions proceed under mild conditions in the system CCl_4–Et_3N to give amides [5] and *O*-esters [6] of phosphinochalcogenoic acids, which are widely used for the design of practically important compounds and materials [7].

The objective of this paper is the development of a one-pot and convenient method for preparation of phosphinochalcogenoic *O*-diesters, and the chemistry of which is being developed very

Correspondence to: Boris A. Trofimov; e-mail: boris_trofimov@irioch.irk.ru.

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intensively during the recent decades [8–14]. These compounds are employed as ligands for metal complexes [8] (including supramolecular complexes [8c]), extractants [9], and flame retardants [10] (including "green, halogen-free" ones [10b]). Phosphinic *O*-diesters, which are structural analogs of myleran, possess antineoplastic activity [11]. Functional diesters of diphenylphosphinic acid are highly selective, sensitive, cell-permeable, red fluorescent probes for detecting of $O_2C^{\bullet-}$ in biological systems [12], whereas their seleno-containing congeners are applied as effective chemosensors for mercury ions in biological systems and drinking water [12c]. Bisphosphinates are employed as the building blocks [13] to design, for example, an effective catalyst for enantioselective ethylation of aldehydes [13a].

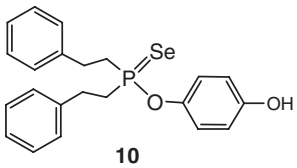
At the same time, the conventional syntheses of phosphinochalcogenoic *O*-diesters are multistep, laborious, and involve utilizing moisture- and air-sensitive phosphorus halides [8–13, 14b–g].

Here, we report for the first time on the reaction of oxidative metal-free cross-coupling of secondary phosphine chalcogenides with benzenediols using the system CCl_4–Et_3N. Also, the paper deals with the development of a one-pot method for the preparation of phosphinochalcogenoic *O*-diesters basing on the above reaction. Initial secondary phosphine oxides, sulfides, and selenides are easily prepared by the "halogen-free" method from red phosphorus, styrenes, and elemental chalcogens [15].

RESULTS AND DISCUSSION

We showed that bis(2-phenylalkyl)phosphine chalcogenides **1–4** reacted with 1,2-, 1,3-, 1,4-benzenediols **5–7**, and 4,4′-isopropylidenebisphenol **8** in the system CCl_4–Et_3N under mild conditions (50–52°C, 1.5–13 h, molar ratio **1–4**:**5–8** = 1:0.4–0.5) to afford bis(2-phenylalkyl)phosphinochalcogenoic *O*-diesters **9a–i** in 62–91% isolated yields (Table 1).

The products of monocondensation, phosphinochalcogenoic *O*-(hydroxyphenyl) esters, were not detected in the resulting reaction mixture obtained under the above conditions. At the same time, on the example of phosphine selenide **3** and 1,4-benzenediol **7**, it was shown that, when the molar ratio of the starting reagents was 1:1, di(2-phenethyl)phosphinoselenoic *O*-(4-hydroxyphenyl) ester **10** was formed in significant amount (30%).



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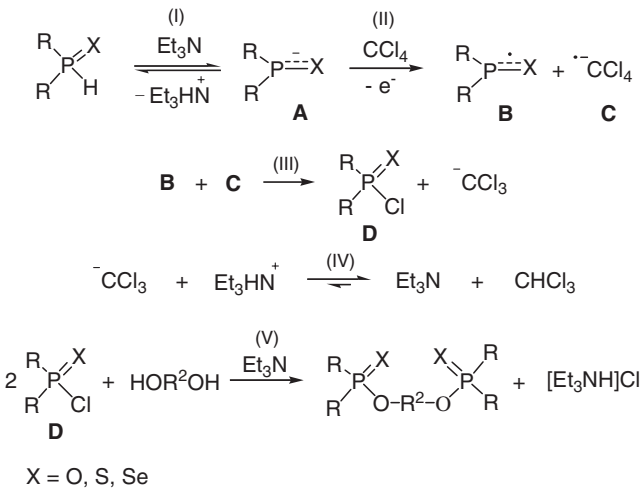


SCHEME 1 A tentative mechanism for the formation of phosphinochalcogenoic *O*-diesters **9a–i**.

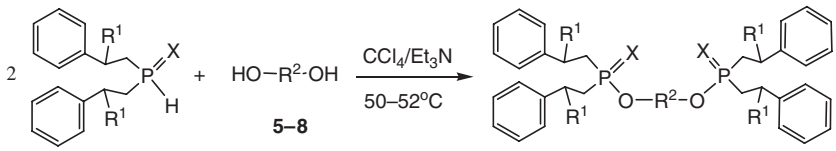
However, the main product of the cross-coupling in this case remained *O*-diester **9g** (yield 57%).

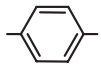
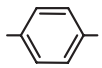
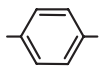
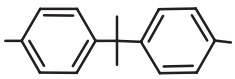
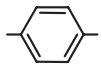
The reactivity of the starting secondary phosphine chalcogenides in oxidative cross-coupling with benzenediols meets the following order: phosphine selenide > phosphine sulfide > phosphine oxide (Table 1, cf. entries 1, 4, 7) that corresponds to the decrease of P—H acidity in the above series of phosphine chalcogenides [16].

The lower reactivity of 1,2-benzenediol **5** as compared to compounds **6,7** (Table 1, cf. entries 5–7) is likely due to steric hindrances imposed by two hydroxyl groups in the orthoposition.

The experimental results obtained are in good agreement with the reaction mechanism (Scheme 1), which we have proposed earlier for the cross-coupling of secondary phosphine chalcogenides with alcohols and phenols [6]. The deprotonation of a secondary phosphine chalcogenide by triethylamine (which proceeds easier in the case of more acidic secondary phosphine selenides and then phosphine sulfides) produces *P,X*-ambident chalcogenophosphinite-anion **A** (Step I). The latter participates in the one-electron transfer toward CCl_4 (oxidizer) to give free radical of secondary phosphine chacogenide **B** and anion radical **C** (Step II). Then the interconversion of the species **B** and **C** affords phosphinochalcogenoic chloride **D** and the $^{-}CCl_3$ carbanion (Step III). The latter is protonated by a triethylammonium cation that leads to regeneration of triethylamine and formation of chloroform (Step IV). The reaction between chloride **D** and benzenediol in the presence of triethylamine results in the final product, phosphinochalcogenoic

TABLE 1 Synthesis of Phosphinochalcogenoic *O*-diesters **9a–i**[a]

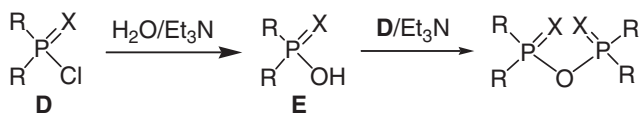


Entry	Phosphine Chalcogenides **1–4**	R^1	X	HOR^2OH **5–8**	R^2	Time (h)	Product	Yield (%) [b]	Yield (%) [c]
1	**1**	H	O	**7**		9.5	**9a**	76	72
2	**2**	H	S	**5**		13	**9b**	66	63
3	**2**	H	S	**6**		5	**9c**	79	73
4	**2**	H	S	**7**		6	**9d**	81	75
5	**3**	H	Se	**5**		11	**9e**	65	62
6	**3**	H	Se	**6**		1.5	**9f**	91	84
7	**3**	H	Se	**7**		4.5	**9g**	93	89
8	**3**	H	Se	**8**		3	**9h**	94	91
9	**4**	Me	Se	**7**		9.5	**9i**	93	90

[a]The reagents **1–4** (1 mmol), Et_3N (1 mmol) and **5** (0.42 mmol) or **6–8** (0.5 mmol), and CCl_4 (4 mL) were used.
[b]Yield was calculated from the ^{31}P NMR spectra of the crude products. Bis(diorganochalcogenophosphoryl)oxides were identified as side organophosphorus compounds (^{13}C and ^{31}P NMR).
[c]Isolated yield.

O-diester, and triethylammonium chloride (Step V). In support of this mechanism, triethylammonium chloride is always isolated from the reaction mixture (by filtration) and $CHCl_3$ is identified by gas chromatography–mass spectrometry.

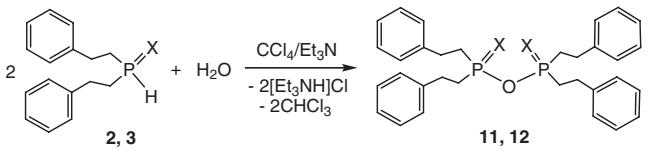
The formation of bis(diorganochalcogenophosphoryl)oxides as by-products is also in agreement with the mechanism proposed (Scheme 2). Phosphinochalcogenoic chloride **D** generated at Stage III apparently undergoes the hydrolysis owing to the presence of trace water in the system to give diorganylphosphinochalcogenoic *O*-acid **E**, which further reacts with chloride **D** in the presence of Et_3N to form bis(diorganylchalcogenophosphoryl)oxides.



SCHEME 2 A tentative mechanism for the formation of bis(diorganylchalcogenophosphoryl)oxides.

On the example of phosphine sulfide **2** and phosphine selenide **3**, it was shown that secondary phosphine chalcogenides did react readily (r.t., 4 h) with water in the system CCl_4–Et_3N to deliver bis(diphenethylchalcogenophosphoryl)oxides **11, 12** in almost quantitative yields (Scheme 3).

In summary, the oxidative transition-metal-free cross-coupling of secondary phosphine chalcogenides and benzenediols using the CCl_4–Et_3N system under mild conditions affords hitherto essentially unknown phosphinochalcogenoic *O*-diesters **9a–i** in high yields. The compounds synthesized are prospective ligands for the preparation of metal



SCHEME 3 Synthesis of bis(diphenethylchalcogenophosphoryl)oxides **11, 12**.

complexes, extractants, flame retardants, and precursors for the design of biologically active compounds.

EXPERIMENTAL

All experiments were carried out under argon. CCl_4 were purified according to standard procedures [17]. Secondary phosphine chalcogenides **1–4** was prepared from styrene or α-methylstyrene and elemental phosphorus and elemental chalcogenes as reported [15]. The reaction was monitored using ^{31}P NMR spectra by the disappearance of peaks of the initial secondary phosphine chalcogenides **1–4** and appearance of new peaks corresponding to phosphinechalcogenoic *O*-diesters **9a–i**. The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded in $CDCl_3$ solutions on a Bruker DPX 400 and Bruker AV-400 spectrometer (Bruker, Germany; 400.13, 100.62, 161.98, and 76.31 MHz, respectively) and referenced to TMS (^{1}H NMR, ^{13}C NMR), H_3PO_4 (^{31}P NMR), and Me_2Se (^{77}Se NMR). IR spectra were run on a Bruker IFS 25 instrument. Mass spectra of electron ionization (70 eV) were obtained on a Shimadzu GCMS–QP5050 *A* (quadruple mass analyzer, the range of detected mass was from 34 to 650 Da); capillary column SPB–5ms (60 m × 0.25 mm × 0.25 μm), gas carrier helium, flow rate 0.7 mL min^{-1}, temperature of injector and ion source 250°C, pressure 100 kPa; temperature programming from 50 to 250°C, 10 deg min^{-1}. Melting points were recorded on a Stuart melting point apparatus and are uncorrected.

*Phosphinechalcogenoic O-Diesters (**9a–i**) (General Procedure)*

A solution of secondary phosphine chalcogenides **1–4** (1.0 mmol) and Et_3N (1.0 mmol) in 4 mL of CCl_4 was stirred at 20–22°C for 10 min. The benzenediols **6–8** (0.5 mmol) or 1,2-benzenediol **5** (0.42 mmol) were added in the reaction mixture. The reaction mixture was stirred at 50–52°C for 1.5-13 h (see also Table 1). The solvent was removed under the reduced pressure, and 1,4-dioxane (3 mL) was added. The precipitated white solid (triethylammonium chloride) was filtered, and 1,4-dioxane was evaporated under vacuum. The residue obtained was washed with Et_2O (2 × 1 mL) and was dried in vacuum to give diesters **9a–i**.

*4-[(Diphenethylphosphoryl)oxy]phenyldiphenethylphosphinate (**9a**).* White powder, yield 0.224 g (72%), mp 116–118°C (hexane). IR (KBr) (cm^{-1}): 1194 (P—O—C), 1172 (P=O). ^{1}H NMR ($CDCl_3$) δ: 2.02–2.18 (m, 8H, CH_2P), 2.82–2.98 (m, 8H, $PhCH_2$), 7.12–7.13, 7.19–7.21, 7.23–7.28 (m, 24H, Ph, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 28.00 ($PhCH_2$), 30.05 (d, CH_2P, $^{1}J_{PC}$ 86.7 Hz), 121.93 (C-2,3,5,6, C_6H_4), 126.60 (C_p), 128.09 (C_o), 128.73 (C_m), 140.36 (d, C_i, $^{3}J_{PC}$ 14.4 Hz), 147.64 (m, C-1,4, C_6H_4). ^{31}P NMR ($CDCl_3$) δ: 56.8. Anal. Calcd for $C_{38}H_{40}O_4P_2$: C, 73.30; H, 6.47; P, 9.95. Found: C, 73.21; H, 6.50; P, 9.89.

*O-{2-[(Diphenethylphosphorothioyl)oxy]phenyl} diphenethylphosphinothioate (**9b**).* Light gray powder, yield 0.173 g (63%), mp 107–109°C (hexane). IR (KBr) (cm^{-1}): 1181 (P—O—C), 617 (P=S). ^{1}H NMR ($CDCl_3$) δ: 2.34–2.46 (m, 8H, CH_2P), 2.87–3.06 (m, 8H, $PhCH_2$), 7.08–7.10, 7.15–7.24 (m, 22H, Ph, H-4,5, C_6H_4), 7.51 (m, 2H, H-3,6, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 29.00 ($PhCH_2$), 36.58 (d, CH_2P, $^{1}J_{PC}$ 65.6 Hz), 123.60 (C-3,6, C_6H_4), 125.38 (C-4,5, C_6H_4), 126.58 (C_p), 128.15 (C_o), 128.72 (C_m), 140.12 (d, C_i, $^{3}J_{PC}$ 16.1 Hz), 142.49 (dd, C-1,2, C_6H_4, $^{2}J_{PC}$ 9.9 Hz, $^{3}J_{PC}$ 4.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 107.0. Anal. Calcd for $C_{38}H_{40}O_2P_2S_2$: C, 69.70; H, 6.16; P, 9.46; S, 9.79. Found: C, 69.72; H, 6.16; P, 9.39; S, 9.73.

*O-{3-[(Diphenethylphosphorothioyl)oxy]phenyl} diphenethylphosphinothioate (**9c**).* White powder, yield 0.239 g (73%), mp 74–76°C (hexane). IR (KBr) (cm^{-1}): 1124 (P—O—C), 629 (P=S). ^{1}H NMR ($CDCl_3$) δ: 2.32–2.49 (m, 8H, CH_2P), 2.92–3.09 (m, 8H, $PhCH_2$), 7.04 (d, 2H, H-4,6, C_6H_4, $^{3}J_{HH}$ 8.2 Hz), 7.16–7.24, 7.26–7.32 (m, 22H, Ph, H-2,5, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 29.02 (d, $PhCH_2$, $^{2}J_{PC}$ 2.4 Hz), 36.46 (d, CH_2P, $^{1}J_{PC}$ 65.9 Hz), 115.88 (t, C-2, C_6H_4, $^{3}J_{PC}$ 4.6 Hz), 118.50 (d, C-4,6, C_6H_4, $^{3}J_{PC}$ 3.6 Hz), 126.70 (C_p), 128.42 (C_o), 128.84 (C_m), 129.99 (C-5, C_6H_4), 130.37 (d, C_i, $^{3}J_{PC}$ 15.6 Hz), 151.20 (d, C-1,3, C_6H_4, $^{2}J_{PC}$ 10.0 Hz). ^{31}P NMR ($CDCl_3$) δ: 105.2. Anal. Calcd for $C_{38}H_{40}O_2P_2S_2$: C, 69.70; H, 6.16; P, 9.46; S, 9.79. Found: C, 69.64; H, 6.14; P, 9.37; S, 9.73.

*O-{4-[(Diphenethylphosphorothioyl)oxy]phenyl} diphenethylphosphinothioate (**9d**).* White powder, yield 0.246 g (75%), mp 69–70°C (hexane). IR (KBr) (cm^{-1}): 1175 (P—O—C), 603 (P=S). ^{1}H NMR ($CDCl_3$) δ: 2.31–2.48 (m, 8H, CH_2P), 2.92-3.10

(m, 8H, $PhCH_2$), 7.15–7.33 (m, 24H, Ph, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 29.09 ($PhCH_2$), 36.49 (d, CH_2P, $^1J_{PC}$ 65.9 Hz), 122.82 (C-2,3,5,6, C_6H_4), 126.77 (C_p), 128.44 (C_o), 128.91 (C_m), 140.43 (d, C_i, $^3J_{PC}$ 15.6 Hz), 147.63 (d, C-1,4, C_6H_4, $^2J_{PC}$ 8.8 Hz). ^{31}P NMR ($CDCl_3$) δ: 104.3. Anal. Calcd for $C_{38}H_{40}O_2P_2S_2$: C, 69.70; H, 6.16; P, 9.46; S, 9.79. Found: C, 69.67; H, 6.15; P, 9.39; S, 9.73.

*O-{2-[(Diphenethylphosphoroselenoyl)oxy]phenyl} diphenethylphosphinoselenoate (***9e***).* White powder, yield 0.195 g (62%), mp 109–111°C (hexane). IR (KBr) (cm^{-1}): 1175 (P—O—C), 572 (P=Se). ^1H NMR ($CDCl_3$) δ: 2.46–2.61 (m, 8H, CH_2P), 2.90–3.09 (m, 8H, $PhCH_2$), 7.10–7.12, 7.20-7.27 (m, 22H, Ph, H-4,5, C_6H_4), 7.53 (m, 2H, H-3,6, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 29.47 ($PhCH_2$), 37.89 (d, CH_2P, $^1J_{PC}$ 55.3 Hz), 123.52 (C-3,6, C_6H_4), 125.44 (C-4,5, C_6H_4), 126.66 (C_p), 128.22 (C_o), 128.77 (C_m), 139.87 (d, C_i, $^3J_{PC}$ 16.6 Hz), 142.72 (dd, C-1,2, C_6H_4, $^2J_{PC}$ 10.3 Hz, $^3J_{PC}$ 4.8 Hz). ^{31}P NMR ($CDCl_3$) δ: 108.6 (+d satellite, $^1J_{PSe}$ 811.1 Hz). ^{77}Se NMR ($CDCl_3$) δ: −239.9 (d, $^1J_{PSe}$ 811.1 Hz). Anal. Calcd for $C_{38}H_{40}O_2P_2Se_2$: C, 60.97; H, 5.39; P, 8.28; Se, 21.10. Found: C, 60.89; H, 5.36; P, 8.21; Se, 20.98.

*O-{3-[(Diphenethylphosphoroselenoyl)oxy]phenyl} diphenethylphosphinoselenoate (***9f***).* Waxy product, yield 0.314 g (84%). IR (neat) (cm^{-1}): 1123 (P—O—C), 582 (P=Se). ^1H NMR ($CDCl_3$) δ: 2.46–2.61 (m, 8H, CH_2P), 2.90–3.09 (m, 8H, $PhCH_2$), 7.04 (d, 2H, H-4,6, C_6H_4, $^3J_{HH}$ 8.1 Hz), 7.20–7.33 (m, 22H, Ph, H-2,5, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 29.47 ($PhCH_2$), 37.89 (d, CH_2P, $^1J_{PC}$ 55.6 Hz), 115.82 (t, C-2, $^3J_{PC}$ 4.6 Hz), 118.56 (d, C-4,6, $^3J_{PC}$ 3.5 Hz), 126.60 (C_p), 128.32 (C_o), 128.69 (C_m), 129.77 (C-5, C_6H_4), 139.91 (d, C_i, $^3J_{PC}$ 15.3 Hz), 151.15 (d, C-1,3, C_6H_4, $^2J_{PC}$ 9.8 Hz). ^{31}P NMR ($CDCl_3$) δ: 108.6 (+d satellite, $^1J_{PSe}$ 811.1 Hz). ^{77}Se NMR ($CDCl_3$) δ: −239.9 (d, $^1J_{PSe}$ 811.1 Hz). Anal. Calcd for $C_{38}H_{40}O_2P_2Se_2$: C, 60.97; H, 5.39; P, 8.28; Se, 21.10. Found: C, 60.89; H, 5.36; P, 8.21; Se, 20.98.

*O-{4-[(Diphenethylphosphoroselenoyl)oxy]phenyl} diphenethylphosphinoselenoate (***9g***).* Light gray powder, yield 0.333 g (89%), mp 148–149°C (hexane). IR (KBr) (cm^{-1}): 1181 (P—O—C), 578 (P=Se). ^1H NMR ($CDCl_3$) δ: 2.45–2.53 (m, 8H, CH_2P), 2.89–3.08 (m, 8H, $PhCH_2$), 7.16–7.23, 7.27–7.30 (m, 24H, Ph, C_6H_4). ^{13}C NMR ($CDCl_3$) δ: 29.55 ($PhCH_2$), 37.80 (d, CH_2P, $^1J_{PC}$ 56.0 Hz), 122.83 (C-2,3,5,6, C_6H_4), 126.80 (C_p), 128.46 (C_o), 128.91 (C_m), 140.14 (d, C_i, $^3J_{PC}$ 15.6 Hz), 147.96 (d, C-1,4, C_6H_4, $^2J_{PC}$ 9.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 109.4 (+d satellite, $^1J_{PSe}$ 803.4 Hz). ^{77}Se NMR ($CDCl_3$) δ: −250.2 (d, $^1J_{PSe}$ 803.4 Hz). Anal. Calcd for $C_{38}H_{40}O_2P_2Se_2$: C, 60.97; H, 5.39; P, 8.28; Se, 21.10. Found: C, 61.01; H, 5.35; P, 8.21; Se, 21.02.

*O-[4-(1-{4-[(Diphenethylphosphoroselenoyl)oxy] phenyl}-1-methylethyl)phenyl]diphenethylphosphinoselenoate (***9h***).* White powder, yield 0.394 g (91%), mp 97–98°C (hexane). IR (KBr) (cm^{-1}): 1170 (P—O—C), 575 (P=Se). ^1H NMR ($CDCl_3$) δ: 1.69 (s, 6H, Me), 2.51–2.60 (m, 8H, $PhCH_2$), 2.98–3.11 (m, 8H, CH_2P), 7.04 (d, 4H, H-2,6, C_6H_4, $^3J_{HH}$ 7.3 Hz) 7.12–7.14 (m, 12H, Ph, H_o, H_p), 7.18 (d, 4H, H-3,5, C_6H_4, $^3J_{HH}$ 7.3 Hz), 7.25 (dd, 8H, H_m, Ph, $^3J_{HH}$ 8.1 Hz, $^3J_{HH}$ 7.3 Hz,). ^{13}C NMR ($CDCl_3$) δ: 29.41 ($PhCH_2$), 30.93 (Me), 37.62 (d, CH_2P, $^1J_{PC}$ 56.3 Hz), 42.38 (*C*Me), 121.16 (d, C-2,6, C_6H_4, $^3J_{PC}$ 3.4 Hz), 126.60 (C-3,5, C_6H_4), 127.88 (C_p), 128.31 (C_o), 128.73 (C_m), 140.12 (d, C_i, $^3J_{PC}$ 15.6 Hz), 147.26 (C-4, C_6H_4), 148.72 (d, C-1, C_6H_4, $^2J_{PC}$ 10.0 Hz). ^{31}P NMR ($CDCl_3$) δ: 104.5 (+d satellite, $^1J_{PSe}$ 799.6 Hz). ^{77}Se NMR ($CDCl_3$) δ: −248.7 (d, $^1J_{PSe}$ 800.9 Hz). Anal. Calcd for $C_{47}H_{50}O_2P_2Se_2$: C, 65.13; H, 5.81; P, 7.15; Se, 18.22. Found: C, 65.08; H, 5.79; P, 7.08; Se, 18.18.

*O-(4-{[Bis(2-phenylpropyl)phosphoroselenoyl] oxy}phenyl)bis(2-phenylpropyl)phosphinoselenoate (***9i***).* Waxy product, yield 0.362 g (90%). IR (neat) (cm^{-1}): 1170 (P—O—C); 550, 575 (P=Se). ^1H NMR ($CDCl_3$) δ: 1.22, 1.28, 1.31, and 1.37 (4d, 12H, *Me*CH, $^3J_{PH}$ 7.0 Hz, $^3J_{PH}$ 7.1 Hz, $^3J_{PH}$ 7.1 Hz, $^3J_{PH}$ 7.1 Hz, respectively), 1.72–1.80, 2.05–2.48 (m, 8H, CH_2P), 3.21–3.31, 3.34–3.49 (m, 4H, PhCH), 6.53, 6.57–6.61, 6.69–6.77, 6.85–6.92 (m, 4H, C_6H_4), 7.09–7.19, 7.22–7.25, 7.27–7.33 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$) δ: 23.58 (d, *Me*CH, $^3J_{PC}$ 11.6 Hz), 23.89 (d, *Me*CH, $^3J_{PC}$ 12.7 Hz), 24.29 (d, *Me*CH, $^3J_{PC}$ 12.4 Hz), 24.42 (d, *Me*CH, $^3J_{PC}$ 12.7 Hz), 35.36, 35.40, 35.61, 35.82 (4s, PhCH), 43.95 (d, CH_2P, $^1J_{PC}$ 55.1 Hz), 44.13 (d, CH_2P, $^1J_{PC}$ 56.3 Hz), 44.30 (d, CH_2P, $^1J_{PC}$ 55.1 Hz), 44.94 (d, CH_2P, $^1J_{PC}$ 55.5 Hz), 122.00–122.23 (m, C-2,3,5,6, C_6H_4), 126.48–126.79, 127.02–127.28, 128.51–128.67 (m, C_o, C_m, C_p), 145.46–145.61, 145.75–145.90 (m, C_i), 147.09–147.29 (m, C-1,4, C_6H_4). ^{31}P NMR ($CDCl_3$) δ: 103.55–103.64, 106.04–106.18, 106.94–107.14 (m). ^{77}Se NMR ($CDCl_3$) δ: −(223.3–223.5), −232.0, −(232.6–233.1), −(233.7–233.9), −242.5, −(243.1÷243.5) (m). Anal. Calcd for $C_{42}H_{48}O_2P_2Se_2$: C, 62.69; H, 6.01; P, 7.70; Se, 19.62. Found: C, 62.65; H, 5.97; P, 7.63; Se, 19.57.

*Phosphinochalcogenoic O-ester (***10***)*

A solution of secondary phosphine selenide **3** (1.0 mmol) and Et_3N (1.0 mmol) in 4 mL of CCl_4 was stirred at 20–22°C for 10 min. The

benzenediol **7** (1.0 mmol) was added in the reaction mixture. The reaction mixture was stirred at 50–52°C for 3 h. The solvent was removed under the reduced pressure, and 1,4-dioxane (3 mL) was added. The precipitated white solid (triethylammonium chloride) was filtered, and 1,4-dioxane was evaporated under vacuum. The residue obtained was consecutively washed with hexane (2 × 1 mL) and Et_2O (3 × 1 mL). The residue was dried in vacuum to give diester **9g** (yield 0.213 g, 57%). Hexane solution was evaporated in vacuum to afford bis(diphenethylselenophosphoryl)oxide **12** (yield 0.02 g, 6%). The ether solution was evaporated in vacuum to give 0.13 g (30%) of *O*-(4-hydroxyphenyl)diphenethylphosphinoselenoate **10** as a waxy product. IR (KBr) (cm^{-1}): 3326 (OH), 1192 (P—O—C), 581 (P=Se). ^{1}H NMR ($CDCl_3$) δ: 2.47–2.54 (m, 4H, CH_2P), 2.94-3.04 (m, 4H, $PhCH_2$), 6.76 (d, H-3.5, $^3J_{HH}$ 8.8 Hz), 6.99 (dd, H-2,6, $^3J_{HH}$ 8.8 Hz, $^4J_{PH}$ 1.6 Hz), 7.20 (m, 6H, H_o, H_p, Ph), 7.30 (dd, $^3J_{HH}$ 8.0 Hz, $^3J_{HH}$ 7.7 Hz, 4H, H_m, Ph). ^{13}C NMR ($CDCl_3$) δ: 29.57 ($PhCH_2$), 38.95 (d, CH_2P, $^1J_{PC}$ 56.7 Hz), 116.10 (C-3,5, C_6H_4), 122.83 (d, $^3J_{PC}$ 4.0 Hz, C-2,6, C_6H_4), 126.66 (C_p), 128.45 (C_m), 128.78 (C_o), 140.12 (d, C_i, $^3J_{PC}$ 15.6 Hz), 143.96 (d, C-1, $^2J_{PC}$ 10.0 Hz), 153.30 (C-4, C_6H_4). ^{31}P NMR ($CDCl_3$) δ: 105.6 (+d satellite, $^1J_{PSe}$ 792.3 Hz). ^{77}Se NMR ($CDCl_3$) δ: −252.6 (d, $^1J_{PSe}$ 792.3 Hz). Anal. Calcd for $C_{22}H_{23}O_2PSe$: C, 61.54; H, 5.40; P, 7.21; Se, 18.39. Found: C, 61.50; H, 5.39; P, 7.18; Se, 18.37.

*Bis(diphenethylchalcogenophosphoryl)oxides (**11, 12**)*

To a solution of phosphine chalcogenides **2, 3** (1.0 mmol) in 4 mL of CCl_4 was added to a solution of Et_3N (1.0 mmol) and H_2O (0.5 mmol) in 1 mL of 1,4-dioxane, and the reaction mixture was stirred at 20–22°C for 4 h. The solvent was removed under the reduced pressure, and 1,4-dioxane (3 mL) was added. The precipitated white solid (triethylammonium chloride) was filtered, and 1,4-dioxane was evaporated under vacuum to give bis(diorganochalcogenophosphoryl)oxides **11, 12**.

*Bis(diphenethylthiophosphoryl)oxide (**11**).* White powder, yield 0.280 g (99%), mp 91–92°C (hexane). IR (KBr) (cm^{-1}): 958 (P—O—P), 615 (P=S). ^{1}H NMR ($CDCl_3$) δ: 2.36–2.56 (m, 8H, CH_2P), 2.97–3.04 (m, 8H, $PhCH_2$), 7.21–7.27, 7.28–7.30 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$) δ: 28.66 ($PhCH_2$), 37.43 (m, CH_2P), 126.26 (C_p), 127.99 (C_o), 128.36 (C_m), 139.91 (2d, C_i, $^3J_{PC}$ 7.7 Hz). Anal. Calcd for $C_{32}H_{36}OP_2S_2$: C, 68.30; H, 6.45; P, 11.01; S, 11.40. Found: C, 68.34; H, 6.43; P, 10.89; S, 11.36.

*Bis(diphenethylselenophosphoryl)oxide (**12**).* White powder, yield 0.325 g (99%), mp 81–82°C (hexane). IR (KBr) (cm^{-1}): 956 (P—O—P), 574 (P=Se). ^{1}H NMR ($CDCl_3$) δ: 2.47–2.68 (m, 8H, CH_2P), 2.96–3.03 (m, 8H, $PhCH_2$), 7.21–7.25, 7.27–7.33 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$) δ: 29.64 ($PhCH_2$), 39.14 (m, CH_2P), 126.84 (C_p), 128.58 (C_o), 128.90 (C_m), 139.88, 139.96 (2 d, C_i, $^3J_{PC}$ 7.7 Hz). ^{31}P NMR ($CDCl_3$) δ: 102.9 (+dd satellites, $^1J_{PSe}$ 817.5 Hz, $^2J_{PP}$ 37.9 Hz). ^{77}Se NMR ($CDCl_3$): δ = −181.3 (d, $^1J_{PSe}$ 817.5 Hz). Anal. Calcd for $C_{32}H_{36}OP_2Se_2$: C, 58.54; H, 5.53; P, 9.44; Se, 24.06. Found: C, 58.48; H, 5.55; P, 9.38; Se, 23.98.

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