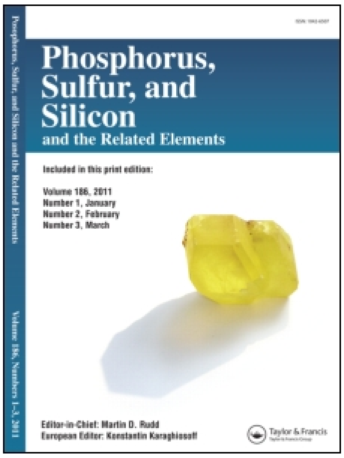

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Synthesis and Characterization of O,O-Dialkyl and Alkylene Dithiophosphoric Acid Adducts of Diphenyl Diselenide

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SYNTHESIS AND CHARACTERIZATION OF O,O-DIALKYL AND ALKYLENE DITHIOPHOSPHORIC ACID ADDUCTS OF DIPHENYL DISELENIDE

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Diphenyl diselenide reacts with O,O-dialkyl and alkylene dithiophosphoric acids in equimolar amounts in refluxing benzene to yield $Ph_2Se_2HS_2P(OR)_2$, $R = Et$, *Pr-n, Pr-i, Bu-i and Ph, and* $Ph_2Se_2HS_2\overline{POGO}$ *where* $G = CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$, *and* $-CMe_2CMe_2-$*. The complexes are sticky solids, soluble in common organic solvents and monomeric in nature. These have been characterized on the basis of elemental analysis, molecular weight determinations, UV, IR, and NMR (*^1H*,* ^{13}C*, and* ^{31}P *NMR). Spectral data reveal addition of dithiophosphate moieties to* Ph_2Se_2*.*

INTRODUCTION

For higher organisms, selenium is an essential trace element,[1] a Se—free diet leads to malfunction of the liver and to hemolytic processes. Selenium plays its biochemical role as a component of glutathione peroxidase, an enzyme that is responsible for the protection of essential SH-groups and for the decomposition of peroxides, thereby acting as an antioxidant.[2] A particularly intriguing idea is to combine organoselenium moieties, which show biocidal activity with organophosphorus moieties, which are also known for their biocidal effect.[3–5] The combination of the two kinds of biological activity in a single molecule could produce a still more powerful and lasting effect and prevent

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the problems associated with development of tolerance to each kind. We initiate this series of papers with a description of the synthesis of the organoselenium dithiophosphate esters. These dithio-ligands are also of interest structurally[6] since several modes of attachment are in principle possible, including mono-dentate,[7–10] bidentate,[11–13] or bridging[14,15] ligands in an oligomeric form, a syn dimer and that of bridging ligand in an associated polymer chain.[16,17] The present article gives new information concerning the donor properties of these acids as neutral ligands.

RESULTS AND DISCUSSION

The reactions of diphenyl diselenide with dialkyl and alkylene dithiophosphoric acids in refluxing benzene with constant stirring, resulted in the formation of addition compounds of 1:1 stoichiometry as shown in Eqs. 1 and 2.

$$Ph_2Se_2 + HS_2P(OR)_2 \longrightarrow Ph_2Se_2\,HS_2P(OR)_2 \tag{1}$$

Where R = Et, Pr-n, Pr-i, Bu-i and Ph

$$Ph_2Se_2 + HS_2\overline{POGO} \longrightarrow Ph_2Se_2HS_2\overline{POGO} \tag{2}$$

$$G = -CH_2CMe_2CH_2-, -CH_2CEt_2CH_2- \text{ and } -CMe_2CMe_2-.$$

The color of the reaction medium changes from orange to yellow with the progress of the reaction. Dialkyl and alkylene dithiophosphoric acid adducts of diphenyl diselenide derivatives are yellow sticky solids in open derivatives and yellow solids in cyclic derivatives. The products were washed with n-hexane several times and finally dried under reduced pressure. These compounds are soluble in common organic solvents such as benzene, dichloromethane, and chloroform, but insoluble in n-hexane. However, attempts to crystallize the solid compounds from benzene/n-hexane mixture were unsuccessful. The molecular weight (Table I) of all these derivatives determined by volumetric titration in ethanol, indicated a monomeric nature of these products.

IR Spectra

The presence of medium intensity bands in the region 2580–2403 cm^{-1} may be assigned to νS—H vibrations.[18] This supports the proposed addition reaction (Table II). The strong intensity bands present in the

TABLE I Synthesis and Physical Properties of Dialkyl and Alkylene Dithiophosphoric Acid Adducts of Diphenyl Diselenide

	Reactants g (mmol)					Elemental analysis		
SI no.	Diphenyl diselenide	Dithiophosphoric acid	Molar ratio	Product g (mmol)	Yield (%)	Se Found/(Calc)	S Found/(Calc)	Mol. wt. Found/(Calc)
1		$HS_2P(OEt)_2$		$Ph_2Se_2HS_2P(OEt)_2$		—	—	—
	0.390 (1.25)	0.233 (1.25)	1:1	0.54 (1.08)	87	(31.69)	(12.87)	(498.37)
2		$HS_2P(OPr\text{-}n)_2$		$Ph_2Se_2HS_2(OPr\text{-}n)_2$		29.23	12.93	514
	0.413 (1.32)	0.284 (1.32)	1:1	0.63 (1.20)	90	(30.00)	(12.18)	(526.42)
3		$HS_2P(OPr\text{-}i)_2$		$Ph_2Se_2HS_2P(OPr\text{-}i)_2$		29.11	13.06	516
	0.480 (1.54)	0.330 (1.54)	1:1	0.75 (1.42)	93	(30.00)	(12.18)	(526.42)
4		$HS_2P(OBu\text{-}i)_2$		$Ph_2Se_2HS_2P(OBu\text{-}i)_2$		27.80	11.25	543
	0.356 (1.14)	0.276 (1.14)	1:1	0.58 (1.05)	91	(28.48)	(11.57)	(554.47)
5		$HS_2P(OPh)_2$		$Ph_2Se_2HS_2P(OPh)_2$		25.70	11.23	585
	0.524 (1.68)	0.474 (1.68)	1:1	0.82 (1.38)	81	(26.57)	(10.79)	(594.46)
6		$HS_2POCH_2CMe_2CH_2O$		$Ph_2Se_2HS_2POCH_2CMe_2CH_2O$		30.12	11.62	498
	0.482 (1.54)	0.306 (1.54)	1:1	0.74 (1.45)	94	(30.95)	(12.57)	(510.28)
7		$HS_2POCH_2CEt_2CH_2O$		$Ph_2Se_2HS_2POCH_2CEt_2CH_2O$		28.53	11.09	527
	0.523 (1.68)	0.379 (1.68)	1:1	0.80 (1.49)	89	(29.34)	(11.91)	(538.33)
8		$HS_2POCMe_2CMe_2O$		$Ph_2Se_2HS_2POCMe_2CMe_2O$		29.67	11.43	516
	0.445 (1.43)	0.302 (1.43)	1:1	0.65 (1.24)	87	(30.12)	(12.23)	(524.31)

TABLE II Some Relevant IR Spectral Data (cm^{-1}) of Dialkyl and Alkylene Dithiophosphoric Acid Adducts of Diphenyl Diselenide

SI no.	Compounds	ν ((P)—O—C)	ν (P—O—(C))	Ring vibration	ν (P=S)	ν (P—S)	ν (S—H)	ν (Se—S)
1	$Ph_2Se_2HS_2P(OEt)_2$	1024.1, s	846.0, s	—	669.3, m	507.2, m	2410.9, m	370, w
2	$Ph_2Se_2HS_2(OPr\text{-}n)_2$	999.1, s	843.0, m	—	671.2, s	515.0, w	2403.1, m	380, m
3	$Ph_2Se_2HS_2P(OPr\text{-}i)_2$	1020.3, s	836.0, m	—	669.3, s	520.0, m	2403.1, m	375, m
4	$Ph_2Se_2HS_2P(OBu\text{-}i)_2$	1020.3, s	848.6, s	—	667.3, s	510.7, w	2403.1, m	370, w
5	$Ph_2Se_2HS_2P(OPh)_2$	1215.1, s	933.0, s	—	669.3,s	508.0, w	2410.2, m	378, w
6	$Ph_2Se_2HS_2\overline{POCH_2CMe_2CH_2O}$	1047.3, s	850.0, m	999.1, s	669.3, s	507.2, s	2579.0, m	377, m
7	$Ph_2Se_2HS_2\overline{POCH_2CEt_2CH_2O}$	1068.5, s	820.0, s	937.3, s	667.3, s	509.2, s	2578.0, m	380, m
8	$Ph_2Se_2HS_2\overline{POCMe_2CMe_2O}$	1022.2, s	848.6, s	929.6, s	667.3, s	586.3, s	2578.0, w	379,m

m = medium absorption bands; s = strong absorption bands; w = weak absorption bands.

region 1215–999 cm^{-1} and 850–820 cm^{-1} may be assigned to ν(P)—O—C and νP—O—(C) vibrations respectively.[19,20] Strong bands assigned to dioxaphospholane and dioxaphosphorinane ring vibrations are present in the region 999–929 cm^{-1} and these are probably coupled with C—C stretching vibrations.[21,22] A sharp band present in the region 688–667 cm^{-1} can be assigned to νP=S vibrations.[23] This band shows notable shifting ($\Delta = 15$ cm^{-1}) toward higher frequency in open chain derivatives, but in cyclic chain derivatives there is a shift toward lower frequency ($\Delta = 13.8$ cm^{-1}) with respect to its position in the free ligands. This shifting is probably due to coordination of sulfur of the P=S group to a selenium atom. The bands of medium intensities in the region 586–507 cm^{-1} may be assigned to νP—S asymmetric and symmetric vibrations.

New bands observed in the region 380–370 cm^{-1} are probably due to νSe—S stretching vibrations.[24,25]

^{1}H NMR Spectra

The ^{1}H NMR spectra (Table III) of these derivatives show the characteristic proton resonance due to corresponding glycoxy and alkoxy groups. The chemical shift as well as the coupling constants are almost the same as those observed for the corresponding ligand dithiophosphoric acids, thus indicating that complexation with selenium does not have any pronounced effect. The S—H protons have been observed in the region (δ 2.68–5.78 ppm),[26] which supports an addition reaction. All the complexes show a shift for the S—H proton (~0.09–0.97 ppm) toward lower field, except diphenyl diselenide diisopropyl and diisobutyl dithiophosphoric acid which show shifts of 2.52 and 2.07 ppm respectively, with comparison to its position in the parent ligands.

The complex multiplets due to the protons of the phenyl groups attached to the selenium atoms were present at δ 7.16–7.73 ppm.

^{13}C NMR Spectra

The ^{13}C NMR spectral data for some of the derivatives (Table IV) of diphenyl diselenide dialkyl and alkylene dithiophosphoric acid adducts were recorded in deuterated chloroform solution. In the spectra of these complexes four signals for phenyl carbons have been observed in the region δ 131.84–127.99 ppm for C_1, $C_{2,6}$, $C_{3,5}$, and C_4 respectively. The appearance of a single set of signals for the carbons of phenyl group show the equivalent nature of the phenyl groups. The signals for dialkyl and alkylene carbons were observed at expected positions.

TABLE III ^{1}H and ^{31}P NMR Spectral Data of Dialkyl and Alkylene Dithiophosphoric Acid Adducts of Diphenyl Diselenide

SI no.	Compounds	^{1}H chemical shift in δ ppm in $CDCl_3$	^{31}P chemical shift in δ ppm (parent acid)
1	$Ph_2Se_2\ HS_2P(OEt)_2$	—	82.087 (85.70)
2	$Ph_2Se_2HS_2P(OPr\text{-}n)_2$	0.94–0.99, t, 6H(CH_3) 1.65–1.79, m, 4H(CH_2) 3.02, s, H(SH) 4.06–4.14, m, 4H(OCH_2) 7.20–7.60, m, 10H(C_6H_5)	85.500 (86.10)
3	$Ph_2Se_2HS_2P(OPr\text{-}i)_2$	1.25–1.52, d, 12H(CH_3) 5.78, s, H(SH) 4.70–4.96, m, 2H(OCH) 7.16–7.72, m, 10H(C_6H_5)	82.453 (82.30)
4	$Ph_2Se_2HS_2P(OBu\text{-}i)_2$	0.93–1.01, d, 12H(CH_3) 1.83–2.08, m, 2H(CH) 3.82–4.04, m, 4H(OCH_2) 5.16, s, H(SH) 7.16–7.73, m, 10H(C_6H_5)	86.412 (85.70)
5	$Ph_2Se_2HS_2P(OPh)_2$	3.98, s, H(SH) 6.89–7.71, m, 20H(C_6H_5 and OC_6H_5)	— (79.90)
6	$Ph_2Se_2HS_2\overline{POCH_2CMe_2CH_2O}$	1.07, s, 6H(CH_3) 3.07, s, H(SH) 4.026–4.078, d, (J = 15.6 Hz), 4H(OCH_2). 7.21–7.64, m, 10H(C_6H_5)	77.273 (77.30)
7	$Ph_2Se_2HS_2\overline{POCH_2CEt_2CH_2O}$	0.853–0.902, t, 6H(CH_3) 1.45–1.53, q, 4H(CH_2) 2.68, s, H(SH) 4.109–4.160, d (J = 15.3 Hz), 4H(OCH_2), 7.21–7.62, m, 10H(C_6H_5)	78.605 (78.50)
8	$Ph_2Se_2HS_2\overline{POCMe_2CMe_2O}$	1.46, s, 12H(CH_3) 4.16, s, H(SH) 7.25–7.63, m, 10H(C_6H_5)	93.303 (93.10)

s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; J = $^{3}J_{(H,P)}$.

TABLE IV ^{13}C NMR Spectral Data of Some Dialkyl and Alkylene Dithiophosphoric Acid Adducts of Diphenyl Diselenide (δ ppm)

		Ph_2Se_2 Carbons				Dialkyl and Alkylene Dithiophosphate				
SI no.	Compound	C_1	$C_{2,6}$	$C_{3,5}$	C_4	CH_3	CH_2	CH	C	CO
3	$Ph_2Se_2HS_2P(OPr\text{-}i)_2$	131.74	131.14	129.46	127.99	23.77, s	—	—	—	73.59, s
6	$Ph_2Se_2HS_2POCH_2C(Me)_2CH_2O$	131.84	131.45	129.61	128.12	21.78, s	—	—	32.78 (d, J = 7.3 Hz)	77.28, s
8	$Ph_2Se_2HS_2POC(Me)_2C(Me)_2O$	131.74	131.30	129.49	128.04	24.32 (d, J = 4.8 Hz)	—	—	—	91.14, s

s = singlet; d = doublet.

^{31}P NMR Spectra

The ^{31}P NMR spectra (Table III) of dialkyl and alkylene dithiophosphoric acid adducts of diphenyl diselenide have been recorded in $CDCl_3$, which show only one signal for each compound, in the region δ 93.1–82 ppm. The differences in chemical shift between some of the parent acids and their addition compounds equal δ 0.71–0.11 ppm toward lower field from their position in the corresponding acids, this is probably due to the dative $P{=}S \rightarrow M$ bonding.

In these complexes, both thiolato and thiono sulfur atoms are potential donors. However, the stoichiometry of the adducts formed indicates that these acids are behaving as monodentate ligands toward diphenyl diselenide.

UV Spectra

The UV spectra of dialkyl and alkylene dithiophosphoric acids are shown in Table V. The comparison of the UV spectra of the starting materials with the UV spectra of the resulting complexes does not show any new peaks, but it shows small shifts in λ_{max}. This proves that the dithiophosphoric acids reacted with diphenyl diselenide as neutral ligands.

The above observations based on molecular weight and spectral data are consistent with trigonal bipyramidal geometry for these complexes with two lone pairs of electrons, two single bonds (phenyl—Se and Se—Se), and one dative bond from S〉 M. Therefore, the dialkyl and alkylene dithiophosphoric acid adducts of diphenyl diselenide complexes may be assigned the following structure:

EXPERIMENTAL

Moisture was carefully excluded throughout the experimental manipulations. Dialkyl[27] and alkylene[20] dithiophosphoric acids were prepared

TABLE V Some Relevant UV Spectral Data (nm) of Dialkyl and Alkylene Dithiophosphoric Acid Adducts of Diphenyl Diselenide

SI no.	Complexes	λ_{max}	Acids and starting material	λ_{max}
3	$Ph_2Se_2HS_2P(OPr\text{-}i)_2$	334.0 240.5	$HS_2P(OPr\text{-}i)_2$	312.5 226.0
6	$Ph_2Se_2HS_2\overline{POCH_2CMe_2CH_2O}$	335.0 233.5	$HS_2\overline{POCH_2CMe_2CH_2O}$	313.0 208.5
			Ph_2Se_2	332.5 238.5

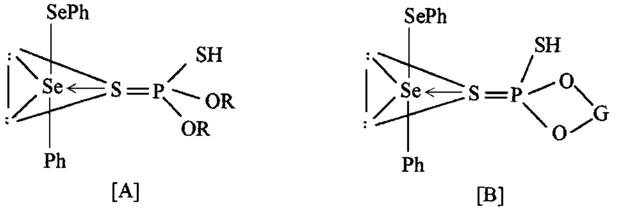

FIGURE 1 Suggested structures of trigonal bipyramidal dialkyl [A] and alkylene [B] dithiophosphoric acid adducts of diphenyl diselenide.

by standard methods. Glycol was distilled before use, diphenyl diselenide (Merck) was used as such. Sulfur was determined by Messenger's method as barium sulfate. Selenium was determined by iodometric titration.

UV spectra were recorded in ethanol in the region 500–200 nm on the UV-visible Spectrophotometer-1601 Shimadzu (Japan). IR spectra were recorded as Nujol mulls using CsI cells in region 4000–200 cm^{-1} on a FT-IR 8201 PC spectrometer. ^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Jeol-FT-NMR spectrometer, LA300, using TMS as internal reference (for ^{1}H and ^{13}C) and H_3PO_4 (for ^{31}P) as external reference.

The following synthetic details for one specific 1:1 addition reaction represent the procedure used to synthesize all compounds.

Reaction between Diphenyl Diselenide with Dialkyl (OPr-i) and Alkylene Dithiophosphoric Acid in 1:1 Molar Ratio

A benzene (~10 ml) solution of $HS_2P(OPr\text{-}i)_2$ (0.330 g, 1.54 mmol) was added to benzene (~15 ml) solution of Ph_2Se_2 (0.480 g, 1.54 mmol) drop wise with constant stirring at room temperature. The reaction mixture was refluxed for ~4 h, during which the color of the reaction mixture changed from orange to yellow. The excess solvent was removed under reduced pressure and the product washed repeatedly by n-hexane the product was finally dried under reduced pressure.

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