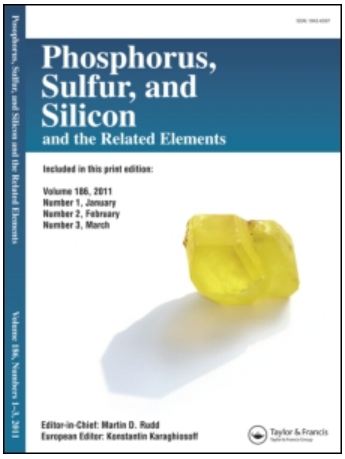

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1,2-Alkatrienephosphonates in the Reactions with Sulfenyl- and Selenenylbromides

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1,2-Alkatrienephosphonates in the Reactions with Sulfenyl- and Selenenylbromides

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The interaction of 1,2-alkatrienephosphonic dichlorides and dialkyl esters with sulfenyl- and selenenylbromides is investigated and a possible mechanism of the reactions is discussed. The possibility to control the structure of the products by variation of the type of the electrophile and of the substrate is also shown.

Keywords 1,2-Alkatrienephosphonates; selenenylbromides; sulfenylbromides

INTRODUCTION

1,2-Alkatrienephosphonates, i.e., 3- and 1-vinylsubstituted 1,2-alkadienephosphonic dichlorides and esters, are interesting substrates, containing both 1,2- and 1,3-dienic fragments in the alkatrienephosphonate system.[1–9] These compounds react with different kinds of electrophilic reagents to a variety of products: 2,5-dihydro-1,2-oxaphosphole derivatives, phosphorus containing thiophenes and selenophenes, as well as adducts.[1–4,6–8,10–15] On the other hand, the interaction of the dialkyl esters of alkatrienephosphonic acids with sulfur dioxide affords cyclic sulphonephosphonates.[11–13]

Here, we report our results on the reactivity of the dichlorides and of the dialkyl esters of 3-methyl-1,2,4-pentatrienyl-1- and 5-methyl-1,3,4-hexatrienyl-3-phosphonic acids with sulfenyl- and selenenylbromides.

RESULTS AND DISCUSSION

The reaction of the dichlorides and of the dialkyl esters of 3-methyl-1,2,4-pentatrienyl-1- and 5-methyl-1,3,4-hexatrienyl-3-phosphonic

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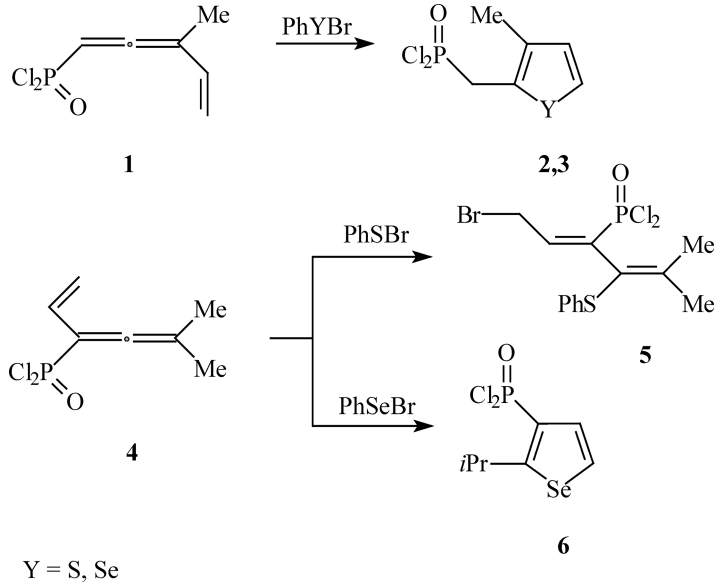
acids with sulfenyl- and selenenylbromides is carried out in methylene chloride at low temperature. As expected, the reactions lead to phosphorylated thiophenes, phosphorylated selenophenes, and to additional products (Scheme 1).

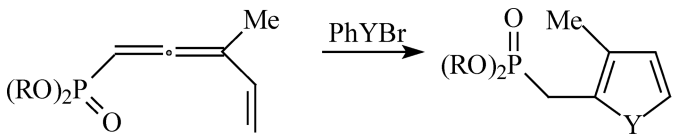


SCHEME 1

The structures of the products confirmed our expectation, that 3-methyl-1,2,4-pentatriene-1-phosphonic dichloride **1** reacts with sulfenyl- and selenenylbromides with formation of a thiophene and selenophene ring to afford the dichloride of (3-methylthiophen-2-yl)methylphosphonic acid **2** and of (3-methylselenophen-2-yl)methylphosphonic acid **3**, respectively. The reaction of the dichloride of 5-methyl-1,3,4-hexatriene-3-phosphonic acid **4** with phenylsulfenylbromide leads to 1-bromo-5-methyl-4-phenylthio-2,4-pentadienyl-3-phosphonic dichloride **5**, while with phenylselenenylbromide 2-isopropyl-3-selenophenephosphonic dichloride the selenophene **6** was isolated.

The reaction of the 3-methyl-1,2,4-pentatriene-1-phosphonic acid dialkyl esters **7a–e** with phenylsulphenyl- and phenylselenenylbromides leads to the corresponding dialkyl esters of (3-methylthiophen-2-yl)methylphosphonic acid **8a–e** and (3-methylselenophen-2-yl)methylphosphonic acid **9a–e**, respectively (Scheme 2).

On the other hand, the reaction of dialkyl esters of 5-methyl-1,3,4-hexatriene-3-phosphonic acid **10a–e** with phenylsulphenylbromide



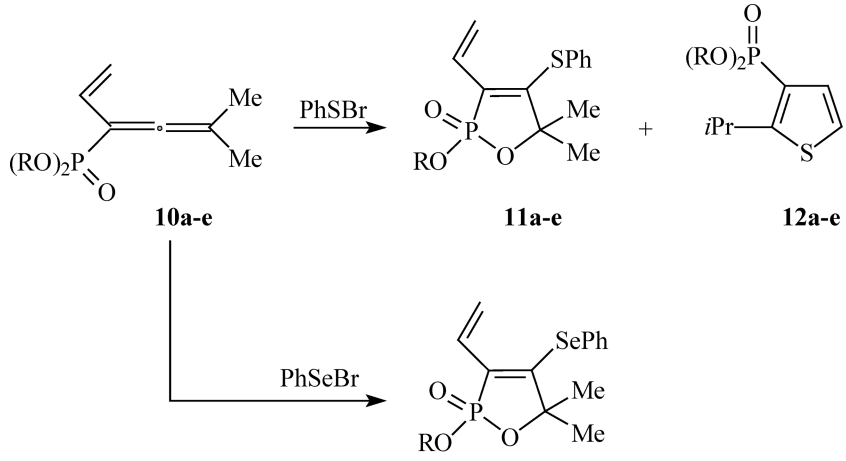
7a-e **8a-e, 9a-e**

Y = S (**8**), Se (**9**)
R = Me (**a**), Et (**b**), Pr (**c**), *i*Pr (**d**), *sec*-Bu (**e**)

SCHEME 2

leads to the corresponding oxaphospholes **11a–e** and thiophenes **12a–e**, respectively. When the same dialkyl esters are reacted with phenylselenenyl bromide cyclization to the vinyl-substituted 2,5-dihydro-1,2-oxaphosphole derivatives **13a–e** takes place (Scheme 3).

Compounds **3**, **6**, **9a–e**, and **13a–e** contain the isotope ^{77}Se, which is magnetically active and interacts with other nuclei. This interaction becomes evident with the protons of the neighboring groups which exhibit symmetric ^{77}Se satellite signals on both sides of the main signal in the ^{1}H NMR spectra.[22]

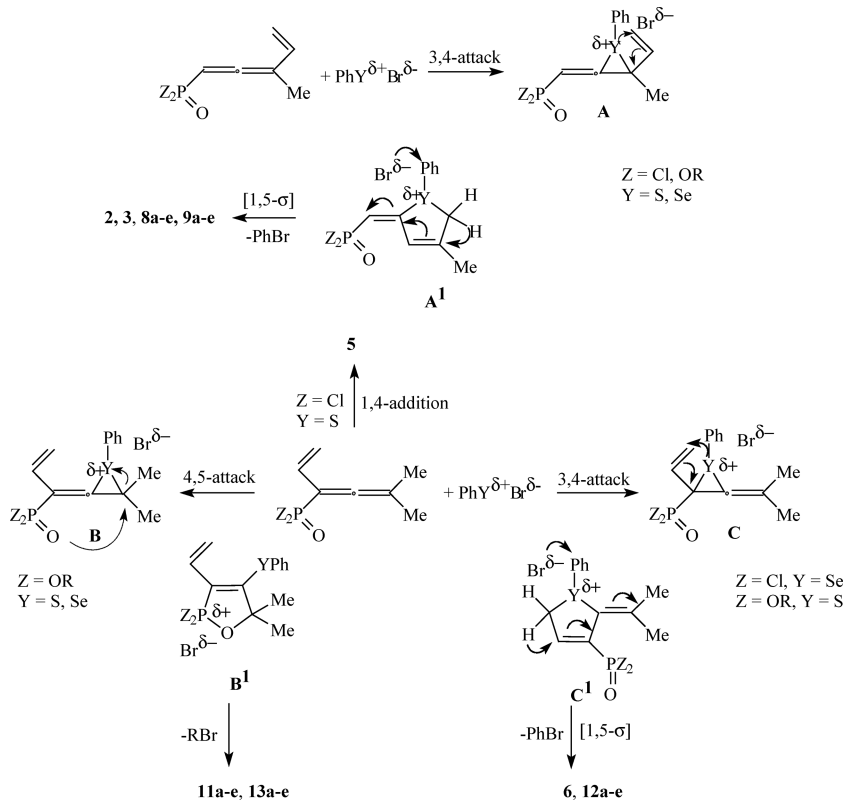


10a-e **11a-e** **12a-e**

13a-e

R = Me (**a**), Et (**b**), Pr (**c**), *i*Pr (**d**), *sec*-Bu (**e**)

SCHEME 3



SCHEME 4

Our previous investigations[11–15] and the isolation of **2,3**, **6**, **8a–e**, **9a–e** and **12a–e** encourage us to propose a mechanism for the reactions of 1,2-alkatrienephosphonates with sulphenyl- and selenenylhalogenides (Scheme 4).

The isolation of bromobenzene from the reaction mixtures of the synthesis of compounds **2,3**, **6**, **8a–e**, **9a–e** and **12a–e** supports the previously suggested reaction mechanism. We believe that the results reported here are in accordance with the assumption [7–21] for the key role of the formation of thiiranium or seleniranium ions **A** and **C** as intermediates resolting from the 3,4 attack of the reagent. They undergo ring expansion due to the anhimeric assistance of the neighboring double bond, forming the more stable cyclic ions $\mathbf{A}^1$ and $\mathbf{C}^1$. Both $\mathbf{A}^1$ and $\mathbf{C}^1$ undergo [1,5]-prototropic shift and elimination of bromobenzene to give the phosphorylated thiophene and selenophene derivatives. The formation of the products **11a–e** and **13a–e** is due to the 4,5 attack

of the reagent. In these cases, both methyl groups stabilize the intermediate **B** and facilitate its interaction with the internal nucleophilic phosphoryl group, leading to the formation of the quasi-phosphonium intermediate $\mathbf{B}^1$. The Arbuzov rearrangement of $\mathbf{B}^1$ (second step) leads to the formation of 4-phenylthio(seleno)-5*H*-1,2-oxaphosphole-2-oxides **11a–e** and **13a–e**.

Having in mind the results reported here, our previous results and literature data, we conclude that:

1. the synthetic potential of the phosphorylated alkatrienes makes them very useful in organic synthesis;
2. by the reactions of these compounds with a number of electrophilic reagents, different kinds of heterocyclic compounds were prepared with good yields;
3. there is a possibility to control the structure of the products by variation of the type of the electrophile and of the substrate; and
4. as far as starting 1-alkynoles are easily available from the corresponding carbonyl compounds and alkynes, the reactions discussed here have to be taken into consideration as useful synthetic protocol for the transformation of carbonyl compounds into the corresponding cyclic products, bearing a phosphonate group.

EXPERIMENTAL

Analytical Methods

The ^{1}H NMR spectra were measured at normal probe temperature on a Jeol JNM-PS-10 spectrometer at 100 MHz using TMS as internal reference in $CDCl_3$ solution. Chemical shifts are given in ppm and are positive downfield from the internal standard. The IR spectra were run on an IR-72 spectrophotometer (Carl Zeiss Jena). Elemental analyses were carried out by the University of Shumen Microanalytical Service Laboratory. The solvents were purified by standard methods. All reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purity on TLC plates.

Starting Materials

The dichlorides **1**,**4** and the dialkyl esters **7a–e** and **10a–e** were prepared according to the procedure described.[22] Phenylselenenylbromide is commercially available. Phenylsulfenylbromide was synthesized according to the procedure described.[22]

Synthesis of Compounds 2, 3, 5, 6: General Procedure

To a solution of 5 mmol of the appropriate dichloride (**1** or **4**) in methylene chloride a solution of 5 mmol phenylsulfenyl- or phenylselenenylbromide was added at low temperature (−12–10°C). The solvent was then removed *in vacuo* and the residue was purified by chromatography (50 g silicagel, hexane/ethyl acetate 1:1).

(3-Methylthiophen-2-yl)methylphosphonic dichloride 2. $C_6H_7Cl_2OPS$; Calcd.: P 13.52, Cl 30.65, S 14.03 %; Found: P 13.43, Cl 30.62, S 14.00%; IR: $\nu(cm^{-1})$ $1262_{(P=O)}$; ^1H NMR ($CDCl_3$): δ 7.08 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 0.8 Hz, 1H, thiophene-H); 6.99 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 1.0 Hz, 1H, thiophene-H); 3.69 (d, $^2J_{PH}$ = 15.0 Hz, 2H, CH_2-P); 2.15 (d $^5J_{PH}$ = 3.4 Hz, 3H, Me-C); ^{31}P NMR ($CDCl_3$): δ 15.5. Oil; yield 53%, b.p. 141–143°C (1.0 Torr).

(3-Methylselenophen-2-yl)methylphosphonic dichloride 3. $C_6H_7Cl_2OPSe$; Calcd.: P 11.22, Cl 25.69 %; Found: P 11.13, Cl 25.62%; IR: $\nu(cm^{-1})$ $1270_{(P=O)}$; ^1H NMR ($CDCl_3$): δ 7.76 (dd,$^3J_{HH}$ = 5.2 Hz, $^5J_{PH}$ = 0.8 Hz, 1H, selenophene-H); 6.99 (dd, $^3J_{HH}$ = 5.2 Hz, $^5J_{PH}$ = 1.2 Hz, 1H, selenophene-H); 4.06 (d, $^2J_{PH}$ = 16.3 Hz, 2H, CH_2-P); 2.16 (d, $^5J_{PH}$ = 3,5 Hz, 3H, Me-C); ^{31}P NMR ($CDCl_3$): δ 17.2. Oil, yield 58%, b.p. 145–146°C (1.0 Torr).

1-Bromo-5-methyl-4-(phenylthio)hexa-2,4-dien-3-ylphosphonic dichloride 5. $C_{13}H_{14}Cl_2BrOPS$; Calcd.: P 7.74, Cl 17.72, Br 19.97, S 8.01%; Found: P 7.70, Cl 17.69, Br 19.94, S 7.98%; IR: $\nu(cm^{-1})$ $1262_{(P=O)}$, 1595, $1620_{(C=C-C=C)}$; ^1H NMR ($CDCl_3$): δ 1.74 (d, $^5J_{PH}$ = 5.3 Hz, 3H, CH_3); 2.04 (d, $^5J_{PH}$ = 7.0 Hz, 3H, CH_3); 4.00 (dd, $^4J_{PH}$ = 2.6 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2—C); 6.91 (dt, $^3J_{PH}$ = 25.6 Hz, 1H); 7.21 - 7.60 (m, 5H, Ph); ^{31}P NMR ($CDCl_3$): 17.5. Oil, yield 51%, b.p. 144–146°C (1.0 Torr).

2-Isopropylselenophen-3-ylphosphonic dichloride 6. $C_7H_9Cl_2OPSe$; Calcd.: P 10.68, Cl 24.45%; Found: P 10.59, Cl 24.42%; IR: $\nu(cm^{-1})$ $1285_{(P=O)}$; ^1H NMR ($CDCl_3$): δ 7.60 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{PH}$ = 2.8 Hz, 1H, selenophene-H); 7.27 (dd, $^4J_{PH}$ = 3.8 Hz, $^3J_{HH}$= 4.8 Hz, 1H, selenophene-H); 3.92 (septett, $^3J_{HH}$ = 5.8 Hz, 1H, C<u>H</u>Me_2); 1.27 (d, $^3J_{HH}$ = 5.8 Hz, 6H, Me); ^{31}P NMR ($CDCl_3$): δ 16.9. Oil, yield 52%, b.p. 145–147°C (1.0 Torr).

Synthesis of Compounds 8a–e and 9a–e: General Procedure

To a solution of 5 mmol of the appropriate dialkyl ester **7a–e** in methylene chloride a solution of 5 mmol of phenylsulphenyl- or phenylselenenylbromide in methylene chloride was added at low temperature (−12–10°C). The solvent was then removed *in vacuo*

and the residue was purified by chromatography (50 g silicagel, hexane/ethyl acetate 1:1).

Dimethyl (3-Methylthiophen-2-yl)methylphosphonate 8a. $C_8H_{13}O_3PS$, Calcd.: P 14.06, S 14.56%; Found: P 14.00, S 14.32%; IR: $\nu(cm^{-1})$ $1279_{(P=O)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 0.8$ Hz, 1H, thiophene-H); 6.99 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 1.0$ Hz, 1H, thiophene-H); 3.67 (d, $^2J_{PH} = 15.1$Hz, 2H, CH_2—P); 2.16 (d, $^5J_{PH} = 3.4$ Hz, 3H, Me-C); 3.76 (d, $^3J_{PH} = 11.2$ Hz, 6H, OMe); ^{31}P NMR ($CDCl_3$): δ 16.7. Oil, yield 53%, b.p. 141–143°C (1.0 Torr).

Diethyl (3-Methylthiophen-2-yl)methylphosphonate 8b. $C_{10}H_{17}O_3PS$, Calcd.: P 12.47, S 12.91%; Found: P 12.35, S 12.88%; IR: $\nu(cm^{-1})$ $1279_{(P=O)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 7.07 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 0.9$ Hz, 1H, thiophene-H); 6.99 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 1.0$ Hz, 1H, thiophene-H); 3.68 (d, $^2J_{PH} = 15.0$ Hz, 2H, CH_2—P); 2.16 (d, $^5J_{PH} = 3.4$ Hz, 3H, Me-C); 1.28 (m, 6H, $OCH_2C\underline{H}_3$); 4.04 (m, 4H, $OC\underline{H}_2CH_3$); ^{31}P NMR ($CDCl_3$): δ 17.7. Oil, yield 53%, b.p. 141–143°C (1.0 Torr).

Dipropyl (3-Methylthiophen-2-yl)methylphosphonate 8c. $C_{12}H_{21}O_3PS$, Calcd.: P 11.20, S 11.60%; Found: P 11.15, S 11.55%; IR: $\nu(cm^{-1})$ $1279_{(P=O)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 0.8$ Hz, 1H, thiophene-H); 6.98 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 1.0$ Hz, 1H, thiophene-H); 3.67 (d, $^2J_{PH} = 15.1$ Hz, 2H, CH_2—P); 2.14 (d, $^5J_{PH} = 3.4$ Hz, 3H, Me-C); 0.85 (t, 6H, $OCH_2CH_2C\underline{H}_3$); 1.58 (m, 4H, $OCH_2C\underline{H}_2CH_3$); 3.96 (m, 4H, $OC\underline{H}_2CH_2CH_3$); ^{31}P NMR ($CDCl_3$): δ 16.2. Oil, yield 53%, b.p. 141–143°C (1.0 Torr).

Diisopropyl (3-Methylthiophen-2-yl)methylphosphonate 8d. $C_{12}H_{21}O_3PS$, Calcd.: P 11.20, S 11.60%; Found: P 11.17, S 11.56%; IR: $\nu(cm^{-1})$ $1279_{(P=O)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 0.7$ Hz, 1H, thiophene-H); 6.89 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 1.0$ Hz, 1H, thiophene-H); 3.67 (d, $^2J_{PH} = 15.1$ Hz, 2H, CH_2—P); 2.16 (d, $^5J_{PH} = 3.4$ Hz, 3H, Me-C); 1.26 (d, 12H, $OCH(C\underline{H}_3)_2$); 4.26 (m, 2H, $OC\underline{H}(CH_3)_2$); ^{31}P NMR ($CDCl_3$): δ 15.6. Oil, yield 53%, b.p. 141–143°C (1.0 Torr).

Di-sec-butyl (3-Methylthiophen-2-yl)methylphosphonate (8e). $C_{14}H_{25}O_3PS$, Calcd.: P 10.17, S 10.53%; Found: P 10.12, S 10.48%; IR: $\nu(cm^{-1})$ $1279_{(P=O)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 0.8$ Hz, 1H, thiophene-H); 6.99 (dd, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 1.0$ Hz, 1H, thiophene-H); 3.67 (d, $^2J_{PH} = 15.1$ Hz, 2H, CH_2—P); 2.16 (d, $^5J_{PH} = 3.4$ Hz, 3H, Me-C); 0.88 (t, 6H, $OCH(Me)CH_2\underline{Me}$); 1.26 (d, 6H, $OCH(\underline{Me})CH_2Me$); 1.76 (m, 4H, $OCH(Me)C\underline{H}_2Me$); 4.26 (m, 2H,

OC<u>H</u>(Me)CH_2Me); ^{31}P NMR ($CDCl_3$): δ 16.7. Oil, yield 53%, b.p. 141–143°C (1.0 Torr).

Dimethyl (3-Methylselenophen-2-yl)methylphosphonate (9a). $C_8H_{13}O_3PSe$, Calcd.: P 11.59%; Found: P 11.55%; IR: ν(cm^{-1}) $1285_{(P=O)}$, $1016_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 0.9 Hz, 1H, selenophene-H); 6.89 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 1.0 Hz, 1H, selenophene-H); 3.67 (d, $^2J_{PH}$ = 15.1 Hz, 2H, CH_2–P); 2.16 (d, $^5J_{PH}$ = 3.4 Hz, 3H, Me-C); 3.76 (d, $^3J_{PH}$ = 11.2 Hz, 6H, OMe); ^{31}P NMR ($CDCl_3$): δ 16.6. Oil, yield 52%, b.p. 145–147°C (1.0 Torr).

Diethyl (3-Methylselenophen-2-yl)methylphosphonate (9b). $C_{10}H_{17}O_3PSe$, Calcd.: P 10.49%; Found: P 10.43%; IR: ν(cm^{-1}) $1285_{(P=O)}$, $1016_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 0.8 Hz, 1H, selenophene-H); 6.99 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 1.0 Hz, 1H, selenophene-H); 3.67 (d, $^2J_{PH}$ = 15.1 Hz, 2H, CH_2–P); 2.16 (d, $^5J_{PH}$ = 3.4 Hz, 3H, Me-C); 1.28 (t, 6H, OCH_2<u>Me</u>); 4.04 (m, 4H, OC<u>H_2</u>Me); ^{31}P NMR ($CDCl_3$): δ 16.7. Oil, yield 52%, b.p. 145–147°C (1.0 Torr).

Dipropyl (3-Methylselenophen-2-yl)methylphosphonate (9c). $C_{12}H_{21}O_3PSe$, Calcd.: P 9.58%; Found: P 9.51%; IR: ν(cm^{-1}) $1285_{(P=O)}$, $1016_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 0.8 Hz, 1H, selenophene-H); 6.99 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 1.0 Hz, 1H, selenophene-H); 3.67 (d, $^2J_{PH}$ = 15.1 Hz, 2H, CH_2–P); 2.16 (d, $^5J_{PH}$ = 3.4 Hz, 3H, Me-C); 0.85 (t, 6H, OCH_2CH_2<u>Me</u>); 1.58 (m, 4H, OCH_2C<u>H_2</u>Me); 3.96 (m, 4H, OC<u>H_2</u>CH_2Me); ^{31}P NMR ($CDCl_3$): δ 17.7. Oil, yield 52%, b.p. 145–147°C (1.0 Torr).

Diisopropyl (3-Methylselenophen-2-yl)methylphosphonate (9d). $C_{12}H_{21}O_3PSe$, Calcd.: P 9.58%; Found: P 9.53%; IR: ν(cm^{-1}) $1285_{(P=O)}$, $1016_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 0.8 Hz, 1H, selenophene-H); 6.99 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 1.0 Hz, 1H, selenophene-H); 3.67 (d, $^2J_{PH}$ = 15.1 Hz, 2H, CH_2–P); 2.16 (d, $^5J_{PH}$ = 3.4 Hz, 3H, Me-C); 1.26 (d, 12H, OCH<u>Me_2</u>); 4.26 (m, 2H, OC<u>H</u>Me_2); ^{31}P NMR ($CDCl_3$): δ 16.5. Oil, yield 52%, b.p. 145–147°C (1.0 Torr).

Di-sec-butyl (3-Methylselenophen-2-yl)methylphosphonate (9e). $C_{14}H_{25}O_3PSe$, Calcd.: P 8.82%; Found: P 8.80%; IR: ν(cm^{-1}) $1285_{(P=O)}$, $1016_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.06 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 0.8 Hz, 1H, selenophene-H); 6.99 (dd, $^3J_{HH}$ = 5.0 Hz, $^5J_{PH}$ = 1.0 Hz, 1H, selenophene-H); 3.67 (d, $^2J_{PH}$ = 15.1 Hz, 2H, CH_2–P); 2.16 (d, $^5J_{PH}$ = 3.4 Hz, 3H, Me-C); 0.88 (t, 6H, OCH(Me)CH_2<u>Me</u>); 1.26 (d, 6H, OCH(<u>Me</u>)CH_2Me); 1.76 (m, 4H, OCH(Me)C<u>H_2</u>Me); 4.26 (m, 2H, OC<u>H</u>(Me)CH_2Me); ^{31}P NMR ($CDCl_3$): δ 14.7. Oil, yield 52%, b.p. 145–147°C (1.0 Torr).

Synthesis of Compounds 11a–e and 12a–e: General Procedure

The syntheses of the compounds **11a–e** and **12a–e** were performed by the procedure described.[3]

4-Phenylthio-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-methoxy-1,2-oxaphosphole-2-oxide (11a). $C_{14}H_{17}O_3PS$, Calcd.: P 10.45, S 10.82%; Found: P 10.40, S 10.79%; IR: $\nu(cm^{-1})$ $1268_{(P=O)}$, $1625_{(CH=CH2)}$, $1585_{(C=C)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}(trans)$ = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^3J_{HH}(trans)$ = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29-7.44 (m, 5H, Ph); 3.76 (d, $^3J_{HH}$ = 11.2 Hz, 3H, OMe) ^{31}P NMR ($CDCl_3$): δ 24.4. Oil, yield 44%, b.p. 145–147°C (1.0 Torr).

4-Phenylthio-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-ethoxy-1,2-oxaphosphole-2-oxide (11b). $C_{15}H_{19}O_3PS$, Calcd.: P 9.98, S 10.33%; Found: P 9.93, S 10.29%; IR: $\nu(cm^{-1})$ $1268_{(P=O)}$, $1625_{(CH=CH2)}$, $1585_{(C=C)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}(trans)$ = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^3J_{HH}(trans)$ = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29-7.44 (m, 5H, Ph); 1.28 (t, 3H, OCH_2<u>Me</u>); 4.04 (m, 2H, O<u>CH_2</u>Me); ^{31}P NMR ($CDCl_3$): δ 24.2. Oil, yield 44%, b.p. 145–147°C (1.0 Torr).

4-Phenylthio-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-n-propoxy-1,2-oxaphosphole-2-oxide (11c). $C_{16}H_{21}O_3PS$, Calcd.: P 9.55, S 9.88%; Found: P 9.49, S 9.81%; IR: $\nu(cm^{-1})$ $1268_{(P=O)}$, $1625_{(CH=CH2)}$, $1585_{(C=C)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}(trans)$ = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^3J_{HH}(trans)$ = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph); 0.85 (t, 3H, OCH_2CH_2<u>Me</u>); 1.58 (m, 2H, OCH_2<u>CH_2</u>Me); 3.96 (m, 2H, O<u>CH_2</u>CH_2Me); ^{31}P NMR ($CDCl_3$): δ 24.8. Oil, yield 44%, b.p. 145–147°C (1.0 Torr).

4-Phenylthio-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-i-propoxy-1,2-oxaphosphole-2-oxide (11d). $C_{16}H_{21}O_3PS$, Calcd.: P 9.55, S 9.88%; Found: P 9.53, S 9.82%; IR: $\nu(cm^{-1})$ $1268_{(P=O)}$, $1625_{(CH=CH2)}$, $1585_{(C=C)}$, $1000_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}(trans)$ = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}(cis)$ = 10.6 Hz, $^3J_{HH}(trans)$ = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH);

1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph); 1.26 (d, 6H, OCH$\underline{Me}_2$); 4.62 (m, 1H, OC$\underline{H}Me_2$); ^{31}P NMR ($CDCl_3$): δ 24.8. Oil, yield 44%, b.p. 145–147°C (1.0 Torr).

4-Phenylthio-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-sec-butoxy-1,2-oxaphosphole-2-oxide (11e). $C_{17}H_{23}O_3PS$, Calcd.: P 9.15, S 9.47%; Found P 9.10, S 9.41%; IR: ν(cm^{-1}) $1268_{(P=O)}$, $1625_{(CH=CH2)}$, $1585_{(C=C)}$, $1000_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}$(*cis*) = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C$\underline{H}$H); 5.62 (ddd, $^3J_{HH}$(*trans*) = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH$\underline{H}$); 6.39 (ddd, $^3J_{HH}$(*cis*) = 10.6 Hz, $^3J_{HH}$(*trans*) = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C$\underline{H}$=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph), 0.88 (t, 3H, OCH(Me)$CH_2\underline{Me}$); 1.26 (d, 3H, OCH($\underline{Me}$)CH_2Me); 1.76 (m, 2H, OCH(Me)C$\underline{H}_2$Me); 4.62 (m, 1H, OCH(Me)CH_2Me); ^{31}P NMR ($CDCl_3$): δ 24.6. Oil, yield 44%, b.p. 145–147°C (1.0 Torr).

Dimethyl 2-Isopropylthiophen-3-ylphosphonate (12a). $C_9H_{15}O_3PS$, Calcd.: P 13.22, S 13.69%; Found: P 13.12, S 13.63%; IR: ν(cm^{-1}) $1279_{(P=O)}$, $1010_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.14 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{PH}$ = 4.0 Hz, 1H, thiophene-H); 7.30 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{PH}$ = 3.0 Hz, 1H, thiophene-H); 3.94 (septett, $^3J_{HH}$ = 6.5 Hz, 1H, C$\underline{H}Me_2$); 1.44 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH$\underline{Me}_2$); 3.77 (d, $^3J_{PH}$ = 11.2 Hz, 6H, OMe); ^{31}P NMR ($CDCl_3$): δ 14.7. Oil, yield 35%, b.p. 145–147°C (1.0 Torr).

Diethyl 2-Isopropylthiophen-3-ylphosphonate (12b). $C_{11}H_{19}O_3PS$, Calcd.: P 11.80, S 12.22%; Found: P 11.78, S 12.18%; IR: ν(cm^{-1}) $1279_{(P=O)}$, $1010_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.14 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{PH}$ = 4.0 Hz, 1H, thiophene-H); 7.30 (dd, $^4J_{PH}$ = 3.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, thiophene-H); 3.94 (septett, $^3J_{HH}$ = 6.5 Hz, 1H, C$\underline{H}Me_2$); 1.44 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH$\underline{Me}_2$); 1.28 (t, 6H, $OCH_2\underline{Me}$); 4.04 (m, 4H, OC$\underline{H}_2$Me); ^{31}P NMR ($CDCl_3$): δ 11.9. Oil, yield 35%, b.p. 145–147°C (1.0 Torr).

Dipropyl 2-isopropylthiophen-3-ylphosphonate (12c). $C_{13}H_{23}O_3$-PS, Calcd.: P 10.67, S 11.04%; Found: P 10.62, S 11.00%; IR: ν(cm^{-1}) $1279_{(P=O)}$, $1010_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.14 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{PH}$ = 4.0 Hz, 1H, thiophene-H); 7.30 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{PH}$ = 3.0 Hz, 1H, thiophene-H); 3.94 (septett, $^3J_{HH}$ = 6.5 Hz, 1H, C$\underline{H}Me_2$); 1.44 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH$\underline{Me}_2$); 0.85 (t, 6H, $OCH_2CH_2\underline{Me}$); 1.58 (m, 4H, $OCH_2C\underline{H}_2$Me); 3.96 (m, 4H, OC$\underline{H}_2CH_2$Me); ^{31}P NMR ($CDCl_3$): δ 12.3. Oil, yield 35%, b.p. 145–147°C (1.0 Torr).

Diisopropyl 2-isopropylthiophen-3-ylphosphonate (12d). $C_{13}H_{23}$-O_3PS, Calcd.: P 10.67, S 11.04%; Found: P 10.64, S 11.00%; IR: ν(cm^{-1}) $1279_{(P=O)}$, $1010_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 7.14 (dd, $^3J_{HH}$ = 4.9 Hz,

$^3J_{PH}$ = 4.0 Hz, 1H, thiophene-H); 7.30 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{PH}$ = 3.0 Hz, 1H, thiophene-H); 3.94 (septett, $^3J_{HH}$ = 6.5 Hz, 1H, C<u>H</u>Me$_2$); 1.44 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH<u>Me</u>$_2$); 1.26 (d, 12H, OCH<u>Me</u>$_2$); 4.26 (m, 4H, OC<u>H</u>Me$_2$); ^{31}P NMR ($CDCl_3$): δ 9.7. Oil, yield 35%, b.p. 145–147°C (1.0 Torr).

Di-sec-butyl 2-isopropylthiophen-3-ylphosphonate (12e). $C_9H_{15}O_3PS$, Calcd.: P 9.73, S 10.07%; Found: P 9.70, S 10.00%; IR: ν(cm^{-1}) 1279$_{(P=O)}$, 1010$_{(P-O-C)}$: ^{1}H NMR ($CDCl_3$): δ 7.14 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{PH}$ = 4.0 Hz, 1H, thiophene-H); 7.30 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{PH}$ = 3.0 Hz, 1H, thiophene-H); 3.94 (septett, $^3J_{HH}$ = 6.5 Hz, 1H, C<u>H</u>Me$_2$); 1.44 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH<u>Me</u>$_2$); 0.88 (t, 6H, OCH(Me)CH$_2$<u>Me</u>); 1.26 (d, 6H, OCH(<u>Me</u>)CH$_2$Me); 1.76 (m, 4H, OCH(Me)C<u>H</u>$_2$Me); 4.26 (m, 2H, OC<u>H</u>(Me)CH$_2$Me); ^{31}P NMR ($CDCl_3$): δ 10.9. Oil, yield 35%, b.p. 145–147°C (1.0 Torr).

Synthesis of the Compounds 13a-e: General Procedure

To a solution of 5 mmol of the appropriate dialkyl ester **10a–e** in methylene chloride a solution of 5 mmol of phenylselenenylbromide in methylene chloride was added at low temperature (−12–−10°C). The solvent was then removed in vacuo and the residue was purified by chromatography (50 g silicagel, hexane / ethyl acetate 1:1).

4-Phenylseleno-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-methoxy-1,2-oxaphosphole-2-oxide (13a). $C_{14}H_{17}O_3PSe$, Calcd.: P 9.02%; Found: P 9.00%; IR: ν(cm^{-1}) 1270$_{(P=O)}$, 1630$_{(CH=CH2)}$, 1580$_{(C=C)}$, 1010$_{(P-O-C)}$;^{1}H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}$(*cis*) = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}$(*trans*) = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}$(*cis*) = 10.6 Hz, $^3J_{HH}$(*trans*) = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph); 3.76 (d, $^3J_{PH}$ = 11.2 Hz, 6H, OMe); ^{31}P NMR ($CDCl_3$): δ 31.7. Oil, yield 56%, b.p. 145–147°C (1.0 Torr).

4-Phenylseleno-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-ethoxy-1,2-oxaphosphole-2-oxide (13b). $C_{15}H_{19}O_3PSe$, Calcd.: P 8.67%; Found: P 8.61%; IR: ν(cm^{-1}) 1270$_{(P=O)}$, 1630$_{(CH=CH2)}$, 1580$_{(C=C)}$, 1010$_{(P-O-C)}$; ^{1}H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}$(*cis*) = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}$(*trans*) = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}$(*cis*) = 10.6 Hz, $^3J_{HH}$(*trans*) = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph); 1.28 (t, 3H, OCH$_2$<u>Me</u>); 4.04 (m, 2H, OC<u>H</u>$_2$Me); ^{31}P NMR ($CDCl_3$): δ 29.0. Oil, yield 52%, b.p. 143–145°C (1.0 Torr).

4-Phenylseleno-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-n-propoxy-1,2-oxaphosphole-2-oxide (13c). $C_{16}H_{21}O_3PSe$, Calcd.: P 8.34%; Found: P 8.29%; IR: $\nu(cm^{-1})$ $1270_{(P=O)}$, $1630_{(CH=CH2)}$, $1580_{(C=C)}$, $1010_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}$*(cis)* = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}$*(trans)* = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}$*(cis)* = 10.6 Hz, $^3J_{HH}$*(trans)* = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph); 0.85 (t, 3H, OCH_2CH_2<u>Me</u>); 1.58 (m, 2H, OCH_2C<u>H_2</u>Me); 3.96 (m 2H, O<u>CH_2</u>CH_2Me); ^{31}P NMR ($CDCl_3$): δ 30.0. Oil, yield 68%, b.p. 145–147°C (1.0 Torr).

4-Phenylseleno-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-i-propoxy-1,2-oxaphosphole-2-oxide (13d). $C_{16}H_{21}O_3PSe$, Calcd.: P 8.34%; Found: P 8.28%; IR: $\nu(cm^{-1})$ $1270_{(P=O)}$, $1630_{(CH=CH2)}$, $1580_{(C=C)}$, $1010_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}$*(cis)* = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}$*(trans)* = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}$*(cis)* = 10.6 Hz, $^3J_{HH}$*(trans)* = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph); 1.26 (d, 6H, OCH<u>Me_2</u>); 4.62 (m, 1H, OC<u>H</u>Me_2); ^{31}P NMR ($CDCl_3$): δ 29.0. Oil, yield 67%, b.p. 145–147°C (1.0 Torr).

4-Phenylseleno-5,5-dimethyl-3-ethenyl-2,5-dihydro-2-sec-butoxy-1,2-oxaphosphole-2-oxide (13e). $C_{17}H_{23}O_3PSe$, Calcd.: P 8.04%; Found: P 8.00%; IR: $\nu(cm^{-1})$ $1270_{(P=O)}$, $1630_{(CH=CH2)}$, $1580_{(C=C)}$, $1010_{(P-O-C)}$; ^1H NMR ($CDCl_3$): δ 5.37 (ddd, $^3J_{HH}$*(cis)* = 10.6 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, CH=C<u>H</u>H); 5.62 (ddd, $^3J_{HH}$*(trans)* = 16.5 Hz, $^2J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 1.0 Hz, 1H, CH=CH<u>H</u>); 6.39 (ddd, $^3J_{HH}$*(cis)* = 10.6 Hz, $^3J_{HH}$*(trans)* = 16.7 Hz, $^3J_{PH}$ = 27.8 Hz, 1H, C<u>H</u>=CHH); 1.44 (s, 3H, Me), 1.49 (s, 3H, Me), 7.29–7.44 (m, 5H, Ph); 0.88 (t, 3H, OCH(Me)CH_2<u>Me</u>); 1.26 (d, 3H, OCH(<u>Me</u>)CH_2Me); 1.76 (m, 2H, OCH(Me)C<u>H_2</u>Me); 4.62 (m, 1H, OCH(Me)CH_2Me); ^{31}P NMR ($CDCl_3$): δ 29.0. Oil, yield 56%, b.p. 175–177°C (1.0 Torr).

REFERENCES

[1] Ch. M. Angelov, M. Kirilov, B. I. Ionin, and A. A. Petrov, *Zh. Obshch. Khim.*, **49,** 2225 (1979).

[2] Ch. M. Angelov, M. Kirilov, K. V. Vachkov, and S. L. Spasov, *Tetrahedron Lett.*, **21,** 3507 (1980).

[3] Ch. M. Angelov and K. V. Vachkov, *Tetrahedron Lett.*, **22,** 2517 (1981).

[4] Ch. M. Angelov, N. M. Stojanov, and B. I. Ionin, *Zh. Obshch. Khim.*, **52,** 178 (1982).

[5] Yu. M. Dangian, G. A. Panosian, M. G. Voskonian, and Sh. O. Badanian, *Zh. Obshch. Khim.*, **53,** 61 (1983).

[6] Ch. M. Angelov and Ch. Zh. Christov, *Phosphorus, Sulfur, and Silicon,* **15,** 373 (1983).
[7] Ch. M. Angelov and Ch. Zh. Christov, *Synthesis*, 664 (1984).
[8] Ch. N. Tancheva, Ch. M. Angelov, and D. M. Mondeshka, *Heterocycles*, **23,** 843 (1985).
[9] Yu. M. Dangian, M. R. Tirakian, G. A. Panosian, and Sh. O. Badanian, *Zh. Obshch. Khim.*, **55,** 1631 (1985).
[10] V. K. Brel, B. I. Ionin, and A. A. Petrov, *Zh. Obshch. Khim.*, **51,** 2625 (1981).
[11] Ch. M. Angelov and D. D. Enchev, *Phosphorus, Sulfur, and Silicon*, **19,** 155 (1984).
[12] D. D. Enchev, Ch. M. Angelov, and M. Kirilov, *Chemica Scripta*, **27,** 295 (1987).
[13] Ch. M. Angelov, D. D. Enchev, and M. Kirilov, *Phosphorus, Sulfur, and Silicon*, **35,** 35 (1988).
[14] D. D. Enchev, *Phosphorus, Sulfur, and Silicon*, **180,** 2211 (2005).
[15] D. D. Enchev, *Heteroatom Chem.*, **16,** 156 (2005).
[16] I. V. Alabugin and V. K. Brel, *Usp. Khim.*, **66,** 225 (1997).
[17] V. Ch. Christov and I. K. Ivanov, *Phosphorus, Sulfur, and Silicon*, **177,** 2445 (2002).
[18] V. Ch. Christov and I. K. Ivanov, *Sulfur Lett.*, **25,** 191 (2002).
[19] V. Ch. Christov and I. K. Ivanov, *Heterocycl. Commun.*, **9,** 629 (2003).
[20] V. Ch. Christov and I. K. Ivanov, *Heterocycles*, **63,** 2203 (2004).
[21] H. Lecher and F. Holschneider; *Ber.*, **57,** 755 (1924).
[22] M. P. Simonin, M. J. Pauet, J. M. Gense, and C. Paumier, *Org. Magn. Reson.*, **8,** 508 (1976).