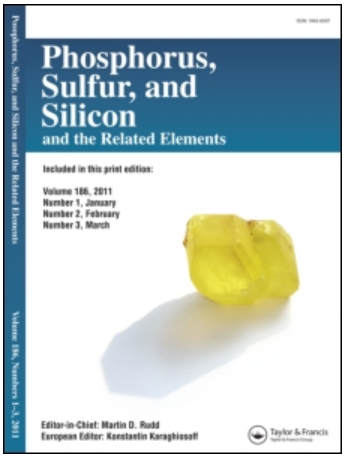

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REACTION OF 2-CHLORO-1,3-ALKADIENYLPHOSPHONIC DIMETHYL ESTERS WITH ARENESELENENYL CHLORIDES

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REACTION OF 2-CHLORO-1,3-ALKADIENYLPHOSPHONIC DIMETHYL ESTERS WITH ARENESELENENYL CHLORIDES

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Reaction of the 3-alkyl-2-chloro-1,3-alkadienylphosphonic dimethyl esters **1** with areneselenenyl chlorides affords mixtures of the 2,5-dihydro-1,2-oxaphosphole 2-oxides **2** and the 3-(1-arylselenoalkyl)-2-chloro-1,3-alkadienylphosphonic dimethyl esters **3**. In contrast, the interaction of the 2-chloro-2-(1-cyclohexenyl)ethenephosphonic dimethyl ester **1d** with areneselenenyl chlorides occurs with six-membered heterocyclization and formation of the 5-arylseleno-4-chloro-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides **4**. The oxidative elimination of the areneselenenyl moiety in the bicyclic compounds **4** yields the 4-chloro-7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides **5**.

Keywords: 2-chloro-1,3-alkadienylphosphonic dimethyl esters; areneselenenyl chlorides; 2,5-dihydro-1,2-oxaphosphole 2-oxides; 3-(1-arylselenoalkyl)-2-chloro-1,3-alkadienylphosphonic dimethyl esters; 5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides; oxidative elimination; 7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides

INTRODUCTION

Previously was shown that the interaction of 1,3-alkadienic hydrocarbons with selenenyl chlorides leads to mixtures of 1,2-, 4,3- and 4,1-adducts which ratio depends on the reaction temperature. [1] As 1,2- and 4,3-adducts readily isomerize into 4,1-adducts the latter arise *via* isomerization of initially former 1,2- and 4,3-adducts. [1c] The selenenyl chlorides add to Si-containing 1,3-alkadienes only at the unfunctionalized double bond in the same manner as sulfenyl chlorides [2a]—the electrophile (RSe^+) attacks the C^4-atom of the conjugated system to give the corresponding 4,3-adducts. [2b] On the other hand the accessibility of the 2-chloro-1,3-alkadienylphosphonates [3] and their rather

interesting system of double bonds provided the grounds in recent years for systematic studies on their reactivity with respect to electrophiles. [4] It was shown that depending on the nature of the reagent they afford various classes of heterocyclic compounds. We have recently reported the reaction of the 2-chloro-1,3-alkadienylphosphonic esters with sulfenyl chlorides which lead to six- or five-membered heterocyclization depending on the type of hydrocarbon moiety in the sulfur atom [5a, 5b]—alkanesulfenyl chlorides give 5,6-dihydro-2H-1,2-oxaphosphorines while arenesulfenyl chlorides lead to 2,5-dihydro-1,2-oxaphospholes. On the other hand the interaction of 2-chloro-2(1-cyclohexenyl)ethenephosphonic dialkyl esters with sulfenyl chlorides affords only six-membered heterocycles irrespective of the type of the sulfenyl chloride. [5c]

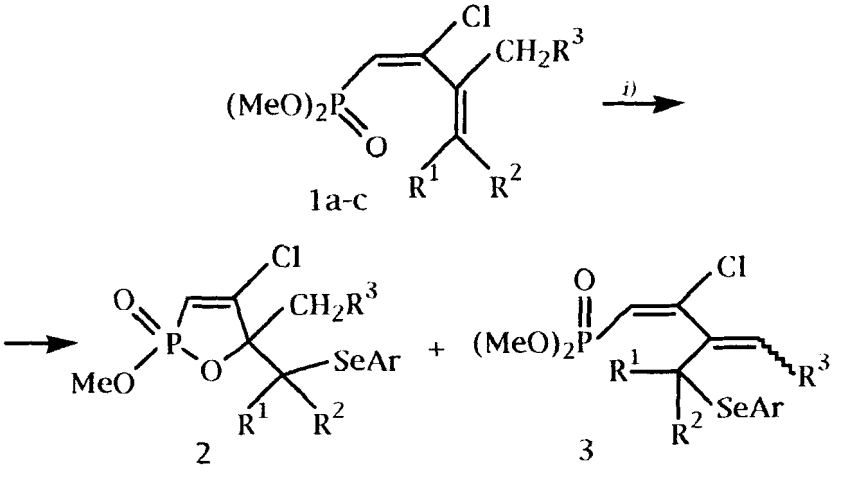
Bearing in mind the fact that selenenyl chlorides are analogous to sulfenyl chlorides it seemed reasonable to expect that the heterocyclization observed with sulfenyl chlorides should also proceed in this case. Based on this consideration we presently describe the results on the reaction of 2-chloro-1,3-alkadienylphosphonic dimethyl esters with areneselenenyl chlorides.

RESULTS

The reaction of the 3-alkyl-2-chloro-1,3-alkadienylphosphonic dimethyl esters **1a-c** with areneselenenyl chlorides was carried out in dry 1,2-dichloroethane at 55-60°C under an argon atmosphere. Under these conditions we found that the interaction led to the formation of mixtures of the 2,5-dihydro-1,2-oxaphosphole 2-oxide **2** and the 3-(1-arylselenoalkyl)-2-chloro-1,3-alkadienylphosphonic dimethyl esters **3** according to Scheme 1. The resulting compounds **2** and **3** were separated by preparative TLC in moderate yields (44-49%) in the ratio **2**:**3** = 2.7−3.1:1. Their structure was established by ^{1}H NMR and IR spectra as well as elemental analysis. Formation of ring compounds is evident from the fact that in the ^{1}H NMR spectra of the crude reaction mixtures a singlet (δ 3.04 ppm) from methyl chloride is observed, and from the fact that integral over the methoxy group corresponds to three hydrogens only. Formation of the five-membered ring was judged on the basis of the signal of the ring methine proton which appears at low field (δ 6.11-6.26 ppm) as a doublet. The coupling constant of this proton with phosphorus (23.0-23.6 Hz) is in agreement with data reported for similar structures. [5a,5b, 6] Moreover, there are signals for protons of the alkyl groups at C^5 atom as well as for the arylseleno moiety in the ^{1}H NMR spectra of the 2,5-dihydro-1,2-oxaphosphole 2-oxides **2**. Some protons resonate at two frequencies which is an indication of the existence of diastereoisomers (chirality

at P, C^5 in **2a** and **2c** and P, C^5 and C^5 (1′) atoms in **2b**). Attempts to separate the individual constituents failed despite considerable efforts. The IR spectra of **2** exhibit absorption bands characteristic for an endocyclic double bond (1585-1587 cm^{-1}), for P=O (1278-1280 cm^{-1}), for the ring P-O-C (991-997 cm^{-1}) and for the P-O-Me function (1025-1030 cm^{-1}).

Comparison of ^1H NMR spectra of the resulting 3-(1-arylselenoalkyl)-2-chloro-1,3-alkadienylphosphonic dimethyl esters **3** with the spectra [3] of the starting 1,3-dienylphosphonates **1** shows differences to a considerable degree. Thus, the spectra of **3** exhibit a doublet signal for the P-CH= proton at δ 6.45-6.51 with coupling constant with phosphorus ($^2J_{HP}$ 27.8-28.3 Hz), while those [3] of **1** show the corresponding peak at higher field (δ 5.80-6.07) with smaller constant (d, $^2J_{HP}$ 10.0-11.0 Hz). Moreover, the signals for protons of the R^1 and R^2 groups appear at higher field, while the signals of the R^3 group are at lower field in the spectra of the products **3**. Furthermore, the multiplet signal for the ArSe protons is also observed. IR spectra of **3** exhibit characteristic absorption bands for the 1,3-dienic system, phosphoryl group and Me-O-P moiety.



1-3	Ar	R^1	R^2	R^3
a	Ph	H	H	H
b	Ph	H	Me	Me
c	p-ClPh	Me	Me	H

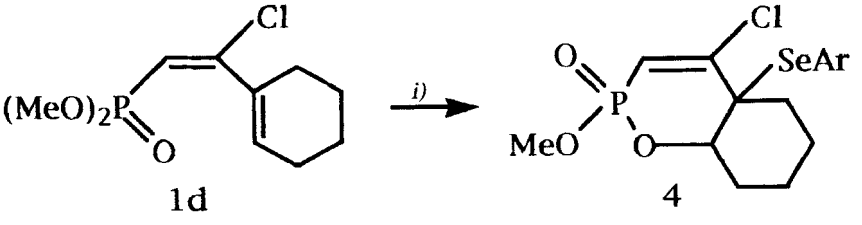
Reagents and Conditions:
i) ArSeCl, $ClCH_2CH_2Cl$, 55-60 °C, 5 h.

Scheme 1

It was established that the configuration of the C^1-C^2 double bond of the starting 2-chloro-1,3-alkadienylphosphonates **1** is (1*E*). [3a, 10] Reaction of **1** with areneselenenyl chlorides occurs, probably, with retention of the (1*E*)-configuration of **3**. Although it was anticipated that the olefinic proton at the C^4 atom of the (1*E*, 3*E*)-isomer of 1,3-diene **3b** would be observed upfield from the corresponding proton of the (1*E*, 3*Z*)-isomer, with the chemical shift value (m, δ 5.78 ppm) alone we cannot determine whether the phosphorylated 1,3-diene **3b** is the (1*E*, 3*Z*)-, (1*E*, 3*E*)-isomer or a mixture of them.

The obtained compounds **2** and **3** contain the isotope ^{77}Se which is magnetically active and interacts with other nuclei. This interaction becomes evident with the protons of the R^1 and R^2 groups which exhibit symmetric satelite signals of the main signal in the ^1H NMR spectra.

The interaction between areneselenenyl chlorides and the 2-chloro-2(1-cyclohexenyl)ethenephosphonic dimethyl ester **1d**, in which the C^3-C^4 double bond is included in the cyclohexene ring system, affords only bicyclic P-, O-containing heterocyclic compounds i.e. 5-arylseleno-4-chloro-2-methoxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides (**4**) in good yield (69-73%) (Scheme 2). The bicyclic compounds **4** were isolated by recrystallization from hexane or heptane and characterized by ^1H NMR and IR spectra. In the ^1H NMR spectra are observed a doublet signal for the olefinic proton (δ 6.21-6.25 ppm) with a coupling constant with phosphorus ($^2J_{HP}$ 9.1-9.2 Hz) typical for six-membered ring system. [5, 6a] The proton at the C^{10} atom gives rise to a complex multiplet (δ 4.70-4.74 ppm) with a considerable coupling constant ($^3J_{HP}$ 7.1-7.5 Hz) confirming in this manner the presence of a P-O-CH moiety in the ring. The proton signals show that these compounds are actually present as a mixture of



4	Ar
a	Ph
b	p-ClPh

Reagents and Conditions:

i) ArSeCl, $ClCH_2CH_2Cl$, 55-60 °C, 5 h.

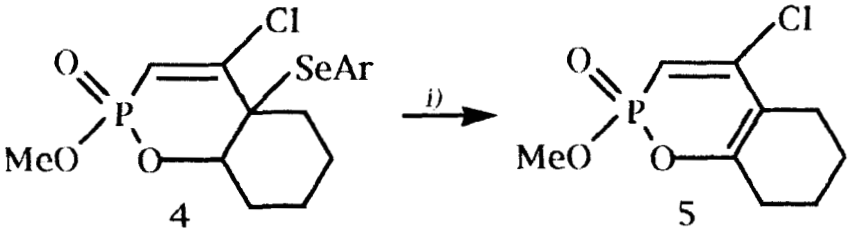
Scheme 2

diastereomers (chirality centers at P, C^5 and C^{10}). The data from the IR spectra and the elemental analysis confirm the structure of the obtained compounds.

It is well known that the *syn*-elimination reaction of selenooxides, containing a β-hydrogen atom, occurs with formation of a double C-C bond. [7] A modification of this reaction is the oxidative elimination of the selenenyl moiety, which have been the subjects of a large number of investigation. [8] Using this method for formation of a double bond, we established that treatment of the bicyclic compounds **4** with hydrogen peroxide in CH_2Cl_2-H_2O at 0°C gives the 4-chloro-2-methoxy-7,8,9,10-tetrahydrobenz-2H-1,2-oxaphosphorine 2-oxide (**5**) in moderate yield (45-48%) (Scheme 3). The formed 1,2-oxaphosphorine 2-oxide was isolated by preparative TLC using as eluent a mixture of hexane: ethyl acetate = 4:1. The ^1H NMR spectrum of **5** shows an absence of multiplet signals for the C^{10} proton and the arylseleno moiety. Moreover, the coupling constant of =CH proton (d, δ 6.12 ppm) with phosphorus ($^2J_{HP}$ 24.8 Hz) is typical for 1,2-oxaphosphorines. [9] The IR spectrum of **5** exhibits absorption bands characteristic for ring double bonds (1592 and 1612 cm^{-1}).

DISCUSSION

We have previously established [10] that the 2-chloro-1,3-alkadienylphosphonates synthesized by chlorination of allenylphosphonic dichlorides [3] exist predominantly in *s-cis* conformation which is favourable for cyclization reactions. All experimental data published earlier on the reaction of selenenyl



Reagents and Conditions: i) H_2O_2, CH_2Cl_2-H_2O, O °C, rt, 3 h.

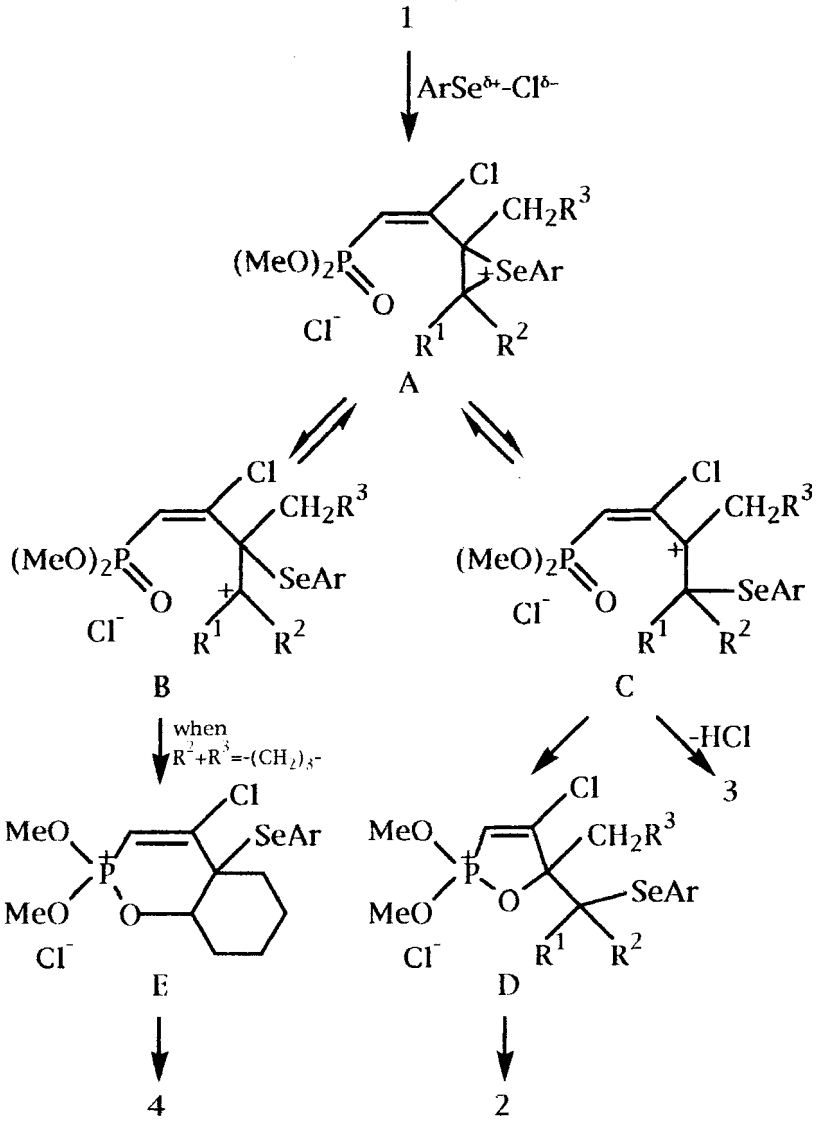
Scheme 3

chlorides with unsaturated compounds confirm the ionic character of these chemical transformations. [11]

We assume the first step of the reaction to be an electrophilic attack of the selenium atom upon the 1,3-dienic double bond system (see Scheme 4). In principle, the electrophilic selenium atom ($ArSe^+$) can attack either of the two double bonds by formation of corresponding episelenonium ions. The attack occurs exclusively at the C^3-C^4 double bond because of the great destabilizing effect of both the electron-withdrawing phosphonate group and the chlorine atom on a C^1-C^2 episelenonium ion (not shown in Scheme 4) compared with the alkyl substituted C^3-C^4 episelenonium ion A shown. This ion, however, exists in equilibrium with the acyclic carbenium ions **B** and **C**. In the case of 3-alkyl-2-chloro-1,3-alkadienylphosphonates **1a-c** as starting compounds, this equilibrium is evidently shifted largely towards the more stabilized carbenium ion C, leading mainly, after P=O attack, to five-membered heterocyclization (intermediate **D**) with subsequent elimination of methyl chloride (second stage of an Arbuzov type rearrangement) and formation of stable products with tetracoordinated phosphorus **2**. Another possibility for stabilization of the carbenium ion **C** is a proton elimination from alkyl group at position 3, leading to the formation of the 3-(1-arylselenoalkyl)-2-chloro-1,3-alkadienylphosphonates **3**.

It is worth noting that regardless of the existing analogy between selenenyl chlorides and sulfenyl chlorides, the interaction between RSCl and the above esters does not afford the 1,3-diene analogous of compounds **3**. A possible explanation lies in the different stabilities of the episelenonium and episulfonium ions. Although sulfur and selenium have almost identical electronegativities (*S* 2.44 and Se 2.48), [12] selenium has a greater covalent radius (1.16 A) [12] than sulfur (1.02 A), [13] which results in a weakening of the carbon-selenium bond in episelenonium ion **A** and, in turn, leads to its easy cleavage and formation of free carbenium ions **B** and **C**.

The formation of only the six-membered bicyclic heterocycles **4** in the reaction of areneselenenyl chlorides with the 2-chloro-2(1-cyclohexenyl)ethenephosphonic dimethyl ester **1d** can be explained on the one hand with the *s-cis* reaction conformation of the 1,3-dienic system in the starting compound **1d** and on the other with the more energetically favoured transition state leading to the sterically more favourable fused bicyclic structure **E** which contains a six-membered ring system in contrast to the spirane (not shown in Scheme 4) which should lead to the five-membered heterocycles.



Scheme 4

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EXPERIMENTAL

Method of analysis

^{1}H NMR spectra were obtained on JEOL JNM-FX-60 (60 MHz) and BRUCKER WM-250 (250.1 MHz) spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

The melting points were measured in open capillary tubes and are uncorrected. Reactions with areneselenenyl chlorides were performed in oven-dried glassware under an argon atmosphere and exclusion of moisture. The solvents were purified by standard methods. All compounds were checked for their purify on TLC plates.

Starting materials

The dimethyl esters **1** were obtained according to the procedure described. [3] The areneselenenyl chlorides were freshly prepared [14] from the corresponding diaryl diselenide and sulfuryl chloride in 1,2-dichloroethane and used without purification.

Reaction of the 2-chloro-1,3-alkadienylphosphonic dimethyl esters 1 with areneselenenyl chlorides. General procedure

A solution of the areneselenenyl chloride (10 mmol) in 1,2-dichloroethane (10 ml) was slowly added at 55-60°C, with stirring, to a solution of the 2-chloro-1,3-alkadienyl phosphonic dimethyl esters (**1**)(10 mmol) in the same solvent (10 ml). The stirring was continued for 5 h at the same temperature. After the solvent was removed using a rotatory evaporater the residue was chromatographed on preparative TLC (silica gel, hexane:ethyl acetate = 1:2)(**2**, **3**) or recrystallized from hexane or heptane (**4**) to give the pure products as light yellow oils (**2a**, **3a**, **3b**) or white crystals (**2b**, **2c**, **3c**, **4a**, **4b**). The products had the following properties:

R^1=R^2=R^3=H, Ar=Ph

Yield: 49%. The ratio of the products was: **2a**:**3a** = 3.1:1. *4-chloro-2-methoxy-5-methyl-5-phenylselenomethyl-2,5-dihydro-1,2-oxaphosphole 2-oxide* (**2a**): oil, $C_{12}H_{14}O_3PClSe$, Calcd., %: P 8.81, Cl 10.08; Found, %: P 8.93, Cl 9.92. IR spectra (neat), cm^{-1}: 997 (P-O-C), 1025 (Me-O-P), 1278 (P=O), 1585 (C=C). ^{1}H NMR spectra, δ: 1.47 (s, 3H, Me), 2.45 (s, 2H, CH_2), 3.77 (d, $^3J_{HP}$ 10.4 Hz, 3H, MeO), 6.11 (d, $^2J_{HP}$ 23.4 Hz, 1H, HC=), 7.41 (m, 5H, Ph).

2-chloro-3-phenylselenomethyl-1,3-butadienylphosphonic dimethyl esters (**3a**): oil,, $C_{13}H_{16}O_3PClSe$, Calcd., %: P 8.47, Cl 9.69; Found, %: P 8.62, Cl 9.86. IR spectra (neat), cm^{-1}: 1012 (Me-O-P), 1267 (P=O), 1595, 1624 (C=C−C=C). ^1H NMR spectra, δ: 3.03 (s, 2H, CH_2Se), 3.69 (d, $^3J_{HP}$ 11.0 Hz, 3H, MeO), 4.88, 5.11 (s, s, 2H, $=CH_2$), 6.48 (d, $^2J_{HP}$ 28.1 Hz, 1H, HC=), 7.53 (m, 5H, Ph).

R^1=H, R^2=R^3=Me, Ar=Ph

Yield: 44%. The ratio of the products was: **2b**:**3b** = 3.0:1. *4-chloro-5-ethyl-2-methoxy-5-(1-phenylselenoethyl)-2,5-dihydro-1,2-oxaphosphole 2-oxide* (**2b**): m.p. 104-5°C, $C_{14}H_{18}O_3PClSe$, Calcd., %: P 8.16, Cl 9.34; Found, %: P 8.23, Cl 9.51. IR spectra (nujol), cm^{-1}: 994 (P-O-C), 1029 (Me-O-P), 1280 (P=O), 1587 (C=C). ^1H NMR spectra, δ: 0.91 (t, 3H, *Me*CH_2), 1.37 (d, $^3J_{HH}$ 6.4 Hz, *Me*CH), 1.93 (m, 2H, Me*CH_2*), 3.48 (m, 1H, Me*CH*), 3.68 (d, $^3J_{HP}$ 10.2 Hz, 3H, MeO), 6.26 (d, $^2J_{HP}$ 23.0 Hz, 1H, HC=), 7.34 (m, 5H, Ph).

2-chloro-3-(1-phenylselenoethyl)-1,3-pentadienylphosphonic dimethyl esters (**3b**): oil, $C_{15}H_{20}O_3PClSe$, Calcd., %: P 7.87, Cl 9.01; Found, %: P 7.98, Cl 9.24. IR spectra (neat), cm^{-1}: 1014 (Me-O-P), 1262 (P=O), 1594, 1625 (C=C−C=C). ^1H NMR spectra, δ: 1.32 (d, $^3J_{HH}$ 5.6 Hz, 3H, *Me*CHSe), 1.78 (d, $^3J_{HH}$ 6.7 Hz, 3H, =CH*Me*), 3.38 (m, 1H, MeC*H*Se), 3.63 (d, $^3J_{HP}$ 10.7 Hz, 3H, MeO), 5.78 (m, 1H, =C*H*Me), 6.45 (d, $^2J_{HP}$ 27.8 Hz, 1H, HC=), 7.43 (m, 5H, Ph).

R^1=R^2=Me, R^3=H, Ar=p-ClPh:

Yield: 45%. The ratio of the products was: **2c**:**3c** = 2.7:1. *4-chloro-2-methoxy-5-methyl-5-[2-(4-chlorophenylseleno)-prop-2-yl]-2,5-dihydro-1,2-oxaphosphole 2-oxide* (**2c**): m.p. 98-9°C, $C_{14}H_{17}O_3PCl_2Se$, Calcd., %: P 7.48, Cl 17.12; Found, %: P 7.62, Cl 17.29. IR spectra (nujol), cm^{-1}: 991 (P-O-C), 1030 (Me-O-P), 1278 (P=O), 1585 (C=C). ^1H NMR spectra, δ: 1.32 (s, 3H, Me), 1.74 (s, 6H, CMe_2), 3.67 (d, $^3J_{HP}$ 10.4 Hz, 3H, MeO), 6.21 (d, $^2J_{HP}$ 23.6 Hz, 1H, HC=), 7.08 (m, 4H, C_6H_4Cl).

2-chloro-3-[2-(4-chlorophenylseleno)-prop-2-yl]-1,3-butadienylphosphonic dimethyl esters (**3c**): m.p. 79-0°C, $C_{15}H_{19}O_3PCl_2Se$, Calcd., %: P 7.23, Cl 16.56; Found, %: P 7.21, Cl 16.72. IR spectra (nujol), cm^{-1}: 1018 (Me-O-P), 1267 (P=O), 1598, 1630 (C=C−C=C). ^1H NMR spectra, δ: 1.87 (s, 6H, CMe_2), 3.61 (d, $^3J_{HP}$ 10.9 Hz, 3H, MeO), 4.91, 5.18 (s, s, 2H, $=CH_2$), 6.51 (d, $^2J_{HP}$ 28.3 Hz, 1H, HC=), 7.08 (m, 4H, C_6H_4Cl).

Ar=Ph:

4-chloro-2-methoxy-5-phenylseleno-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxide (**4a**): Yield: 73%, m.p. 108-9°C, $C_{15}H_{18}O_3PClSe$, Calcd., %: P 7.91, Cl 9.05; Found, %: P 7.83, Cl 9.19. IR spectra (nujol), cm^{-1}: 979 (P-O-C), 1026 (Me-O-P), 1281 (P=O), 1590 (C=C). ^1H NMR spectra, δ: 1.64, 2.31, 4.70 (s, s, m, $^3J_{HP}$ 7.1 Hz, 9H, cyclohexyl), 3.61 (d, $^3J_{HP}$ 8.4 Hz, 3H, MeO), 6.21 (d, $^2J_{HP}$ 9.1 Hz, 1H, HC=), 7.31 (m, 5H, Ph).

Ar=p-ClPh:

4-chloro-5-(4-chlorophenylseleno)-2-methoxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxide (**4b**): Yield: 69%, m.p. 113-4°C, $C_{15}H_{17}O_3PCl_2Se$, Calcd., %: P 7.27, Cl 16.64; Found, %: P 7.19, Cl 16.81. IR spectra (nujol), cm^{-1}: 976 (P-O-C), 1028 (Me-O-P), 1278 (P=O), 1588 (C=C). ^1H NMR spectra, δ: 1.67, 2.29, 4.74 (s, s, m, $^3J_{HP}$ 7.5 Hz, 9H, cyclohexyl), 3.66 (d, $^3J_{HP}$ 8.6 Hz, 3H, MeO), 6.25 (d, $^2J_{HP}$ 9.2 Hz, 1H, HC=), 7.13 (m, 4H, C_6H_4Cl).

Oxidative elimination reaction of the 5-arylseleno-4-chloro-2-methoxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides (**4**). *General procedure*: To a solution of the 5-arylseleno-4-chloro-2-methoxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides (**4a,b**) (7 mmol) in dichloromethane (5 ml) at 0°C was added dropwise hydrogen peroxide (35%, 3.6 ml, 35.5 mmol) in water (5 ml). The mixture was stirred at this temperature for 1 h and 3 h at room temperature. After a conventional work-up, the residue was chromatographed on preparative TLC (silica gel, hexane:ethyl acetate = 4:1) to give **5**.

4-chloro-2-methoxy-7,8,9,10-tetrahydrobenz-2H-1,2-oxaphosphorine 2-oxide (**5**): Yield: 48% (from **4a**) and 45% (from **4b**), oil, $C_9H_{12}O_3PCl$, Calcd., %: P 13.20, Cl 15.11; Found, %: P 13.13, Cl 15.29. IR spectra (neat), cm^{-1}: 934 (P-O-C), 1012 (Me-O-P), 1254 (P=O), 1592, 1612 (C=C−C=C). ^1H NMR spectra, δ: 1.26, 2.02 (s, s, 8H, $4CH_2$), 3.54 (d, $^3J_{HP}$ 8.0 Hz, 3H, MeO), 6.12 (d, $^2J_{HP}$ 24.8 Hz, 1H, HC=).

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