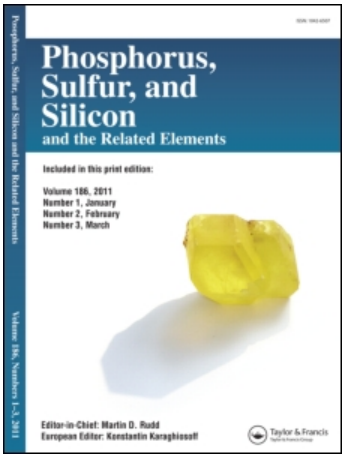


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHEMO-, REGIO- AND STEREOSELECTIVITY OF THE REACTION OF DIALKYL-1,2-ALKADIENYLPHOSPHONATES WITH SELENENYL CHLORIDES. 1,3-SIGMATROPIC REARRANGEMENT OF 2,3-ADDUCTS

Diana M. Mondeshka[a]; Chonka N. Tancheva[a]; Christo M. Angelov[b]
[a] Department of Organic Chemistry, Higher Institute of Chemical Technology, Sofia, Bulgaria [b] Department of Chemistry, Higher Pedagogical Institute, Shoumen, Bulgaria

To cite this Article Mondeshka, Diana M. , Tancheva, Chonka N. and Angelov, Christo M.(1987) 'CHEMO-, REGIO- AND STEREOSELECTIVITY OF THE REACTION OF DIALKYL-1,2-ALKADIENYLPHOSPHONATES WITH SELENENYL CHLORIDES. 1,3-SIGMATROPIC REARRANGEMENT OF 2,3-ADDUCTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 31: 1, 89 — 99
To link to this Article: DOI: 10.1080/03086648708079346
URL: http://dx.doi.org/10.1080/03086648708079346

Phosphorus and Sulfur, 1987, Vol. 31, pp. 89–99
Photocopying permitted by license only

CHEMO-, REGIO- AND STEREOSELECTIVITY OF THE REACTION OF DIALKYL-1,2-ALKADIENYLPHOSPHONATES WITH SELENENYL CHLORIDES. 1,3-SIGMATROPIC REARRANGEMENT OF 2,3-ADDUCTS

DIANA M. MONDESHKA and CHONKA N. TANCHEVA
Department of Organic Chemistry, Higher Institute of Chemical Technology 1156 Sofia, Bulgaria.

CHRISTO M. ANGELOV
Department of Chemistry, Higher Pedagogical Institute, 9700 Shoumen, Bulgaria.

(Received May 7, 1986; in final form July 7, 1986)

By spectral and chromatographic studies, the chemo-, regio- and stereoselectivity of the reaction of dialkyl-1,2-alkadienylphosphonates with selenenyl chlorides has been investigated in detail.

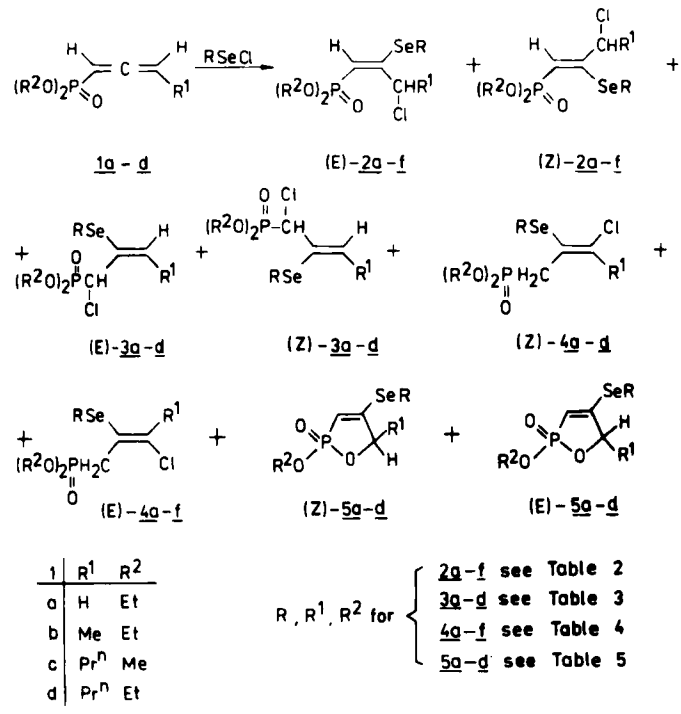
INTRODUCTION

In the past 15–20 years the electrophilic addition to allenes and their derivatives is studied very intensively.[1–4] The literature data show that the addition of selenenyl chlorides was studied some years ago.[5–7] Recently it has been shown that the reaction of phosphorylated allenes with selenenyl chlorides mainly gives the heterocyclic products -2,5-dihydro-1,2-oxaphosphole 2-oxides.[8–10] In contrast to 3,3-disubstituted allenylphosphonates which give only five-membered heterocycles, we found that 3-mono- and 3-non-substituted allenylphosphonates with methyl- and phenylselenenyl chlorides lead to the formation of complex reaction mixtures in which we identify oxaphosphole derivatives as well as 2,3-adducts.[11] In the present paper we describe the results of a detailed study of the reaction mixtures with chromatographic methods which allow to follow all reaction routes of the interaction between C-3 substituted and non-substituted dialkyl-1,2-alkadienylphosphonates with selenenyl chlorides.

The obtained experimental data to draw some conclusions about the chemo-, regio- and stereoselectivity of the reaction of 1,2-alkadienylphosphonates with selenenyl chlorides.

RESULTS

In order to carry out the chromatographic study we obtained reaction mixtures from dialkyl-1,2-alkadienylphosphonates and methyl- or phenylselenenyl chlor-



Scheme 1

ides according to the procedure described earlier.[11] The chromatographic separation shows that the reaction of 3,3-disubstituted allenylphosphonic dialkyl esters with selenenyl chlorides leads only to the formation of five-membered P,O-containing heterocycles. Applying the same conditions 3-mono- and 3-non-substituted allenylphosphonic dialkyl esters give complex reaction mixtures where 2,3-adducts **2a–f** are obtained in insignificant amounts. The amount of 2,5-dihydro-1,2-oxaphosphole 2-oxides **5a–d** considerably increased when the reaction proceeds with phenylselenenyl chloride. Moreover in the reaction mixtures, the alkylphosphonates **4a–f** are discovered, which are obtained as a result of a 1,3-sigmatropic rearrangement of the 2,3-adducts **2a–f** (see Scheme 1).

In the Table I the correlation (in per cent) of all compounds contained in the reaction mixtures are shown. All reaction products have been isolated in pure form by means of column and TL chromatography.

The diethyl propadienylphosphonate **1a** with methyl- and phenylselenenyl chlorides give 2,3-adducts. It should be noted that when sleenium is embed to a phenyl group the (*Z*)-stereoselectivity of the reaction is significantly increased. Along with the 2,3-adducts **2a, b** from the reaction mixtures, (*E*)- and (*Z*)-isomers of diethyl-3-chloro-2-methyl(phenyl)seleno-2-propenylphosphonates **4a, b** in considerable amounts (see Table I) are isolated. The late alkenylphosphonates probably are formed during the reaction by 1,3-sigmatropic rearrangement of 2,3-adducts.

The most complex reaction mixtures for chromatographic separation were

TABLE I

A correlation (in %) of the reaction products obtained by interaction of dialkyl-allenylphosphonates with methyl- and phenylselenenyl chlorides (^{1}H NMR and chromatographic data)

Reaction	Config.	Adducts 1,2-	Adducts 2,3-	1,3-sig-Trop. isom. products	Oxaphosphole 2-oxides
1a + MeSeCl	*E*	—	23	18	—
	Z	—	26	31	—
1a + PhSeCl	*E*	—	9	15	—
	Z	—	62	12	—
1b + MeSeCl	*E*	1.5	18	4	12
	Z	3	39	12	8
1c + MeSeCl	*E*	traces	22	1	10
	Z	5	52	7	
1c + PhSeCl	*E*	—	5	2	30
	Z	1	28	6	25
1d + MeSeCl	*E*	6	11	5	8
	Z	11	50	8	

obtained from 3-monosubstituted allenyl phosphonic dialkyl esters **1b–d** and selenenyl chlorides. Nevertheless, we succeeded to isolate in pure form all (*E*)- and (*Z*)-isomers of the 1,2- (**3a–d**) and 2,3-adducts (**2c–f**) as well as a diastereomeres of 2,5-dihydro-1,2-oxaphosphole derivatives **5a–d**. In this case the products of the sigmatropic rearrangement of the 2,3-adducts are considerably less than those obtained from 2,3-adducts **2a–b**. The structure of isolated compounds and their isomers were confirmed by IR and ^{1}H-NMR spectra, and of the main products by elemental analysis too (Tables II–V).

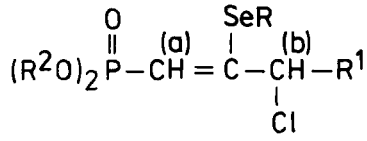
The ^{1}H-NMR spectra of (*E*)- and (*Z*)-2,3-adducts are quite characteristic and essentially differed from one another (Table II). The great difference in the chemical shift of the protons of the =CH and CHCl groups of both isomers can be explained by the deshielding effects on the part of the P=O and C—Cl groups when they are in cis-position in relation to a given proton. It is possible that the great H^1 deshielding in the (*Z*)-isomer, respectively H^3 deshielding in the (*E*)-isomer is due to the inductive, respectively magnetic anisotropic effect of the chlorine and the phosphoryl group. But here it is conceivable to observe the Buckingham effect[12] too. Moreover the $^4J_{HP}$ in both isomers are different (Table II). The cis-allylic interaction being a bit greater than the trans one,[13] the configuration of the both isomers could be determined. The supposed configuration of the isolated (*E*)- and (*Z*)-2,3-adducts we confirmed recently[14] by the vicinal coupling constant $^3J_{CP}$, by the observed Overhauser effect in the spectra of the (*Z*)-isomers and by the value of the vicinal ^{13}C—^{1}H coupling constant between CHCl and =CHP(O). The configuration of the 1,2-adducts **3a–d** isolated in small amounts was determined by their ^{1}H-NMR spectra which are similar to those of sulfur analogues.[15]

In the literature, the dialkyl 2-methyl(phenyl)seleno-3-chloro-2-alkenylphosphonates **4a–f** are not described. We suggest their configuration on the basis of the difference in the chemical shift of the CH_2 group, which appeared under the influence of the chlorine atom in cis-position in (*E*)-isomer at low field.

The structure of the 2,3-adducts **2a–d** and the alkenylphosphonates **4a–f** has

TABLE II

TLC and ^{1}H NMR data of dialkyl 3-chloro-2-methyl(phenyl)-seleno-1-alkenylphoshonetes **2a–f**



No	R	R^1 (R^2)	Config.	R_f	Chem. shifts, δ (Coupling constants, J Hz) Ha (Ha–P)	Hb (Hb–P)	R	R^1
2a	Me	H	*E*	0.60	5.45 brd (10.2)	4.68 brd (1.9)	2.18 s	4.68 brd
		(Et)	*Z*	0.49	6.19 dt (13.8)	4.29 dd (1.0)	2.23 s	4.29 dd
b	Ph	H	*E*	0.73	5.29 brd (11.0)	4.67 brd (2.4)	7.16–7.50 m	4.67 brd
		(Et)	*Z*	0.64	6.31 dt (13.1)	3.86 dd (1.5)	7.08–7.52 m	386 d
c	Me	Me	*E*	0.62	5.35 d (10.3)	5.91 dq (2.0)	2.18 s	1.73 d
		(Et)	*Z*	0.50	6.42 brd (12.8)	4.72 dq (1.0)	2.29 s	1.74 d
d	Me	Pr^n	*E*	0.61	5.26 brd (10.1)	5.64 dt (1.9)	2.12 s	Me—0.88 t, CH_2— 1.42 m, 1.84 m
		(Me)	*Z*	0.44	6.30 dd (13.2)	4.50 ddd (1.0)	2.28 s	Me—0.91 t CH_2—1.48 m, 2.03 m
e	Me	Pr^n	*E*	0.70	5.29 brd (10.2)	5.68 dt (1.9)	2.11 s	Me—0.90 t, CH_2—1.44 m, 167 m
		(Et)	*Z*	0.61	6.26 dd (12.6)	4.46 ddd (1.2)	2.21 s	Me—0.89 t, CH_2—1.50 CH_2—1.85 m, 1.96 m
f	Ph	Pr^n	*E*	0.57	5.11 brd (10.9)	5.76 dt (2.1)	7.12–7.60 m	Me—0.89 t, CH_2—1.50 m, 1.90 m
		(Me)	*Z*	0.42	6.40 dd (12.9)	4.18 ddd (1.1)	7.10–7.56 m	Me—0.89 t CH_2—1.30 m, CH_2—1.68 m, 1.90 m

Ir Spectra (film, cm^{-1}): 1256–1262 (P=O), 1580–1600 (C=C), 965–990 (R^2—O—P).

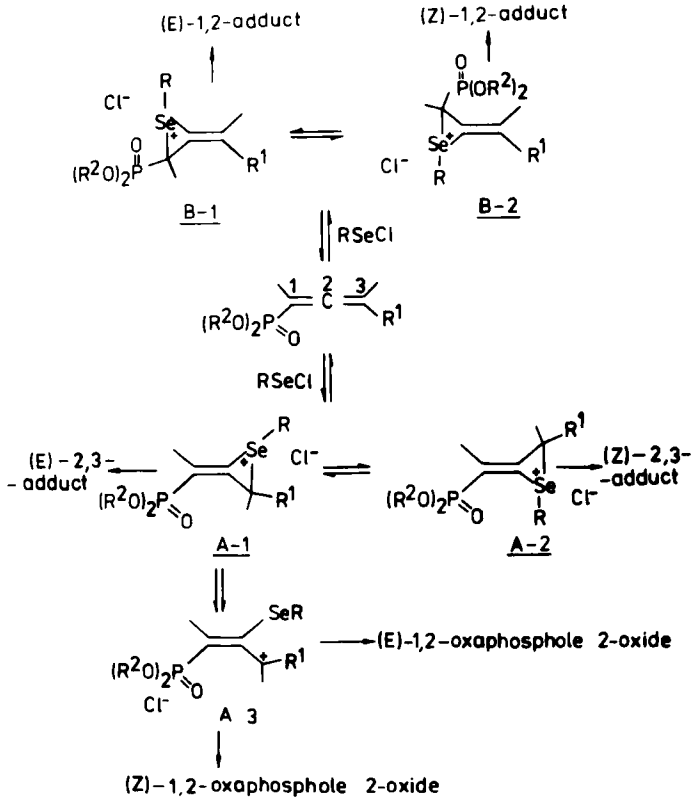
been established by their mass-spectra (see the experimental section). All compounds have an identical molecular ion and a peak corresponding to the fragment M-SeR(Ar) and M-^{35}Cl. These data confirm that both **2a–d** and **4a–f** have an isomeric structure.†

DISCUSSION

All experimental data published earlier on the reactions of selenenyl chlorides with unsaturated compounds confirm the ionic character of these chemical

† The full discussion of mass spectra will be published later.

transformations.[1-3] In our case most probably the intermediates of the reaction are the episelenonium ions A-1, A-2 and B-1, B-2:



Scheme 2

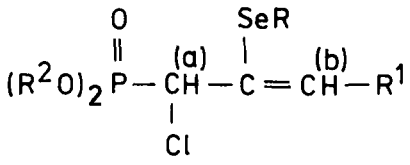
It is obvious that under the influence of the electron accepting P=O group the ions B-1 and B-2 will be formed more slowly as the ions A-1 and A-2, i.e. the amounts of the 1,2-adducts obtained will be smaller as the 2,3-adducts, which is in agreement with our experimental data. The 2,3-adducts are formed through the ions A-1 and A-2. When we use PhSeCl, the intermediate A-3 stabilizes by heterocyclization.

Our experimental results show that when the reagent add to the C^2—C^3 double bond a (*Z*)-stereoselectivity of the reaction is observed. This fact we explain with the sterical hinderance of the alkyl substituents at C-3 atom on the attack of the chlorine anion. Thus, when the methyl group at C-3 was changed to the *n*-propyl group the (*Z*)-stereoselectivity considerably increases (Table I and II).

The above results allow us to draw the following conclusions: 1. The interaction of 3,3-disubstituted allenylphosphonic dialkyl esters with selenenyl chlorides is a highly chemo-, regio- and stereoselective reaction leading to five-membered heterocycles. 2. The interaction of the 3-monosubstituted allenylphosphonic dialkyl esters preserves its regioselectivity which explains the formation of a complex mixture of addition and cyclization products. 3. The reaction of the

TABLE III

TLC and ^{1}H-NMR data of dialkyl 1-chloro-2-methyl (phenyl)seleno-2-alkenylphosphonates **3a–d**



					Chemical shift, δ (Coupling constants, J Hz)			
No	R	R^1 (R^2)	Config.	R_f	Ha (Ha-P)	Hb (Hb-P)	R	R^1(R^1-P)
3a	Me	Me	*E*	0.65	4.69 brd (15.2)	5.57 dq (2.2)	2.13 s	2.09 dd (2.5)
		(Et)	*Z*	0.57	4.17 brd (14.5)	6.49 dq (3.8)	2.11 s	1.91 dd (3.9)
b	Me	Pr^n	*E*	0.69	traces			
		(Me)	*Z*	0.63	4.58 brd (14.2)	6.33 dt (3.6)	2.16 s	Me—0.92 t, CH_2—1.66m, CH_2—2.38 m (3.7)
c	Me	Pr^n	*E*	0.72	4.84 brd (15.5)	5.68 dt (2.1)	2.13 s	Me—0.91 t, CH_2—1.71 m CH_2—2.23 m (3.1)
		(Et)	*Z*	0.66	4.5 brd (14.4)	6.34 dt (3.7)	2.17 s	Me—0.93 t, CH_2—1.80 m CH_2—2.35 m (3.8)
d	Ph	Pr^n	*E*		absent			
		(Me)	*Z*	0.60	4.78 brd (14.0)	6.46 dt (3.2)	7.05–7.58 m	Me—0.97 t, CH_2—1.85 m, CH_2—2.38 m (3.4)

Ir Spectra (film, cm^{-1}): 960–980 (R^2—O—P), 1250–1260 (P=O), 1585–1603 (C=C).

propadienylphosphonic dialkyl esters with selenenyl chlorides are chemo- and regioselective and to a great extent stereoselective.†

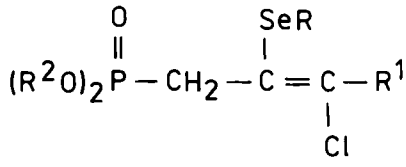
EXPERIMENTAL

Analytical Methods. The IR spectra were carried out on a IR-10 or IR-72 spectrophotometer (Carl Zeiss Jena, GDR). The ^{1}H-NMR spectra were measured at normal temperature on a Jeol JNM-PS-100 (100 MHz) and Brucker WM-250 (250.1 MHz) in $CDCl_3$ with HMSO or TMS as internal standard. The mass spectra were performed on a LKB.

† *Chemoselectivity* will be related to the preference for attack of the one double bond of the cumulated dienic system.
Regioselectivity is related to the relative positions of nucleophile and electrophile on the reacting double bond.
(*E*)/(*Z*) *Stereoselectivities* refer to the geometrical isomerism of the ethylenic adducts.

TABLE IV

TLC and ^{1}H-NMR data of dialkyl 3-chloro-2-methyl (phenyl)seleno-2-alkenylphosphonates **4a–f**



No	R	R^1 (R^2)	Con-fig.	Chemical shift, δ				Coupling constants, J Hz	
				R_f	CH_2	R	R^1	CH_2–P	R^1–P
4a	Me	H	*E*	0.56	3.07 brd	2.17 s	6.07 dt	22.0	5.0
		(Et)	*Z*	0.47	2.85 dd	2.21 s	6.30 dt	21.5	5.8
b	Ph	H	*E*	0.55	2.87 dd	7.05–7.46 m	5.25 dt	21.4	4.7
		(Et)	*Z*	0.38	2.55 dd	7.07–7.50 m	6.43 dt	19.5	5.4
c	Me	Me	*E*	0.59	3.19 brd	2.16 s	2.32 d	22.0	6.0
		(Et)	*Z*	0.45	2.92 brd	2.20 s	2.18 d	21.0	4.5
d	Me	Pr^n	*E*	0.58		traces			
		(Me)	*Z*	0.39	2.93 d	2.19 s	Me –0.98 t CH_2 1.90 m CH_2 2.40 m	21.5	3.1
e	Me	Pr^n	*E*	0.63	3.17 d	2.15 s	Me 0.95 t CH_2 1.85 m CH_2 2.41 m	21.8	3.1
		(Et)	*Z*	0.54	2.89 brd	2.18 s	Me 0.95 t CH_2 1.80 m CH_2 2.35 m	21.0	3.0
f	Ph	Pr^n	*E*	0.48	2.88 brd	7.04–7.50 m	Me 0.95 t CH_2 1.95 m CH_2 2.45 m	21.0	3.4
		(Me)	*Z*	0.39	2.73 brd	7.10–7.52 m	Me 0.96 t CH_2 1.92 m CH_2 2.40 m	20.2	2.8

IR Spectra (film, cm^{-1}): 955–980 (R^2—O—P), 1265–1284 (P=O), 1595–1610 (C=C).

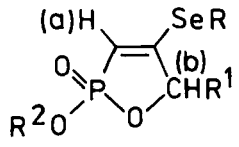
Starting Materials. The crude reaction mixtures of **1a–d** with selenenyl chlorides were obtained according our data published earlier.[11]

Column and TL Chromatography. The qualitative TLC investigations and the R_f value determinations of the isolated substances were carried out on silicagel "Merck" 60 F_{254} pre-coated sheets, using ethylacetate-hexane 1:2.1 as a mobile phase with two- or threefold development. The column chromatographic separation was performed on silicagel "Merck" 60 (0.063–0.200 mm).

Column Chromatographic Separation of the Reaction Mixtures. General Procedure. 0.5 To 1.2 g of the reaction mixture, adsorbed on silicagel were inserted into the column containing 50 to 120 g silicagel in hexane. Then

TABLE V

TLC and ^{1}H-NMR data of 4-methyl(phenyl)seleno-5-alkyl-2-alkoxy-2,5-dihydro-1,2-oxaphosphole 2-oxides **5a–d**



No	R	R^1 (R^2)	Con-fig.	R_f	Chemical shift, δ (Coupling const., J Hz) Ha (Ha–P)	Hb (Hb–P)	R	R^1(R^1–P)
5a	Me	Me	*E*	0.29	5.65 dd (27.5)	4.82 ddq (12.5)	2.27 s	1.42 dd (4.2)
		(Et)	*Z*	0.32	5.63 dd (27.0)	4.84 ddq (12.8)	2.28 s	1.45 dd (4.8)
b	Me	Pr^n	*E*	0.32	5.65 dd	4.78 m	2.26 s	Me 0.92 t, CH_2 1.45 m CH_2 1.80 m (4.2)
		(Me)	*Z*	mixture 0.35	(27.6)	(10.2)		
c	Me	Pr^n	*E*	0.34	5.66 dd	4.76 m	2.25 s	Me 0.92 t, CH_2 1.46 m CH_2 1.80 m (4.4)
		(Et)	*Z*	mixture 0.36	(27.5)	(10.0)		
d	Ph	Pr^n	*E*	0.23	5.39 dd (29.9)	4.88 m (9.0)	7.26–7.49 m	Me 0.92 t, CH_2 1.52 m CH_2 1.78 m (4.0)
		(Me)	*Z*	0.26	5.37 dd (29.3)	4.92 m (8.6)	7.28–7.50 m	Me 0.91 t, CH_2 1.50 m CH_2 1.73 m (4.5)

IR Spectra (cm^{-1}): 995–1015 (R^2—O—P), 1252–1262 (P=O), 1535–1545 (C=C).

TABLE VI

Analyses and mass spectra of **2a–d, f, 3a, 4a–d, 5a, b, d**

No	Con-fig.	Calculated C (H)	Calculated P (Cl)	Formula	Found C (H)	Found P (Cl)	Mass-spectra (70 eV) m/e (rel. intensity)
1	2	3		4	5		6
2a	*E*	31.40 (5.28)	10.13 (11.60)	$C_8H_{16}ClO_3Pse$	31.18 (5.17)	9.92 (11.37)	306 (16, M^+ for ^{35}Cl, ^{80}Se), 213/211 (31/90, M—SeMe)
	Z				31.25 (5.12)	9.85 (11.46)	306 (14, M^+ for ^{35}Cl, ^{80}Se), 213/211 (26/75, M—SeMe)
2b	*E*	42.46 (4.93)	8.42 (9.64)	$C_{13}H_{18}ClO_3PSe$	42.30 (4.93)	8.13 (9.48)	368 (9, M^+ for ^{35}Cl, ^{80}Se), 213/211 (34/100, M—SePh)
	Z				42.26 (4.88)	8.25 (9.56)	368 (17, M^+ for ^{35}Cl, ^{80}Se), 213/211 (33/100, M—SePh)

TABLE VI (*Cont'd.*)

No	Con-fig.	Calculated C (H)	Calculated P (Cl)	Formula	Found C (H)	Found P (Cl)	Mass-spectra (70 eV) m/e (rel. intensity)
1	2	3		4	5		6
2c	*E*	33.82 (5.68)	9.70 (11.09)	$C_9H_{18}ClO_3PSe$	33.68 (5.50)	9.48 (10.85)	320 (15, M^+ for ^{35}Cl, ^{80}Se), 227/225 (30/88, M—SeMe)
	Z				33.70 (5.72)	9.53 (11.17)	320 (13, M^+ for ^{35}Cl, ^{80}Se), 227/225 (24/69, M—SeMe)
2d	*E*	33.82 (5.68)	9.70 (11.09)	$C_9H_{18}ClO_3PSe$	33.56 (5.50)	9.54 (10.85)	
	Z				33.60 (5.75)	9.46 (11.16)	
2f	*E*	44.05 (5.28)	8.11 (9.29)	$C_{14}H_{20}ClO_3PSe$	43.90 (5.11)	(9.35)	
	Z				43.82 (5.15)	7.90	
3a	*E*	33.82 (5.68)	9.70 (11.70)	$C_9H_{18}ClO_3PSe$	33.60 (5.73)	(10.95)	
	Z				33.63 (5.49)	9.58	
4a	*E*	31.40 (5.28)	10.13 (11.60)	$C_8H_{16}ClO_3PSe$	31.20 (5.19)		306 (21, M^+ for ^{35}Cl, ^{80}Se), 213/211 (21/61, M—SeMe)
	Z				31.23 (5.10)	9.92 (11.48)	306 (17, M^+ for ^{35}Cl, ^{80}Se), 213/211 (18/52, M—SeMe)
4b	*E*	42.46 (4.93)	8.42 (9.64)	$C_{13}H_{18}ClO_3PSe$	42.28 (4.80)		368 (13, M^+ for ^{35}Cl, ^{80}Se), 213/211 (35/100, M—SePh)
	Z				42.20 (4.78)	8.28 (9.53)	368 (24, M^+ for ^{35}Cl, ^{80}Se), 213/211 (33/100, M—SePh)
4c	*E*	33.82 (5.68)	9.70 (11.09)	$C_9H_{18}ClO_3PSe$		9.54	320 (23, M^+ for ^{35}Cl, ^{80}Se), 227/225 (17/50, M—SeMe)
	Z				33.60 (5.73)	(10.95)	320 (19, M^+ for ^{35}Cl, ^{80}Se), 227/225 (13/38, M—SeMe)
4d	*Z*	33.82 (5.68)	9.70 (11.09)	$C_9H_{18}ClO_3PSe$	33.70 (5.49)	(10.90)	
5a	*E*	32.95 (5.14)	12.15	$C_7H_{13}O_3PSe$	32.71 (4.97)	11.93	
	Z				32.80 (5.02)	12.23	
5b	*E/Z*	35.70 (5.62)	11.51	$C_8H_{15}O_3PSe$	35.58 (5.51)	11.27	
5d	*E*	47.14 (5.17)	9.36	$C_{13}H_{17}O_3PSe$	46.95 (5.04)	9.16	
	Z				47.01 (4.98)	9.22	

hexane/ethylacetate mixtures with increasing polarities (5:1 versus 1:3) and finally pure ethylacetate were used as eluent. Fractions of each 40 or 70 ml were collected at a rate of about 100 drops/min.

Chromatographic separation of the reaction mixture obtained by interaction of diethyl-1-1,2-propadienylphosphonate **1a** *and MeSeCl.* Starting with a mixture of 0.508 g the following products were isolated:

Fractions	Compounds	g	%
4–7	(*E*) – **2a**	0.101	20
8–9	(*E*) – **2a** + (*E*) – **4a**	0.036	7
10–12	(*E*) – **4a**	0.061	12
13–19	(*Z*) – **2a**	0.119	22
20–21	(*Z*) – **2a** + (*Z*) – **4a**	0.105	10
22–27	(*Z*) – **4a**	0.127	25

Chromatographic separation of the reaction mixture obtained by interaction of diethyl-1,2-propadienylphosphonate **1a** *and MeSeCl.* Starting with a mixture of 0.508 g the following products were isolated:

Fractions	Compounds	g	%
7–8	(*E*) – **2b**	0.036	7
9–10	*E*/*Z* – **2b**	0.056	11
11–17	(*Z*) – **2b**	0.271	53
19–22	(*E*) – **4b**	0.077	15
24–28	(*Z*) – **4b**	0.062	12

Chromatographic separation of the reaction mixture obtained by interaction of diethyl-1,2-butadienylphosphonate **1b** *with MeSeCl.* Starting with a mixture of 1.236 g the following products were isolated:

Fractions	Compounds	g	%
18–19	(*E*) – **3a**	0.015	1.2
20–21	(*E*) – **3a** + (*E*) – **2c**	0.042	4.3
21–30	(*E*) – **2c**	0.180	18
32–38	(*Z*) – **3a** + (*E*) – **4c**	0.090	9
40–53	(*Z*) – **2c**	0.380	34
54–57	(*Z*) – **2c** + (*Z*) – **4c**	0.080	8
58–63	(*Z*) – **4c**	0.120	10.2
66–78	(*E*) + (*Z*) – **5a**	0.240	20

Applying the preparative TLC on the fractions 32–38 pure (*Z*)-**3a** and (*E*)-**4c** were isolated. (*E*)-**5a** and (*Z*)-**5a** were obtained in pure form by the separation of the fractions 66–78 (hexane/ethylacetate (1.2:2) threefold development).

Chromatographic separation of the reaction mixture obtained by interaction of dimethyl-1,2-hexadienylphosphonate **1c** *with MeSeCl.* Starting with 0.520 g of

the reaction mixture the following compounds were isolated through column and preparative TLC: 0.025 g (5%) of (*Z*)-**3b** mixed with small amount of (*E*)-**3b**; 0.10 g (21%) of (*E*)-**2d**; 0.012 g (2%) a mixture of (*e*)-**2d** and (*E*)-**4d**; 0.256 g (51%) of (*Z*)-**2d**; 0.035 g (7%) of (*Z*)-**4d** and 0.050 g (9.4%) of (*E*)/(*Z*) mixture of **5b**.

Chromatographic separation of the reaction mixture obtained by interaction of dimethyl-1,2-hexadienylphosphonate **1c** *and PhSeCl.* Starting with 0.490 g of the reaction mixture the following compounds were isolated: 0.023 g (5%) of (*E*)-**2f**; 0.136 g (28%) of (*Z*)-**2f**; 0.026 g (6%) of (*Z*)-**4f**; 0.147 g (32%) of (*E*)-**5d** and 0.122 g (25%) of (*Z*)-**5d** and small amounts of (*Z*)-**3d** and (*E*)-**4f** proved by means of ^{1}H NMR and TLC.

ACKNOWLEDGMENT

The authors are indebted to Dr. B. Koumanova (Higher Institute of Chemical Technology, Sofia) for the measurement of the mass spectra.

REFERENCES

1. P. B. D. De la Mare and R. Bolton, "Electrophilic Addition to Unsaturated Systems", Elsevier, Amsterdam, 1982, pp. 317–325.
2. T. L. Jacobs, In "The Chemistry of the Allenes", Ed. S. R. Landor, Academic Press, New York, 1982, vol. 2, Chapter 4, pp. 417–510.
3. W. Smadja, *Chem. Rev.*, **83,** 263 (1983).
4. Ch. M. Angelov, *Phosphorus and Sulfur,* **15,** 177 (1983).
5. D. G. Garratt, P. L. Beaulieu and M. D. Ryan, *Tetrahedron,* **36,** 1507 (1980).
6. G. H. Schmid, D. G. Garratt and P. L. Beaulieu, *Chemica Scripta,* **15,** 128, (1980).
7. D. G. Garratt, P. L. Beaulieu, V. M. Morisset and M. Ujjainwalla, *Can. J. Chem.*, **58,** 2745 (1980).
8. Ch. M. Angelov and Ch. Zh. Christov, *Zh. Obshch. Khim.*, **50,** 1981 (1980).
9. Ch. M. Angelov and Ch. Zh. Christov, *Phosphorus and Sulfur,* **15,** 205 (1983).
10. R. S. Macomber, G. A. Krudy, K. Seffand and L. E. Rendon-Diazmiron, *J. Org. Chem.*, **48,** 1425 (1983).
11. Ch. M. Angelov and T. N. Tancheva, *Zh. Obshch. Khim.*, **55,** 33 (1985).
12. J. W. Emsley, J. Feeney and L. H. Sutcliffe, In "High resolution NMR spectroscopy", Ed. "Mir", Moskow, 1968, Vol. 1, pp. 131; H. Günther In "NMR Spectroscopy", Ed. John Willey & Sons, 1980, pp. 86.
13. T. N. Timofeeva, V. M. Ignat'ev, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **39,** 2446 (1968).
14. S. L. Spassov, L. Markova, D. M. Mondeshka, Ch. N. Tancheva and Ch. M. Angelov, *Magn. Reson. Chem.*, **23,** 578 (1985).
15. Ch. M. Angelov, D. M. Mondeshka, Ch. N. Tancheva and S. L. Spassov, unpublished data.