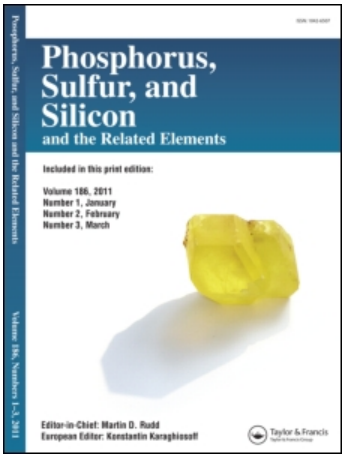

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INTERACTION OF 1,2-ALKADIENEPHOSPHONIC DIALKYL ESTERS WITH SULFENYL CHLORIDES—REACTION PATHWAYS AND STEREOCHEMISTRY

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Chromatographic and NMR-spectroscopic studies permitted the determination of the reaction pathways and stereochemistry in the case of interaction of dialkyl-1,2-alkadienephosphonates with sulfenyl chlorides. The structure of the 1,2-adducts has been verified.

Key words: Electrophilic addition of sulfenyl chlorides; synthesis of oxaphospholes and alkenephosphonates; NMR; stereochemistry; regioselectivity; chemoselectivity.

INTRODUCTION

The electrophilic addition of sulfenyl chlorides to dialkyl-1,2-alkadienephosphonates has been the subject of several studies during the last decade.[1–9] The results indicate that the reaction route depends considerably on the degree of substitution at the allene system as well as on the substituent at the sulfur atom. Thus, 1,3,3- and 1,3-alkylsubstituted 1,2-alkadienephosphonates yield only five membered heterocycles[6,8] whereas the 3,3-dialkylsubstituted esters yield in addition a small amount of 1,2-adducts.[7] The addition of phenylsulfenyl chloride to dialkylpropadienephosphonates occurs along the C_1—C_2^1 or the C_2—C_3^4 double bond of the allenic system whereas the use of alkylsulfenyl chlorides leads to formation of 2,3-adducts only,[5] eventually mixed with unindentified compounds.[6] According to Reference 6, 3-monoalkyl-substituted allenephosphonates under similar conditions yield oxaphosphole derivatives and 1,2-adducts with anti-Markovnikov orientation, whereas other authors obtained a mixture of oxaphospholes, 2,3- and 1,2-adducts, the latter corresponding to Markovnikov orientation. However, the structural conclusions (based mainly on ^{1}H-NMR spectra of

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reaction mixtures) are not fully convincing, especially as far as the stereochemistry of the addition products with respect to both double bonds is concerned.

The present paper describes the results of a comprehensive study of the reactions of sulfenyl chlorides and dialkyl esters of unsubstituted and 3-monoalkyl-substituted allenylphosphonic acids with the aim to isolate individual compounds from the reaction mixture and to determine their structure and stereochemistry.

RESULTS

The reactions of allenylphosphonates with sulfenyl chlorides were carried out under experimental conditions described in:[5,6,8] with equimolar amounts of reactants in carbon tetrachloride or chloroform solution at −12 to −8°C. The quantitative composition of the reaction maxtures as determined on the basis of the amounts of chromatographically isolated products and the integral intensities of the corresponding signals in the ^{1}H-NMR spectra are presented on Table I.

As can be seen, the main reaction products of the dialkyl propadienylphosphonates both in the case of alkyl- as well as phenylsulfenyl chloride are the 2,3-adducts **2a–c**, for which one of the stereoisomers dominates. The hitherto unknown (E)- and (Z)-isomers of 2-alkyl (aryl)thio-3-chloro-2-propenylphosphonic esters **4a–c** were also isolated in significant amounts; they were most probably formed via prototropic rearrangement of the 2,3-adducts. The reaction mixtures contain also small amounts of 2,5-dihydro-1,2-oxaphosphole-2-oxides **5a–c**, the latter not described till now as products of the reaction.[4–6]

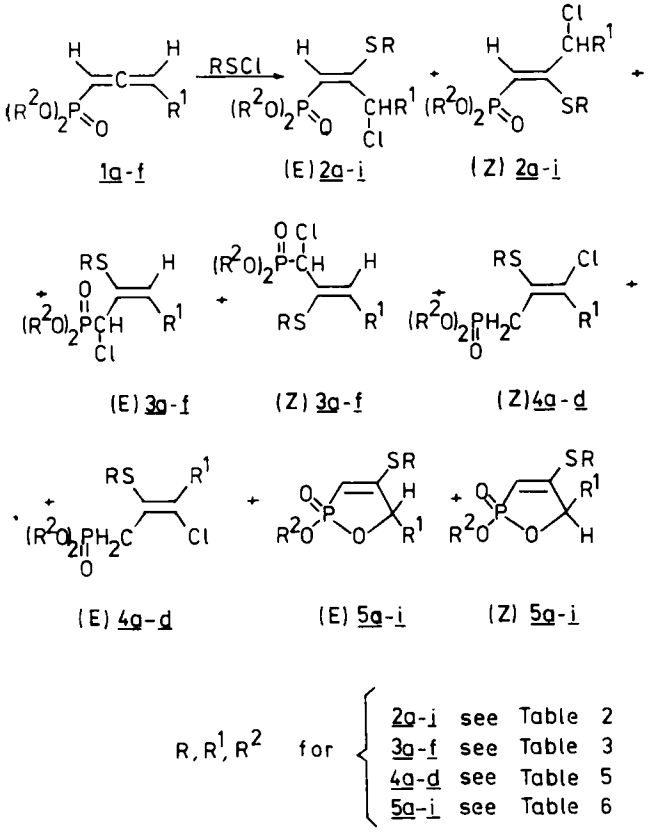
TABLE I

Composition (in %) of the reaction products obtained by interaction of dialkyl-allenephosphonates with alkyl(phenyl)sulfenyl chlorides (^{1}H-NMR and chromatographic data)

Reaction	Config.	Adducts 1,2-	Adducts 2,3-	Prototrop. isom. products	Oxaphosphole 2-oxides
1a + EtSCl	E	—	57	15	2
	Z	—	11	14	
1b + MeSCl	E	—	56	14	3
	Z	—	9	16	
1b + PhSCl	E	—	45	38	5
	Z	—	3	8	
1c + Pr^{i}SCl	E	10	6	—	54
	Z	27	2	—	
1d + PhSCl	E	traces	11	—	73
	Z	14	1	—	
1e + MeSCl	E	7	12	2	60
	Z	14	4	—	
1e + Pr^{i}SCl	E	14	8	—	51
	Z	23	2	—	
1e + PhSCl	E	traces	12	—	66
	Z	18	2	—	
1f + Pr^{i}SCl	E	22	6	—	33
	Z	36	2	—	

The 3-monoalkyl-1,2-alkadienylphosphonates yield with alkyl- as well as phenylsulfenyl chloride complex reaction mixtures, as seen from TLC and ^{1}H-NMR. However, careful chromatographic separation permitted the isolation of all reaction products. Thus, it was established that the reaction mixtures contain mainly the diastereoisomers of the corresponding oxaphosphole derivatives **5d–i** as well as E, Z-isomers of the 1,2-adducts **3a–f** one of which dominates. In the case of phenylsulfenyl chloride as reactant only one of the isomers is formed in noticeable amount. The E, Z-isomers of the 2,3-adducts **2d–i** were also formed, one of them in insignificant amount. The alkenephosphonates obtained via prototropic rearrangement of the 2,3-adducts were observed in traces in the mixtures obtained with the 1,2-butadienylphosphonic esters (**4d**) and were not even chromatographically detected among the reaction products of 1,2-hexadienylphosphonic esters where the 2,3-adducts are also in small amounts (Table I). We consider this as an indifect evidence for the formation of the alkenephosphonates **4** from the 2,3-adducts.

The experimental results suggest the following scheme for the reaction of dialkyl-1,2-alkadienylphosphonates with sulfenyl chlorides:



R, R^1, R^2 for
- 2a-i see Table 2
- 3a-f see Table 3
- 4a-d see Table 5
- 5a-i see Table 6

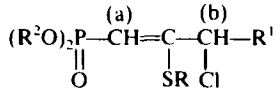
It can be seen from Table I that in the case of 3-monoalkylsubstituted 1,2-alkadienylphosphonates the main reaction with phenylsulfenyl chloride is the

heterocyclization whereas with alkylsulfenyl chlorides both the heterocyclization and the classical addition to the allenic double bonds occur in comparable degrees. Increasing the alkyl chain in the allenephosphonates as well as in the sulfenyl chlorides hampers the heterocyclization as well as the 2,3-addition.

The IR-spectra of the (E)- and (Z)-isomers of the adducts are very similar and

TABLE II

TLC and ^{1}H-NMR data of dialkyl-3-chloro-2-alkyl(phenyl)thio-1-alkenephosphonates **2a–i**



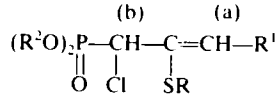
No.	R	R^1 (R^2)	Con-fig.	R_f	Chem. shifts, δ (Coupling const. *J*, Hz)			
					Ha (Ha-P)	Hb (Hb-P)	R	R^1
1	2	3	4	5	6	7	8	9
2a	Me	H	E	0.56	5.52 brd (9.8)	4.64 brd (1.9)	2.26 s	4.64 brd
		(Et)	Z	0.50	5.86 dt (13.1)	3.90 dd (1.2)	2.29 s	3.90 dd
2b	Et	H	E	0.56	5.26 brd (9.4)	4.61 brd (1.8)	1.37 t 2.93 q	4.61 brd
		(Me)	Z	0.46	5.94 dd (13.0)	3.98 dd (1.1)	1.97 t 2.97 q	3.98 dd
2c	Ph	H	E	0.67	4.90 brd (10.2)	4.51 brd (2.0)	7.0–7.4 m	4.57 brd
		(Et)	Z	0.41	5.70 dd (11.8)	3.80 dd (1.9)	7.1–7.4 m	3.80 dd
2d	Me	Pr^n	E	0.50	4.98 brd (9.7)	5.72 td (1.7)	2.19 s	Me 0.89 t CH_2 1.42, 1.85 m
		(Et)	Z	0.53	6.01 d (13.2)	4.40 brd (1.0)	2.23 s	Me 0.89 t CH_2 1.48, 1.83 m
2e	Pr^i	Me	E	0.38	5.17 dd (9.7)	5.91 qd (2.4)	CH 3.21 sept CH_3 1.31, 1.34 d	1.58 d
		(Me)	Z	0.35	6.17 d (13.8)	4.52 brd (0.7)	CH 3.18 sept CH_3 1.30, 1.35 d	1.66 d
2f	Pr^i	Pr^n	E	0.61	5.13 brd (9.8)	5.74 td (2.2)	CH 3.20 sept CH_3 1.28, 1.30 d	CH_3 0.88 t CH_2 1.38, 1.78 m
		(Et)	Z	0.50	6.19 d (13.5)	4.28 brd (0.7)	CH 3.23 sept CH_3 1.29, 1.32 d	CH_3 0.90 t CH_2 1.40, 1.83 m
2g	Pr^i	Pr^n	E	0.43	5.20 brd (9.8)	5.73 td (1.7)	CH 3.23 sept CH_3 1.29, 1.32 d	CH_3 0.92 t CH_2 1.42, 1.96 m
		(Pr^n)	Z	0.45	6.20 d (13.9)	4.22 brt (1.0)	CH 3.25 sept CH_3 1.30, 1.34 d	CH_3 0.92 t CH_2 1.30, 1.94 m
2h	Ph	Pr^n	E	0.72	4.86 d (10.3)	5.80 td (1.9)	7.28 brs	CH_3 0.96 t CH_2 1.48, 2.00 m
		(Me)	Z	0.60	6.22 d (13.7)	4.80 t (1.0)	7.31 brs	CH_3 0.98 t CH_2 1.50, 1.98 m
2i	Ph	Pr^n	E	0.67	4.75 d (10.4)	5.76 td (1.8)	7.05–7.4 m	CH_3 0.92 t CH_2 1.46, 1.98 m
		(Et)	Z	0.50	6.25 d (14.0)	4.75 t (1.0)	7.1–7.4 m	CH_3 0.88 t CH_2 1.42, 2.03 m

IR-spectra (film, cm^{-1}): 970–992 (R^2—O—P), 1250–1269 (P=O), 1582–1608 (C=C).

also close to those of there selene analogues,[10] thus excluding any stereochemical conclusions. However, the ^{1}H-NMR-spectra differ significantly and are very characteristic. Thus, for the 2,3-adducts (Table II) the chemical shift difference for the CHCI- and =CH-protons in both isomers is large, due probably to the deshielding effect of the C—CI and P=O groups when cis-oriented to the respective proton. The most important stereochemical information is obtained from the coupling constants. On the basis of literature data for the stereospecifity of $^4J_{HP}$- and $^4J_{HH}$-values[11] as well as of $^2J_{HP}$-values[12] in similar compounds it may be concluded that the dominant 2,3-adduct possesses (E)-configuration, unlike the case of the analogous reactions with selenenyl chlorides.[10] In the 1,2-adducts (Table III), the lowestfield signal due to the olefinic proton is observed as a quartet (triplet) of doublets as a result of the spin coupling with the methyl(methylene) protons and the phosphorus, the chemical shift difference between the two stereoisomers being 0.65–0.95 ppm. Using similar arguments as

TABLE III

TLC and ^{1}H-NMR data of dialkyl-1-chloro-2-alkyl(phenyl)thio-2-alkenephosphonates **3a–f**

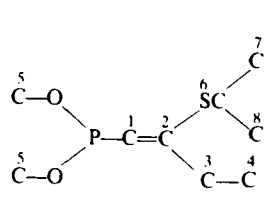


No.	R	R^1 (R^2)	Config.	R_f	Chemical shift, δ ppm, (Coupling constants, J, Hz) Ha (Ha-P)	Hb (Hb-P)	R	R^1(R^1-P)
1	2	3	4	5	6	7	8	9
		Pr^n	E	0.64	5.80 td (1.8)	4.89 brd (15.5)	2.16 s	Me 0.87 t, CH_2 1.44 m CH_2 2.30 m, (2.6)
3a	Me	(Et)	Z	0.60	6.32 td (3.6)	4.48 brd (14.3)	2.18 s	Me 0.86 t, CH_2 1.34 m CH_2 2.32 m (3.8)
		Me	E	0.51	6.06 qdd (2.2)	4.95 brd (15.9)	3.24 sept 1.18 d	1.82 dd (3.4)
3b	Pr^i	(Me)	Z	0.45	6.70 qdd (3.8)	4.52 brd (14.4)	3.14 sept 1.19 d	1.89 ddd (4.1)
		Pr^n	E	0.51	5.96 td (1.9)	4.91 brd (15.7)	3.21 sept 1.17 d	Me 0.86 t, CH_2 1.42 m CH_2 2.26 (2.9)
3c	Pr^i	(Et)	Z	0.43	6.58 td (3.4)	4.47 brd (14.1)	3.16 sept 1.19 d	Me 0.88 t, CH_2 1.42 m CH_2 2.28 m (3.8)
		Pr^n	E	0.64	5.95 td (2.0)	4.56 brd (15.9)	3.21 sept 1.16 d	Me 0.87 t, CH_2 1.50 m CH_2 2.26 m (3.1)
3d	Pr^i	(Pr^n)	Z	0.58	6.62 td (3.7)	4.97 brd (14.7)	3.15 sept 1.20 d	Me 0.89 t, CH_2 1.44 m CH_2 2.30 m (3.6)
		Pr^n	E	traces				
3e	Ph	(Me)	Z	0.60	6.60 td (3.8)	4.32 brd (14.7)	7.1–7.38 m	Me 0.87 t, CH_2 1.47 m CH_2 2.34 m (3.6)
		Pr^n	E	traces				
3f	Ph	(Et)	Z	0.63	6.64 td (4.0)	4.25 brd (14.8)	7.04–7.36 m	Me 0.86 t, CH_2 1.42 m CH_2 2.30 m (3.7)

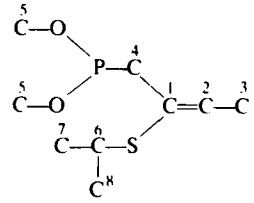
IR-spectra (film, cm^{-1}): 960–985 (R^2—O—P), 1255–1276 (P=O), 1585–1607 (C=C).

TABLE IV

^{13}C-NMR data of alkenephosphonates **2b** and **3e**



3e



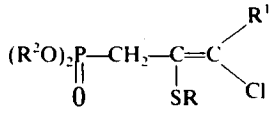
2b

No.	Config.	Chemical shift, δ, ppm (Coupling constants, J, Hz)							
		C-1 (C_1—P)	C-2 (C_2—P)	C-3 (C_3—P)	C-4 (C_4—P)	C-5 (C_5—P)	C-6	C-7	C-8
2b	(E)-1,2-	127.8 (5.6)	138.01 (10.9)	15.5 (2)	51.5 (164.01)	54.4, 54.6 (7.00) (7.2)	37.6 —	25.5 —	22.6 —
2b	(Z)-1,2-	128.0 (4.3)	147.5 (7.7)	16.6 (2)	55.2 (157.1)	54.1, 54.5 (7.01) (7.2)	37.5 —	29.9 —	23.2 —
3e	(E)-2,3-	105.5 (190.9)	165.3 (9.3)	54.9 (7.6)	24.7 —	52.2, 52.5 (5.5) (5.8)	35.2 —	21.8 —	22.0 —

TABLE V

TLC and ^{1}H-NMR data of dialkyl-3-chloro-2-alkyl(phenyl)thio-2-alkenephosphonates **4a–d**

alkenephosphonates **4a–d**



No.	R	R^1 (R^2)	Con-fig.	R_f	Chemical shift, δ, ppm (Coupling const, J, Hz)				
					CH_2	R	R^1	CH_2—P	R^1—P
4a	Me	H	E	0.42	2.98 brd	2.27 s	5.84 brd	22.5	5.4
		(Et)	Z	0.37	2.80 dd	2.35 s	6.13 dd	21.8	6.1
4b	Et	H	E	0.49	2.93 brd	1.35 t 2.98 q	5.76 brd	22.0	5.1
		(Me)	Z	0.44	2.77 dd	1.38 t 3.02 q	6.02 dd	21.5	5.9
4c	Ph	H	E	0.55	2.72 brd	7.12–7.32 m	5.21 brd	22.3	4.6
		(Et)	Z	0.47	2.48 dd	7.10–7.28 m	6.37 m	21.6	5.3
4d	Me	Pr^n	E	0.39	2.90 d	2.26 s	Me 0.98 t CH_2 1.95–2.4 m	21.7	2.1
		(Et)	Z	traces					

IR-spectra (film, cm^{-1}): 970–990 (R^2—O—P), 1268–1280 (P=O), 1598–1612 (C=C).

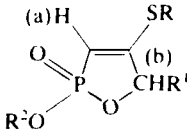
for the 2,3-adducts, we ascribed (Z)-configuration to the isomer with the olefinic proton at lower field and larger $^4J_{HP}$- and $^5J_{HP}$-values.

The ^{13}C-NMR-spectra of the (E)- and (Z)-isomers of compound **3c** differ significantly from those of the 2,3-adducts,[12] resp. comp. **2e** (Table IV) and are also in agreement with the structure of 2-isopropylthio-1-chloro-2-butene-phosphonic esters but not of 1-isopropylthio-2-chloro-2-butenylphosphonates as assumed in.[5] This conclusion is mainly supported by the chemical shift of the phosphorus-bonded carbon (corresponding to that of a CHCl group) as well as by the large $^1J_{CP}$-value caused by the electronegative effect of the chlorine atom.[13]

The structure and configuration of compounds **4a–d** were determined on the

TABLE VI

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



No.	R	$R^1(R^2)$	Con-fig.	R_f	Chemical shift, δ, ppm (Coupling const., J, Hz) Ha (Ha–P)	Hb (Hb–P)	R	R^1 (Ha–Hb)
1	2	3	4	5	6	7	8	9
5a	Et	H (Me)	—	0.20	5.50 dd (28.8)	4.54 dd (7.0)	1.23 t 3.26 q	4.54 dd (1.4)
b	Me	H (Et)	—	0.19	5.54 dd (28.9)	4.56 dd (7.0)	2.40 s	4.56 dd (1.4)
c	Ph	H (Et)	—	0.28	5.28 dd (29.8)	4.53 dd (7.0)	7.32 s	4.53 dd (1.5)
d	Me	Pr^n	E	0.21	5.36 dd (27.0)	4.69 m	2.32 s	Me 0.87 t (1.7) CH_2 1.42, 1.74 m
		(Et)	Z	0.25	5.39 dd (26.8)	4.67 m	2.35 s	Me 0.88 t (1.3) CH_2 1.44, 1.78 m
e	Pr^i	Me	E	0.26	5.44 dd (28.0)	4.74 m	Me 1.47 d CH 3.32 sept	1.35 d (1.8)
		(Me)	Z	0.27	5.46 dd (27.5)	4.72 m	Me 1.42 d CH 3.36 sept	1.37 d (1.4)
f	Pr^i	Pr^n	E	0.25	5.51 dd (27.0)	4.67 m	Me 1.30 d CH 3.37 sept	Me 0.95 t (1.4) CH_2 1.44, 1.80 m
		(Et)	Z	0.29	5.52 dd (26.5)	4.59 m	Me 1.28 d CH 3.34 sept	Me 0.96 t (1.0) CH_2 1.46, 1.84 m
g	Pr^i	Pr^n	E	0.26	5.59 dd (28.5)	4.74 m	Me 1.30 d CH 3.40 m	Me 0.94 t (1.6) CH_2 1.43, 1.80 m
		(Pr^n)	Z	0.30	5.62 dd (28.0)	4.72 m	Me 1.29 d CH 3.36 m	Me 0.94 t (1.2) CH_2 1.43, 1.80 m
h	Ph	Pr^n	E	0.31	5.07 dd (26.5)	4.83 m	7.34 s	Me 0.90 t (1.6) CH_2 1.49, 1.90 m
		(Me)	Z	0.34	5.09 dd (26.0)	4.78 m	7.31 s	Me 0.93 t (1.1) CH_2 1.51, 1.96 m
i	Ph	Pr^n	E	0.35	5.03 dd (27.6)	4.79 m	7.32 s	Me 0.90 t (1.8) CH_2 1.50, 1.91 m
		(Et)	Z	0.38	5.05 dd (27.0)	4.74 m	7.30 s	Me 0.92 t (1.3) CH_2 1.52, 1.94 m

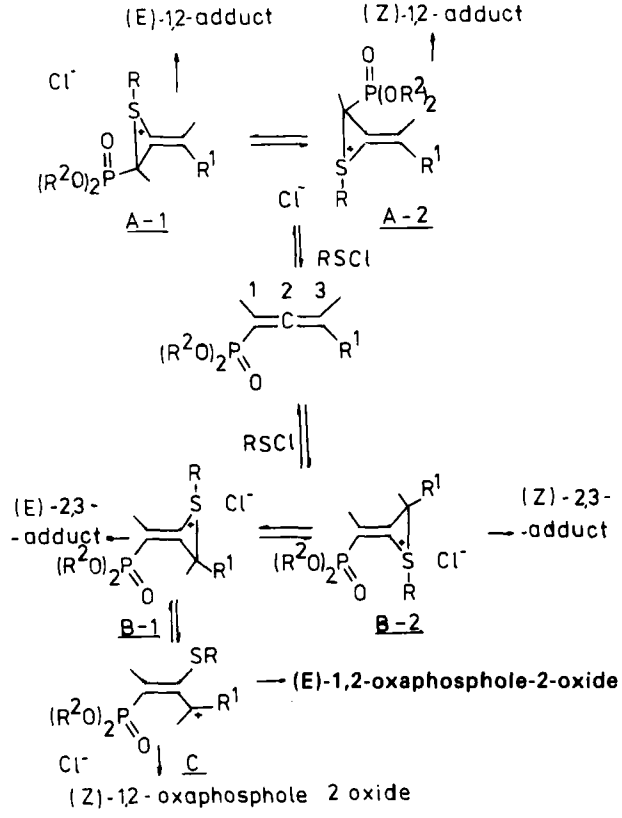
basis of their ^{1}H-NMR-spectra (Table V) using similar criteria as for the selene analogues.[10]

Our conclusion that the alkenephosphonates **2, 3** and **4** are structural isomers is also supported by their mass spectra possessing a molecular ion peak at the same m/z-value but with different intensity.[14]

The structure and configuration of the oxaphospholes **5a–e** in the form of (E)/(Z)-mixtures or pure stereoisomers (Table VI) were determined by spectral comparison with literature data for similar compounds with configuration proven by X-ray analysis[8] as well as on the basis of the $^4J_{HH}$-values measured for the two isomers.

DISCUSSION

The published data concerning the reaction of allenes with nonacidic electrophiles are in favour of an A_E2 mechanism.[15–17] The (E), (Z)-diastereoselectivity observed in some cases as well as other experimental data are in agreement with the initial formation of a δ-complex with onium structure the stability of which depends on the biphylicity of the heteroatom and the nature of substituents at the terminal allene carbons. It is known that sulfur tends to form relatively stable onium ions which appear in the rate-determining step and possess a partial thiyranium structure.[17] In our case reacting intermediates are the episulfonium ions **A-1**, **A-2**, **B-1** and **B-2**:



The presence of the electron-accepting phosphoryl group should facilitate the formation of the ions **B-1** and **B-2** leading to 2,3-adducts and cyclic compounds, which is in agreement with the experimental observations. The formation of significant amounts of 1,2-adducts via the **A-1** and **A-2** ions could be attributed to the domination of steric control in the episulfonium ion formation. The (Z)-stereoselection observed could be attributed to the phosphoryl group influenced decrease in participation of thiyranium structure of the ions **A-1** and **A-2** which should increase the mobility of the halide and facilitate the trans-approach to the C-3 atom resulting in formation of (Z)-1,2-adducts.

The product formation upon 2,3-addition significantly depends on the degree of substitution at the C-3 atom. In the case of secondary C-3 atom the ions **B-1** and **B-2** will be in an equilibrium with the acyclic ion **C**, resulting in two reaction pathways: heterocyclization and addition, in agreement with the experimental data. The first route is strongly represented if the sulfur is bonded to an aryl substituent destabilizing the cyclic ions. In the case of primary C-3 atom the acyclic ions are formed with difficulty and the heterocyclization occurs in insignificant degree. The (E)-stereoselection observed for the addition reaction could be attributed to the stronger participation of the thiyranium structure for the ions **B-1** and **B-2** as well as to the less mobile nucleophile resulting in a favoured cis-approach to the C-3 atom. The following conclusions could be drawn from the experimental data:

1. The interaction of dialkyl propadienylphosphonates with sulfenyl chlorides is a chemoselective and regioselective reaction with a pronounced (E)-stereoselectivity.

2. The reactions of the 3-monoalkylsubstituted allenephosphonic esters retain only the regioselectivity and otherwise take several directions, the 1,2-addition exhibiting (Z)- and the 2,3-addition-(E)-stereoselectivity, unlike the behaviour of the selenenyl chlorides under similar conditions.

EXPERIMENTAL

Analytical methods. IR spectra were obtained on a UR-10 or IR-72 (Carl Zeiss, Jena) infrared spectrophotometers. ^{1}H-NMR-spectra were recorded at normal temperature on a JEOL JNM-PS-100 (100 MHz) or Brucker WM-250 (250.1 MHz) resp. Brucker WH-400 (400 MHz)-FT-spectrometers in $CDCl_3$ using HMDSO or TMS as internal reference. ^{13}C-NMR-spectra were measured on a Brucker WM-250 (62.9 MHz) or Brucker WH-400 (100.6 MHz) FT-spectrometers in $CDCl_3$ with TMS as internal reference.

Starting materials. The crude reaction mixtures of **1a–f** with sulfenyl chlorides were prepared according to References 5, 6 and 8.

Column and TL chromatography—general procedure. The qualitative TLC investigations were performed on silica gel "Merck" $60F_{254}$ pre-coated sheets, using ethyl acetate-hexane (23:10) mixture as eluant with two- or threefold development. Preparative TLC was performed on silica gel with the same eluant. The column chromatographic separation was carried out on silica gel "merck" 60 (0.063–0.200 mm).

Column chromatographic separation of the reaction mixtures. General procedure. 0.6 to 1.5 g of the reaction mixture, adsorbed on silica gel were inserted into the column containing 60 to 150 g silica gel in hexane. Then hexane- ethyl acetate mixtures with increasing polarity (9:1 to 1:2) and finally pure ethyl acetate were used as eluant. Fractions of each 30 or 60 ml were collected at a rate of about 90 drops/min.

Chromatographic separation of the reaction mixture obtained by interaction of diethyl-1,2-propadienylphosphonate **1a** *and MeSCl.* Starting with a mixture of 0.61 g, the following products were isolated:

Fractions	Compounds	g	%
18–26	(E)-**2a**	0.317	52
27–47	(E)-**2a** + (Z)-**2a**	0.049	8
48–53	(Z)-**2a**	0.030	5
54–59	(E)-**4a**	0.067	11
60–70	(E)-**4a** + (Z)-**4a**	0.043	7
71–82	(Z)-**4a**	0.073	12
89–93	**5a**	0.018	3

Chromatographic separation of the reaction mixture obtained by interaction of diethyl-1,2-propadienylphosphonate **1a** *with PhSCl.* Starting from a mixture of 0.59 g the following products were isolated:

Fractions	Compounds	g	%
12–26	(E)-**2c**	0.236	40
27–32	(E)-**2c** + (E)-**4c**	0.083	14
33–40	(E)-**4c**	0.171	29
47–51	(Z)-**2c**	0.012	2
52–54	(Z)-**4c** + (Z)-**2c**	0.053	9
55–58	**5b**	0.030	5

Chromatographic separation of the reaction mixture obtained by interaction of dimethyl-1,2-butadienylphosphonate **1c** *with Pr^{i}SCl.* From a mixture of 0.92 g were isolated the following products:

Fractions	Compounds	g	%
40–43	(E)-**3b**	0.037	4
44–53	(E)-**3b** + (Z)-**3b**	0.230	25
54–61	(Z)-**3b**	0.067	7
62–68	(E)-**2e** + (Z)-**3b**	0.018	2
69–76	(E)-**2e**	0.064	7
77–80	(E)-**2e** + **5d**	0.028	3
81–98	(E)/(Z)-**5d**	0.460	50

Applying preparative TLC on the fractions 44–53 (hexane-ethyl acetate 40:13) pure (E)-**3b** was obtained. (Z)-**2e** was obtained through separation of the fractions 77–80 (hexane-ethyl acetate 10:25).

Chromatographic separation of the reaction mixture obtained by interaction of diethyl-1,2-hexadienylphosphonate **1e** *and PhSCl.* Starting with 0.83 g of the reaction mixture the following compounds were isolated through column and preparative TL chromatography:

Fractions	Compounds	g	%
21–25	(E)-**2i**	0.050	6
26–32	(E)-**2i** + (Z)-**3f**	0.100	12
33–35	(Z)-**3f**	0.083	10
36–38	(Z)-**3f** + (Z)-**2i**	0.033	4
39–56	(E)/(Z)-**5h**	0.548	66

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