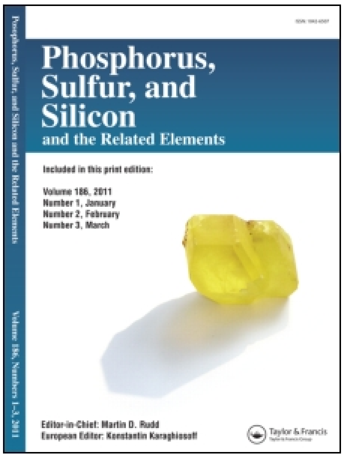

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FIVE-MEMBERED PHOSPHORUS HETEROCYCLES BY THE REACTION OF SULFENYL-AND SELENENYL CHLORIDES WITH 2-(1,2-ALKADIENYL)-1,3,2- DIOXAPHOSPHOLANE-2-OXIDES

Christo M. Angelov[a]; Christo Zh. Christov[a]
[a] Department of Chemistry, Higher Pedagogical Institute, Shoumen, Bulgaria

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FIVE-MEMBERED PHOSPHORUS HETEROCYCLES BY THE REACTION OF SULFENYL- AND SELENENYL CHLORIDES WITH 2-(1,2-ALKADIENYL)-1,3,2-DIOXAPHOSPHOLANE-2-OXIDES

CHRISTO M. ANGELOV* and CHRISTO ZH. CHRISTOV

Department of Chemistry, Higher Pedagogical Institute,
9700 Shoumen, Bulgaria

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It was found that in the reaction of sulfenyl and selenenyl chlorides with 2-(1,2-alkadienyl)-1,3,2-dioxaphospholane-2-oxides cyclization occurred to give 2-oxo-1,2-oxaphosphol-3-ene derivatives. The sulfenyl chlorides with the cyclic esters also afford 1,2-adducts in temperature dependent amounts.

INTRODUCTION

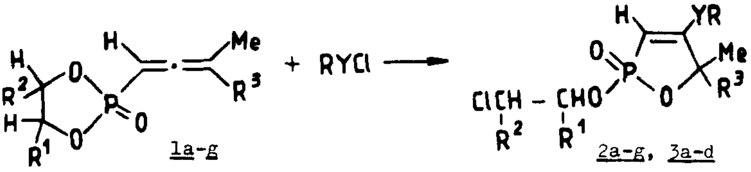
It was recently reported that the interaction of sulfenyl chlorides and selenenyl analogues with 3,3-disubstituted allenylphosphonic esters proceed via the elimination of alkyl chlorides and formation of five-membered heterocyclic systems.[1-3] It was found by means of column chromatography that in the case of sulfenyl chlorides besides the cyclic esters, minor amounts of the 1,2-adducts are formed, too.[4]

The easy access to 2-(1,2-alkadienyl)-1,3,2-dioxaphospholane-2-oxides permitted us to continue our studies on the five-membered heterocyclization of the allenylphosphonate system of π-bonds.[5] It is known that dioxaphospholanes are highly reactive compounds, often participating in ring opening reactions.[6] This was also corroborated by us in the halogenation of the phosphonates, **1a–g**. Addition of the reagent takes place during the reaction, followed by opening of the dioxaphospholane ring and formation of a new 1,2-oxaphosphol-3-ene.[7] As a continuation of these investigations we presently report the results of the interaction of sulfenyl or selenenyl chlorides with the dioxaphospholanes, **1a–g**.

RESULTS

The reaction of sulfenyl and selenenyl chlorides with the 2-(1,2-alkadienyl)-1,3,2-dioxaphospholane-2-oxides, **1a–g** was carried out in dry CCl_4 or $CHCl_3$ at 15 to 20°C or at -60°C. The results indicate that the main reaction proceeds via dioxaphospholane ring opening, followed by addition of the reagent and formation of

1,2-oxaphosphol-3-ene-2-oxides:



1	R^1	R^2	R^3
a	H	H	Me
b	H	H	Et
c	H	H	Pr^n
d	Me	H	Me
e	Me	H	Et
f	Me	Me	Me
g	Me	Me	Et

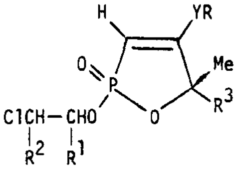
2a–2g and **3a–3d**: see Table I.

SCHEME 1

The reaction mixtures obtained during the interaction of 2-(3-methyl-1,2-butadienyl)-1,3,2-dioxaphospholane-2-oxide **1a** and methylsulfenyl or methylseleneny1 chloride in chloroform at 20°C and −60°C were examined with a view of assessing the extent of the cyclization and the side reactions. The ^{1}H-nmr spectral data indicate that when sulfenyl chloride was used at 20°C, alongside the cyclic ester **2a**, the product of addition to the C^1—C^2 double bond **4a** was also formed (Fig. 1). The oxaphospholene vs. 1,2-adduct ratio is 4 : 1, i.e. the latter amounts to almost 25% of the total reaction product. At −60°C the amount of the 1,2-adduct formed is about 5% of the total. In contrast to sulfenyl chloride, in the presence of methylselenenyl chloride the reaction proceeds, irrespective of the temperature, solely with the conversion of the allenylphosphonate **1a** into the 1,2-oxaphosphol-3-ene **3a** (Fig. 2). While sulfenyl chlorides form 1,2-adducts (**4a–d, 4f**) also with other allenyl dioxaphospholanes (Table II), selenenyl chlorides in none of our experiments afforded addition products. It has to be noted that after two vacuum distillations from the reaction mixtures of **1a–g** with sulfenyl chlorides only the oxaphosphol-3-enes **2a–g** were isolated. The structure of **2a–g** and **3a–d** was determined on the basis of ir, ^{1}H-nmr spectra and elemental analysis (Tables I and III). Compounds **2b–g** and **3b–d** contain more than one chiral center and exist as diastereoisomeric mixtures. The presence of diastereoisomers is partially observed in the ^{1}H-nmr spectra of these substances (see Table I). Especially noteworthy is the characteristic signal ascribed to the C^3 ring proton appearing at weaker fields. The presence of diastereoisomers in the mixture is reflected in the appearance of several doublets ($^2J_{HP}$ 25.2–28.4 Hz) of varying intensities. Fig. 3 shows the signal of this proton for compound **3d**, involving four centers of chirality. In ir spectra of **2a–g** and **3a–d** there are absorbtion bans from the C—C double bond (1530–1545 cm^{-1}), from the phosphoryl group (1240–1275 cm^{-1}) and from the C—O—P group (1000–1100 cm^{-1}). The 1,2-oxaphosphol-3-enes, **2a–g** and **3a–d** are viscous liquids some of which crystallize after distillation.

TABLE I

^{1}H-nmr data for 1,2-oxaphosphol-3-ene-2-oxides, **2a–g** and **3a–d**

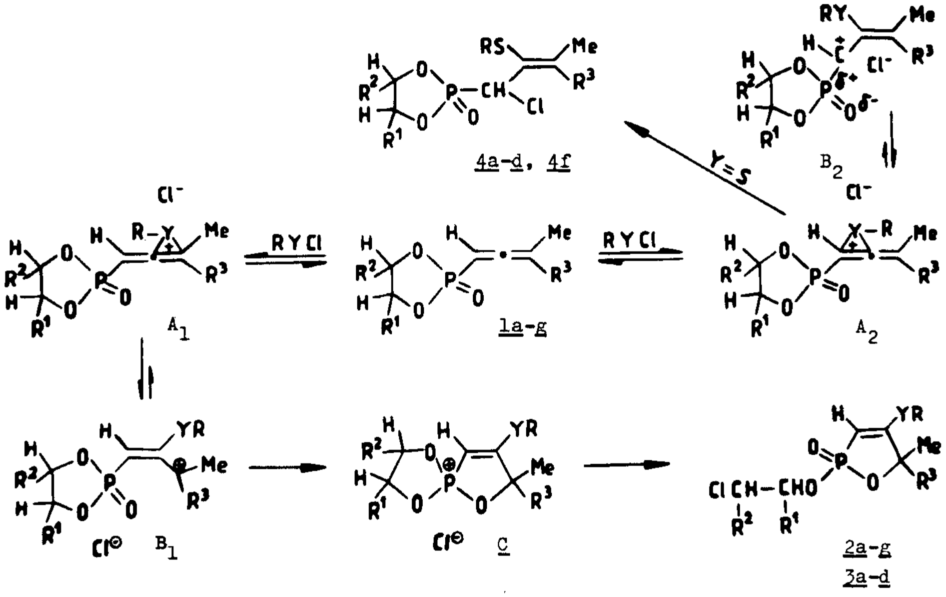


No	R (Y)	R^1 (R^2)	R^3	Chemical Shifts, δ					J Hz		
				H	R	CHR^1	CHR^2	R^3	Me	H—P	R^1CH—P
2a	Me (S)	H (H)	Me	5.60d	2.43s	4.18dt	3.65t	1.49s	1.52s	26.4	10.0
b	Me (S)	H (H)	Pr^n	5.49d	2.37s	4.25dt	3.63t	Me 0.89t CH_2CH_2	1.51s 1.53s	26.4	9.6
c	Me (S)	Me (H)	Me	5.44d 5.48d	2.42s	H 4.66m Me 1.43d	1.65m 3.58d	1.55s	1.58s	25.2	9.6
d	Pr^i (S)	Me (H)	Me	5.64d	CH 3.44q Me 1.32d	H 4.67m Me 1.40d	3.60d	1.50s	1.54s	25.6	9.6
e	Pr^i (S)	Me (H)	Et	5.63d	CH 3.22q Me 1.31d	H 4.64m Me 1.38d	3.52d	CH_2 1.72q Me 0.83t	1.38s 1.42s	26.0	9.4
f	Me (S)	Me (Me)	Me	5.43d 5.47d	2.38s	H 4.52m Me 1.38d	H 4.08dq Me 1.38d	1.48s	1.52s	26.0	9.0
g	Pr^i (S)	Me (Me)	Et	5.53d 5.54d 5.60d	H 3.36q Me 1.34d	H 4.75m Me 1.42d	H 4.13dq Me 1.42d	CH_2 1.84q Me 0.90t	1.52s 1.54s	26.2	9.4
3a	Me (Se)	H (H)	Et	5.60d	2.26s	4.20dt	3.62t	1.48s	1.52s	26.8	9.4
b	Ph (Se)	H (H)	Et	5.28d	7.48m	4.23dt	3.61t	CH_2 1.92q Me 1.00t	1.58s 1.62s	28.4	10.0
c	Ph (Se)	Me (H)	Me	5.27d 5.33d	7.50m	H 4.68m Me 1.38d	3.54d	1.64s	1.68s	28.4	10.0
d	Me (Se)	Me (Me)	Et	5.70d 5.72d 5.77d	2.34s	H 4.74m Me 1.42d	H 4.14dq Me 1.42d	CH_2 1.81q Me 0.92t	1.51s 1.54s 1.57s	28.0	11.8

s- singlet, d- doublet, t- triplet, q- quartet, m- multiplet, dt- doublet-triplet, dq- doublet-quartet
IR Spectra, cm^{-1}: $1530–1545_{(C=C)}$, $1240–1275_{(P=O)}$, $1000–1100_{(C-O-P)}$.

DISCUSSION

The reactions described above are assumed to proceed via an ionic pathway since it is well known that sulfenyl and selenenyl chlorides are polar compounds ($RY^{\delta+}Cl^{\delta-}$). The electrophilic sulfur or selenium atom can attack, in principle, either of the two double bonds of the allenic system by formation two π-complexes (onium ions):



SCHEME 2

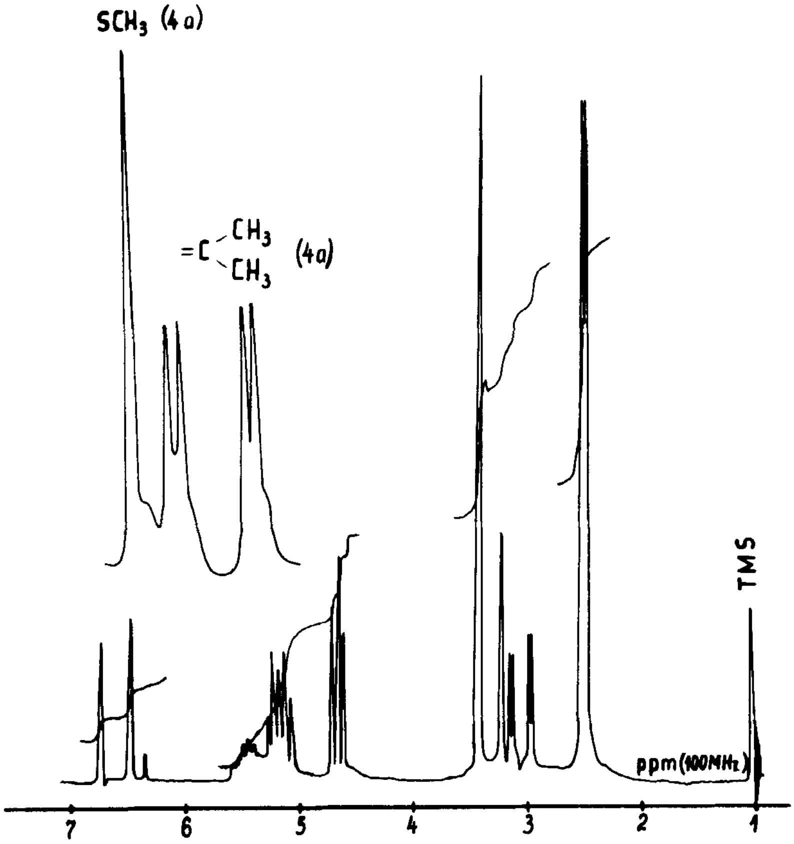


FIGURE 1 ^{1}H-nmr spectrum of the reaction mixture obtained from 2-(3-methyl-1,2-butadienyl)-1,3,2-dioxaphospholane-2-oxide **1a** and MeSCl, containing 4-methylthio-5,5-dimethyl-2-(2-chloroethoxy)-1,2-oxaphosphol-3-ene-2-oxide **2a** and 2-(1-chloro-2-mehtylthio-3-methyl-2-butenyl)-1,3,2-dioxaphospholane-2-oxide **4a**.

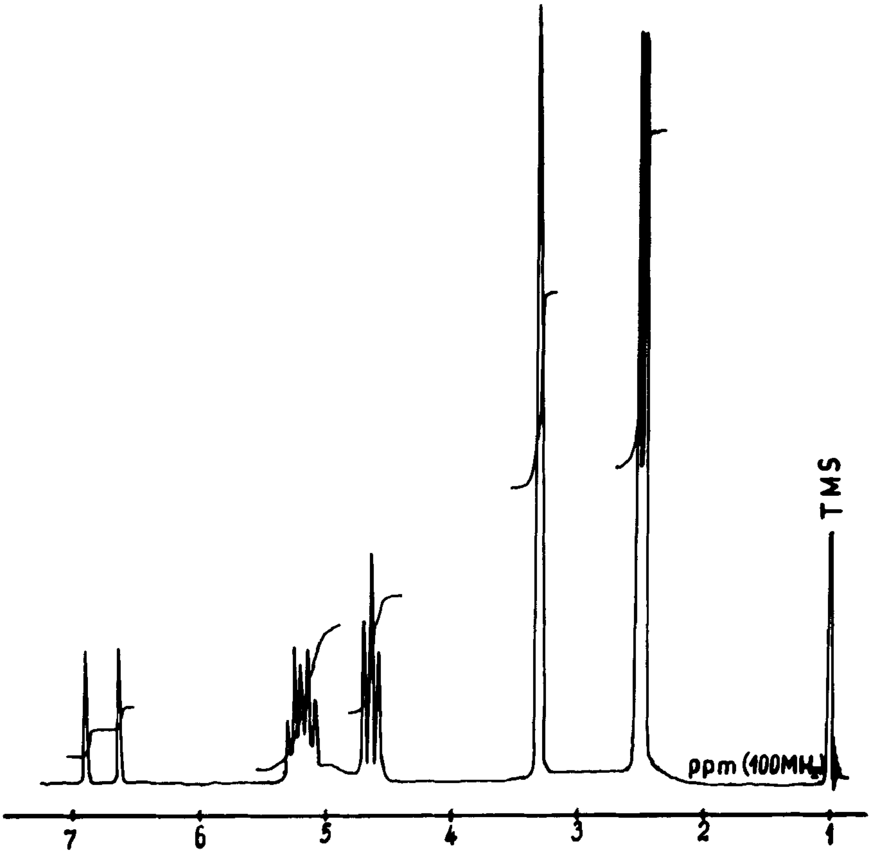


FIGURE 2 ^{1}H-nmr spectrum of the reaction mixture obtained from 2-(3-methyl-1,2-butadienyl)-1,3,2-dioxaphospholane-2-oxide **1a** and MeSeCl, containing 4-methylseleno-5,5-dimethyl-2-(2-chloroethoxy)-1,2-oxaphosphol-3-ene-2-oxide **3a**.

It is obvious that A_1 would be formed in preference to A_2. This was confirmed by the observation of varying quantities of the 1,2-adducts on treating **1a–g** with sulfenyl chlorides depending on the reaction temperature. The significant decrease of addition across the C^1—C^2 double bond at low temperature undoubtedly reflects its decreased reactivity. Although sulfur and selenium have almost identical electronegativities (S 2.44 and Se 2.48)[8] and in spite of the expected similar stability of the A_1 and A_2 intermediates, formation of 1,2-adducts is not observed when selenenyl chloride is employed. The non-formation of the 1,2-adduct in this case can be explained by the greater covalent radius of selenium (1.16 Å),[8] as against that of sulfur (1.02 Å)[9] which results in a weakening of the carbon–selenium bond in A_1 and A_2 and, in turn, leads to their easy cleavage and formation of free carbenium ions B_1 and B_2. The partially positive P-atom (see Scheme 2) renders the formation of B_1 difficult and shifts the equilibrium towards the ion B_2, facilitating in this way

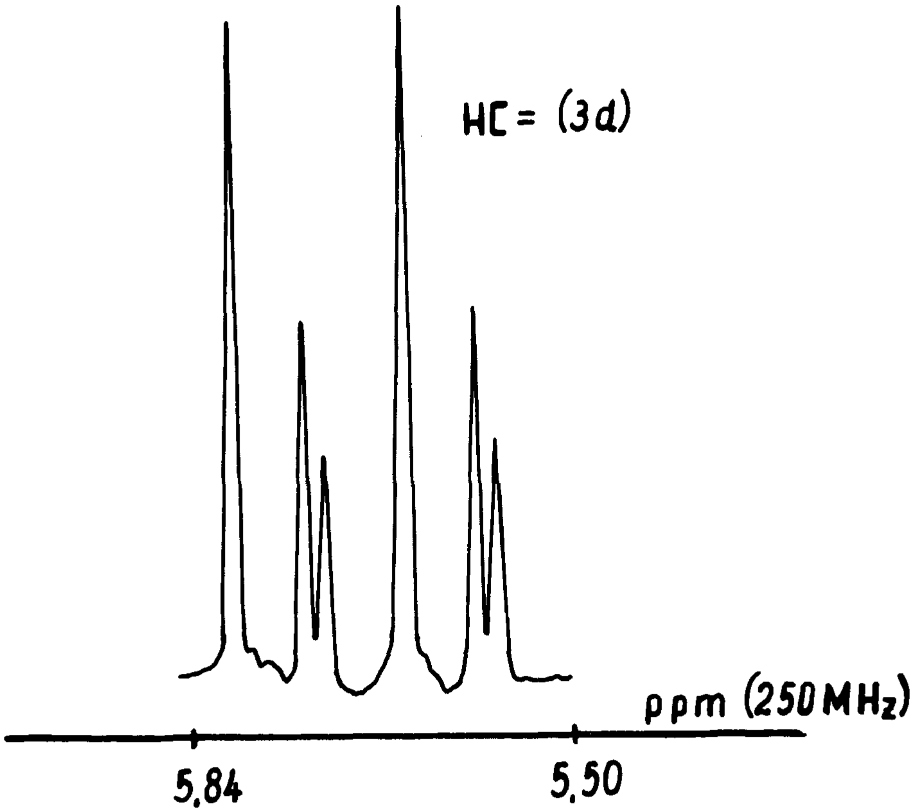
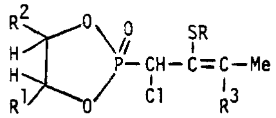


FIGURE 3 The ^{1}H-nmr signal of the proton at the double bond (^{3}H) in the 1,2-oxaphosphol-3-ene **3d** with four centers of chirality.

TABLE II

^{1}H-nmr spectra of the 1,2-adducts, **4a–d**, **4f**



	Chemical Shifts, δ						J Hz		
No	H	R	CHR^1	CHR^2	R^3	Me	H—P	Me—P	R^3—P
4a	5.32d	2.23s	4.46m	4.46m	1.97d	2.13d	13.2	3.0	2.4
b	5.22d	2.28s	4.22m	4.22m	Me 0.89t CH_2CH_2 1.60m	Z 1.92d E 2.10d	13.8	2.2 3.0	—
c	5.26d	2.26s	CH 3.98m Me 1.41d	4.62m	1.98d	2.15d	14.0	3.8	2.4
d	5.30d	CH 3.42q Me 1.30d	CH 3.92m Me 1.40d	4.50m	2.06d	2.12d	14.4	3.2	2.4
f	5.26d	2.20s	CH 4.40m Me 1.42d	CH 4.40m Me 1.42d	1.96d	2.10d	12.8	3.2	2.4

R, R^1, R^2 and R^3: see Table I.
s- singlet; d- doublet; t- triplet; q- quartet; m- multiplet.

TABLE III

Physical constants and analyses of compounds **2a–g**, **3a–d**

No	Yield %	bp°C (mm)	n_D^{20} (d_4^{20})	Found, %			Formula	Calculated, %		
				P	Cl	Y		P	Cl	Y
2a	71	155–156 (1.0)	1.5262 (1.3076)	12.06	14.02	12.33	$C_8H_{14}ClO_3PS$	12.06	13.80	12.50
b	67	162–163 (1.0)	1.5172 (1.2256)	10.82	12.62	11.23	$C_{10}H_{18}ClO_3PS$	10.87	12.44	11.27
c	74	145–146 (1.0)	1.5192 (1.2584)	11.41	13.15	11.77	$C_9H_{16}ClO_3PS$	11.43	13.09	11.85
d	66	150–151 (1.0)	1.5093 (1.1660)	10.32	11.67	10.57	$C_{11}H_{20}ClO_3PS$	10.36	11.86	10.74
e	75	153–154 (1.0)	1.5072 (1.1968)	9.85	11.48	10.25	$C_{12}H_{22}ClO_3PS$	9.90	11.33	10.26
f	67	145–146 (1.0)	1.5118 (1.2159)	10.79	12.15	11.38	$C_{10}H_{18}ClO_3PS$	10.87	12.44	11.27
g	71	156–157 (1.0)	1.5068 (1.1566)	9.40	10.79	9.70	$C_{13}H_{24}ClO_3PS$	9.47	10.84	9.82
3a	70	165–166 (1.0)	1.5342 (—)	10.28	11.58	—	$C_8H_{14}ClO_3PSe$	10.20	11.67	—
b	68	198–199 (1.0)	1.5702 (—)	8.18	9.34	—	$C_{14}H_{18}ClO_3PSe$	8.15	9.33	—
c	65	192–193 (1.0)	1.5632 (—)	8.00	9.39	—	$C_{14}H_{18}ClO_3PSe$	8.15	9.33	—
d	73	147–148 (1.0)	1.5202 (—)	8.95	10.14	—	$C_{11}H_{20}ClO_3PSe$	8.96	10.26	—

cyclization. The absence of a 2,3-adduct, arising from the addition of chloride ion to the C^3 atom, is probably due to the geometry of the transition state in which the C^3 atom is moved closer to the phosphoryl oxygen, as a result of the geminal effect of the alkyl groups; in this manner nucleophilic attack is facilitated. This reaction probably proceeds through a spiro intermediate *C* which then rapidly intramolecularly rearranges with cleavage of the dioxaphospholane ring and restoration of the tetracoordination of the P-atom. The greater amount of 1,2-adducts (20–25%) on treating compounds **1a–g** with sulfenyl chloride, in comparison to the amounts of the same adducts when using the 3,3-disubstituted allenylphosphonic esters (8–12%)[4] is probably due to the greater strength of the carbon–oxygen bond in the P—O—C grouping in the dioxaphospholane ring which hinders the second stage of the oxaphospholene cyclization—an Arbuzov type rearrangement. In spite of this, at lower temperature the five-membered heterocyclization of the allenylphosphonate system of π-bonds takes place because of the decreased reactivity of the C^1—C^2 double bond, as a result of the electron-withdrawing properties of the P=O function.

EXPERIMENTAL

Methods of analysis

^{1}H-nmr spectra were determined on a "Jeol" JNM-PS-10 (100 MHz) spectrometer as solutions in $CDCl_3$ with TMS as internal standard. The ir spectra were recorded on a spectrophotometer IR-72 (Carl Zeiss, Jena, DDR).

Starting materials

The 2-(1,2-alkadienyl)-1,3,2-dioxaphospholanes was prepared from phosphorus trichloride, 1,2-alkanedioles and α-alkynols.[5] The sulfenyl and selenenyl chlorides was synthezised in solution from the corresponding disulfides or diselenides and chlorine or sulfuryl chloride.

General method for preparation of 2-oxo-1,2-oxaphosphol-3-ene derivatives **2a–g**, **3a–d**

A solution of 0.03 mole of sulfenyl or selenenyl chloride in dry CCl_4 or $CHCl_3$ is slowly added, with stirring, at 15–20°C or at −60°C, to a solution of 0.03 mole of 2-(1,2-alkadienyl)-1,3,2-dioxaphospholane-2-oxide in the same solvent. Stirring of the reaction mixture is continued for 1 h. After the solvent is removed the residue is distilled twice in vacuo. Yields 65–75%.

REFERENCES

1. Ch. M. Angelov, K. V. Vachkov, B. I. Ionin and M. Kirilov, *Zh. Obshch. Khim.*, **49**, 2438 (1979).
2. Ch. M. Angelov, K. V. Vachkov, M. Kirilov, B. I. Ionin and A. A. Petrov, *C.r. Acad. bulg. Sci.*, **32**, 611 (1979); *Chem. Abst.*, **92**: 22561k (1980).
3. Ch. M. Angelov and Ch. Zh. Christov, *Zh. Obshch. Khim.*, **50**, 1891 (1980).
4. Ch. M. Angelov, K. V. Vachkov, J. Petrova and M. Kirilov, *Phosphorus and Sulfur*, in press.
5. Ch. M. Angelov and Ch. Zh. Christov, *C.r. Acad. bulg. Sci.*, in press.
6. A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier Publ. Comp., Amsterdam, London, New York, 1967, p. 211, 322, 339, 342, 349.
7. Ch. M. Angelov and Ch. Zh. Christov, *Heterocycles*, in press.
8. A. J. Gordon, R. A. Ford, "The Chemist's Companion", John Wiley & Sons, New York, 1972, p. 84.
9. Encyclopedia of Chemical Technology, Vol. 17, John Wiley & Sons, New York, 1968, p. 881.