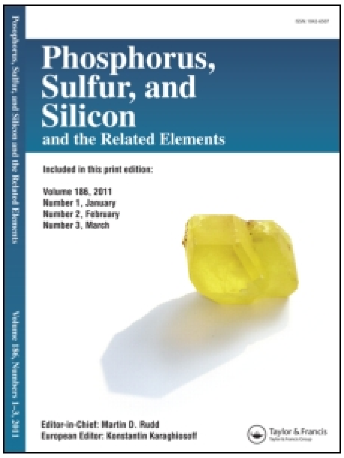

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THE REACTIONS OF ALLENIC PHOSPHONYL DICHLORIDES WITH SULFENYL CHLORIDES

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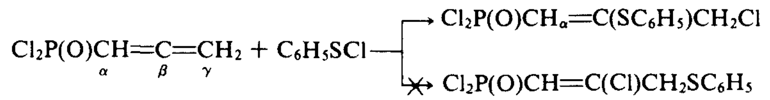
The structure of the product of the interaction of dichlorides of allenylphosphonic acids with sulfenyl chlorides depends on the nature of sulfenyl chlorides and substituents at the terminal carbon atom of allenic system. Arylsulfenyl chlorides and dichlorides of γ,γ-dialkylsubstituted allenylphosphonic acids form diene products. Phosphonesulfenyl chloride acts as chlorinating agent to form 4-chlorooxaphospholenes. The dichloride of propadienephosphonic acid reacts with phenylsulfenyl chloride yielding the addition product.

INTRODUCTION

The reactions of sulfenyl chlorides with allenic systems represents one of the poorly studied areas of electrophilic addition.[1] Up to recent times there were practically no data about the interaction of sulfenyl chlorides with phosphorus-containing allenes.[2–4] We considered it of interest to investigate the influence of substituents at the phosphorus atom and the terminal carbon atom in phosphonyl allenes upon the direction of addition of sulfenyl chlorides to these compounds and upon the structure of products formed.

RESULTS AND DISCUSSION

We have established that the dichloride of propadienephosphonic acid adds phenylsulfenyl chloride at the β, γ-double bond with an attack of the phenylthio group on the central carbon atom of the system of cumulative double bonds and with the formation of the product of anti-Markovnikov addition. This conclusion follows from the analysis of the ^1H NMR spectrum of the product of addition (Figure 1):



$$Cl_2P(O)\underset{\alpha}{CH}=\underset{\beta}{C}=\underset{\gamma}{CH_2} + C_6H_5SCl \left\{ \begin{array}{l} \rightarrow Cl_2P(O)CH_\alpha=C(SC_6H_5)CH_2Cl \\ \cancel{\rightarrow} Cl_2P(O)CH=C(Cl)CH_2SC_6H_5 \end{array} \right.$$

The presence of the phenylthio group at the β-carbon atom of the dichloride of 2-phenylthio-3-chloro-1-propenephosphonic acid contributes to an upfield shift of the resonance signal of H_α in comparison with the value of its chemical shift in the ^1H NMR spectrum of dichloride of 2,3-dichloro-1-propenephosphonic acid.[5] The comparison of the ^1H and ^{31}P NMR spectra of the crude reaction mixture at −20°C and the distilled product testifies to the absence of isomerization of the initial product of addition. The attribution of proton signals to the E-isomer was made on the basis of calculated chemical shift of the olefinic proton H_α for the corresponding E- and Z-configurational isomers with the use of increments for the C_6H_5S- and $ClCH_2$-

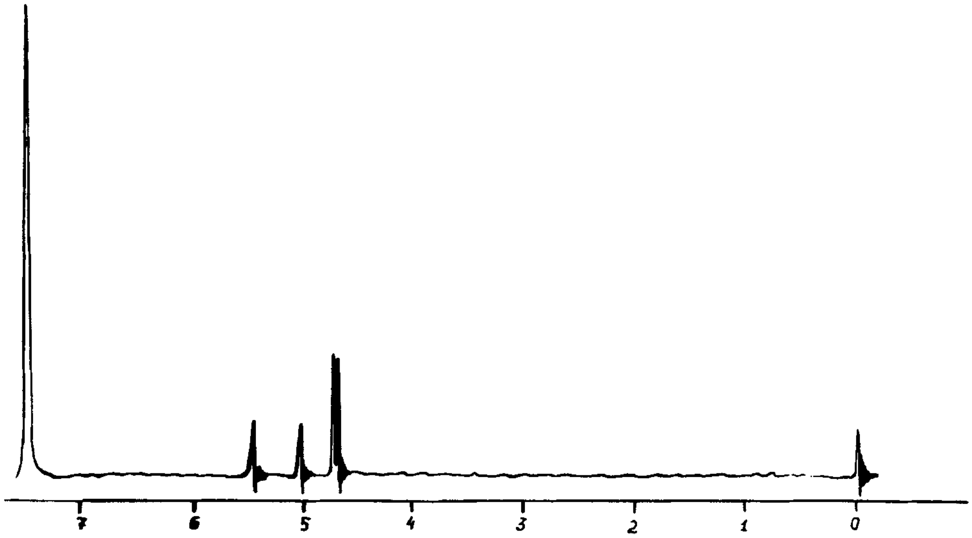
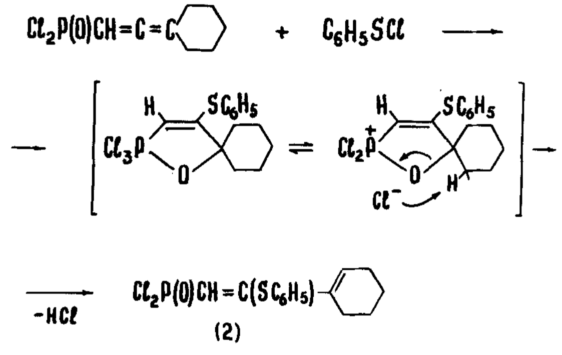


FIGURE 1 ^{1}H NMR spectrum of the dichloride of 2-phenylthio-3-chloro-1-propenephosphonic acid (1).

groups.[6] The stereospecific course of this reaction with the formation of E-configuration isomer 1 could be explained by lesser spatial obstacles during the trans-attack (relative to the phosphonyl group) of the phenylsulfenyl chloride molecule upon the β-carbon atom of cumulene.

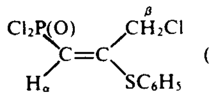
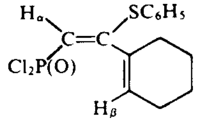
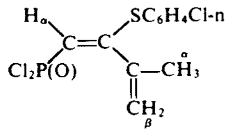
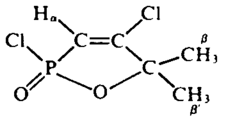
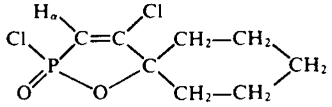
Introduction of substituents onto the γ-carbon atom of phosphorylated allenes leads to a change of the structure of the reaction products. It has been shown earlier that esters of γ,γ-disubstituted allenylphosphonic acids react with sulfenyl chlorides to form heterocyclic compounds,[2-4] mainly oxaphospholenes. We found that the interaction of the dichloride of cyclohexylidene vinylphosphonic acid with phenylsulfenyl chloride led to the formation of 1-dichlorophosphoryl-2-phenylthio-2-(cyclohex-1-enyl)ethene (2), the diene structure of which has been established by ^{1}H NMR and IR spectroscopy. In the ^{1}H NMR spectrum of (2), the CH_2— protons of the cyclohexene ring are non-equivalent and are observed as two widened resonance lines with δ 1.6 ppm (—CH_2—CH_2—) and δ 2.2 ppm (—CH_2—C═C—CH_2—) (Table I). Elimination of hydrogen chloride accompanying the formation of (2) is confirmed by elementary analysis. The formation of (2) could be explained by the following scheme:



SCHEME 1

TABLE I

Products of interaction of sulfenyl chlorides with dichlorides of allenylphosphonic acids

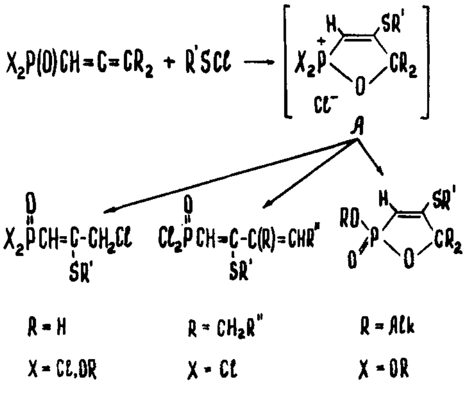
N	Product	Yield (%)	B.p. °C/mm or M.p.	Formula	Found %	Calc. %	NMR, δ (ppm)	
							^{31}P	^{1}H
1.[a]	 (E)	70	133–134°/0.1	$C_9H_8OPSCl_3$	C 36.73 H 2.88 P 9.99	35.82 2.65 10.28	25	5.20(H_α,d, $^2J_{PH}$ 26 Hz) 4.70(H_β,d, $^4J_{PH}$ 2 Hz)
2.		63	M.p. 87–90°	$C_{14}H_{15}OPSCl_2$	C 50.27 H 4.55 P 9.50	50.43 4.35 9.31	40	5.26(H_α,d, $^2J_{PH}$ 32 Hz) 5.97(H_β,m)
3.		49	170–172°/0.2	$C_{11}H_{10}OPSCl_3$	C 38.53 H 3.02 P 9.66	38.29 3.16 9.79	—	5.25(H_α,d, $^2J_{PH}$ 31 Hz) 5.20(H_β,q, $^4J_{HH}$ 1 Hz) 2.05(H_γ,t, $^4J_{HH}$ 1 Hz)
4.[b]		76	M.p. 47°	$C_5H_7O_2PCl_2$	C 30.01 H 4.02 P 15.06	29.85 3.48 15.42	33	6.49(H_α,d, $^2J_{PH}$ 28 Hz) 1.59(H_β,s) 1.60(H'_β,s)
5.		79	M.p. 59–61°	$C_8H_{11}O_2PCl_2$	C 39.84 H 4.69 P 13.09 Cl 30.02	39.89 4.56 12.86 29.46	34	6.50(H_α,d, $^2J_{PH}$ 28 Hz) 1.7 (—CH_2—, 10H, br.s)

[a] $d_4^{20} = 1.4176$, $n_D^{20} = 1.6175$; [b] Lit. data[7]: M.p. 46–48°C, δ31P 30.7, δH_α 6.54, $^2J_{PH}$ 28Hz; δCH_3 1.65, 1.67.

Nucleophilic assistance of phosphoryl oxygen to the electrophilic attack by sulfenyl chloride at the central carbon atom of the allene leads to formation of a quasiphosphonium intermediate of type *A* which can exist in equilibrium with a phosphorane structure. The formation of *A* as a white semicrystalline mass can be observed in the course of the reaction at low temperature (—20°C). The intermediate *A* also persists in the reaction mixture during 10–20 minutes at room temperature. It is impossible to confirm its formation by spectral methods, because on being dissolved, *A* eliminates hydrogen chloride and transforms into the diene (**2**). The ^{31}P NMR spectra of the crude reaction mixture and of the distilled product (**2**) show the only signal at δ 40 ppm.

The formation of an intermediate of the *A* type has been also observed in the course of the interaction of dichloride of γ,γ-dimethylallenylphosphonic acid with arylsulfenyl chlorides. The product of reaction of p-chlorophenylsulfenyl chloride with the dichloride of γ,γ-dimethylallenylphosphonic acid has the diene structure (**3**). Parameters of ^{1}H NMR spectrum of (**3**) are given in the Table. In the IR spectrum of (**3**) there are absorption bands as follows (ν, cm^{-1}): 580 (C—S), 1285 (P=O), 1535,1582,1660 (benzene ring and diene group).

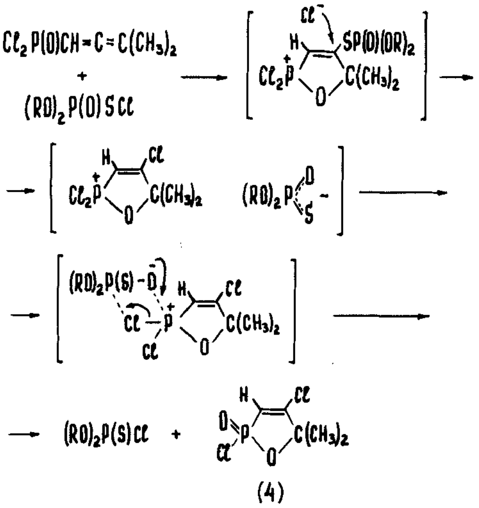
We suppose that the initial formation of the intermediate of the *A* type occurs in the course of the interaction of sulfenyl chloride both with substituted in γ-position, and with the unsubstituted dichloride of allenylphosphonic acid. However, its further stabilization essentially depends upon the character of the unsaturated agent. In case of the unsubstituted phosphorus-containing allene, the attack of the chloroanion is directed at the endocyclic sp^3-hybridized carbon atom, and the reaction results in the formation of 1-dichlorophosphonyl-2-aryl(alkyl)thio-3-chloro-1-propene. In case of the substituted cumulene, the protons on the sp^3 carbon atom in the ring take part in an interaction leading to the corresponding phosphono-1,3-diene as a result of dehydrochlorination. Analyses of literature data[2-4] give evidence of the fact that the interaction of ethers of allenylphosphonic acids with sulfenyl chlorides also proceed with the formation of intermediate quasiphosphonium compounds, which are stabilized in a manner similar to the second stage of the Arbusov reaction.



SCHEME 2

Thus, the reactions of sulfenyl chlorides with derivatives of allenylphosphonic acids, apparently, always proceed through quasiphosphonium intermediate formation, further transformation of which essentially depends on the character of the substituents at the phosphorus atom and at the terminal carbon atom of the cumulene. Continuing these investigations, we studied the reactions of the dichlorides of γ,γ-disubstituted allenylphosphonic acids with phosphorylated sulfenyl chlorides. Thus, in the ^{31}P NMR spectrum of the crude reaction mixture of diisopropylphosphonesulfenyl chloride with the dichloride of γ,γ-dimethylallenylphosphonic acid, two signals were found at 67 ppm and 33 ppm. When distilling the reaction mixture, we obtained the chloride of diisopropylthiophosphorus acid (δ ^{31}P, 65 ppm) and 2,4-dichloro-5,5-dimethyl-2-oxo-1,2-oxaphosphol-3-en (**4**), δ ^{31}P, 33 ppm. The structure of (**4**) was established by the analysis of its ^{1}H NMR spectrum (Table I). Protons of two non-equivalent CH_3 groups resonate in the form of two singlet signals with δ 1.59 and 1.60.

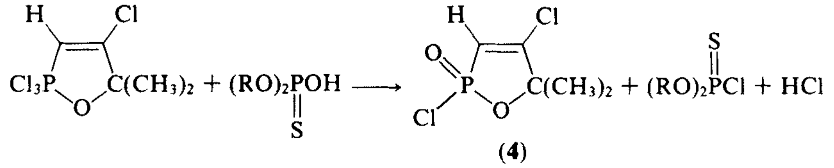
Interaction of the dichloride of γ,γ-dimethylallenylphosphonic acid with 0,0-dimethylphosphonylsulfenyl chloride also leads to the formation of (**4**). We suppose that the formation of dichlorooxaphospholene (**4**) proceeds according to the following scheme:



(4)

SCHEME 3

At stage *a*, a nucleophilic substitution of the thiophosphonyl group by the chloroanion takes place. In order to confirm the possibility of stage *b*, the interaction of 2,2,2,4-tetrachloro-5,5-dimethyl-1,2-oxaphospholene-3[8] with the diisopropyl ester of thiophosphorus acid has been studied. It resulted in the formation of dichlorooxaphospholene (**4**) and the chloride of the thiophosphorus acid:



(**4**)

The interaction of dimethylphosphono- and diisopropylphosphono-sulfenyl chlorides with the dichloride of cyclohexylidenevinylphosphonic acid proceed with the formation of 1-oxa-2,4-dichloro-2-phosphaspiro-4,5-3-decene (**5**), the composition and structure of which have been proved by elementary analysis and spectral methods. Protons of the cyclohexane ring in the ^{1}H NMR spectrum of (**5**) appear in the form of a widened line at strong field (δ 1.7 ppm). Integral intensities of the signals correspond to the structure of compound (**5**). In the IR spectrum of (**5**) there are absorption bands at 1270 (P=O) and 1580 (C=C) cm^{-1}.

Thus, the structure of products of the interaction of sulfenyl chloride with phosphorylated allenes is determined not only by the character of substituents at the phosphorus atom and the terminal carbon atom of the cumulene, but also depends on the nature of the functional group connected to the sulfur atom.

EXPERIMENTAL

NMR spectra were obtained with a Varian T-60 spectrometer. The chemical shifts are reported in δ, using TMS as reference, in CCl_4 as solvent. ^{31}P NMR spectra were recorded by a KGU-4 spectrometer with frequency of 10.2 MHz, using as an inner standard 85% H_3PO_4.

The Interaction of Sulfenyl Chlorides with Dichlorides of Allenylphosphonic Acids

A solution of 0.2 mole of sulfenyl chloride in 10 ml of CCl_4 was added dropwise to 0.2 mole of the phosphonoallene, dissolved in 10 ml of CCl_4 at the temperature of −25 to −15°C. The mixture was kept overnight at room temperature, then the solvent was removed and the residue was distilled in vacuum. The data are summarized in Table I.

The Interaction of the Diisopropyl Ester of Thiophosphorus Acid with 2,2,2,4-Tetrachloro-5,5-dimethyl-1,2-oxaphosphol-3-ene

A 0.1 mole of thiophosphate was added to the solution of 0.1 mole of tetrachlorooxaphospholene[8] in 15 ml of CCl_4 at a temperature of −20° to −15°C. The mixture was stored overnight, the solvent was removed, and the residue was distilled.

The chloride of O,O-diisopropylthiophosphorus acid was obtained, b.p. 38–40°C (0.9 mm), $n_D^{25} = 1.4622$, ^{31}P NMR: 65 ppm (lit.[9] b.p. 61–63°C (3 mm), $n_D^{25} = 1.4601$, ^{31}P NMR: 65.1 ppm), and 2,4-dichloro-5,5-dimethyl-2-oxo-1,2-oxaphosphol-3-ene, m.p. 48°C.

REFERENCES

1. L. P. Rasteikene, D. I. Greichute, M. L. Linkova and I. L. Knunyanz, *Uspekhi Khim.*, **46**, 1041 (1977).
2. A. N. Pudovik, N. G. Khusainova and E. A. Berdnikov, *Dokl. AN SSSR*, **250**, 116 (1980).
3. Ch. M. Angelov, K. V. Vachkov, B. I. Ionin and M. Kirilov, *Zh. Obshch. Khim.*, **49**, 2438 (1979).
4. Ch. M. Angelov, M. Kirilov, K. V. Vachkov and S. L. Spassov, *Tetrahedron Lett.*, **21**, 3507 (1980).
5. A. M. Shehade, V. I. Zaharov, V. M. Ignatjev, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **48**, 55 (1978).
6. A. Zhunke, *Nuclear Magnetic Resonance for Organic Chemists*, M., "Mir", p. 32 (1974) (in Russian).
7. T. S. Mihailova, Ch. M. Angelov, V. M. Ignatjev, A. V. Dogadina, V. I. Zaharov, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **47**, 2701 (1977).
8. T. S. Mihailova, Ch. M. Angelov, V. M. Ignatjev, B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **49**, 570 (1979).
9. T. H. Fletcher, I. C. Hamilton, I. Hechenbleikner and E. I. Hoigberg, *J. Am. Chem. Soc.*, **72**, 2461 (1950).