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Christo M. Angelov^a; Kolyo V. Vachkov^a

^a Department of Chemistry, Higher Pedagogical Institute, Shoumen, Bulgaria

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STRUCTURAL EFFECTS OF SULFENYL CHLORIDES IN THEIR REACTION WITH 3,3-DISUBSTITUTED 1,2-ALKADIENYL- PHOSPHONIC DICHLORIDES

CHRISTO M. ANGELOV* and KOLYO V. VACHKOV

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

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The reaction of 3,3-disubstituted allenylphosphonic dichlorides with sulfenyl chlorides in the presence of sulfur dioxide proceeds with formation of mixtures of 2,5-dihydro-1,2-oxaphospholes and 1,2-adducts. The influence of hydrocarbon substituent in the electrophilic sulfur on the reaction road has been investigated in detail.

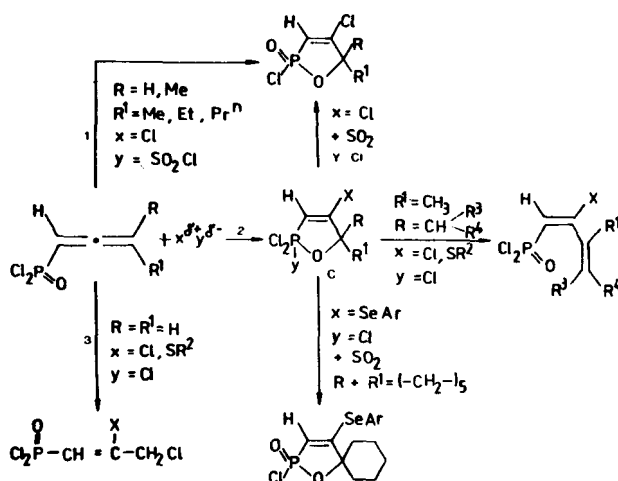
INTRODUCTION

Recently the reaction of 1,2-alkadienylphosphonic derivatives with electrophilic reagents has been studied intensively mainly because in many cases a five-membered heterocyclization of the initial phosphonates was observed. In the review¹ it was shown, that this cyclization depends on the allenylphosphonate structure, on the electrophile's nature and on the reaction conditions. It has been established^{2–10} that 1,2-alkadienylphosphonic dichlorides in this reaction undergo different chemical transformations according to the Scheme 1.

A. N. Pudovik *et al.* have shown that sulfenyl chlorides react through the second (2) pathway giving 2-arylthio-1,3-alkadienylphosphonic dichlorides.^{9,10} The same authors assume that the reaction proceeds via a five-membered intermediate C, followed by elimination of hydrogen chloride.¹⁰ The yields in this case are lower (57–63%) than in the halogenation of the same 1,2-alkadienylphosphonates (85–95%).^{3–5} It seems that the lower yields are due to polymerization or to other side processes in the reaction course. The latter assumption is confirmed also by the fact that in the reaction of sulfenyl chlorides with esters of mono- and disubstituted 1,2-alkadienylphosphonic acids together with 2,5-dihydro-1,2-oxaphosphol-2-oxides the 1,2-adducts are formed.^{11,12}

In the present paper we report about the reactivity of 3,3-disubstituted allenylphosphonic dichlorides against different alkylsulfenyl chlorides and benzene-sulfenyl chloride in the presence of sulfur dioxide. With these studies we confirmed the assumption for the formation of the oxyphosphorane C as reaction intermediate and estimated the presence of other products in the reaction system.

*Author to whom all correspondence should be addressed.



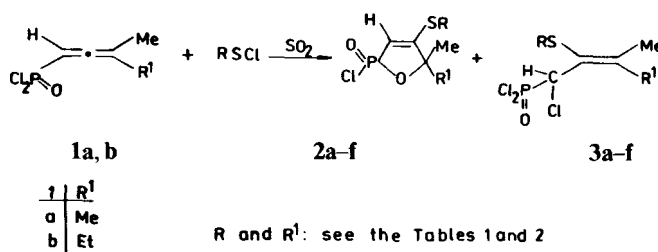
SCHEME 1

RESULTS

The reaction of 3,3-disubstituted allenylphosphonic dichlorides with sulfenyl chlorides was carried out in carbon tetrachloride at low temperature (-10 or $-25^\circ C$) in the presence of sulfur dioxide (gas). The 1H -nmr studies on the reaction products obtained before and after the first distillation have shown that the reaction is going on mainly through two parallel pathways.

In 1H -nmr spectra of reaction mixtures the proton's signals of **2a-f** and **3a-f** (Tables I and II) are seen. In the spectra of **2a-f** the most characteristic from these signals is a doublet for the olefinic proton at the double bond in the ring (δ 5.93–6.05), whose coupling constant with ^{31}P ($^2J_{HP}$ 31.6–32.0 Hz) is typical for 2,5-dihydro-1,2-oxaphospholes.^{5–10}

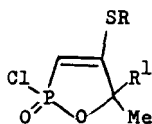
We tried to synthesize the cyclic chlorides **2a-c**, **g** and **i** from the corresponding 2-alkoxy-2,5-dihydro-1,2-oxaphosphol-2-oxides¹³ by treatment with thionyl chloride. The 1H -nmr spectra of the reaction products proved to be identical with those of the products obtained as described above (see Table I): Table III summarizes the results for the yields, physical constants and elemental analysis data for the oxaphospholes obtained according to Scheme 3.



SCHEME 2

TABLE I

¹H-NMR and IR spectral data of 2-chloro-4-alkyl(phenyl)-thio-5-methyl-5-alkyl-2,5-dihydro-1,2-oxaphosphol 2-oxides



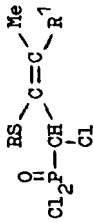
No.	R	R ¹	Chemical Shift, δ				² J _{HP} Hz	IR Spectra, cm ⁻¹	
			R	R ¹	Me	H		P=O	C=C
2a	Me	Me	2.52 s	1.62 s	1.62 s	6.02 d	31.6	1280	1525
			2.51 s*	1.59 s	1.59 s	6.03 d	32.0		
			1.43 t	1.60 s	1.60 s	5.96 d	31.6	1277	1530
b	Et	Me	Me						
			CH ₂						
			Me*	1.59 s	1.59 s	6.03 d	32.2		
			CH ₂						
c	Pr ⁱ	Me	Me						
			CH						
			Me*	1.59 s	1.59 s	6.02 d	32.0	1280	1525
			CH						
d	Bu ⁿ	Me	Me						
			CH ₂ S						
			CH ₂ CH ₂	1.52 m	1.60 s	1.60 s	5.93 d	31.2	1275
e	Ph	Me	Me						
			CH ₂ S						
			CH ₂ CH ₂	7.32 m	1.55 s	1.55 s	5.13 d	33.2	1270
f [†]	Me	Et	Me						
			CH ₂	0.96 t	1.60 s	6.04 d	31.6		
			Me	1.87 m	1.58 s	6.05 d	31.8	1276	1540
g [†]	Pr ⁱ	Et	Me*	0.90 t	1.61 s	6.01 d	33.2	1250	1532
			CH						
			CH ₂	1.85 m	1.54 s	6.04 d	32.6		
i ⁺	Et	Et	Me*	0.96 t	1.60 s	6.08 d	32.0	1275	1532
			CH						
			CH ₂	3.03 q	1.87 m	1.58 s	6.12 d	32.4	

*The compounds are obtained by the reaction of 2-alkoxy-4-alkylthio-2,5-dihydro-1,2-oxaphosphol 2-oxides with thionyl chloride.

[†]The ratio of the two diastereomers is: **2f** 1 : 1.3, **2g** 1 : 1.8, **2i** 1 : 1.4. s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet.

The formation of 1,2-adducts were proved by the following ¹H-nmr data: (i) If two methyl groups are present at C³ of the allene bond in the ¹H-nmr spectra of the substances **3a–e** two doublets are observed (Table II) each of them corresponding to three protons. The coupling constants of these protons with ³¹P are characteristic for cis (δ 2.06–2.12, ⁵J_{HP} 4.0–4.4 Hz) and trans (δ 2.21–2.24, ⁵J_{HP} 5.6–6.0 Hz) position with respect to the phosphorus atom.^{15,16} (ii) The signal for proton at C¹ is a doublet (δ 5.56–5.73) with a relatively small HP coupling constant (²J_{HP} 6.6–8.2 Hz) and correlates well with the data for other 1,2-adducts synthesized before.¹⁶ The presence of this signal in a relatively low field is not astonishing taking into account the strong negative induction effect of the dichlorophosphonic group and the chlorine atom connected with C¹.¹⁷ (iii) If 2,3-adducts formation takes place, additional splitting of the signals from the different groups of protons must be observed due to the formation of E- and Z-isomers, even in the case of equal substituents at C³. It can be seen from the ¹H-nmr spectra that in the mixture of the compounds **2a–e** and **3a–e** do not show any sign of the presence of isomers. Compounds with different

TABLE II
¹H-NMR and IR spectral data of (1-chloro-2-alkyl(phenyl)-thio-3-methyl-2-alkenyl)phosphonic dichlorides

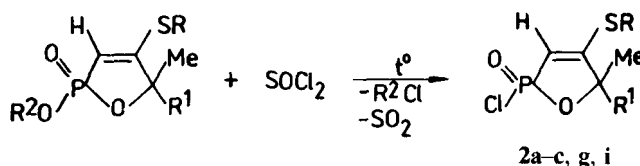


No.	R	R ¹	Chemical shift, δ				Coupling constants		J Hz	IR Spectra, cm ⁻¹	
			R	R ¹	Me	H	H-P	P-P		P=O	C=C
3a	Me	Me	2.27 s	Z 2.07 d	E 2.24 d	5.73 d	6.6		Z 4.0 E 5.6 Z 4.0	1280	1585
b	Et	Me	Me 1.25 t CH ₂ 2.79 q Me 1.27 d	Z 2.07 d	E 2.21 d	5.63 d	7.2		E 6.0 Z 4.0	1277	1586
c	Pr ⁱ	Me	CH 3.41 m Me 0.92 t CH ₂ S 2.74 t CH ₂ CH ₂ 1.52 m	Z 2.12 d	E 2.21 d	5.56 d	8.2		E 5.8 Z 4.0	1280	1590
d	Bu ⁿ	Me		Z 2.06 d	E 2.21 d	5.60 d	7.6		E 6.0 Z 5.2	1275	1583
e	Ph	Me	7.04 m	Z 2.06 d	E 1.95 d	5.54 d	7.8		E 6.8 Z 4.4	1270	1580
f	Me	Et	2.27 s	Me 0.90 t CH ₂ 2.87 q	Z 2.28 d E 2.31 d	5.85 d 5.87 d	7.0		E 6.0	1276	1586

s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet.

TABLE III
Physical constants and analyses of **2a-c**, **2g** and **2i**

No.	Yield %	bp, °C (p, mm)	n_D^{20}	d_4^{20}	Found, %		Formula	Calcul., %	
					Cl	S		Cl	S
2a	63	131–132/0.5	1.5324	1.5616	16.40	15.17	C ₆ H ₁₀ ClO ₂ PS	16.67	15.07
b	71	133–134/0.5	1.5307	1.5596	15.44	14.02	C ₇ H ₁₂ ClO ₂ PS	15.64	14.14
c	65	136–137/0.5	1.5297	1.5586	14.41	13.13	C ₈ H ₁₄ ClO ₂ PS	14.72	13.32
g	68	137–138/0.5	1.5276	1.5581	13.92	12.19	C ₉ H ₁₆ ClO ₂ PS	14.03	12.69
i	72	135–136/0.5	1.5285	1.5589	14.90	13.09	C ₈ H ₁₄ ClO ₂ PS	14.72	13.32



SCHEME 3

substituents at C³, however, show splitting of most of the signals both for cyclic chlorides and for 1,2-adducts. This is observed in the spectrum of the mixture of **2f** and **3f** (see Tables I and II). In the IR spectra of the reaction mixtures of **2a-f** and **3a-f** the absorption bands for the double bonds are observed (see Tables I and II). In the spectra of the compounds **2a-f** synthesized according to Schemes 2 and 3, an absorption band for P—O—C bond (900–1000 cm⁻¹) is seen too, whose presence is an additional support for the formation of a five-membered ring.

The experimental data show that the ratio between the **2a-f** and **3a-f** in the reaction mixtures depends on the structure of the hydrocarbon substituent bonds with the sulfur atom and on the reaction temperature as well. As Table IV shows with the change of the alkyl from methyl to butyl at a constant temperature (–10°C) and R¹ = Me the ratio between the cyclic compound and the 1,2-adduct is changed in the favour of the latter. The change of the alkyl group to phenyl leads to

TABLE IV
Molecule Ratio of 2-Chloro-4-alkyl(phenyl)thio-5-methyl-5-alkyl-2,5-dihydro-1,2-oxaphosphol
2-oxides **2a-e**, **2f** to (1-Chloro-2-alkyl(phenyl)thio-3-
methyl-2-alkenyl)phosphonic dichlorides **3a-f** in the reaction mixtures
after the first distillation (¹H-NMR spectral data)

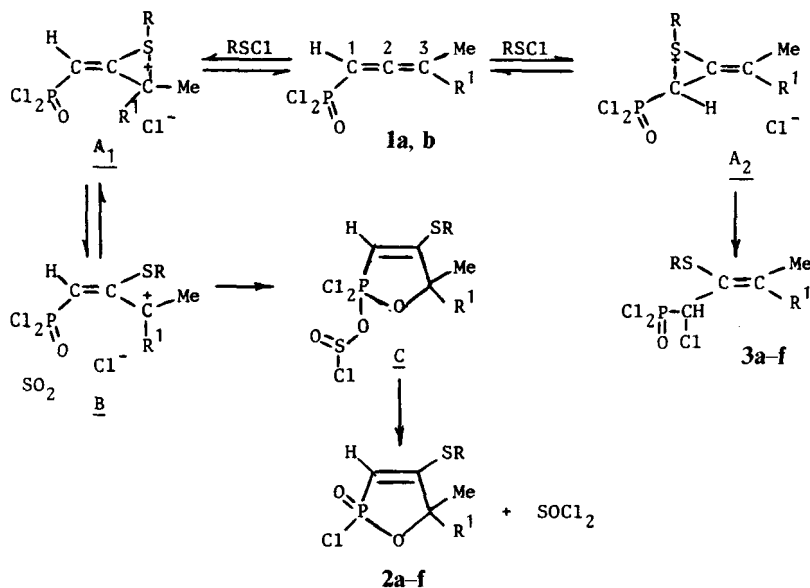
Compt.	–10°C	–25°C
2a	3.5	1.8
b	0.4	
c	0.3	0.1
d	0.3	
e	5.7	
f	3.8	

the formation of the oxaphosphole **2e** as a main reaction product, the amount of the 1,2-adduct being only about 15%. The decrease of temperature to -25°C keeping all other reaction conditions unchanged results in increase of the 1,2-adduct in the reaction mixture. When $\text{R} = \text{Me}$ the oxaphosphole again dominates in the mixture, and when $\text{R} = \text{Pr}^i$ the reaction follows the pathway to the formation of the 1,2-adduct as a main reaction product (Table IV).

DISCUSSION

As it was already mentioned above, the formation of 1,2-adducts was observed before at the interaction of sulfonyl chlorides with esters of substituted 1,2-alkadienylphosphonic acids,^{12,13} and now at the reaction of the same reagents with dichlorides of the corresponding acids. This fact is explained with attack of the electrophilic sulfur on the central carbon atom C^2 of the allenic bond followed by the formation of two episulfonium ions A_1 and A_2 .

The equilibrium between the ion A_1 and the free carbenium ion B depends on the stabilization of the positive charge on sulfur or on C^3 atom. The positive charge on sulfur is influenced by the positive induction effect of the alkyl substituents in the order¹⁸ $\text{Me} < \text{Et} < \text{Pr}^i < \text{Bu}^i$ increasing the stability of the ion A_1 and decreasing the formation of the free carbenium ion B . Our studies up to now have shown, however, that the heterocyclization of the allenylphosphonic system of π -bonds depends on the possibility for formation of free carbenium ions and on the nucleophilicity of the phosphorylic oxygen atom as well.¹ Both parameters influence negatively on the cyclization in the reaction of allenylphosphonic dichlorides **1a, b**



SCHEME 4

with sulfenyl chlorides. In this case C^3 is charged positively only to a small extent, and the two chlorine atoms at phosphorus decrease sufficiently the oxygen nucleophilicity. The exchange of the alkyl substituent to phenyl having a negative induction effect,¹⁸ however, stabilized the ion *B* and the reaction leads to the formation mainly of oxaphosphole. On the other hand the localization of the positive charge on sulfur in the ion A_2 decreases the influence of the electron-acceptor dichlorophosphonylic group bonded with C^1 on the rate of its formation. The 1,2-adduct here is formed as a result of rear attack of the chloride ion to the episulfonium ion A_2 . The increase of the 1,2-adduct's yield when temperature is lowered is connected to the cyclic ion intermediates being favoured over the free carbenium ions.

EXPERIMENTAL

Methods of Analysis. 1H -nmr spectra were obtained on "Tesla" BS 487 B (80 MHz) and "Jeol" JNM-PS-10 (100 MHz) spectrometers of solutions in $CDCl_3$ with TMS as internal standard. The IR spectra were run on a IR-72 spectrophotometer (Carl Zeiss Jena GDR).

Starting Materials. (3-Methyl-1,2-alkadienyl)phosphonic dichlorides were synthesized according to the literature.¹⁹ Alkyl and phenyl sulfenyl chlorides were freshly prepared from the corresponding disulfides and chlorine or sulfuryl chloride and used without purification.

Interaction of (3-methyl-1,2-alkadienyl)phosphonic dichlorides with sulfenyl chlorides in the presence of sulfur dioxide. Through a solution of 0.02 mol of (3-methyl-1,2-alkadienyl)phosphonic dichloride in carbon tetrachloride at $-10^\circ C$ or $-25^\circ C$ was bubbled sulfur dioxide for 20–30 min. Continuing the admission of SO_2 with stirring, a solution of 0.02 mol of the sulfenyl chloride in CCl_4 was added dropwise. The reaction mixture was stirred for one hour and then the solvent was removed and the residue was distilled *in vacuo*.

2-Chloro-4-alkylthio-5-methyl-5-alkyl-2,5-dihydro-1,2-oxaphosphol-2-oxides. 0.03 mol 4-alkylthio-5-methyl-5-alkyl-2-alkoxy-2,5-dihydro-1,2-oxaphosphol-2-oxide was added to 20 ml thionyl chloride at room temperature. The reaction mixture was boiled for 4–5 hours, thionyl chloride was removed in a water pump and the residue was distilled at low pressure. Yield 60–70%.

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