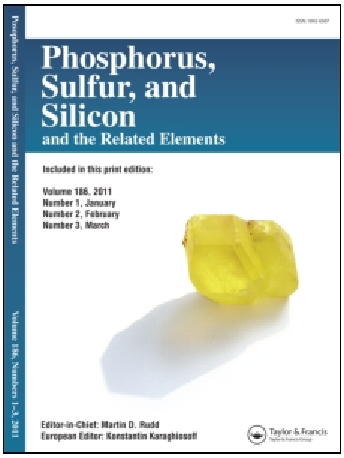

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2,5-DIHYDRO-1,2-OXAPHOSPHOLENE DERIVATIVES BY THE REACTION OF 1,2-ALKADIENEPHOSPHONATES AND PHOSPHORUS PSEUDOHALOGENES

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2,5-DIHYDRO-1,2-OXAPHOSPHOLENE DERIVATIVES BY THE REACTION OF 1,2-ALKADIENEPHOSPHONATES AND PHOSPHORUS PSEUDOHALOGENES

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The interaction of 1,2-alkadienephosphonic derivatives with phosphorus containing pseudohalogenes affords 2,5-dihydro-1,2-oxaphospholene derivatives. The structure of the new compounds is determined by NMR and IR spectroscopy.

Key words: 1,2-alkadienephosphonates; 2,5-dihydro-1,2-oxaphospholene derivatives; heterocyclization; phosphorus containing pseudohalogenes.

INTRODUCTION

It is well known that in the reaction of alkyl(aryl)sulfenyl chlorides with 1,2-alkadienephosphonic derivatives a heterocyclization of the allenephosphonic system takes place and 2,5-dihydro-1,2-oxaphospholene derivatives are obtained.[1–8]

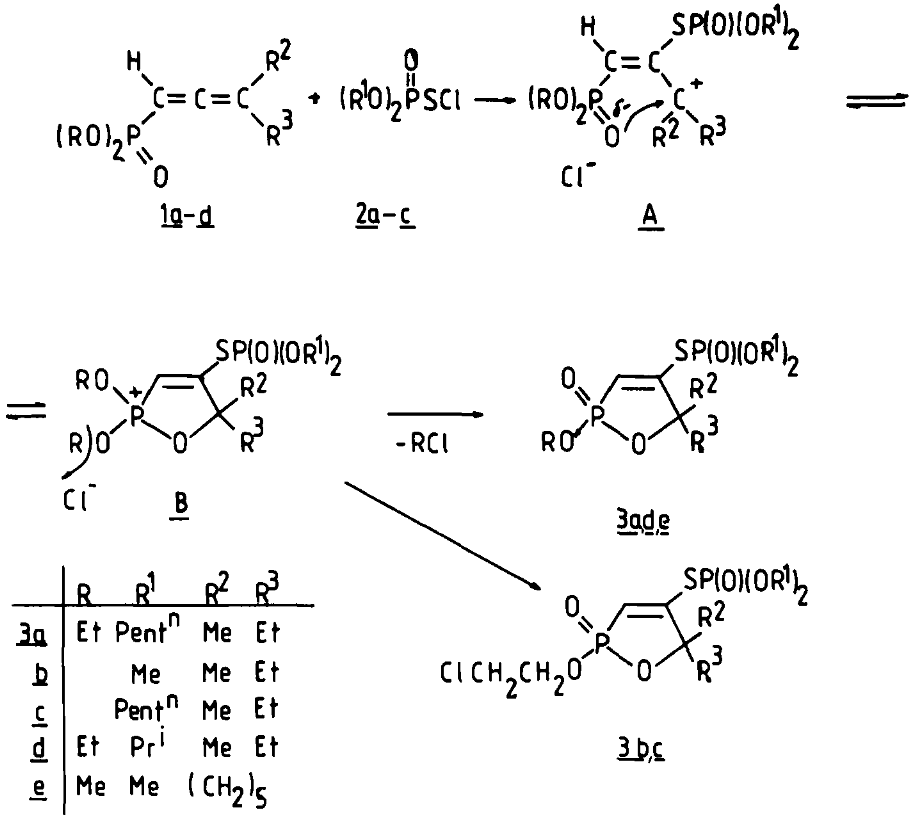
On the other hand, there are only two publications concerning the interaction between allenephosphonic derivatives and phosphorus containing pseudohalogenes (dialkoxyoxophosphorane sulfenyl chlorides).[9,10]

In the present paper we report the results of our investigations of heterocyclization of allenephosphonic esters and phosphine oxides in the reaction with phosphorus containing pseudohalogenes.

RESULTS AND DISCUSSION

We established that when dialkyl esters of allenephosphonic acids react with phosphorus containing pseudohalogenes the 2,5-dihydro-1,2-oxaphospholene derivatives are obtained in all cases with good yield. The reaction is carried out in methylene chloride at low temperature (−10 to −8°C) and under an argon atmosphere. The solution of the appropriate allenephosphonic esters **1a–d** is added dropwise to an equimolar amount of the phosphorus containing pseudohalogenes

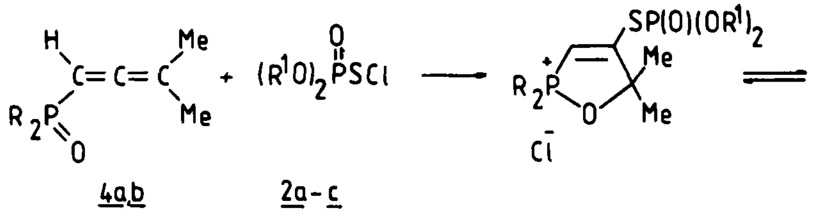
2a–c in the same solvent under an argon atmosphere. After one hour stirring at the same temperature the solvent is removed and the residue is distilled. The reaction takes place following the scheme:

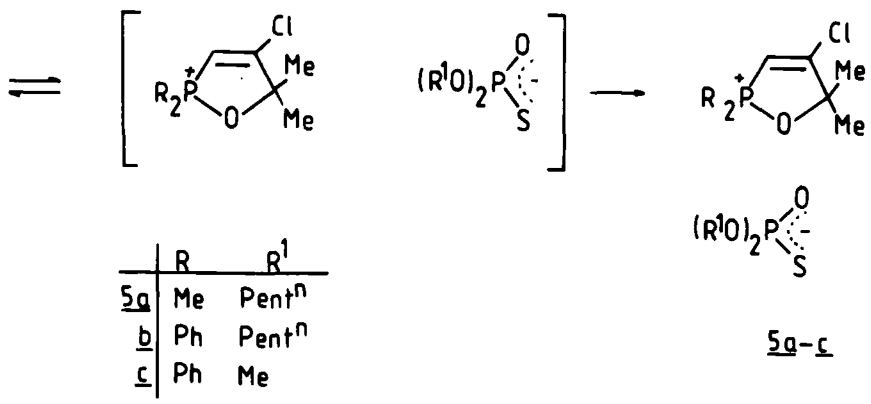


	R	R1	R2	R3
3a	Et	Pent^n	Me	Et
b		Me	Me	Et
c		Pent^n	Me	Et
d	Et	Pr^i	Me	Et
e	Me	Me	$(CH_2)_5$	

We assume that the electrophilic part of the phosphorus containing pseudohalogene attacks the allenic system forming tertiary carbenium ion *A* which react with the internal nucleophilic—O-atom from the phosphoryl group of the allenephosphonate system. As a result, the intermediate with quasiphosphonium structure *B* is obtained. After elimination of alkyl halide the final products **3a–d** are formed.

Continuing our investigations we established that in the reaction of allenephosphine oxides **4a,b** with the same phosphorus containing pseudohalogenes **2a–c** stable oxaphosphonium salts **5a–c** are formed. The spectroscopic investigation of the above mentioned reaction shows that the interaction in this case is similar to the reaction described by Pudovik et al:[9]





	R	R^1
5a	Me	Pent^n
b	Ph	Pent^n
c	Ph	Me

5a-c

EXPERIMENTAL

Analytical methods. The ^{1}H-nmr spectra were recorded on spectrometers "Jeol" JNM-PS-10 (100 MHz) Institute of Chemical Technologie Sofia, Bulgaria and "Brucker" MSL (300 MHz) Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland.

The ^{31}P-nmr spectra were recorded on spectrometer "Jeol" C-60 JNM-FX-60 TF (60 MHz) Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Poland.

The IR spectra were run on IR-72 spectrophotometer (Carl Zeiss Jena, GDR).

Starting materials. The phosphorus containing pseudohalogenes were prepared by a procedure described earlier.[11]

Synthesis of 4-thiodialkoxyphosphonyl-2-alkoxy-2,5-dihydro-1,2-oxaphospholene-2-oxides **3a–e**

General procedures: To a solution of 5 mM allenic dialkyl esters in 10 ml methylene chloride a solution of 5 mM phosphorus containing pseudohalogene is dropwise added at low temperature (−10 to −8°C) and under an argon atmosphere. After one hour of stirring the solvent is removed under low pressure (water pump) and the residue is distilled under vacuum.

Synthesis of 4-chloro-2,2-dimethyl(diphenyl)-5,5-dimethyl-2,5-dihydro-1,2-oxaphosphonium salts **5a–c**

General procedure: To a solution of 5 mM allenic dimethyl(diphenyl)phosphine oxide in 10 ml methylene chloride is added dropwise a solution of 5 mM phosphorus containing pseudohalogene at low temper-

TABLE I

Physical constants and analyses of **3a–e** and **5a–c**

No	R (R^1)	R^2 (R^3)	Yield %	b.p. °C	Calculated P	 S	 Cl	Formula	Found P	 S	 Cl
3a	Et (Me)	Et (Pent^n)	77	109–110	14.00	7.24	—	$C_{18}H_{36}O_6P_2S$	13.78	7.17	—
b	ClEt (Me)	Et (Pent^n)	75	110–112	16.98	8.79	9.72	$C_{10}H_{19}O_6P_2SCl$	16.79	8.71	9.69
c	ClEt (Me)	Et (Me)	76	106–108	12.98	6.72	7.43	$C_{18}H_{35}O_6P_2SCl$	12.89	6.70	7.39
d	Et (Me)	Et (Pr^i)	78	105–107	16.03	8.29	—	$C_{14}H_{28}O_6P_2S$	15.98	8.23	—
e	Me	(Me)	80	110–112	18.09	9.36	—	$C_{11}H_{20}O_6P_2S$	17.99	9.29	—
5a	Me (Me)	Me (Pent^n)	86	—	14.31	7.40	8.19	$C_{17}H_{35}O_4P_2SCl$	14.29	7.37	8.11
b	Ph (Me)	Me (Pent^n)	85	—	11.12	5.75	6.36	$C_{27}H_{39}O_4P_2SCl$	10.98	5.71	6.31
c	Ph (Me)	Me (Me)	85	—	13.92	7.20	7.96	$C_{19}H_{23}O_4P_2SCl$	13.90	7.19	7.92

TABLE II

^{1}H, ^{31}P and IR spectral data of **3a–e** and **5a–c**

No	R (R^1)	R^2 (R^3)	Chemical shift Ha	 R	 R^1	 R^2	 R^3	 Pa	 Pb	Coupling H Ha—Pa
3a	Et (Me)	Et (Pent^n)	6.47d	Me–3.82t $CH_2$4.13m	1.53d	Me–0.97s CH_2–1.32	Me–0.98s CH_2–3.78	33.09	16.84	35.54
b	ClEt (Me)	Et (Pent^n)	6.48d	CH_2–4.35m	1.42d	Me–0.97s CH_2–1.56	Me–0.96s CH_2–3.77	33.69	16.44	27.09
c	ClEt (Me)	Et (Me)	6.06d	CH_2–4.15m	1.33d	Me–0.69 CH_2–1.64	Me–3.69	34.12	16.95	23.79
d	Et (Me)	Et (Pr^i)	6.59d	Me–3.81 CH_2–4.08	1.22d	Me–0.81 CH_2–1.58	CH–4.60m	33.70	16.85	24.00
e	Me	(Me)	5.98	Me–3.78		$(CH_2)_5$–1.70m	Me–3.90	29.80	16.94	22.50
5a	Me (Me)	Me (Pent^n)	6.19d	Me–1.70	0.94	Me–0.94	Me–0.97 CH_2–3.68	110.00	16.55	23.12
b	Ph (Me)	Me (Pent^n)	5.95d	7.75	1.41	Me–0.67	Me–0.98 CH_2–3.84	109.87	16.39	24.73
c	Ph (Me)	Me (Me)	6.12d	7.80	1.52	Me–0.81	Me–0.95	107.90	16.34	24.89

ature (− 10 to − 8°C) and under an argon atmosphere. Just after adding the reagents, the white precipitate starts forming. After one hour stirring the precipitate is filtered and washed with heptane.

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