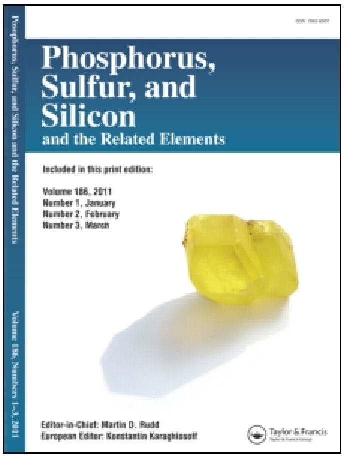

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HETEROCYCLIZATION OF 2-(2-CHLORO-1,3-ALKADIENYL)-1,3,2-DIOXAPHOSPHOLANE 2-OXIDES IN THE REACTION WITH SULFENYL CHLORIDES

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The reaction of sulfenyl chlorides with 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides proceeds nonselectively affording five- or six-membered heterocycles depending on the nature of the hydrocarbon moiety in the sulfenyl chloride. The structures of the compounds are determined by NMR and IR spectra.

Key words: 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides; heterocyclization; 5,6-dihydro-2H-1,2-oxaphosphorines; 2,5-dihydro-1,2-oxaphospholes; sulfenyl chlorides.

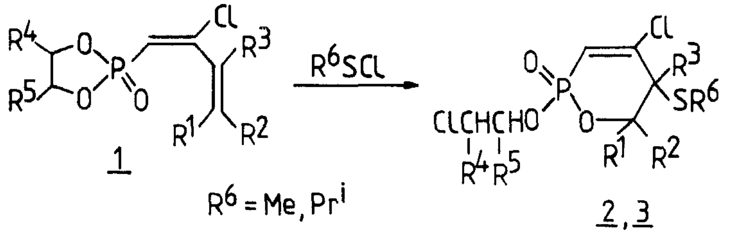
INTRODUCTION

Recently was shown that the interaction of electrophilic reagents with 1,3-alkadienylphosphonic derivatives proceeds with heterocyclization of the 1,3-dienephosphonic system.[1–8] The reaction between sulfenyl chlorides and 1,3-alkadienylphosphonic dialkyl esters leads to five- or six-membered heterocyclization depending on the nature of the substituent on the sulfur. Thus, alkylsulfenyl chlorides give six-membered 5,6-dihydro-2H-1,2-oxaphosphorines,[7] while arylsulfenyl chlorides lead to five-membered 2,5-dihydro-1,2-oxaphospholes.[7] Halogenation of the 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides proceeds with the formation of only six-membered P, O-containing heterocycles.[8]

Continuing our investigation in this field, in the present paper we report the results of the interaction of sulfenyl chlorides with 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides and the study of the influence of the dioxaphospholane ring on the course of the reaction.

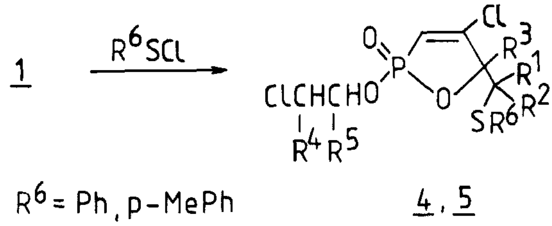
RESULTS AND DISCUSSION

The reaction of sulfenyl chlorides with 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides 1 was carried out in dry chloroform or 1,2-dichloroethane and heating to 50–55°C. We found that the reagent attacks the C^3—C^4-double bond and at the same time a heterocyclization of the 1,3-dienylphosphonic system (O=P—C=C—C=C) of π-bonds takes place. We established that depending on the nature of the substituent on the sulfur atom, 5,6-dihydro-2H-1,2-oxaphosphorine or 2,5-dihydro-1,2-oxaphosphole derivatives are formed. When the reagent



R¹, R², R³, R⁴ and R⁵: see Table I

Scheme 1



R¹, R², R³, R⁴ and R⁵: see Table II

Scheme 2

is alkylsulfenyl chloride (methyl or isopropyl), the six-membered heterocycles 2 and 3 are the main reaction products (Scheme 1).

With arylsulfenyl chlorides (phenyl or p-tolyl), however, five-membered heterocyclization takes place yielding 2,5-dihydro-1,2-oxaphosphole derivatives 4 and 5 (Scheme 2).

The results indicate that the above reactions proceed via dioxaphospholane ring opening, followed by addition of the reagent and formation of five- or six-membered heterocycles 2–5. The compounds 2–5 are viscous light yellow liquids some of which crystallize after vacuum distillation.

Detailed investigations were carried out with the view of establishing the course of the reactions between 1 and methylsulfenyl chloride or 1 and phenylsulfenyl chloride. The crude products 2a or 4a were subjected to column chromatography on Silica gel (Merck 60, 0,063–0,200 nm) using as eluent a hexane-ethyl acetate mixture of a continuously increasing polarity. The separation was monitored by thin-layer chromatography. These studies revealed that the reaction proceed with the sole formation of six- or five-membered heterocycles i.e., no side products were found in the individual fractions. Diastereomeric mixtures were isolated (yield 2a 60%, 4a 61%), however attempts to separate the individual constituents failed despite considerable efforts.

EXPERIMENTAL

Method 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 run on an IR-72 spectrophotometer (Carl Zeiss Jena, Germany).

TABLE I

Yields, physical constants, analyses and IR spectral data of 2 and 3

No.	R^1 (R^2)	R^3 (R^4)	R^5 (R^6)	Yield %	bp, °C/mmHg	Found, %			Molecular formula	Calculated, %			IR spectra, cm^{-1}		
						P	Cl	S		P	Cl	S	P=O	C=C	P-O-C
2a	H (Me)	Et (H)	H (Me)	57	148-9/0.5	9.57	10.94	9.97	$C_{10}H_{17}O_3SCl_2P$	9.70	11.11	10.04	1239	1578	968, 1024
b	H (Me)	Et (Me)	H (Me)	54	154-5/0.5	9.37	10.49	9.50	$C_{11}H_{19}O_3SCl_2P$	9.29	10.62	9.62	1248	1578	974, 1016
c	H (Me)	Et (H)	H (Pr^i)	52	148-9/0.5	8.85	10.50	9.11	$C_{12}H_{21}O_3SCl_2P$	8.92	10.21	9.23	1247	1579	985, 1019
3a	Me (Me)	Me (H)	H (Me)	55	167-8/1.0	9.79	10.23	9.88	$C_{10}H_{17}O_3SCl_2P$	9.70	11.11	10.04	1250	1582	991, 1026
b	Me (Me)	Me (Me)	H (Me)	57	166-7/0.5	9.12	10.38	9.49	$C_{11}H_{19}O_3SCl_2P$	9.29	10.64	9.62	1241	1580	993, 1020
c	Me (Me)	Me (Me)	Me (Me)	52	180-1/0.5	9.06	10.07	9.31	$C_{12}H_{21}O_3SCl_2P$	8.92	10.21	9.26	1247	1575	980, 1024

TABLE II

Yields, physical constants, analyses and IR spectral data of 4 and 5

No.	R^1 (R^2)	R^3 (R^4)	R^5 (R^6)	Yield %	bp, °C/mmHg	Found, %			Molecular formula	Calculated, %			IR spectra, cm^{-1}		
						P	Cl	S		P	Cl	S	P=O	C=C	P-O-C
4a	H (Me)	Et (H)	H (Ph)	53	152-3/0.5	8.25	9.15	8.57	$C_{15}H_{19}O_3SCl_2P$	8.12	9.30	8.41	1258	1589	991, 1040
b	H (Me)	Et (Me)	H (Ph)	52	160-1/0.5	7.90	9.06	8.26	$C_{16}H_{21}O_3SCl_2P$	7.83	8.97	8.11	1256	1591	993, 1038
c	H (Me)	Et (Me)	Me (Ph)	50	179-0/1.0	7.46	8.79	8.01	$C_{17}H_{23}O_3SCl_2P$	7.57	8.66	7.83	1265	1592	978, 1037
d	H (Me)	Et (H)	H (p-MePh)	51	184-5/0.5	7.71	9.04	8.24	$C_{16}H_{21}O_3SCl_2P$	7.83	8.97	8.11	1261	1594	995, 1041
5a	Me (Me)	Me (H)	H (Ph)	54	170-1/1.0	7.95	9.47	8.28	$C_{15}H_{19}O_3SCl_2P$	8.12	9.30	8.41	1258	1588	990, 1042
b	Me (Me)	Me (Me)	H (Ph)	51	167-8/0.5	7.98	9.79	8.30	$C_{16}H_{21}O_3SCl_2P$	7.83	8.97	8.11	1256	1590	988, 1040

Starting materials. 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides (1) were synthesized according to the literature.[8] The alkyl- and arylsulfenyl chlorides were freshly prepared from the corresponding disulfides and sulfuryl chloride in chloroform or 1,2-dichloroethane and used without purification.

Interaction of 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides (1) with alkyl(aryl)sulfenyl chlorides.

General procedure. A solution of alkyl- or arylsulfenyl chloride (10 mmol) in dry chloroform or 1,2-dichloroethane (10 ml) is added dropwise with stirring to 2-(2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholane 2-oxides (1) (10 mmol) dissolved in the same solvent (10 ml) at 50–55°C. The reaction mixture is kept for 4 h at the same temperature the solvent removed and the residue is distilled in the vacuum to give the product as a light yellow liquid.

^{1}H-NMR spectra, ppm: 2a 6.09d (1H, $^2J_{HP}$ 8.5 Hz); 4.54qq (1H, $^3J_{HP}$ 13.4 Hz); 4.29m (2H); 3.64m (2H); 2.16q (2H); 2.09s (3H); 1.59dd (3H); 0.93t (3H); 4a 6.27d (1H, $^2J_{HP}$ 22.8 Hz); 4.36m (2H); 3.82m (2H); 3.48m (1H); 1.92m (2H); 1.48d (3H); 0.99m (3H); 7.39m (5H). Other data are summarized in Tables I and II.

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