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BICYCLIC SIX-MEMBERED HETEROCYCLES FROM THE REACTION OF SULFENYL CHLORIDES WITH DIALKYL 2-CHLORO-2(1-CYCLOHEXENYL)ETHENE PHOSPHONATES

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The interaction of alkyl(aryl)sulfonyl chlorides with dialkyl 2-chloro-2(1-cyclohexenyl)ethene phosphonates affords six-membered bicyclic derivatives of 5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine. The structure of the new compounds is determined by NMR and IR spectroscopy.

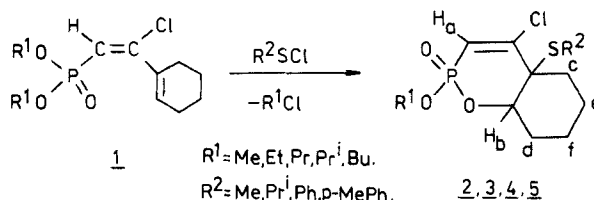
INTRODUCTION

Several methods have been developed in recent years for the preparation of phosphorylated 1,3-alkadienes.¹⁻³ Closely related to these investigations are the studies on the reaction of these compounds with electrophiles which is reported to lead to 5,6-dihydro-2H-1,2-oxaphosphorine⁴⁻⁷ and/or 2,5-dihydro-1,2-oxaphosphole⁸⁻¹⁰ derivatives via heterocyclization of the 1,3-diene phosphonate system of double bonds ($\text{O}=\text{P}-\text{C}=\text{C}-\text{C}=\text{C}$). The reaction between sulfonyl chlorides and 2-chloro-3-alkyl-1,3-alkadiene phosphonates proceeds nonregioselectively affording six- or five-membered heterocycles depending on the type of hydrocarbon moiety in the sulfonyl chloride. Thus, alkylsulfonyl chlorides give six-membered P-, O-containing heterocycles,¹⁰ while arylsulfonyl chlorides lead to five-membered heterocycles.¹⁰ We presently wish to report the results from the interaction between sulfonyl chlorides and dialkyl esters of 2-chloro-2(1-cyclohexenyl)ethene phosphonic acid; the latter the C^3-C^4 double bond is included in the cyclohexene ring system and could affect in a particular way the course of the reaction with sulfonyl chlorides.

RESULTS AND DISCUSSION

The reaction between dialkyl 2-chloro-2(1-cyclohexenyl)ethene phosphonates 1 and sulfonyl chlorides gives bicyclic P-, O-containing heterocyclic compounds in high yields (70-78%) i.e. 4-chloro-5-alkyl(aryl)thio-2-alkoxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides (2, 3, 4 and 5). These six-membered heterocycles are formed regardless of the type of substituent at the sulfur atom i.e. whether it is alkyl or aryl: Scheme 1.

The reaction proceeds in chloroform or 1,2-dichloroethane on gentle heating



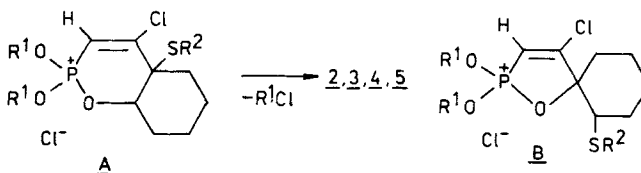
(45–50°) to afford the products which are purified by vacuum distillation or recrystallization from heptane.

The bicyclic compounds **2–5** were characterized by ^1H NMR and IR spectroscopy (see Table I). In the ^1H NMR spectra of **2–5** can be seen a doublet which we ascribe to the H_a proton (δ 6.17–6.24 ppm) with a spin-spin coupling constant with phosphorus typical for six-membered ring systems^{5,6,8,9} ($^2J_{\text{HP}}$ 9.0–9.8 Hz). The proton at $\text{C}^{10}(\text{H}_b)$ gives rise to a complex multiplet (δ 4.56–4.85 ppm) with a considerable constant of spin-spin interaction with phosphorus ($^3J_{\text{HP}}$ 7.2–8.6 Hz) confirming in this manner the presence of a $\text{P}-\text{O}-\text{CH}$ moiety in the molecule. The proton signals in the spectra of **2–5** show that these compounds are actually present as mixtures of diastereomers (chirality centers at P, C^5 and C^{10}). The chemical shifts for phosphorus in the ^{31}P NMR spectra of compounds **2a** and **4a** (7.5 and 7.8 ppm) agree well with the data from the literature for six-membered phosphorus-containing heterocycles.^{5,6,8–11}

Detailed investigations were carried out with the view to establishing the course of the reaction between methylsulphenyl chloride and dimethyl 2-chloro-2(1-cyclohexenyl)ethene phosphonate. The crude product **2a** was subjected to column chromatography on silica gel (Merck 60, 0.063–0.200 mm) using as eluant a hexane-ethyl acetate mixture of a continuously increasing polarity.⁶ The separation was monitored by thin-layer chromatography.

These studies revealed that the reaction proceeds with the sole formation of six-membered heterocycles i.e. no side products were established in the individual fractions. A diastereomeric mixture was isolated in 76% yield, however the attempts to separate the individual constituents failed despite considerable efforts. This observation is in agreement with attempts to resolve another similar mixture of diastereomeric halogenated bicyclic compounds.⁵

It appears likely that the reaction leading to the heterocyclic compounds **2–5** proceeds via an intermediate of a quasiphosphonium structure **A**:



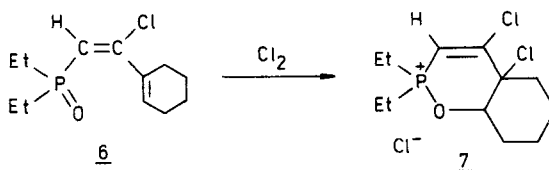
The formation of only the six-membered bicyclic heterocycles **2–5** regardless of the substituents in the sulphenyl chloride can be explained on the one hand with the *s-cis* reaction conformation of the 1,3-diene system^{12,13} in the starting compound **1** and on the other with the more energetically favoured transition state leading to the sterically more favourable fused bicyclic structure **A** which

TABLE I
¹H-NMR and IR spectral data for 4-chloro-5-aryl(aryl)thio-2-alkoxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxides 2-5

No.	R ¹ (R ²)	H _a	H _b	Chemical Shifts, δ		R ²	H _{c,d}	H _{e,f}	J, Hz			IR-spectra, cm ⁻¹		
				R ¹					² J _{HP}	³ J _{HP}	P=O	C=C	R ¹ -O-PP-O-CH	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	
2a	Me (Me)	6.19 d	4.62 m	3.77 d	2.06 s	2.05 s	1.56 s	9.5	7.2	1230	1590	1036	985	
c	Pr ⁿ (Me)	6.24 d	4.68 m	Me 0.97 t CH ₂ 1.67 m CH ₂ O 4.08 m	2.03 s	2.18 s	1.64 s	9.6	8.5	1281	1587	1025	985	
d	Pr ⁱ (Me)	6.22 d	4.85 m	Me 1.36 d CHO 4.85 m	2.09 s	2.20 s	1.66 s	9.8	8.2	1280	1592	1023	984	
e	Bu (Me)	6.20 d	4.63 m	Me 1.23 t CH ₂ 1.89 m CH ₂ O 3.88 m	2.05 s	2.17 s	1.55 s	9.8	8.4	1278	1588	1037	980	
3a	Me (Pr ⁱ)	6.19 d	4.56 m	3.68 d	Me 1.30 d CHS 2.86 m	2.16 s	1.64 s	9.3	8.5	1277	1582	1035	978	
3d	Pr ⁱ (Pr ⁱ)	6.20 d	4.64 m	Me 1.32 d CHO 4.88 m	Me 1.38 d CHS 2.76 m	2.18 s	1.66 s	9.0	8.2	1278	1590	1008	971	
4a	Me (Ph)	6.22 d	4.64 m	3.75 d	7.35 m	2.12 s	1.60 s	9.0	8.4	1285	1590	1037	974	
b	Et (Ph)	6.21 d	4.61 m	Me 0.86 t CH ₂ O 3.90 m	7.20 m	2.16 s	1.56 s	9.1	8.3	1275	1589	1025	979	
d	Pr ⁱ (Ph)	6.20 d	4.62 m	Me 1.33 d CHO 4.78 m	7.18 m	2.10 s	1.57 s	9.1	8.3	1261	1587	1003	962	
5a	Me (p-MePh)	6.17 d	4.65 m	3.63 d	Me 2.26 s Ph 7.20 m	2.26 s	1.60 s	9.0	8.6	1279	1593	1040	976	

contains a six-membered ring system in contrast to the spirane *B* which should lead to the five-membered heterocycles.

Diethyl(2-chloro-2(1-cyclohexenyl)ethenyl)phosphine oxide **6** gives the stable bicyclic phosphonium salt **7** on chlorination confirming in this manner the structure of the intermediate **A**:



EXPERIMENTAL

Method of analysis

$^1\text{H-NMR}$ 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, GDR).

Starting materials

Dialkyl 2-chloro-2(1-cyclohexenyl)ethene phosphonates were synthesized according to the literature.² 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 dialkyl 2-chloro-2(1-cyclohexenyl)ethene phosphonates with alkyl(aryl)sulfenyl chlorides
General procedure: A solution of alkyl- or arylsulfenyl chlorides (20 mmol) in dry chloroform or 1,2-dichloroethane (20 ml) is added dropwise with stirring to dialkyl 2-chloro-2(1-cyclohexenyl)ethene phosphonate (20 mmol) dissolved in the same solvent (15 ml) at 45–50°C. The reaction mixture is kept for 2h at the temperature the solvent removed and residue is distilled to give the product as light yellow liquid. The solid residue is recrystallized from heptane to give light yellow crystals (Table II).

TABLE II
Physical constants and analyses of 2–5

No.	Yield %	bp, °C /mm Hg	Found, %			Molecular Formula	Calculated, %		
			P	Cl	S		P	Cl	S
2a	78	mp 92–93	10.81	12.30	11.19	$\text{C}_{10}\text{H}_{16}\text{O}_3\text{SCIP}$	10.95	12.54	11.34
c	70	163–164/0.5	10.05	11.44	10.37	$\text{C}_{12}\text{H}_{20}\text{O}_3\text{SCIP}$	9.97	11.41	10.32
d	72	166–167/1.0	10.09	11.38	10.49	$\text{C}_{12}\text{H}_{20}\text{O}_3\text{SCIP}$	9.97	11.41	10.32
e	77	153–154/0.5 mp 67–68	9.90	11.70	10.11	$\text{C}_{13}\text{H}_{22}\text{O}_3\text{SCIP}$	9.53	10.91	9.87
3a	75	134–135/0.5	10.12	11.50	10.35	$\text{C}_{12}\text{H}_{20}\text{O}_3\text{SCIP}$	9.97	11.41	10.32
d	71	157–158/0.5	9.38	10.59	9.60	$\text{C}_{14}\text{H}_{24}\text{O}_3\text{SCIP}$	9.14	10.46	9.46
4a	73	168–169/1.0	8.69	10.02	9.09	$\text{C}_{15}\text{H}_{18}\text{O}_3\text{SCIP}$	8.98	10.28	9.30
b	74	165–166/0.5	8.60	9.98	8.91	$\text{C}_{16}\text{H}_{20}\text{O}_3\text{SCIP}$	8.63	9.88	8.94
d	70	mp 51–52	8.29	9.64	8.72	$\text{C}_{17}\text{H}_{22}\text{O}_3\text{SCIP}$	8.31	9.51	8.59
5a	74	170–171/0.5	8.52	9.10	8.84	$\text{C}_{16}\text{H}_{20}\text{O}_3\text{SCIP}$	8.63	9.88	8.94

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