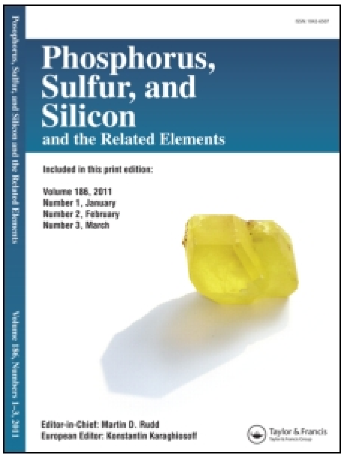

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HETEROCYCLIC PHOSPHONIUM SALTS BY CHLORINATION OF DIALKYL (2-CHLORO-1,3-ALKADIENYL) PHOSPHINE OXIDES

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HETEROCYCLIC PHOSPHONIUM SALTS BY CHLORINATION OF DIALKYL (2-CHLORO-1,3-ALKADIENYL) PHOSPHINE OXIDES

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Dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides **2** have been prepared by reaction of the 2-chloro-1,3-alkadienylphosphonic dichlorides **1** with alkylmagnesium iodides (Grignard reagents). The chlorination of **2** takes place with formation of 4,5-dichloro-5,6-dihydro-2H-1,2-oxaphosphorinium chlorides.

Keywords: 2-chloro-1,3-alkadienylphosphonic dichlorides; alkylmagnesium iodides (Grignard reagents); dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides; chlorination; 4,5-dichloro-5,6-dihydro-2H-1,2-oxaphosphorinium chlorides

INTRODUCTION

In the past 20 years the reactions of phosphorylated 1,3-alkadienes with electrophilic reagents[1] were studied mainly with 1,3-alkadienylphosphonic dialkyl esters,[2] dichlorides[3] and acids.[4] It was shown that the reactions proceed with heterocyclization of the 1,3-alkadienylphosphonic system of double bonds (O=P-C=C-C=C) in most cases. The reaction of 2-chloro-1,3-alkadienylphosphonic esters with sulfenyl chlorides leads to six- or five-membered heterocycles, depending on the type of the hydrocarbon moiety at the sulfur atom[2f,2i]- alkylsulfenyl chlorides give 5,6-dihydro-2H-1,2-oxaphosphorines, while arylsulfenyl chlorides lead to 2,5-dihydro-1,2-oxaphospholes. The interaction of 2-chloro-2 (1-cyclohexenyl) ethenephosphonic dialkyl esters with sulfenyl chlorides affords only six-membered heterocycles, irrespective of the type of the sulfenyl chloride.[2g] Moreover, it has been shown that depending on the nature of the substituents at the phosphorus atom (Cl, RO, OH) as well as on the position of the phosphorus moiety in the 1,3 diene system (1- or 2-), the reaction with halogens leads to the formation of adducts,[2b] five-[2c] or six-membered[2a,2d,2e,2h,3b] heterocyclic compounds, mixtures of them,[2b] addition-elimination products *via* five-membered heterocyclic intermediates[3a] or a mixture of six-membered heterocycles and addition products.[4] In the case of heterocyclization it was proposed[1–3] that the reaction probably passed through a phosphonium intermediate, but it was not sufficiently stable to be isolated because of the fast intramolecular rearrangement of the Arbuzov type compound.

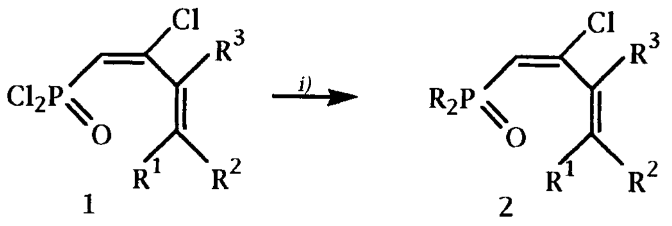
The aim of this paper as a part of our continuing study on the reactions of phosphorylated 1,3-alkadienes with electrophilic reagents,[1] was to synthezise dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides and investigate the influence of the phosphorus moiety [$R_2P(O)$] on the course of the chlorination reaction of the dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides with respect to products formed.

RESULTS AND DISCUSSION

The dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides **2** were obtained in good yield (38–43%) by reaction of the 2-chloro-1,3-alkadienylphosphonic dichlorides **1** with alkylmagnesium iodides, generated *in situ* from alkyl iodides and magnesium, according to **Scheme 1:**

The resulting dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides **2** were isolated by recrystalization or distillation *in vacuo* and characterized by ^1H and ^{31}P NMR and IR spectra and elemental analyses.

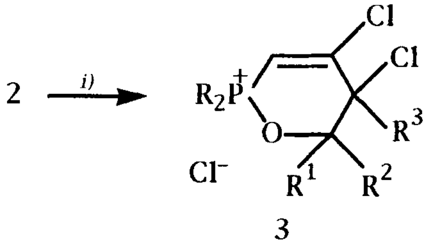
The phosphine oxides **2** obtained in preparative amounts allowed us to study their chemical behavior in the reaction with chlorine. This study, however, is quite interesting, because in this case if a heterocyclization of the 1,3-alkadienylphosphonic system of π-bonds is carried out, it would lead to the formation of stable phosphonium salts. The reaction proceeded in 1,2-dichloroethane on heating to 55–60 °C. Under these conditions we found that a heterocyclization of the 1,3-alkadienylphosphonic system took place and only 4,5-dichloro-5,6-dihydro-2H-1,2-oxaphosphorinium chlorides were isolated in 61–68% yields **(Scheme 2):**



1,2	R	R^1	R^2	R^3
a	Me	H	Me	Et
b	Et	H	-$(CH_2)_4$-	
c	Me	Me	Me	Me

Reagents and Conditions: i) RMgI, ether, -20 °C, rt, 2h.

SCHEME 1



Reagents and Conditions: i) Cl_2 or SO_2Cl_2, $ClCH_2CH_2Cl$, 55-60 °C, rt, 3h.

SCHEME 2

The heterocyclic salts **3** exhibited correct ^1H NMR spectroscopic properties in agreement[2–4] with the proposed structure. The chemical shift of ^{31}P as determined with respect to 85% H_3PO_4 appears at lower field for the cyclic 5,6-dihydro-2H-1,2-oxaphosphorinium chlorides **3** (δ 84.8–86.3 ppm) than for the starting dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides **2** (δ 29.4–31.15 ppm), which is in accordance with the literature data.[2,3,6]

In summary, we have found that the dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides, in contrast to the 2-chloro-1,3-alkadienylphosphonic dichlorides,[3] esters[2a-2e,2h] and acids[4], react with chlorine giving stable phosphonium salts. The above results confirm the assumption that the heterocyclization reactions of 2-chloro-1,3-alkadienylphosphonates with electrophilic reagents probably proceed through a phosphonium intermediate.[1-3]

EXPERIMENTAL

Method of analysis

NMR spectra were obtained on a BRUCKER WM-250 spectrometer for solutions in $CDCl_3$ or CF_3COOH operating at 250.1 (^1H) and 161.9 MHz (^{31}P). Chemical shifts are in parts per million downfield from internal TMS (^1H) and external 85% H_3PO_4 (^{31}P).

IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

The boiling points are uncorrected. The melting points were measured in open capillary tubes and are uncorrected. Chlorination reactions were carried out under an argon atmosphere and exclusion of moisture. The solvents were purified by standard methods.

Starting materials

2-Chloro-1,3-alkadienylphosphonic dichlorides (**1**) were synthesized by chlorination reaction of allenylphosphonic dichlorides according to the literature.[5]

Preparation of dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides (2)

General procedure

To a solution of alkylmagnesium iodide (Grignard reagent) prepared from Magnesium (60 mmol) and alkyl iodide (60 mmol) in dry ether (50 ml) was added dropwise with stirring a solution of 2-chloro-1,3-alkadienylphosphonic dichloride (**1**) (30 mmol) in the same solvent (20 ml) under cooling (-20 °C). The stirring was continued for 1h at the same temperature and 2h at room temperature. The complex was hydrolyzed with saturated NH_4Cl at −20 to −15 °C and the ether solution was separated. The residue was extracted with chloroform (3 × 30 ml) and both solutions were united and dried over $MgSO_4$ for 24h. The solvents were removed on a rotatory evaporator and the residue was distilled *in vacuo* or recrystalized from hexane or heptane to give the pure products as light yellow oil (**2b**) or white crystals (**2a, 2c**). Yield: 38–43%.

The products had the following properties:

Dimethyl (2-chloro-3-ethyl-1,3-pentadienyl) phosphine oxide (2a)

Yield: 41%; m. p. 78–9 °C; $C_9H_{16}OClP$, Calcd., %: Cl 17.16, P 14.99; Found, %: Cl 17.39, P 15.18. IR spectra, cm^{-1}: 1164 (P=O), 1598, 1639 (C=C-C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.19 (t, $^3J_{H\text{-}H}$ 6.2 Hz, 3H, $CH_2\text{-}\underline{Me}$), 1.49 (d, $^2J_{HP}$ 15.1 Hz, 6H, 2Me); 1.90 (d, $^3J_{H\text{-}H}$ 5.9 Hz, 3H, $=CH\text{-}\underline{Me}$), 2.22–2.43 (m, $^3J_{H\text{-}H}$ 6.2 Hz, 2H, $\underline{CH_2}\text{-}Me$), 5.45–5.71 (m, $^3J_{H\text{-}H}$ 5.9 Hz, 1H, $=C\underline{H}\text{-}Me$), 6.04 (d, $^2J_{H\text{-}P}$ 15.2 Hz, 1H, =CH); ^{31}P NMR spectra, δ: 29.4.

Diethyl [2-chloro-2(1-cyclohexenyl)ethenyl] phosphine oxide (2b)

Yield: 38%; b. p. 145-6 °C/0.5 mm Hg; $C_{12}H_{20}OClP$, Calcd., %: Cl 14.37, P 12.55; Found, %: Cl 14.49, P 12.85. IR spectra, cm^{-1}: 1160 (P=O), 1601, 1640 (C=C-C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.43 (tt, $^3J_{HP}$ 14.8 Hz, $^3J_{HH}$ 5.8 Hz, 6H, $2\underline{Me}CH_2$), 1.87, 2.29, 6.01–6.29 (s, s, m, 9H, cyclohexenyl), 4.00–4.34 (m, $^2J_{HP}$ 14.4 Hz, $^3J_{HH}$ 5.8 Hz, 4H, $2Me\underline{CH_2}$), 5.93 (d, $^2J_{HP}$15.8 Hz, 1H, =CH).

Dimethyl (2-chloro-3,4-dimethyl-1,3-pentadienyl) phosphine oxide (2c)

Yield: 43% ; m. p. 84–5 °C; $C_9H_{16}OClP$, Calcd., %: Cl 17.16, P 14.99; Found, %: Cl 17.42, P 15.15. IR spectra, cm^{-1} : 1162 (P=O), 1603, 1641 (C=C-C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.41 (d, $^2J_{HP}$15.0 Hz, 6H, 2Me), 1.82, 1.96 (s, s, 9H, 3Me), 6.08 (d, $^2J_{H\text{-}P}$ 15.2 Hz, 1H, =CH); ^{31}P NMR spectra, δ: 31.15.

Chlorination of dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides (2)

General procedure

To a solution of dialkyl (2-chloro-1,3-alkadienyl) phosphine oxides (**2**)(10 mmol) in dry 1,2-dichloroethane (10 ml) at 55–60 °C was added dropwise with stirring a solution of chlorine (0.78 g, 11 mmol) or sulfuryl chloride (1.48 g, 11 mmol) in the same solvent (10 ml). The stirring was continued for 3h at the same temperature and lh at room temperature. The resulting upper oily layer was separated and dried *in vacuo*. After drying, the products **2a** and **2c** were crystallized but **2b** was an oil. The salts **2** were not dissolved in organic solvents as C_6H_6, CCl_4, $CHCl_3$, $ClCH_2CH_2Cl$, CH_2Cl_2, CH_3NO_2 etc., but were dissolved in water and CF_3COOH. The pure samples were obtained by washing with organic solvents and drying in a vacuum desiccator. Yield: 61–68 %.

The products had the following properties:

4, 5-Dichloro-2,2-dimethyl-5-ethyl-6-methyl-5, 6-dihydro-2H-1,2-oxaphosphorinium chloride (3a)

Yield: 61 %; m. p. 104–6 °C; $C_9H_{16}0Cl_3P$, Calcd., %: Cl 38.32, P 11.16; Found, %: Cl 38.48, P 11.35. IR spectra (nujol), cm^{-1}: 981 (P-O-C), 1592 (C=C). ^1H NMR spectra (CF_3COOH), δ: 0.88 (t, 3H, $^3J_{H\text{-}H}$ 5.96 Hz, $\underline{Me}$-CH_2), 1.57 (d, $^3J_{H\text{-}H}$ 6.1 Hz, 3H, CH-$\underline{Me}$, 1.83 (d, 6H, $^2J_{H\text{-}P}$15.6 Hz, 2Me), 2.12–2.43 (m, 2H, Me-$C\underline{H_2}$), 4.57–4.86 (m, $^3J_{H\text{-}P}$ 10.0 Hz, $^3J_{H\text{-}H}$ 6.1 Hz, 1H, C$\underline{H}$-Me), 6.41 (d, $^3J_{H\text{-}P}$ 9.65 Hz, 1H, =CH); ^{31}P NMR spectra (CF_3COOH), δ: 86.3.

4,5-Dichloro-2,2-diethyl-5, 6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorinium chloride (3b)

Yield: 68 %; oil, $C_{12}H_{20}OCl_3P$, Calcd., %: Cl 33.49, P 9.75; Found, %: Cl 32.88, P 12.54. IR spectra (nujol), cm^{-1} : 984 (P-O-C), 1589 (C=C). ^1H NMR spectra (CF_3COOH), δ: 1.29 (tt, $^3J_{HP}$6.6 Hz, $^3J_{HH}$ 4.1 Hz, 6H, 2$\underline{Me}CH_2$), 1.79, 2.35, 4.67–4.98 (s, s, m, 9H, cyclohexyl), 3.27–3.54 (m, 4H, 2Me$\underline{CH_2}$), 6.52 (d, $^2J_{HP}$ 9.8 Hz, 1H, =CH).

4,5-Dichloro-2, 2-dimethyl-5, 6, 6-trimethyl-5,6-dihydro-2H-1,2-oxaphosphorinium chloride (3c)

Yield: 62 %; m. p. 110–1 °C; $C_9H_{16}OCl_3P$, Calcd., %: Cl 38.32, P 11.16; Found, %: Cl 38.53, P 11.29. IR spectra (nujol), cm^{-1}: 988 (P-O-C), 1590 (C=C). ^1H NMR spectra (CF_3COOH), δ: 1.81 (d, $^2J_{HP}$ 15.9 Hz, 6H, 2Me), 1.88, 2.03 (s, s, 9H, 3Me), 6.38 (d, $^2J_{H\text{-}P}$ 9.4 Hz, 1H, =CH). ^{31}P NMR spectra (CF_3COOH), δ: 84.8.

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