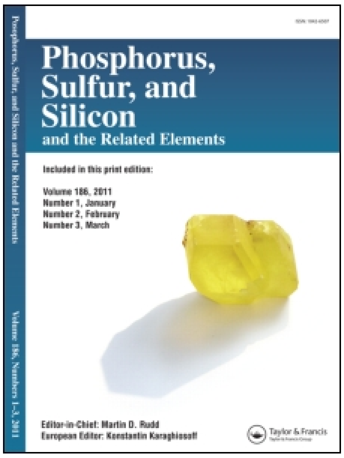

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CYCLIC PHOSPHONIUM SALTS BY CHLORINATION OF BENZO[c]-2-(2-CHLORO-1,3-ALKADIENYL)-2-OXO-1,3,2-DIOXAPHOSPHOLANES

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Benzo[c]-2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes **2** have been prepared by reaction of the 2-chloro-1,3-alkadienylphosphonic dichlorides **1** with catechol in the presence of triethylamine. The chlorination of **2** takes place with formation of benzo[c]-1,3,2-dioxaphospholane-2-spiro-2′-(4′,5′-dichloro-5′,6′-dihydro-2H-1′,2′-oxaphosphorinium) chlorides.

Keywords: 2-chloro-1,3-alkadienylphosphonic dichlorides; catechol; benzo[c]-2-(2-chloro-1,3 alkadienyl)-2-oxo-1,3,2-dioxaphospholanes; chlorination; benzo[c]-1,3,2-dioxaphospholane-2-spiro-2′-(4′,5′-dichloro-5′,6′-dihydro-2H-1′,2′-oxaphosphorinium) chlorides; 4,5-dihydro-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine-2-spiro-2′-(benzo[c]-1′,3′,2′-dioxaphospholanium) chloride

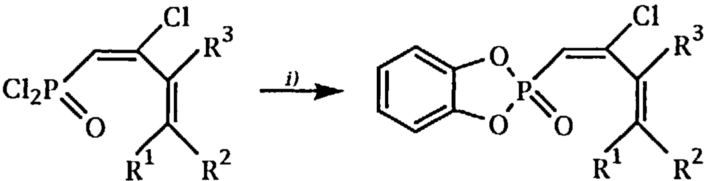
INTRODUCTION

Recently was shown that the reactions of phosphorylated 1,3-alkadienes with electrophilic reagents proceed with heterocyclization of the 1,3-alkadienylphosphonic system of double bonds in most cases.[1] Halogenation reactions of the phosphorylated 2-chloro-1,3-alkadienes are studied with 1,3-alkadienylphosphonic dialkyl esters,[2] dichlorides[2b,3]and acids[4] as well as the corresponding phosphine oxides.[5] On the other hand, the halogenation of the 2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes proceeds with six-membered ring heterocyclization with associated cleavage of the dioxaphospholane ring and addition of halogen across the carbon-oxygen bond.[6] The interaction of the same 1,3,2-dioxaphospholanes with sulfenyl chlorides leads to six- or five-membered heterocycles depending on the type of hydrocarbon moiety in the sulfur atom[7] – alkylsulfenyl chlorides give 5,6-dihydro-2H-1,2-oxaphosphorines while arylsulfenyl chlorides afford 2,5-dihydro-1,2-oxaphospholes.

The aim of this paper as a part of our continuing interest on the reactions of phosphorylated 2-chloro-1,3-alkadienes with electrophilic reagents[1] was to synthezise benzo[c]-2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes and investigate the influence of the benzo[c]-1,3,2-dioxaphospholane ring on the course of the chlorination reaction with respect to products formed.

RESULTS AND DISCUSSION

The benzo[c]-2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes **2** were prepared in good yield (48–53%) by substitution reaction of the two chlorine atoms in the starting 2-chloro-1,3-alkadienylphosphonic dichlorides **1** with catechol in the presence of triethylamine, according to **Scheme 1**:



1

2

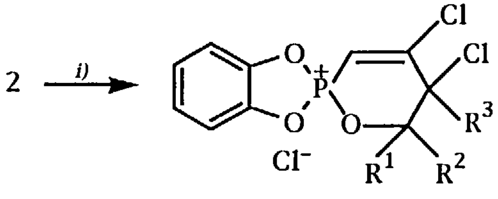
1,2	R^1	R^2	R^3
a	H	Me	Et
b	H	$-(CH_2)_4-$	
c	Me	Me	Me

Reagents and Conditions: i) pyrocatechol, Et_3N, ether, –20 °C, rt, 2h.

SCHEME 1

The resulting 1,3,2-dioxaphospholanes **2** were isolated by recrystallization from hexane or heptane and characterized by ^1H NMR and IR spectra and elemental analyses. ^1H NMR spectra of **2** show a multiplet signal for the aromatic protons in the benzo[c]-1,3,2-dioxaphospholane ring (δ 7.48–7.79 ppm) in addition to the signals of the protons due to the initial dichlorides **1**. The IR spectra of **2** exhibit characteristic absorption bands (1031–1038 cm^{-1}) due to the Ar-O-P bonds.

The benzo[c]-1,3,2-dioxaphospholanes **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-alkadienylphosphonate system is carried out, it would lead either to formation of stable phosphonium salts as in the chlorination reaction of the dialkyl (2-chlgro-1,3-alkadienyl) phosphine oxides[5] or to cleavage of one of the C-O bonds, opening of the benzo[c]-1,3,2-dioxaphospholane ring and addition of chlorine atom to the benzene ring like the reaction of the (2-chloro-1,3-alkadienyl)-1,3,2-dioxaphospholanes with halogens[6] and sulfenyl chlorides[7]. The reaction proceeded in 1,2-dichloroethane on heating at 55–60 °C. Under this conditions we established that a six-membered ring heterocyclization took place and only benzo[c]-1,3,2-dioxaphospholane-2-spiro-2′-(4′,5′-dichloro-5′,6′-dihydro-2H-1′,2′-oxaphosphorinium) chlorides were isolated in 54–60 % yields (Scheme 2):



3

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

SCHEME 2

Heterocyclic phosphonium salts **3** were not dissolved in organic solvents and pure examples were obtained by washing with organic solvents. Their structure were determined by means of ^1H NMR and IR spectra. Formation of the six-membered rings was judged on the basis of the signal of the olefinic proton in the ring which appears at low field (δ 6.19–6.23 ppm) as a doublet in the ^1H NMR spectra. The coupling constants of this proton with phosphorus ($^2J_{HP}$ 10.2–10.8 Hz) are in agreement with data reported for similar structures.[2–7] Moreover, in compound **3a**, the proton at C^6

atom (m, δ 4.61–4.89 ppm) shows considerable H-P coupling ($^3J_{HP}$ 7.7 Hz) which is characteristic for the P-O-CH moiety in the ring. The IR spectra of **3** exhibit absorption bands characteristic for the endocyclic double bond (1588–1593 cm^{-1}), for the P-O-C (977–982 cm^{-1}) and Ar-O-P (1040–1048 cm^{-1}) functions and absence of a band for the phosphoryl group.

The above experimental results show that the chlorination reaction of the benzo[c]-2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes proceeds regiospecifically with formation of stable 5,6-dihydro-2H-1,2-oxaphosphorinium salts. Benzo[c]-1,3,2-dioxaphospholane ring cleavage and chlorine addition[6,7] to the benzene ring did not occur probably because of the greater stability of the benzo[c]-1,3,2-dioxaphospholane ring in comparison with the 1,3,2-dioxaphospholane ring. Moreover, these results again[5] 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

^{1}H NMR spectra were obtained on a BRUCKER WM-250 spectrometer (250.1 MHz) for solutions in $CDCl_3$ or CF_3COOH. Chemical shifts are in parts per million downfield from internal TMS. IR spectra were recorded (in nujol) with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

The melting points were measured in open capillary tubes and are uncorrected. All 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.[8]

Synthesis of benzo[c]-2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes (2)

General procedure

To a solution of catechol (1.1 g, 10 mmol) and triethylamine (2.22 g, 22 mmol) in dry diethyl ether (30 ml) was added dropwise with stirring a solution of 2-chloro-1,3-alkadienylphosphonic dichloride (**1**) (10 mmol) in the same solvent (10 ml) under cooling (-20 °C). The stirring was continued for 1 h at the same temperature and 2 h at room temperature. Then the precipitate of triethylamine hydrochloride was filtered off, the solvent was removed using a rotatory evaporater and the residue was recrystallized from hexane or heptane to give the pure products as white crystals. Yield: 48–53%. The products had the following properties:

Benzo[c]-2-(2-chloro-3-ethyl-1,3-pentadienyl)-2-oxo-1,3,2-dioxaphospholane (**2a**): Yield: 49 %; m.p. 91–2 °C; $C_{13}H_{14}O_3PCl$, Calcd., %: P 10.88, Cl 12.46; Found, %: P 10.73, Cl 12.51. IR spectra, cm^{-1} : 1033 (Ar-O-P), 1280 (P=O), 1601, 1644 (C=C-C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.10 (t, $^3J_{H\text{-}H}$ 6.0 Hz, 3H, CH_2-$\underline{Me}$), 1.95 (d, $^3J_{H\text{-}H}$ 6.3 Hz, 3H, =CH-$\underline{Me}$), 2.35–2.54 (m, $^3J_{H\text{-}H}$ 6.0 Hz, 2H, $\underline{CH_2}$-Me), 5.33–5.58 (m, $^3J_{H\text{-}H}$ 6.3 Hz, 1H, =$\underline{CH}$-Me), 6.09 (d, $^2J_{H\text{-}P}$ 15.6 Hz, 1H, =CH), 7.59–7.79 (m, 4H, Ph).

Benzo[c]-2-[2-chloro-2-(1-cyclohexenyl)ethenyl]-2-oxo-1,3,2-dioxaphospholane (**2b**): Yield: 51 %; m.p. 113–4 °C; $C_{14}H_{14}O_3PCl$, Calcd., %: P 10.44, Cl 11.95; Found, %: P 10.57, Cl 12.07. IR spectra, cm^{-1}: 1038 (Ar-O-P), 1285 (P=O), 1605, 1655 (C=C-C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.67, 2.31, 6.08–6.32 (s, s, m, 9H, cyclohexenyl), 6.14 (d, $^2J_{HP}$ 15.3 Hz, 1H, =CH), 7.54–7.78 (m, 4H, Ph).

Benzo[c]-2-(2-chloro-3,4-dimethyl-1,3-pentadienyl)-2-oxo-1,3,2-dioxaphospholane (**2c**): Yield: 53 %; m.p. 89–0 °C; $C_{13}H_{14}O_3PCl$, Calcd., %: P 10.88, Cl 12.46; Found, %: P 10.83, Cl 12.57. IR spectra, cm^{-1} : 1031 (Ar-O-P), 1282 (P=O), 1603, 1647 (C=C-C=C). ^1H NMR spectra ($CDCl_3$), δ: 1.80, 1.93 (s, s, 9H, 3Me), 6.11 (d, $^2J_{H\text{-}P}$ 15.4 Hz, 1H, =CH), 7.48–7.66 (m, 4H, Ph).

Synthesis of benzo[c]-1,3,2-dioxaphospholane-2-spiro-2′-(4′,5′-dichloro-5′,6′-dihydro- 2H-1′,2′-oxaphosphorinium) chlorides (3)

General procedure

To a solution of benzo[c]-2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholane (**2**) (5 mmol) in dry 1,2-dichloroethane (10 ml) at 55–60 °C was added dropwise with stirring a solution of chlorine (0.43 g, 6 mmol) or sulfuryl chloride (0.81 g, 6 mmol) in the same solvent (10 ml). The stirring was continued for 1 h at the same temperature and 3 h at room temperature. The resulting precipitate was filtered and dried *in vacuo.*The salts **3** were not dissolved in organic solvents, but were dissolved in water and trifluoroacetic acid. The pure samples were obtained by washing with organic solvents and drying in a vacuum exicator as light yellow crystals. Yield: 54–60 %. The products had the following properties:

Benzo[c]-1,3,2-dioxaphospholane-2-spiro-2′-(4′,5′-dichloro-5′-ethyl-6′-methyl-5′,6′-dihydro-2H-1,2-oxaphosphorinium) chloride (**3a**): Yield: 54 %; m.p. 123–4 °C ; $C_{13}H_{14}O_3PCl_3$, Calcd., %: P 8.71, Cl 29.91; Found, %: P 8.79, Cl 30.11. IR spectra, cm^{-1}: 978 (C-O-P), 1042 (Ar-O-P), 1589 (C=C). ^{1}H NMR spectra (CF_3COOH), δ: 0.84 (t, 3H, $^3J_{H\text{-}H}$ 6.1 Hz, $\underline{Me}$-CH_2), 1.54 (d, $^3J_{H\text{-}H}$ 6.5 Hz, 3H, CH-$\underline{Me}$), 2.21–2.45 (m, 2H, Me-C$\underline{H}_2$), 4.61–4.89 (m, $^3J_{H\text{-}P}$7.7 Hz, $^3J_{H\text{-}H}$ 6.5 Hz, 1H, C$\underline{H}$-Me), 6.19 (d, $^3J_{H\text{-}P}$ 10.2 Hz, 1H, =CH), 7.31–7.55 (m, 4H, Ph).

4,5-Dihydro-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine-2-spiro-2′-(benzo[c]-1′,3′,2′-dioxaphospholanium) chloride (**3b**): Yield: 58 %; m.p. 166–7 °C; $C_{14}H_{14}O_3PCl_3$, Calcd., %: P 8.43, Cl 28.94; Found, %: P 8.39, Cl 29.07. IR spectra, cm^{-1} : 982 (C-O-P), 1048 (Ar-O-P), 1593 (C=C). ^{1}H NMR spectra (CF_3COOH), δ: 1.81, 2.43, 4.55–4.92 (s, s, m, 9H, cyclohexyl), 6.23 (d, $^2J_{HP}$10.8 Hz, 1H, =CH), 7.34–7.58 (m, 4H, Ph).

Benzo[c]-1,3,2-dioxaphospholane-2-spiro-2′-(4′,5′-dichloro-5′,6′,6′-trimethyl-5′,6′-dihydro-2H-1′,2′-oxaphosphorinium) chloride (**3c**): Yield: 60 %; m.p. 119–0 °C ; $C_{13}H_{14}O_3PCl_3$, Calcd., %: P 8.71, Cl 29.91; Found, %: P 8.82, Cl 30.02. IR spectra, cm^{-1}: 977 (C-O-P), 1040 (Ar-O-P), 1588 (C=C). ^{1}H NMR spectra (CF_3COOH), δ: 1.76, 2.18 (s, s, 9H, 3Me), 6.22 (d, $^2J_{H\text{-}P}$ 10.4 Hz, 1H, =CH), 7.35–7.59 (m, 4H, Ph).

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