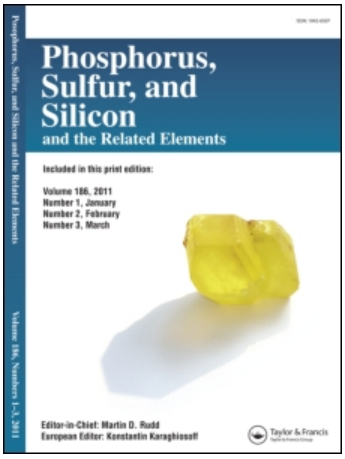

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SYNTHESIS AND HALOGENATION OF 2-CHLORO-1,3-ALKADIENYLPHOSPHONIC ACIDS

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SYNTHESIS AND HALOGENATION OF 2-CHLORO-1,3-ALKADIENYLPHOSPHONIC ACIDS

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2-Chloro-1,3-alkadienylphosphonic acids **2** have been synthesized by hydrolysis of the 2-chloro-1,3-alkadienylphosphonic dichlorides **1**. The chlorination of **2** takes place with formation of 2-hydroxy-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides, but their bromination yields mixtures of 2-hydroxy-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides and phosphorylated 2-chloro-1,2,3-tribromoalkanes.

Keywords: 2-chloro-1,3-alkadienylphosphonic acids; halogenation; 2-hydroxy-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides; 2-chloro-1,2,3-tribromoalkanephosphonic acids

INTRODUCTION

Although halogenation of 1,3-alkadienes is a well studied reaction there is, however, scant information on this reaction with 1,3-dienic compounds containing electron-withdrawing groups adjacent to the conjugate bond system.[1] Thus, only the halogenation of 1,3-alkadienecarboxylic acids[2] and of their esters[3] have been investigated in detail. On the other hand, convenient methods for the preparation of phosphorylated 1,3-alkadienes were elaborated in the past twenty years,[4] thus making them available for systematic studies of their reactivity. Recently was shown that the reaction of 1,3-alkadienylphosphonic derivatives with electrophilic reagents proceeds with heterocyclization of the 1,3-alkadienylphosphonic system of double bonds (O=P-C=C-C=C) in most cases. Clearly,

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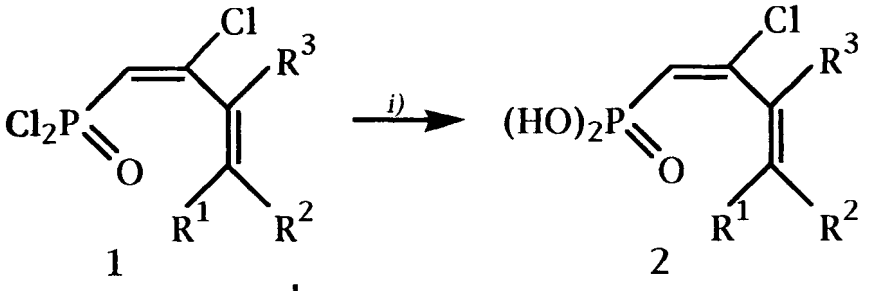
the preferential s-cis conformation[5] of the 1,3-diene system is particularly favourable for the cyclization. The reaction of 2-chloro-1,3-alkadienylphosphonic esters with sulfenyl chlorides leads to six- or five-membered heterocyclization depending on the type of hydrocarbon moiety in the sulfur atom[6a,6c] - 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.[6b] Moreover, it has shown that depending on the nature of the substituents at the phosphorus atom (Cl, RO, etc.) 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,[7] five-[8] or six-membered[9] heterocyclic compounds, or mixtures of them,[7] or addition-elimination products *via* five-membered heterocyclic intermediates.[10]

The aim of this paper as a part of our continuing study on the reactions of phosphorylated 1,3-alkadienes with electrophilic reagents,[6,9] was to synthezised 2-chloro-1,3-alkadienylphosphonic acids and investigate the influence of the phosphorus moiety [$(HO)_2P(O)$] on the course of the halogenation reactions of the 2-chloro-1,3-alkadienylphosphonic acids with respect to products formed.

RESULTS AND DISCUSSION

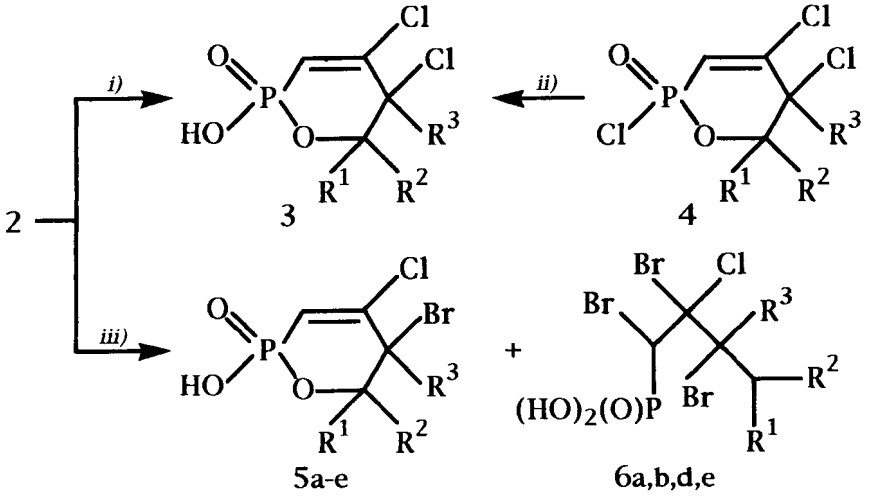
The 2-chloro-1,3-alkadienylphosphonic acids **2** are obtained in high yield (77–90%) by hydrolysis of 2-chloro-1,3-alkadienylphosphonic dichlorides **1** according to Scheme 1: The resulting 1,3-dienes **2** were isolated by recrystallization and characterized by ^{1}H NMR and IR spectra and elemental analyses.

The acids **2** obtained in preparative amounts allowed us to study their chemical behavior in the reaction with halogens. We established that irrespective of the halogen, heterocyclization of the 1,3-dienylphosphonic system predominantly proceeded with formation of six-membered heterocyclic compounds (Scheme 2). In the case of chlorination, only 4,5-dichloro-2-hydroxy-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides **3** were isolated in 66–71% yields. The same heterocycles **3** were successfully synthesized in 73–84% yields by hydrolysis of the cyclic chlorides **4**, which were prepared from the reaction of 2-chloro-1,3-alkadienylphosphonic dichlorides with sulfuryl chloride.[9b] On the other hand, the bromination of 2-chloro-1,3-dienylphosphonic acids **2** yielded mixtures of the cyclic compounds **5a-e** and the 2-chloro-1,2,3-tribromoalkanephosphonic acids **6a,b,d,e** in the ratio 2:1 with the exception of the 2-chloro-2(1-cyclohexenyl)-ethenephosphonic acid **2c**, which gave only the

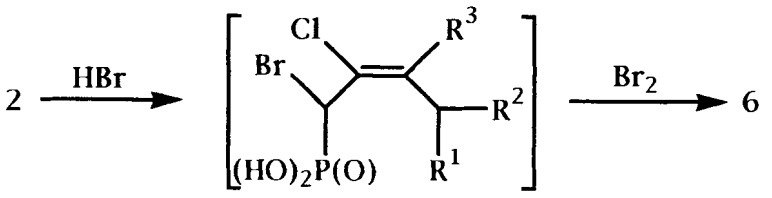


1, 2	R^1	R^2	R^3
a	H	H	Me
b	H	Me	Et
c	H	$-(CH_2)_4-$	
d	Me	Me	Me
e	Me	Me	Pr^i

Reagents and Conditions: *i)* H_2O, acetone, 0-10°C, 1h, rt, 3h;



Reagents and Conditions: *i)* Cl_2 or SO_2Cl_2, $ClCH_2CH_2Cl$, 55-60°C, 3h, rt, 24h;
ii) H_2O, reflux, 1h;
iii) Br_2, $ClCH_2CH_2Cl$, 55-60°C, 3h, rt, 24h;



4,1-adduct

5-bromo-4-chloro-2-hydroxy-5,6,7,8,9,10-hexahydro-benz-2H-1,2-oxaphosphorine 2-oxide **5c** (Scheme 2): Heterocyclic compounds **3** and **5** exhibited correct spectroscopic properties in agreement[6,7,9] with the proposed structure. The structure of the 2-chloro-1,2,3-tribromoalkanephosphonic acids **6** were assigned on the basis of their ^1H and ^{13}C NMR data. Thus, the ^1H NMR spectra showed singlet peak for OH proton, doublet signal at low field (δ 5.26–5.31 ppm, J_{HP} 15.76–16.83 Hz) for BrCH-P proton and peaks at high field for other protons. The ^{13}C NMR spectra exhibited peaks only for sp^3 carbon atoms and the C-1 carbon atom was a doublet signal with coupling between carbon and phosphorus ($^1J_{CP}$ 219.34–221.20 Hz). The ratio of the products **5** and **6** was determined by comparison of the intensity of the signals for the =CH of **5** and the BrCH-P protons of **6** in the ^1H NMR spectra and the C-1 resonances of **5** and **6** in the ^{13}C NMR spectra of the mixtures.

As shown in Scheme 3, the formation of the 2-chloro-1,2,3-tribromoalkanephosphonic acids **6** can be explained by the addition reaction of hydrogen bromide, which eliminated in the heterocyclization reaction, to 2-chloro-1,3-alkadienylphosphonic acids **2** to yield the 4,1-adduct, followed by addition of bromine to afford compounds **6**. The fact that the adduct **6c** was not obtained may be due to the influence of the cyclohexene ring on the stability of the intermediate carbenium ion, which formed after protonation with HBr.

In summary, we have found that the 2-chloro-1,3-alkadienylphosphonic acids, in contrast to their dichlorides[9b] and esters,[7,9a,9c,9d,9e] react with halogens peculiarly - the chlorination reaction leads to formation of 5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides, while the bromination yields mixtures of six-membered heterocyclic compounds and addition products - the phosphorylated 2-chloro-1,2,3-tribromoalkanes.

EXPERIMENTAL

Method of analysis

NMR spectra were obtained on a BRUCKER WM-250 spectrometer for solutions (in $CDCl_3$:d_6-DMSO = 5:1) operating at 250.1 (^1H), 100.6 (^{13}C) and 161.9 MHz (^{31}P). Chemical shifts are in parts per million downfield from internal TMS

(^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). 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. Halogenation 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.[4a,4b,4c] 2,4,5-Trichloro-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides (**4**) were prepared according to the established procedure.[9b]

Synthesis of 2-chloro-1,3-alkadienylphosphonic acids (2). General procedure

A solution of 2-chloro-1,3-alkadienylphosphonic dichloride **1** (50 mmol) in acetone (5 ml) was slowly added dropwise, with stirring, at 0–10°C to distilled water (20 ml). The reaction mixture was stirred for 1h at the same temperature and 3h at room temperature. Then the precipitate was filtered, washed with water, dried and recrystallized from hexane or heptane to give the pure products as white crystals. The products had the following properties:

2-Chloro-3-methyl-1,3-butadienylphosphonic acid (2a)

had the same physical and spectral data as the described one in the literature.[4a]

2-Chloro-3-ethyl-1,3-pentadienylphosphonic acid (2b)

Yield: 84%, m.p. 82–3°C, $C_7H_{12}O_3PCl$, Calcd., %: P 14.71, Cl 16.83; Found, %: P 14.98, Cl 17.02; IR spectra, cm^{-1}: 1268 (P=O), 1601, 1652 (C=C-C=C); ^1H NMR spectra, δ: 1.04 (t, J_{H-H} 6.8 Hz, 3H, CH_2-*Me*), 1.72 (d, J_{H-H} 6.4 Hz, 3H, =CH-*Me*), 2.26 (q, J_{H-H} 6.8 Hz, 2H, *CH_2*-Me), 5.47 (q, J_{H-H} 6.4 Hz, 1H, =*CH*-Me), 6.06 (d, J_{H-P} 9.7 Hz, 1H, =CH), 10.38 (s, 2H, 2HO);

2-Chloro-2(1-cyclohexenyl)ethenephosphonic acid (2c)

Yield: 90%, m.p. 127–8°C, $C_8H_{12}O_3PCl$, Calcd., %: P 13.91, Cl 15.94; Found, %: P 13.85, Cl 15.78; IR spectra, cm^{-1}: 1275 (P=O), 1589, 1625 (C=C-C=C); ^1H NMR spectra, δ: 1.56, 2.09, 5.93–6.09 (s, s, m, 9H, cyclohexenyl), 5.78 (d, J_{H-P} 11.2 Hz, 1H, =CH), 9.81 (s, 2H, 2HO);

2-Chloro-3,4-dimethyl-1,3-pentadienylphosphonic acid (2d)

Yield: 81%, m.p. 94–5°C, $C_7H_{12}O_3PCl$, Calcd., %: P 14.71, Cl 16.83; Found, %: P 14.87, Cl 17.12; IR spectra, cm^{-1}: 1281 (P=O), 1602, 1659 (C=C-C=C); ^1H NMR spectra, δ: 1.70, 1.77, 1.83 (s, s, s, 9H, 3Me), 5.98 (d, J_{H-P} 10.6 Hz, 1H, =CH), 10.47 (s, 2H, 2HO);

2-Chloro-3-isopropyl-4-methyl-1,3-pentadienylphosphonic acid (2e)

Yield: 77%, m.p. 104–5°C, $C_9H_{16}O_3PCl$, Calcd., %: P 12.98, Cl 14.86; Found, %: P 13.17, Cl 15.12; IR spectra, cm^{-1}: 1283 (P=O), 1601, 1656 (C=C-C=C); ^1H NMR spectra, δ: 1.03 (d, J_{H-H} 6.4 Hz, 6H, $CHMe_2$), 1.68, 1.77, (s, s, 6H, 2Me), 2.56 (m, 1H, $CHMe_2$), 5.96 (d, J_{H-P} 10.2 Hz, 1H, =CH), 10.67 (s, 2H, 2HO);

Synthesis of 4,5-dichloro-2-hydroxy-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides (3): Method a: Chlorination of 2-chloro-1,3-alkadienylphosphonic acids (2). General procedure

To a solution of 2-chloro-1,3-alkadienylphosphonic acid **2** (10 mmol) in dry 1,2-dichloroethane (5 ml) at 55–60°C during 0.5h 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 (15 ml). The stirring was continued for 3h at the same temperature. The flask was stoppered and kept at room temperature for 24h. 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: 66–71%.

Method b: Hydrolysis of 2,4,5-trichloro-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxides (4): General procedure

A mixture of 2,4,5-trichloro-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide **4** (5 mmol) and 5 ml distilled water was refluxed for 1h. The crystals were dissolved. After cooling of the solution, the product was crystallized. The pure samples were obtained by recrystallization from hexane or heptane. Yield: 73–84%.

The products had the following properties:

4,5-dichloro-2-hydroxy-5-methyl-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (3a)

Yield: 71% (method a), 79% (method b); m.p. 75–6°C, $C_5H_7O_3PCl_2$, Calcd., %: P 14.27, Cl 32.68; Found, %: P 14.41, Cl 32.86; IR spectra, cm^{-1}: 1239 (P=O), 1607 (C=C); ^1H NMR spectra, δ: 2.04 (s, 3H, Me), 4.48 (A), 4.31 (B)(ABX-system, J_{A-P} 12.37 Hz, J_{B-P} 18.89 Hz, J_{A-B} 11.44 Hz, 2H, CH_2-O-P), 6.34 (d, J_{H-P} 7.76 Hz, 1H, =CH), 8.54 (s, 1H, OH); ^{13}C NMR spectra, δ: 28.41 (C-5), 43.12 (C-3), 65.09 (C-4), 123.33 (C-1, J_{C-P} 171.23 Hz), 144.42 (C-2).

4,5-dichloro-5-ethyl-2-hydroxy-6-methyl-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (3b)

Yield: 68% (*method a*); m.p. 94–5°C, $C_7H_{11}O_3PCl_2$, Calcd., %: P 12.64, Cl 28.94; Found, %: P 12.75, Cl 29.09; IR spectra cm^{-1}: 1243 (P=O), 1606 (C=C); ^1H NMR spectra, δ: 0.91 (t, 3H, *Me*-CH_2), 1.69 (d, J_{H-H} 6.7 Hz, 3H, CH-*Me*), 2.33 (q, 2H, Me-*CH_2*), 4.74–4.98 (m, J_{H-P} 13.2 Hz, J_{H-H} 6.7 Hz, 1H, *CH*-Me), 6.32 (d, J_{H-P} 8.86 Hz, 1H, =CH), 8.89 (s, 1H, OH); ^{13}C NMR spectra, δ: 9.3 (C-6), 17.4 (C-7), 33.0 (C-5), 47.10 (C-3), 67.43 (C-4), 121.55 (C-1, J_{C-P} 168.23 Hz), 146.22 (C-2).

4,5-dichloro-2-hydroxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxide (3c)

Yield: 69% (*method a*), 84% (*method b*); m.p. 107–8°C, $C_8H_{11}O_3PCl_2$, Calcd., %: P 12.05, Cl 27.58; Found, %: P 12.13, Cl 27.74; IR spectra, cm^{-1}: 1239 (P=O), 1599 (C=C); ^1H NMR spectra, δ: 1.74, 2.18, 4.66–4.81 (s, s, m, 9H, cyclohexyl), 6.20 (d, J_{H-P} 8.60 Hz, 1H, =CH), 12.05 (s, 1H. OH); ^{13}C NMR spectra, δ: 23.85 (C-6), 28.35 (C-5), 33.65 (C-7), 72.45 (C-3, J_{C-P} 6.7 Hz), 67.6 (C-4, J_{C-P} 5.5 Hz), 118.9 (C-1, J_{C-P} 178.45 Hz), 143.7 (C-2, J_{C-P} 11.4 Hz); ^{31}P NMR spectra, δ: 7.30.

4,5-dichloro-2-hydroxy-5,6,6-trimethyl-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (3d)

Yield: 68% (*method a*), 73% (*method b*); m.p. 95–6°C, $C_7H_{11}O_3PCl_2$, Calcd., %: P 12.64, Cl 28.94; Found, %: P 12.80, Cl 29.18; IR spectra, cm^{-1}: 1245 (P=O), 1604 (C=C); ^1H NMR spectra, δ: 1.65, 1.80 (s, s, 9H, 3Me), 6.25 (d, J_{H-P} 8.57 Hz, 1H, =CH), 8.92 (s, 1H, OH).

4,5-dichloro-6,6-dimethyl-5-isopropyl-2-hydroxy-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (3e)

Yield: 66% (*method a*), 75% (*method b*); m.p. 105–6°C, $C_9H_{15}O_3PCl_2$, Calcd., %: P 11.34, Cl 25.96; Found, %: P 11.42, Cl 26.11; IR spectra, cm^{-1}: 1241 (P=O), 1600 (C=C); ^1H NMR spectra, δ: 1.41 (d, 6H, CH*Me*$_2$), 1.72 (s, s, 6H, 2Me), 2.58–2.77 (m, 1H, C*H*Me$_2$), 6.37 (d, J_{H-P} 7.97 Hz, 1H, =CH), 9.12 (s, 1H, OH).

Bromination of 2-chloro-1,3-alkadienylphosphonic acids (2). General procedure

To a solution of 2-chloro-1,3-alkadienylphosphonic acid **2** (10 mmol) in dry 1,2-dichloroethane (5 ml) at 55–60°C during 0.5h was added dropwise with stirring a solution of bromine (1.76 g, 11 mmol) in the same solvent (15 ml). The stirring was continued for 3h at the same temperature. The flask was stoppered and kept at room temperature for 24h. The solvent was removed using a rotatory evaporater and the residue was washed with hexane and dried to give the mixture of products as light yellow crystals.

$R^1 = R^2 = H$, $R^3 = Me$: Yield: 51%, m.p. 89–2°C;

Ratio (by NMR spectra): **5a:6a** = 2.0:1.0.

5-bromo-4-chloro-2-hydroxy-5-methyl-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (5a)

IR spectra, cm^{-1}: 1246 (P=O), 1614 (C=C); ^1H NMR spectra, δ: 2.10 (s, 3H, Me), 4.55 (A), 4.38 (B)(ABX-system, J_{A-P} 12.78 Hz, J_{B-P} 19.08 Hz, J_{A-B} 11.67 Hz, 2H, CH_2-O-P), 6.37 (d, J_{H-P} 7.68 Hz, 1H, =CH), 8.34 (s, 1H, OH); ^{13}C NMR spectra, δ: 28.35 (C-5), 43.09 (C-3), 64.93 (C-4, J_{C-P} 16.10 Hz), 121.85 (C-1, J_{C-P} 181.11 Hz), 146.24 (C-2); ^{31}P NMR spectra, δ: 5.89.

2-chloro-3-methyl-1,2,3-tribromobutanephosphonic acid (6a)

IR spectra, cm^{-1}: 1273 (P=O); ^1H NMR spectra, δ: 1.92, 1.95 (s, s, 6H, 2Me), 5.28 (d, J_{H-P} 15.76 Hz, 1H, Br-CH), 8.34 (s, 2H, 2OH); ^{13}C NMR spectra, δ: 17.80 (C-4), 20.08 (C-5), 33.40 (C-3), 35.50 (C-2), 42.59 (C-1, J_{C-P} 219.34 Hz); ^{31}P NMR spectra, δ: 9.81, 9.96.

$R^1 = H$, $R^2 = Me$, $R^3 = Et$: Yield: 50%, m.p. 93–5°C;

Ratio (by NMR spectra): **5b:6b** = 2.2:1.0.

5-bromo-4-chloro-5-ethyl-2-hydroxy-6-methyl-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (5b)

IR spectra. cm^{-1}: 1239 (P=O), 1590 (C=C); ^1H NMR spectra, δ: 1.12 (t, 3H, *Me*-CH_2), 1.75 (d, J_{H-H} 6.8 Hz, 3H, CH-*Me*), 2.39 (q, 2H, Me-*CH*$_2$), 4.90–5.08 (m, J_{H-P} 13.2 Hz, J_{H-H} 6.9 Hz, 1H, C*H*-Me), 6.44 (d, J_{H-P} 9.0 Hz, 1H, =CH), 9.08 (s, 1H, OH); ^{13}C NMR spectra, δ: 10.13 (C-6), 17.93 (C-7), 33.4 (C-5), 47.35 (C-3), 68.78 (C-4), 123.11 (C-1, J_{C-P} 169.30 Hz), 146.17 (C-2); ^{31}P NMR spectra, δ: 6.56.

2-chloro-3-ethyl-1,2,3-tribromopentanephosphonic acid (6b)

IR spectra, cm^{-1}: 1268 (P=O); ^1H NMR spectra, δ: 0.89 (t, 6H, 2*Me*-CH_2), 2.15 (q, 4H, 2Me-C*H*$_2$), 5.23 (d, J_{H-P} 16.65 Hz, 1H, Br-CH), 9.08 (s, 2H, 2OH); ^{13}C NMR spectra, δ: 19.11 (C-7), 20.08 (C-5), 27.94 (C-6), 29.82 (C-4), 31.08 (C-3), 34.16 (C-2), 43.61 (C-1, J_{CP} 221.20); ^{31}P NMR spectra, δ: 10.08, 10.43.

R^1 = H, R^2 + R^3 = $-(CH_2)_4$-: 5-bromo-4-chloro-2-hydroxy-5,6,7,8,9,10-hexahydrobenz-2H-1,2-oxaphosphorine 2-oxide (5c)

Yield: 58%; m.p. 114-5°C, $C_8H_{11}O_3PClBr$, Calcd., %: P 10.27, Cl 11.76; Br 26.50; Found, %: P 10.38, Cl 11.85; Br 26.71; IR spectra, cm^{-1}: 1244 (P=O), 1602 (C=C); ^1H NMR spectra, δ: 1.80, 2.21, 4.68–4.87 (s, s, m, 9H, cyclohexyl), 6.31 (d, J_{H-P} 8.56 Hz, 1H, =CH), 12.44 (s, 1H, OH); ^{13}C NMR spectra, δ: 24.05 (C-6), 29.05 (C-5), 32.95 (C-7), 74.23 (C-3, J_{C-P} 6.5 Hz), 67.70 (C-4, J_{C-P} 5.8 Hz), 119.45 (C-1, J_{C-P} 177.09 Hz), 146.92 (C-2, J_{C-P} 10.9 Hz); ^{31}P NMR spectra, δ: 7.77.

R^1 = R^2 = R^3 = Me: Yield: 47%, m.p. 109–1°C;

Ratio (by NMR spectra): **5d:6d** = 2.1:1.0.

5-bromo-4-chloro-2-hydroxy-5,6,6-trimethyl-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (5d)

IR spectra, cm^{-1}: 1250 (P=O), 1610 (C=C); ^1H NMR spectra, δ: 1.69, 1.89 (s, s, 9H, 3Me), 6.33 (d, J_{H-P} 8.47 Hz, 1H, =CH), 9.13 (s, 1H, OH).

2-chloro-3,4-dimethyl-1,2,3-tribromopentanephosphonic acid (6d)

IR spectra, cm^{-1}: 1274 (P=O); ^1H NMR spectra, δ: 1.77 (s, 3H, Me), 1.44 (d, 6H, CH*Me*$_2$), 2.49–2.79 (m, 1H, *CH*Me$_2$), 5.31 (d, J_{H-P} 16.83 Hz, 1H, Br-CH), 9.13 (s, 2H, 2OH).

$R^1 = R^2 = Me$, $R^3 = Pr^i$: Yield: 48%, m.p. 121–3°C;
Ratio (by NMR spectra): **5e:6e** = 2.0:1.0.

5-bromo-4-chloro-6,6-dimethyl-5-isopropyl-2-hydroxy-5,6-dihydro-2H-1,2-oxaphosphorine 2-oxide (5e)

IR spectra, cm^{-1}: 1254 (P=O), 1609 (C=C); ^1H NMR spectra, δ: 1.35 (d, 6H, $CHMe_2$), 1.88 (s, 6H, 2Me), 2.51–2.74 (m, 1H, $CHMe_2$), 6.50 (d, $J_{H\text{-}P}$ 8.09 Hz, 1H, =CH), 9.54 (s, 1H, OH).

2-chloro-3-isopropyl-4-methyl-1,2,3-tribromopentanephosphonic acid (6e)

IR spectra, cm^{-1}: 1273 (P=O); ^1H NMR spectra, δ: 1.56 (d, 12H, $2CHMe_2$), 2.34–2.68 (m, 2H, $2CHMe_2$), 5.26 (d, $J_{H\text{-}P}$ 16.66 Hz, 1H, Br-CH), 9.54 (s, 2H, 2OH).

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