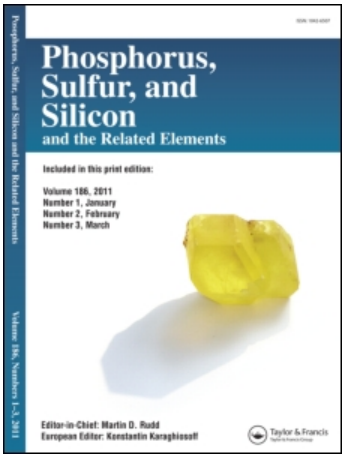

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New Derivatives of 1,2-Alkadienephosphonic Acids

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NEW DERIVATIVES OF 1,2-ALKADIENEPHOSPHONIC ACIDS

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The preparations of new cyclic derivatives of 1,2-alkadienephosphonic acids have been reported and the reactions of these compounds with bromine have been investigated.

Keywords: allenephosphonates; alkadienephosphonate derivatives; electrophilic addition reactions

INTRODUCTION

The chemistry of the phosphorylated 1,2-alkadiene hydrocarbons attracts permanently the interest of scientists because of the combination between phosphoryl group and with 1,2-dienyc system of double bonds in their molecules[1-5].

There are number of known methods for the preparation of the above mentioned compounds[6-12], which can to be separated in two main groups. Methods connected with the application of completely new approaches for the synthesis and modified methods which are already established.

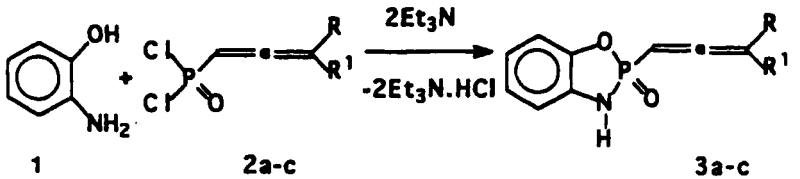
In this paper we report the synthesis of new cyclic derivatives of 1,2-alkadienephosphonic acids based on the well known reactivity of the dichlorides of 1,2-alkadienephosphonic acids in substitution reactions.

* Corresponding Author.

RESULTS AND DISCUSSION

The high reactivity of the dichlorides of 1,2-alkadienephosphonic acids in the substitution reactions are well documented[13–22]. We decided to investigate the interaction of the dichlorides of 1,2-alkadienephosphonic acids with bifunctional organic compounds such as 2-aminophenol and some hydroxycarboxylic acids. During the investigation of the reactions between 2-aminophenol and the dichlorides of 1,2-alkadienephosphonic acids we obtained cyclic derivatives of the 1,2-alkadienephosphonic acids, namely 2-(1,2-alkadienyl)-2-oxo-benzo-[b]-1,3,2-oxazaphospholanes **2a-c**

The reaction follow the scheme:



1 **2a-c** **3a-c**

	R	R^1
a	Me	Me
b	Me	Et
c	$-(CH_2)_2-$	

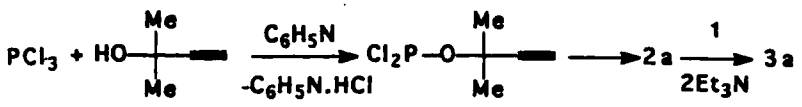
The successful synthesis of **3a-c** was confirmed by their IR, ^{1}H- and ^{31}P-NMR spectral data as well as by elemental analysis data.

In the IR spectra of **3a-c** besides of the bands at 1250–1270cm^{-1} and at 1950–1980cm^{-1} for the phosphoryl group and for the allenic system respectively, there are also bands at 900 – 1000cm^{-1} for the P-O-C bonds and at 3500cm^{-1} for the N-H bond. The bands chracteristic for the aromatic ring appear at 1600cm^{-1}.

The ^{1}H-NMR spectra also confirm the suggested structure. For example in the ^{1}H-NMR spectra of **3a** there is a signal for the olefinic proton at 5.04 ppm with a coupling constant with the phosphorus atom of $^2J_{HP}$ 6.8Hz. There are also signals at 7.8ppm for the protons of the aromatic ring as well as at 1.68ppm for the protons of the methyl groups. The ^{31}P-NMR of ***3a-c*** are in accordance with those for phosphorylated 1,2-alkadienes, namely in the range of 16 – 18ppm.

The above mentioned spectral data and those given in the experimental part confirm the suggested structure of **3a-c**. We also tried to synthesize the compounds **3a-c** in a one pot reaction, namely without isolation of the dichlorides of 1,2-alkadienephosphonic acids.

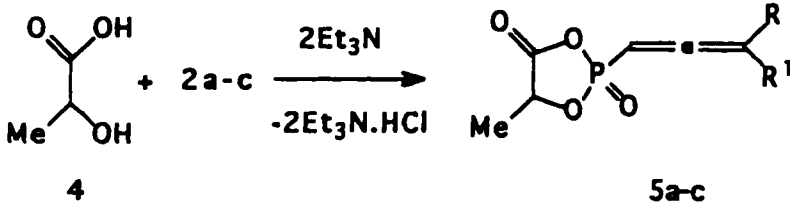
The reaction follows the scheme:



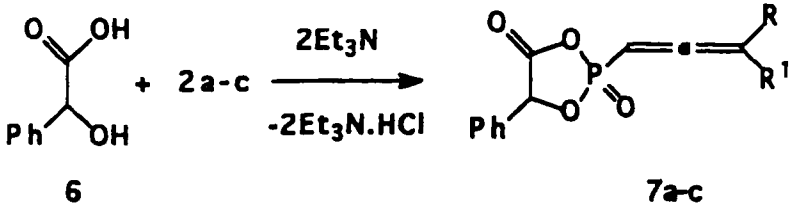
The structures of the obtained compounds are confirmed by their IR, ^{1}H- and ^{31}P-NMR spectra. The spectral data and those from the elementhal analysis are identical with that for **3a-c**, synthesized according to the first procedure.

We also examine the reaction of the dichlorides of 1,2-alkadienephosphonic acids with α-hydroxycarboxylic acids. As a result we successfully synthesized 1,3,2-dioxaphospholanes **5a-c** and **7a-c**.

The following schemes ilustrate the reactions:



4 5a-c



6 7a-c

The confirmation of the structure of the compounds **5a-c** and **7a-c**comes from their IR, ^{1}H- and ^{31}P-NMR spectra as well as from the data of the

elemental analyses. Thus in IR spectra of the compounds **5a-c** there are characteristic bands for the allenic system at 1950–1970cm^{-1}, for the phosphoryl group at 1255–1260cm^{-1} and for the P-O-C bonds at 1020 – 960cm^{-1}. Besides these characteristic bands in the IR spectra of **7a-c** there are bands at 1600cm^{-1} for the benzene ring.

The characteristic bands for the carbonyl group are particulary suitable for establishing the structure of **5a-c** and **7a-c**. There is a significant shift of the appearance of these bands up to 1800cm^{-1}. The mentioned IR spectral data are in accordance with our previous results and with those reported by others[23].

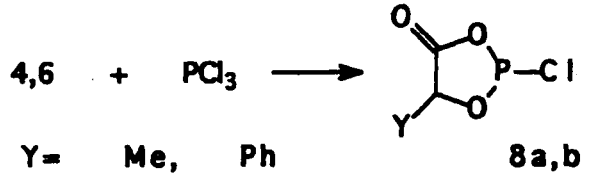
In the ^{1}H-NMR spectra of the compounds **5a-c** and **7a-c** there is a very characteristic signal at 5.02ppm for the olefinic proton at the C1 atom from the allenephosphonate system of double bonds with a characteristic coupling constant of $^2J_{HP}$ 6.8Hz with the phosphorus atom. In the spectra are also present signals for other protons(see experimental part).

The ^{31}P-NMR are in accordance with those for phosphorylated allenes.

In the ^{1}H-NMR spectra of compounds **7a-c**, besides of the mentioned signals, there are also signals for the protons of the benzene ring.

To confirm the synthesis of the compounds **5a-c** and **7a-c** we tried to synthesize cyclic chlorophosphites from the corresponding α-hydroxycarboxylic acids and phosphorus trichoride and then to cause these cyclic chlorophosphites to react with α-acetylenic alcoholes.

The reactions follow the scheme:

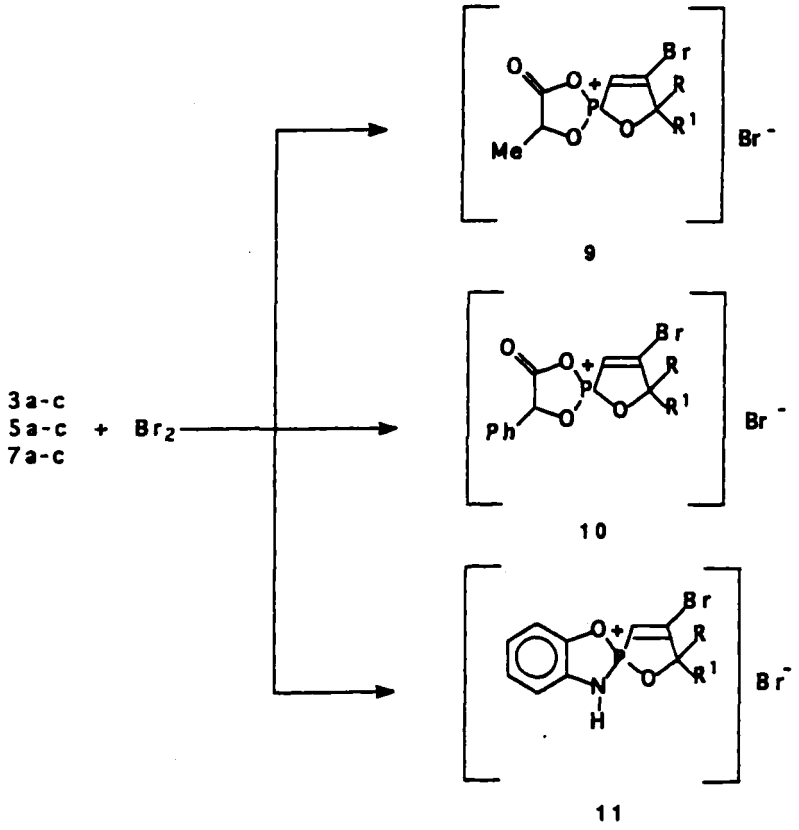


The spectral data of the synthesized compounds **5a-c** and **7a-c** are identical to those synthesized via the previously mentioned reaction pathway(see experimental part).

Continuing our investigations of the reactivity of the allenephosphonate derivatives we investigated the interaction of the synthesized compounds **3a-c**, **5a-c** and **7a-c** with bromine in nonpolar media.

In all cases we isolated with good yield cyclic spirophosphonium salts. The isolated compounds are colored powders which are insoluble in organic solvents but have very good solubility in water.

The reaction follows the scheme:.



The proposals for the structure of the compounds **9**, **10** and **11** were made on the basis of spectral investigations. Thus in the IR spectra of these compounds the chracteristic bands for the allenic system of the double bonds and for the phosphoryl group at 1950–1980 and 1255–1270cm^{-1}, respectively, disappear while characteristic bands at 1585–1595cm^{-1} for an endocyclic double bond appear.

The ^{1}H-NMR and ^{31}P-NMR spectral data also confirm the suggested structure.

One of the most convenient information which supports the suggested structure were their ^{31}P-NMR spectra. The signals for the phosphorus atom in the compounds **9**, **10** and **11** were in the range of 107 – 110ppm, typical for the structures of phosphonium salts[24] of this type.

EXPERIMENTAL

1. Starting materials

Phosphorus trichloride, acetylenic alcoholes, triethylamine and salicylic acid are commercially available from Fluka.

All the reagents are purified using standart procedures.

2. Analytical methods

IR spectra are registered on IR 72 Karl Zeiss Jena spectrophotometer.

1H-nmr spectra are registered on Tesla BS(80 MHz) at normal temperature as $CDCl_3$ solution with TMS as an internal standard.

Synthesis of 2-(1,2-alkadlenyl)-2-oxo-benzo-[b]-1,3,2-oxazaphospholanes 3a-c I

General procedure

A solution of 0.2mol of 2-aminophenol and 0.4mol of triethylamine in 500ml of dry benzene was heated to 45–50°C. After that under stirring a solution of 0.2mol of the appropriate dichloride of 1,2-alkadienephosphonic acid in the same solvent was added dropwise for an hour. The reaction mixture was stirred an additional hour at the same conditions and cooled to room temperature. The precipitate was filtered off, the solvent was removed and the residue was purified by column chromatography(50g silicagel, heptane/benzene)

3a, ^{1}H NMR 5.04d(1H, $^{2}J_{HP}$6.8Hz), 1.67d(6H), 7.8m; $C_{11}H_{12}O_2NP$; Calcd. P(%) 14.00, N (%) 6.33; Found P(%) 13.95, N(%) 6.29; m.p. °C

122–124; Yield (%) 72; IR (cm^{-1}) $1260_{\nu(P=O)}$, $1989_{\nu(C=C=C)}$, $3495_{\nu(N-H)}$, $1020_{\nu(P-O-C)}$

3b, ^1H NMR 5.02d(1H, $^2J_{HP}$6.8Hz), 1.68d(6H), 7.8m; $C_{12}H_{14}O_2NP$; Calcd. P(%) 13.17, N (%) 5.95; Found P(%) 13.10, N(%) 5.74; m.p. °C 125–128; Yield (%) 68; IR (cm^{-1}) $1255_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $3500_{\nu(N-H)}$, $1010_{\nu(P-O-C)}$

3c, ^1H NMR 5.04d(1H, $^2J_{HP}$6.6Hz), 1.69d(6H), 7.8m; $C_{14}H_{16}O_2NP$; Calcd. P(%) 11.85, N (%) 5.36; Found P(%) 11.78, N(%) 5.26; m.p. °C 135–138; Yield (%) 70; IR (cm^{-1}) $1260_{\nu(P=O)}$, $1989_{\nu(C=C=C)}$, $3490_{\nu(N-H)}$, $1020_{\nu(P-O-C)}$

Synthesis of 2-(1,2-alkadlenyl)-2-oxo-benzo-[b]-1,3,2-oxazaphospholanes 3a-c II

General procedure

To 0.2mol of phosphorus trichloride dissolved in 500ml of dry diethyl ether at −5°C and under stirring 0.2mol of pyridin were added dropwise. After 15min the temperature of the mixture was lowered to −8 to −10°C and 0.2mol of the appropriate α-acetylenic alcohol were added. After an hour stirring at the same condition a mixture of 0.2mol of 2-aminophenol and 0.4mol of triethylamine were added. The reaction mixture was stirred an additional hour at the same conditions and was let stand over night. Then the precipitate was filtered off, the solvent was removed and the residue was purified by column chromatography(50g silicagel, heptane/benzene).

3a, ^1H NMR 5.04d(1H, $^2J_{HP}$6.9Hz), 1.68d(6H), 7.9m; $C_{11}H_{12}O_2NP$; Calcd. P(%) 14.00, N (%) 6.33; Found P(%) 13.97, N(%) 6.30; m.p. °C 122–124; Yield (%) 70; IR (cm^{-1}) $1284_{\nu(P=O)}$, $1990_{\nu(C=C=C)}$, $3490_{\nu(N-H)}$, $1020_{\nu(P-O-C)}$

3b, ^1H NMR 5.02d(1H, $^2J_{HP}$6.5Hz), 1.68d(6H), 7.8m; $C_{12}H_{14}O_2NP$; Calcd. P(%) 13.17, N (%) 5.95; Found P(%) 13.12, N(%) 5.75; m.p. °C 125–128; Yield (%) 69; IR (cm^{-1}) $1285_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $3500_{\nu(N-H)}$, $1010_{\nu(P-O-C)}$

3c, ^1H NMR 5.04d(1H, $^2J_{HP}$6.8Hz), 1.69d(6H), 7.7m; $C_{14}H_{16}O_2NP$; Calcd. P(%) 11.85, N (%) 5.36; Found P(%) 11.78, N(%) 5.26; m.p. °C 135–138; Yield (%) 70; IR (cm^{-1}) $1285_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $3495_{\nu(N-H)}$, $1020_{\nu(P-O-C)}$.

Synthesis of 2-(1,2-alkadlenyl)-2,5-dioxo-4-methyl-1,3,2-dioxaphospholanes 5a-c.I

General procedure

To a solution of 0.2mol of 2-hydroxy-propionic acid in 500ml of dry benzene at 45–50°C and stirring, a solution of 0.2mol of the appropriate dichloride of the 1,2-alkadienephosphonic acids and 0,4mol of triethylamine in the same solvent were added dropwise for an hour. The reaction mixture was stirred an additional hour at the same conditions and was let stand over night. Then the precipitate was filtered off, the solvent was removed and the residue was purified by column chromatography(50g silicagel, heptane/ benzene)

5a ^{1}H NMR 5.04d(1H, $^2J_{HP}$6.8Hz), 1.67d(6H), 4.18m; $C_8H_{10}O_4P$; Calcd. P(%) 14.43, Found P(%) 14.3,; Yield (%) 65; IR (cm^{-1}) $1266_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $1789_{\nu(C=O)}$, 1020, $930_{\nu(P-O-C)}$

5b, ^{1}H NMR 5.02d(1H, $^2J_{HP}$6.8Hz), 1.68d(6H), 4.15m; $C_9H_{12}O_4P$; Calcd. P(%) 14.39, Found P(%) 14.22; Yield (%) 70; IR (cm^{-1}) $1255_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $1790_{\nu(C=O)}$, 1010, $920_{\nu(P-O-C)}$

5c, ^{1}H NMR 5.04d(1H, $^2J_{HP}$6.6Hz), 1.69d(6H), 4.16m; $C_{11}H_{14}O_4P$; Calcd. P(%) 12.84; Found P(%) 12.78; Yield (%) 70; IR (cm^{-1}) $12860_{\nu(P=O)}$, $1989_{\nu(C=C=C)}$, $1789_{\nu(C=O)}$, 1020, $930_{\nu(P-O-C)}$

Synthesis of 2-chloro-4-methyl-5-oxo-1,3,2-dioxaphospholane 8a

To a solution of 0.1mol of phosphorus trichloride in dry 1,2-dichloroethane at room temperature a solution of 0.1mol of 2-hydroxypropionic acid was added. The mixture was stirred 6 hours at the same condition. After degassing of the reaction mixture and removing of the solvent the residue was purified by distillation.

Yield 85%

Synthesis of 2-(1,2-alkadlenyl)-2,5-dioxo-4-methyl-1,3,2-dioxaphospholanes 5a-c.II

General procedure

To a solution of 0.1mol of 2-chloro-4-methyl-5-oxo-1,3,2-dioxaphospholane **8a** in 200ml of dry diethyl ether at –8°C and stirring a solution of

0.1mol of the appropriate a-acetylenic alcohol and 0.2mol of triethylamine in the same solvent were added. The reaction mixture was stirred an additional hour at the same conditions and was let stand over night. Then the precipitate was filtered off, the solvent was removed and the residue was purified by column chromatography(50g silicagel heptane/benzene).

5a, ^{1}H NMR 5.02d(1H, $^2J_{HP}$6.7Hz), 1.67d(6H), 4.12m; $C_8H_{10}O_4P$; Calcd. P(%) 14.43, Found P(%) 14.35; Yield (%) 68; IR (cm^{-1}) $1260_{\nu(P=O)}$, $1985_{\nu(C=C=C)}$, $1790_{\nu(C=O)}$, 1020, $930_{\nu(P\text{-}O\text{-}C)}$

5b, ^{1}H NMR 5.02d(1H, $^2J_{HP}$6.9Hz), 1.68d(6H), 4.17m; $C_9H_{12}O_4P$; Calcd. P(%) 14.39, Found P(%) 14.24; Yield (%) 72; IR (cm^{-1}) $1260_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $1795_{\nu(C=O)}$, 1010, $920_{\nu(P\text{-}O\text{-}C)}$

5c, ^{1}H NMR 5.04d(1H, $^2J_{HP}$6.8Hz), 1.67d(6H), 4.16m; $C_{11}H_{14}O_4P$; Calcd. P(%) 12.84; Found P(%) 12.80; Yield (%) 71; IR (cm^{-1}) $1280_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $1792_{\nu(C=O)}$, 1020, $930_{\nu(P\text{-}O\text{-}C)}$

Synthesis of 2-(1,2-alkadienyl)-2,5-dioxo-4-phenyl-1,3,2-dioxaphospholanes 7a-c. I

General procedure

To a solution of 0.2mol of 2-hydroxy-2-phenyl-acetic acid in 500ml of dry benzene at 45–50°C and stirring, a solution of 0.2mol of the appropriate dichloride of the 1,2-alkadienephosphonic acids and 0,4mol of triethylamine in the same solvent were added dropwise for an hour. The reaction mixture was stirred an additional hour at the same conditions and was let stand over night. Then the precipitate was filtered off, the solvent was removed and the residue was purified by column chromatography(50g silicagel, heptane/benzene)

7a ^{1}H NMR 5.04d(1H, $^2J_{HP}$6.8Hz), 1.67d(6H), 7.8m, 4.15m; $C_{13}H_{12}O_4P$; Calcd. P(%) 11.77, Found P(%) 11.65; Yield (%) 65; IR (cm^{-1}) $1266_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $1789_{\nu(C=O)}$, $1605_{\nu(phenyl)}$ 1020, $930_{\nu(P\text{-}O\text{-}C)}$

7b, ^{1}H NMR 5.02d(1H, $^2J_{HP}$6.8Hz), 1.68d(6H), 7.8m, 4.20m; $C_{14}H_{14}O_4P$; Calcd. P(%) 11.17, Found P(%) 11.02; Yield (%) 75; IR (cm^{-1}) $1255_{\nu(P=O)}$, $1980_{\nu(C=C=C)}$, $1790_{\nu(C=O)}$, $1605_{\nu(phenyl)}$ 1010, $920_{\nu(P\text{-}O\text{-}C)}$

7c, ^{1}H NMR 5.04d(1H, $^2J_{HP}$6.6Hz), 1.69d(6H), 7.8m, 4.15m; $C_{16}H_{16}O_4P$; Calcd. P(%) 10.21; Found P(%) 10.15; Yield (%) 72; IR

(cm^{-1}) $1260_{\nu(P=O)}$, $1989_{\nu(C=C=C)}$, $1789_{\nu(C=O)}$, $1600_{\nu(phenyl)}$ 1020, $930_{\nu(P-O-C)}$

Synthesis of 2-chloro-4-phenyl-5-oxo-1,3,2-dioxaphospholane 8b

To 0.5mol of 2-hydroxy-2-phenylacetic acid and 0.032mol of water 60ml of phosphorus trichloride were added under stirring and at room temperature. After an hour 24.2ml of phosphorus trichloride were added and the obtained reaction mixture was heated on a water bath for 2.5 hours. After degassing of the reaction mixture and removing of the solvent the residue was purified by distillation.

Yield 85%

Synthesis of 2-(1,2-alkadienyl)-2,5-dioxo-4-phenyl-1,3,2-dioxaphospholanes 7a-c. II

General procedure

To a solution of 0.1mol of 2-chloro-4-phenyl-5-oxo-1,3,2-dioxaphospholane **8b** in 200ml of dry diethyl ether at −8°C and stirring a solution of 0.1mol of the appropriate α-acetylenic alcohol and 0.2mol of triethylamine in the same solvent were added. The reaction mixture was stirred an additional hour at the same conditions and was let stand over night. Then the precipitate was filtered off, the solvent was removed and the residue was purified by column chromatography(50g silicagel heptane/benzene).

7a ^1H NMR 5.02d(1H, $^2J_{HP}$6.7Hz), 1.67d(6H), 7.9m, 4.20m; $C_{13}H_{12}O_4P$; Calcd. P(%) 11.77, Found P(%) 11.62; Yield (%) 63; IR (cm^{-1}) $1270_{\nu(P=O)}$, $1985_{\nu(C=C=C)}$, $1798_{\nu(C=O)}$, $1600_{\nu(phenyl)}$ 1020, $930_{\nu(P-O-C)}$

7b, ^1H NMR 5.04d(1H, $^2J_{HP}$6.8Hz), 1.69d(6H), 7.8m, 4.15m; $C_{14}H_{14}O_4P$; Calcd. P(%) 11.17, Found P(%) 11.08; Yield (%) 70; IR (cm^{-1})

$1260_{\nu(P=O)}$, $1985_{\nu(C=C=C)}$, $1790_{\nu(C=O)}$, $1600_{\nu(phenyl)}$ 1010, $920_{\nu(P-O-C)}$

7c, ^1H NMR 5.04d(1H, $^2J_{HP}$6.9Hz), 1.69d(6H), 7.8m, 4.12m; $C_{16}H_{16}O_4P$; Calcd. P(%) 10.21; Found P(%) 10.15; Yield (%) 70; IR (cm^{-1}) $1266_{\nu(P=O)}$, $1990_{\nu(C=C=C)}$, $1790_{\nu(C=O)}$, $1605_{\nu(phenyl)}$ 1020, $930_{\nu(P-O-C)}$

Synthesis of the spirophosphonium salts 9, 10, 11

General procedure

To 0.05mole of the compounds **3a-c**, **5a-c** or **7a-c**, respectively, dissolved in dry 1,2-dichloroethane at 0 – 5 °C and stirring a solution of 0.05mol of bromine in the same solvent were added dropwise. The reaction mixture was stirred an additional hour at the same conditions and the solvent was removed. The residue was purified by washing with heptane.

9, ^{1}H-NMR 6.35d($^2J_{HP}$7.0Hz), 1.69d(6H), 7.8m; ^{31}P 107s; IR cm^{-1} $1590_{\nu(C=C)}$, $1257_{\nu(P=O)}$, $920_{\nu(P\text{-}O\text{-}C)}$, $3487_{\nu(N\text{-}H)}$, $C_{11}H_{12}O_2NBr_2P$; Calcd. P(%) 8.13, Br(%) 41.94, N(%) 3.67, Found P(%) 8.09, Br(%) 41.89, N(%) 3.62; Yield(%) 82

10, ^{1}H-NMR 6.30d($^2J_{HP}$6.8Hz), 1.69d(6H), 4.15m; ^{31}P 108s; IR cm^{-1} $1590_{\nu(C=C)}$, $1257_{\nu(P=O)}$, 1035, $1038_{\nu(P\text{-}O\text{-}C)}$, $C_8H_{10}O_4Br_2P$, Calcd. P(%) 8.58, Br(%) 44.27, Found P(%) 8.49, Br(%) 44.22; Yeld(%) 85

11, ^{1}H-NMR 6.40d($^2J_{HP}$7.0Hz), 1.68d(6H), 7.5m, 4.18m; ^{31}P 107s; IR cm^{-1} $1590_{\nu(C=C)}$, $1257_{\nu(P=O)}$, 1030, $1040_{\nu(P\text{-}O\text{-}C)}$, $C_{13}H_{12}O_4Br_2P$, Calcd. P(%) 7.32, Br(%) 37.78, Found P(%) 7.29, Br(%)37.72; Yeld(%) 83

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