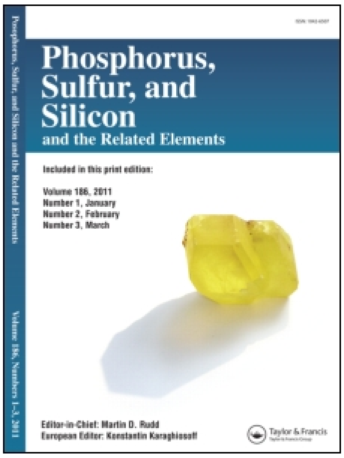


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1,2-Alkadienephosphonic Dichlorides in the Reactions with Sulphenyl- and Selenenylbromides

D. D. Enchev[a]
[a] Department of Organic Chemistry and Technology, Konstantin Preslavsky University, Shumen, Bulgaria

To cite this Article Enchev, D. D.(2005) '1,2-Alkadienephosphonic Dichlorides in the Reactions with Sulphenyl- and Selenenylbromides', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 10, 2211 — 2215
To link to this Article: DOI: 10.1080/104265090917745
URL: http://dx.doi.org/10.1080/104265090917745

Phosphorus, Sulfur, and Silicon, 180:2211–2215, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090917745

1,2-Alkadienephosphonic Dichlorides in the Reactions with Sulphenyl- and Selenenylbromides

D. D. Enchev
Department of Organic Chemistry and Technology, Konstantin Preslavsky University, Shumen, Bulgaria

The reactivity of the titled compounds towards sulphenyl- and selenenylbromides has been investigated.

Keywords 1,2-Alkadienephosphonic dichlorides; selenenylbromides; sulphenylbromides

INTRODUCTION

In the past several years, there has been a particular interest in the chemistry of high unsaturated organophosphorus compounds. It is due probably to the large number of methods for their preparative preparations and to the interesting reactions in which they took part.

We have a large amount of data for the reactivity of the 1,2-alkadienephosphonic derivatives in the reactions with different electrophilic reagents on the basis of our investigations of this subject for more then 20 years.[1]

Now we wish to report our first results in the investigations of the 1,2-alkadienephosphonic dichlorides with sulphenyl- and selenenyl bromides.

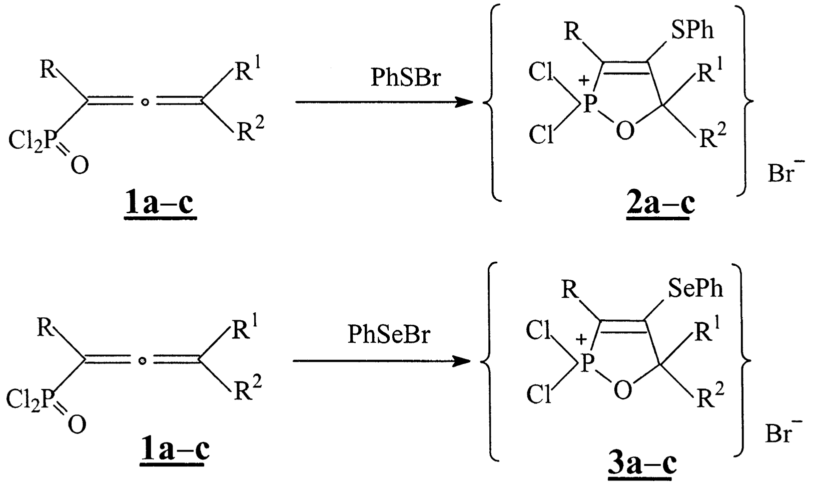
As far as 1,2-alkadienephosphonic dichlorides are good precursors for synthesis of different kind of 1,2- and 1,3-alkadienephosphonic derivatives, the results we wish to report here should be taken as initial data for the investigation of the reactivity of 1,2- and 1,3-alkadienephosphonate derivatives towards sulphenyl- and selenenylbromides.

Received October 26, 2004; accepted November 11, 2004.

Address correspondence to Dobromir D. Enchev, Konstantin Preslavsky University, Department of Organic Chemistry and Technology, Shumen 9700, Bulgaria. E-mail: rector@shu-bg.net

RESULTS AND DISCUSSION

We established that 1,2-alkadienephosphonic dichlorides, synthesized by the procedure described earlier,[2] undergo 2,5-dihydro-1,2-oxaphosphole cyclization in the reactions with phenylsulphenyl- and phenylselenenyl bromides. The reactions follow Scheme 1:



1,2,3	R	R¹	R²
a	H	Me	Me
b	H	Me	Et
c	H	-$(CH_2)_5$-	

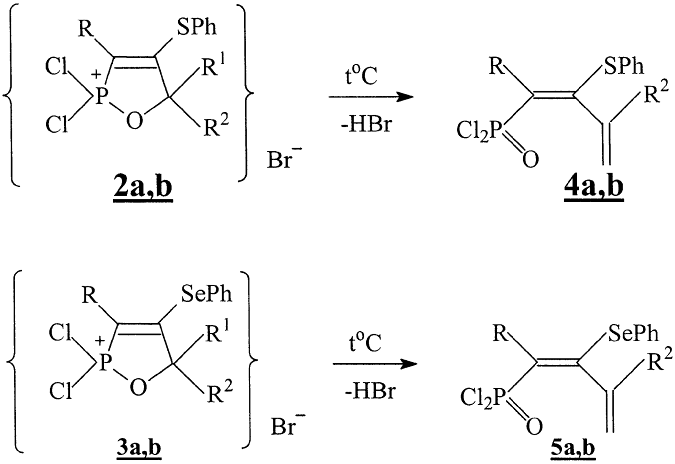
SCHEME 1

The structures of **2a–c** and **3a–c** were determinated by ^{1}H- and ^{31}P-NMR spectral data and elemental analysis.

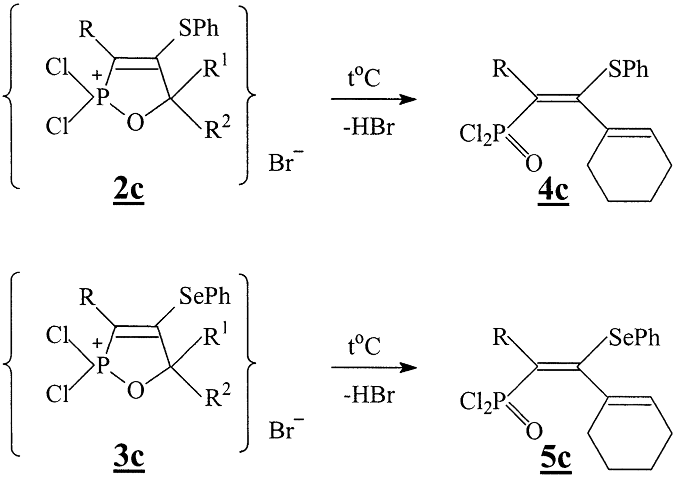
The formation of cyclic phosphonium salts were confirmed by the very characteristic signal in ^{31}P-NMR, i.e., in the area of 101–109 ppm.

The chromatographic investigations do not indicate the presence of other products. The successful synthesis only of **2a–c** and **3a–c** are due probably to the significant stabilization of the quasiphosphonium intermediate from the bromine anion compared to chlorine anion.[3]

The attempts for isolation of the cyclic products by distillation lead to spontaneous crystallization of the products. Heating of the cyclic phosphonium salts **2a–c** and **3a–c** lead to the derivatives of the dichlorides



2–5	R	R^1	R^2
a	H	Me	Me
b	H	Me	Et



2 - 5	R	R^1	R^2
c	H	$-(CH_2)_5-$	

SCHEME 2

of the 1,3-alkadienephosphonic acids, similar to the results described by others [4–6] (Scheme 2):

EXPERIMENTAL

Methods of Analysis

^{1}H- and ^{31}P-NMR spectra were determinated on a Jeol PX 10 and FX-90 Q spectrometers in normal temperature as solution in $CDCl_3$ with TMS as internal standard. The IR-spectra were recorded on a spectrophotometer IR-72 (Karl Zeiss Jena).

Starting Materials

The phenylsulphenyl- and phenylseleneneyl bromides were prepared from diphenyl disulfide and diphenyl diselenyde (commercially available) and bromine in nonpolar media.

Preparation of 4-Phenylthio-2-alkoxy-2,5-dihydro-1,2-oxaphosphoniu salts 2a–c. General Procedure

To a solution of 5 mM of the 1,2-alkadienephosphonic dichlorides **1a–c** in methylene chloride, a solution of 5 mM phenylsulfenyl bromide at the same solvent is dropwise added at low temperature (–8–10°C) and under argon atmosphere. After one hour of stirring, the solvent was evaporated and the residue spontaneously crystallized.

2a

Yield% 85, Found% P 8.26, S 8.54, Cl 18.92, Br 21.31, Formula $C_{11}H_{12}BrCl_2OPS$ Calcd.% P 8.28, S 8 = 57, Cl 18.95, Br 21.36, ^{1}H NMR 6.36d($2J_{HP}$ 7.0 Hz), 1.46, 1.51, 7.9 m, ^{31}P 102 s, IR cm^{-1} $1590_{\nu(C=C)}$, $1256_{\nu(P=O)}$, $930_{\nu(P-O-C)}$.

2b

Yield% 82, Found% P 7.94, S 8.22, Cl 18.21, Br 20.53, Formula $C_{12}H_{14}BrCl_2OPS$, Calcd. % P 7.98, S 8.22, Cl 18.27, Br 20.59, ^{1}H NMR 6.38d($2J_{HP}$ 7.1 Hz), 1.51, 0.92, 1.89, 7.8 m, ^{31}P 107 s, IR cm^{-1} $1588_{\nu(C=C)}$, $1259_{\nu(P=O)}$, $930_{\nu(P-O-C)}$.

2c

Yield% 86, Found% P 7.44, S 7.39, Cl 17.08, Br 19.22, Formula $C_{14}H_{16}BrCl_2OPS$, Calcd.% P 7.48, S 7.42, Cl 17.12, Br 19.29, , ^{1}H NMR 6.40d($2J_{HP}$ 7.0 Hz), 1.68, 7.9 m, ^{31}P 108 s, IR cm^{-1} $1582_{\nu(C=C)}$, $1257_{\nu(P=O)}$, $930_{\nu(P-O-C)}$.

Preparation of 4-Phenylseleno-2-alkoxy-2,5-dihydro-1,2-oxaphosphoniu Salts 3a–c General Procedure

To a solution of 5 mM of the 1,2-alkadienephosphonic dichlorides **1a–c** in methylene chloride, a solution of 5 mM phenylselenenyl bromide at the same solvent is dropwise added at low temperature (−8–10°C) and under argon atmosphere. After one hour of stirring the solvent was evaporated and the residue spontaneously crystallized.

3a

Yield % 85, Found % P 7.32, Cl 16.80 , Br 18.93 , Formula $C_{11}H_{12}BrCl_2OPSe$ Calcd.% P 7.36, Cl 16.84, Br 18.98, ^1H NMR 6.36d($2J_{HP}$ 7.0 Hz), 1.57, 1.53, 7.7 m, ^{31}P 105 s, IR cm^{-1} $1594_{\nu(C=C)}$, $1257_{\nu(P=O)}$, $930_{\nu(P-O-C)}$.

3b

Yield % 82, Found % P 7.09, Cl 16.27, Br 18.33, Formula $C_{12}H_{14}BrCl_2OPSe$, Calcd. % P 7.12, Cl 16.30, Br 18.37, ^1H NMR 6.38d($2J_{HP}$ 7.1 Hz), 1.50, 0.90, 1.88, 7.9 m, ^{31}P 109 s, IR cm^{-1} $1589_{\nu(C=C)}$, $1260_{\nu(P=O)}$, $930_{\nu(P-O-C)}$.

3c

Yield % 86, Found % P 6.69, Cl 15.32, Br 17.30, Formula $C_{14}H_{16}BrCl_2OPSe$, Calcd.% P 6.72, Cl 15.38, Br 17.33, ^1H NMR 6.40d($2J_{HP}$ 7.0 Hz), 1.68, 7.8 m, ^{31}P 108s, IR cm^{-1} $1584_{\nu(C=C)}$, $1258_{\nu(P=O)}$, $930_{\nu(P-O-C)}$.

REFERENCES

[1] D. D. Enchev and J. I. Tacheva, *Phosphorus, Sulfur, Silicon, and the Related Elements*, **178,** 505 (2003); Ch. M. Angelov, *Phosphorus, Sulfur, Silicon, and the Related Elements*, **15,** 177 (1983); Ch. M. Angelov and D. D. Enchev, *Phosphorus, Sulfur, Silicon, and the Related Elements*, **37,** 125 (1988); Ch. M. Angelov and D. D. Enchev, *Phosphorus, Sulfur, Silicon, and the Related Elements*, **34,** 163 (1988); Ch. M. Angelov and D. D. Enchev, *Phosphorus, Sulfur, Silicon, and the Related Elements*, **57,** 242 (1991).

[2] T. S. Mikhailova, Ch. M. Angelov, V. M. Ignatiev, A. V. Dogadina, V. I. Zakharov, B. I. Ionin, *et al.*, *J. Obch. Khim.*, **47,** 2701 (1977).

[3] *Comprehensive Organic Chem.*, Pergamon Press: Elmsford: NY, Russ. Transl., 638, 32 (1985).

[4] V. M. Ignatiev, Ch. M. Angelov, B. I. Ionin, and A. A. Petrov, *J. Obch. Khim.*, **45,** 2342 (1975).

[5] Ch. M. Angelov, T. S. Mikhailova, V. M. Ignatiev, A. V. Dogadina, V. I. Zakharov, B. I. Ionin, et al., *J. Obch. Khim.*, **48,** 1487 (1977).

[6] V. M. Ignatiev, Ch. M. Angelov, B. I. Ionin, S. V. Golubkov, N. V. Vershin, and A. A. Petrov, *USSR Patent*, N 536189 (1976).