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Interaction of 1,2-Alkadienephosphonic Dialkyl Esters with Sulfenyl- and Selenenylbromides

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ABSTRACT: *The reactivity of dialkyl esters of 1, 2-alkadienephosphonic acids toward sulfenyl- and selenenyl-bromides has been investigated.* Heteroatom Chem 16:156–158, 2005; DOI 10.1002/hc.20083

INTRODUCTION

The phosphorylated 1,2-alkadienes provide an unusual system of centers of unsaturation. Their preparation as well as their reactions attracts permanent interest [1–4]. An increasing number of reactions involving phosphorylated 1,2-alkadienes as well as concepts of their reactivity are noticed [5–18].

RESULTS AND DISCUSSION

The study of the reactivity of these compounds, as well as the creation of methods for their preparation, is one of the topics in our investigations for more than 20 years [8–14].

In this paper, we wish to report our results from the investigations of the interaction of dialkyl esters of 1,2-alkadienephosphonic acids with phenylsulfenyl- and phenylselenenyl-bromides. The mentioned reagents were chosen because of their similarity to sulfenyl- and selenenyl-chlorides, as well as because of some differences between them of course, i.e.: (1) Energy and bond length of the S—Cl (255 kJ/mol, 207 nm) and S—Br (217 kJ/mol, 227 nm) [19], (2) the higher dealkylation rate (Arbuzov reaction) in case of bromide anion as compared to chloride anion [20], (3) the degree of stabilization of quasiphosphonium intermediate, in general, is more significant in the case of bromide than in the case of chloride anion [21].

As starting compounds in our investigation, we synthesized dichlorides of 1,2-alkadienephosphonic acids **2** following the procedure described earlier [18]. The nucleophilic displacement of the two chlorine atoms at phosphorus with alkoxy-groups leads to the titled compounds, **3, 5** in very good yields (Scheme 1).

The reactions of **3, 5** with phenylsulfenyl- and phenylselenenyl-bromides were performed in polar solvent, at low temperature and argon atmosphere (see Scheme 2).

Obtaining of the 2,5-dihydro-1,2-oxaphosphole derivatives **4,6** and **7,8** was confirmed by their ^{1}H, ^{31}P NMR, and IR spectra as well as by elemental analysis (see Experimental). Very good yields of these compounds and the absence of other products are probably due to the combined influence of the factors mentioned above, especially to the increased stability of the quasiphosphonium intermediate of the

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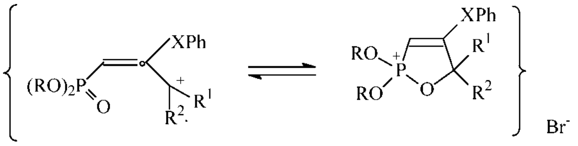
reaction:



The literature data and the results we reported here confirm the direction of the reaction of dialkyl esters of 3,3-disubstituted 1,2-alkadienephosphonic acids with sulfenyl- and selenenyl-halogenides, i.e. irrespective to the kind of the reagent in all cases oxaphospholic derivatives were isolated.

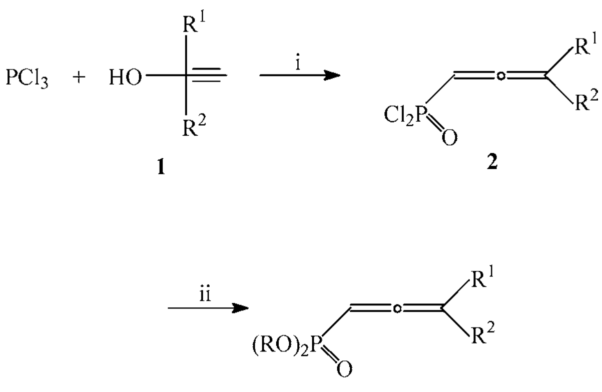
EXPERIMENTAL

^{1}H and ^{31}P NMR spectra were determined on 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 (Carl Zeiss Jena).

The phenylsulfenyl- and phenylselenenyl-bromides were prepared from diphenyl disulfide and diphenyl diselenide, commercially available, and bromine in nonpolar media.

Preparation of 4-Phenylthio-2-alkoxy-2,5-dihydro-1,2-oxaphosphol-2-oxides **4a–x, 6a–h**

General Procedure. To the solution of 0.05 mol of **3a–x, 5a–h** in 50 mL dry methylene chloride under argon atmosphere and stirring, at −10 to −8°C, a solution of 0.05 mol of phenylsulfenyl bromide in the same solvent was added dropwise in 30 min. Then the solvent was evaporated and the residue was distilled in vacuum.



1 **2**

3a–x, 5a–h

i = Pyr., –Pyr. HCl
ii = 2 ROH, 2 Pyr.

3 R^2 = Me
5 $R^1 + R^2 = -(CH_2)_5-$
for R^1 see Tables 1, 2

SCHEME 1

TABLE 1 R and R^1 for Compounds **3, 4, 7**

	R	*R¹*
a	Me	Me
b	Et	Me
c	Pr^n	Me
d	Pr^i	Me
e	Bu^n	Me
f	Bu^t	Me
g	$PhCH_2$	Me
h	$Ph(CH_2)_2$	Me
i	Me	Et
j	Et	Et
k	Pr^n	Et
l	Pr^i	Et
m	Bu^n	Et
n	Bu^t	Et
o	$PhCH_2$	Et
p	$Ph(CH_2)_2$	Et
q	Me	Pr^i
r	Et	Pr^i
s	Pr^n	Pr^i
t	Pr^i	Pr^i
u	Bu^n	Pr^i
v	Bu^t	Pr^i
w	$PhCH_2$	Pr^i
x	$Ph(CH_2)_2$	Pr^i

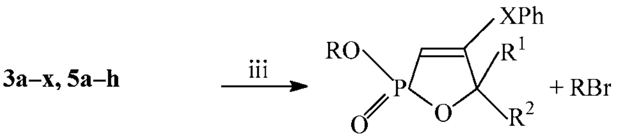
4a: Yield 85%; found P, 12.94; S, 13.42; formula $C_{12}H_{15}OPS$; calcd. P, 12.99; S, 13.46. ^{1}H NMR 6.36 (d $^{2}J_{HP}$ 7.0 Hz), 1.46, 1.51, 7.8 m; ^{31}P 33.09, IR 1590 ν(C=C), 1256 ν(P=O), 930 ν(P–O–C) cm^{-1}.

4i: Yield 82%; found P, 12.24; S, 12.68; formula $C_{13}H_{17}OPS$; calcd. P, 12.27; S, 12.71; ^{1}H NMR 6.38 (d $^{2}J_{HP}$ 7.1 Hz), 1.51, 0.92, 1.89, 7.8 m, ^{31}P 33; IR 1588 ν(C=C), 1259 ν(P=O), 930 ν(P–O–C) cm^{-1}.

6a: Yield; 86%; found P, 11.10; S, 11.49; formula $C_{15}H_{19}OPS$; calcd. P, 11.13; S, 11.52; ^{1}H NMR 6.40 (d $^{2}J_{HP}$ 7.0 Hz), 1.68, 7.9 m, ^{31}P 32.9; IR 1582 ν(C=C), 1257 ν(P=O), 930 ν(P–O–C) cm^{-1}.

TABLE 2 R for Compounds **5, 6, 8**

	R
a	Me
b	Et
c	Pr^n
d	Pr^i
e	Bu^n
f	Bu^t
g	$PhCH_2$
h	$Ph(CH_2)_2$



4a–x, 6a–h X = S
7a–x, 8a–h X = Se

iii = PhSBr or PhSeBr −10 to −8°C, CH_2Cl_2 for R and R^1 see Tables 1,2

SCHEME 2

Preparation of 4-Phenylseleno-2-alkoxy-2, 5-dihydro-1,2-oxaphosphol-2-oxides **7a–x, 8a–h**

General Procedure. To the solution of 0.05 mol of **3a–x, 5a–h** in 50 mL dry methylene chloride under argon atmosphere and stirring, at −10 to −8°C, a solution of 0.05 mol of phenylselenenyl bromide in the same solvent was added dropwise in 30 min. Then the solvent was evaporated and the residue was distilled in vacuum.

7a: Yield 85%; found P, 10.82; formula $C_{12}H_{15}OPSe$; calcd. P, 10.86; ^{1}H NMR 6.36 (d $^{2}\mathbf{J}_{HP}$ 7.0 Hz), 1.57, 1.53, 7.7 m, ^{31}P 32; IR 1594 ν(C=C), 1257 ν(P=O), 930 ν(P—O—C) cm^{-1}.

7i: Yield 84%; cryst. found P, 10.31; formula $C_{13}H_{17}OPSe$; calcd. P, 10.35; ^{1}H NMR 6.38 (d$^{2}\mathbf{J}_{HP}$ 7.1 Hz), 1.50, 0.90, 1.88, 7.9 m, ^{31}P 33; IR 1589 ν(C=C), 1260 ν(P=O), 930 ν(P—O—C) cm^{-1}.

8a: Yield 87%; found P, 9.50; formula $C_{15}H_{19}OPSe$; calcd. P, 9.52; ^{1}H NMR 6.40 (d $^{2}\mathbf{J}_{HP}$ 7.0 Hz), 1.68, 7.8 m, ^{31}P 31.9; IR 1584 ν(C=C), 1258 ν(P=O), 930 ν(P—O—C) cm^{-1}.

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