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Interaction of 1,2-Alkadienephosphonic thioesters with sulphenyl- and selenenylbromides

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Abstract*: The reactivity of thioesters of 1,2-alkadienephosphonic acids toward sulphenyl- and selenenyl bromides has been investigated.*

Keywords*: 1,2-alkadienephosphonates, phenylsulphenyl bromide, phenylselenenyl bromide*

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 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 thioesters of 1,2-alkadienephosphonic acids with phenylsulphenyl- and phenylselenenyl bromides.

The reagents were chosen because of their similarity to sulphenyl- 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 compared to S-Br [19],
2). The dealkylation rate in case of bromide anion is higher compared to those in case of chloride anion [20],
3). The stabilization of quaziphosphonium intermediate in general is more significant in the case of bromide compared to chloride anion [21].

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

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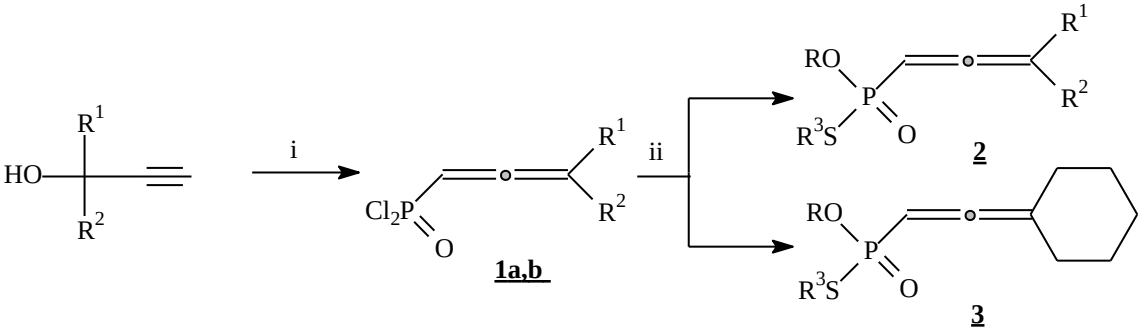
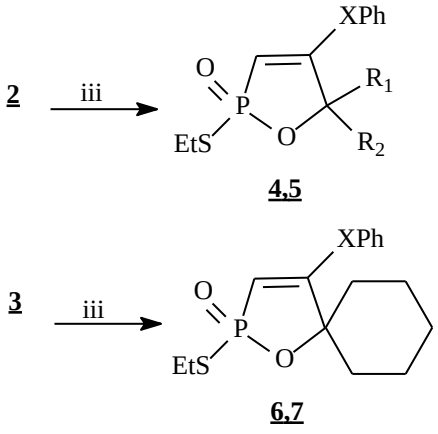


i = PCl_3, Pyr., - Pyr.HCl — R^1=R^2=Me; R^1+R^2=-$(CH_2)_2$-

ii = ROH, R^3SH, 2Pyr. — R^3=Et; R=Me

Scheme 1. Synthesis of compounds **2** and **3**

The reaction of **2** and **3** with phenylsulphenyl- and phenylselenenyl bromides were performed in polar solvent, at low temperature and under inert atmosphere (Scheme 2)



iii = PhSbr, PhSeBr, -10 - -8°C, CH_2Cl_2

Scheme 2. Interaction of compounds **2** and **3** with sulphenyl- and selenenylbromides

Obtaining of the 2,5-dihydro-1,2-oxaphosphole derivatives **4,5** and **6,7** was confirmed by their ^1H, ^{31}P NMR and IR spectra as well as by elemental analysis (see Experimental section).

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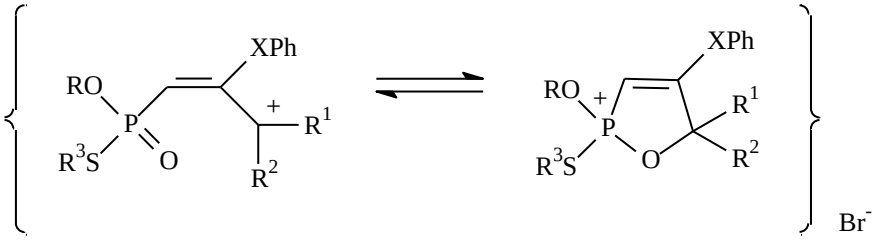
Compounds **5** and **7**, contain the isotope Se^{77} which is magnetically active and interacts with other nuclei. This interaction becomes evident with the protons from the neighboring groups which exhibit symmetric satellite signals of the main signal in the ^{1}H NMR spectra [22].

The yields of these compounds and the absence of the other products are probably due to the combined influence of the factors mentioned above, especially to the increased stability of the quaziphosphonium intermediate of the reaction:



Scheme 3. Probable structural equilibrium of the intermediate of the reaction dicussed

The literature data and the results reported here confirm the direction of the reaction of thioesters of 1,2-alkadienephosphonic acids with sulphenyl- and selenenyl halogenides, i.e. irrespective to the kind of the reagent in all cases oxaphosphole derivatives were isolated.

Experimental

General procedures The melting points are uncorrected. The ^{1}H- and ^{31}P NMR spectra were obtained on Jeol JNM PS 10 and FX 90 Q spectrometers with TMS and H_3PO_4 as internal standards as $CDCl_3$ solution. The IR spectra were run on Shimadzu IRAffinity spectrophotometer. The phenylsulphenyl bromide and phenylselenenyl bromide were prepared from diphenyl disulfide and diphenyl diselenide, commercially available and bromine in nonpolar media.

General procedure for preparation of S-ethyl-O-methyl-3-methyl-1,2-butadienephosphonate 2
To a solution of 0.05mol of phosphorus trichloride in 200ml dry diethyl ether under argon atmosphere, stirring and at low temperature(-10 - -8^{o}C) a solution of 0.05mol pyridine in the same solvent was added. After that a solution of 0.05mol of 3-methyl-1-butyn-3-ol in the same solvent was added. The reaction mixture was stirring for one hour and rest for a night. Then the precipitate was filtered off, the solvent was evaporated and the residue was distilled in vacuum.
Yield 80%

Compound characterization

S-ethyl-O-methyl-3-methyl-1,2-butadienephosphonate 2 pale-yellow liquid, b.p. 85-87^{o}C *Anal*., Calcd. P 15.02, S 15.54, $C_8H_{15}PO_2S$, Found P 15.00, S 15.48 IR ν (cm^{-1}) $1980_{(C=C=C)}$, $1256_{(P=O)}$, $960_{(P-O-C)}$; ^{1}H-NMR(100MHz, $CDCl_3$) δ/ppm 5.04 (d $^{2}J_{HP}$ 7.7Hz, 1H), 1.68 (d $2CH_3$, 6H), 3.76 (d CH_3O, 3H), 4.15 (m $SC\underline{H}_2CH_3$, 2H), 1.58 (s $SCH_2C\underline{H}_3$, 3H), ^{31}P NMR($CDCl_3$) δ/ppm: ^{31}P 17.1

General procedure for preparation of S-ethyl-O-methyl-2-(1-cyclohexelyden)etenephosphonate 3

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To a solution of 0.05mol of phosphorus trichloride in 200ml dry diethyl ether under argon, stirring and at low temperature(-10 - -8°C) a solution of 0.05mol pyridine in the same solvent was added. After that a solution of 0.05mol of 1-ethynylcyclohexanol in the same solvent was added. The reaction mixture was stirring for one hour and rest for a night. Then the precipitate was filtered off, the solvent was evaporated and the residue was distilled in vacuum.
Yield 72%

Compound characterization

S-ethyl-O-methyl-2-(1-cyclohexelyden)etenephosphonate 3 red liquid, b.p. 115-117°C *Anal*., Calcd. P 12.57, S 13.02, $C_{11}H_{19}PO_2S$, Found P 12.45, S 13.00 IR ν (cm^{-1}) $1970_{(C=C=C)}$, $1260_{(P=O)}$, $960_{(P-O-C)}$; ^{1}H-NMR(100MHz, $CDCl_3$) δ/ppm 5.05 (d $^2J_{HP}$ 7.7Hz, 1H), 1.72 (m cyclohexyl, 12H), 3.76 (d CH_3O, 3H), 4.15 (m $SC\underline{H}_2CH_3$, 2H), 1.58 (s $SCH_2C\underline{H}_3$, 3H), ^{31}P NMR($CDCl_3$) δ/ppm: ^{31}P 16.8

General procedure for preparation of 2-ethylthio -4-phenylthio-5,5-dimethyl -2,5-dihydro-1,2-oxaphosphole-2-oxide 4
To the solution of 0.05mol of **2** in 50 ml dry methylenechloride under argon atmosphere and stirring, at -10 - -8°C, a solution of phenylsulphenyl bromide in the same solvent was added dropwise in 30 min. Then the solvent was evaporated and the residue was recrystalized in hexane/benzene 2:1.
Yield 75%

Compound characterization

2-ethylthio -4-phenylthio-5,5-dimethyl -2,5-dihydro-1,2-oxaphosphole-2-oxide 4 cryst., m.p. 105-107°C *Anal*., Calcd. P 10.31, S 21.35, $C_{13}H_{17}PO_2S_2$, Found P 10.25, S 21.22 IR ν (cm^{-1}) $1589_{(C=C)}$, $1260_{(P=O)}$, $960_{(P-O-C)}$; ^{1}H-NMR(100MHz, $CDCl_3$) δ/ppm 5.88 (d $^2J_{HP}$ 24.2 Hz, 1H), 1.51 (s CH_3, 3H,), 1.58 (s CH_3, 3H), 4.15 (m $SC\underline{H}_2CH_3$, 2H), 1.55 (s $SCH_2C\underline{H}_3$, 3H), 7.24 (m arom., 5H), ^{31}P NMR($CDCl_3$) δ/ppm: ^{31}P 24.4

General procedure for preparation of 2-ethylthio -4-phenylthio-1-oxa-2-phospha-spyro[4,5]dec-3-ene 2-oxide 5
To the solution of 0.05mol of **3** in 50 ml dry methylenechloride under argon and stirring, at -10 - -8°C, a solution of phenylsulphenyl bromide in the same solvent was added dropwise in 30 min. Then the solvent was evaporated and the residue was recrystalized in hexane/benzene 2:1.
Yield 77%

Compound characterization

2-ethylthio -4-phenylthio-1-oxa-2-phospha-spyro[4,5]dec--3-ene 2-oxide 5 cryst., m.p. 118-120°C *Anal*., Calcd. P 9.09, S 18.83, $C_{16}H_{21}PO_2S_2$, Found P 9.00, S 18.78 IR ν (cm^{-1}) $1587_{(C=C)}$, $1256_{(P=O)}$, $960_{(P-O-C)}$; ^{1}H-NMR(100MHz, $CDCl_3$) δ/ppm 5.87 (d $^2J_{HP}$ 24.0 Hz, 1H), 1.72 (m cyclohexyl, 12H), 4.15 (m $SC\underline{H}_2CH_3$, 2H), 1.58 (s $SCH_2C\underline{H}_3$, 3H), 7.24 (m arom., 5H), ^{31}P NMR($CDCl_3$) δ/ppm: ^{31}P 24.2

General procedure for preparation of 2-ethylthio -4-phenylseleno-5,5-dimethyl -2,5-dihydro-1,2-oxaphosphole-2-oxide 6
To the solution of 0.05mol of **2** in 50 ml dry methylenechloride under argon and stirring, at -10 - -8°C, a solution of phenylsulphenyl bromide in the same solvent was added dropwise in 30 min. Then the solvent was evaporated and the residue was recrystalized in hexane/benzene 2:1.
Yield 66%

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Compound characterization

2-ethylthio -4-phenylseleno-5,5-dimethyl -2,5-dihydro-1,2-oxaphosphole-2-oxide 6 cryst., m.p. 108-110^{o}C *Anal*., Calcd. P 8.92, S 9.23, $C_{13}H_{17}PO_2SSe$, Found P 8.88, S 9.12 IR ν (cm^{-1})) $1589_{(C=C)}$, $1256_{(P=O)}$, $960_{(P\text{-}O\text{-}C)}$; ^{1}H-NMR(100MHz, $CDCl_3$) δ/ppm 5.88 (d $^{2}J_{HP}$ 24.2 Hz, 1H), 1.51 (s CH_3, 3H), 1.58 (s CH_3, 3H), 4.15 (m SCH_2CH_3, 2H), 1.55 (s SCH_2CH_3, 3H), 7.24 (m arom., 5H), ^{31}P NMR($CDCl_3$) δ/ppm: ^{31}P 26.4

General procedure for preparation 2-ethylthio -4-phenylseleno-1-oxa-2-phospha-spyro[4,5]dec-3-ene 2-oxide 7

To the solution of 0.05mol of **3** in 50 ml dry methylenechloride under argon and stirring, at -10 - -8^{o}C, a solution of phenylsulphenyl bromide in the same solvent was added dropwise in 30 min. Then the solvent was evaporated and the residue was recrystalized in hexane/benzene 2:1.
Yield 70%

Compound characterization

2-ethylthio -4-phenylseleno-1-oxa-2-phospha-spyro[4,5]dec-3-ene 2-oxide 7 cryst., m.p. 119-121^{o}C *Anal*., Calcd. P 7.99, S 8.28, $C_{16}H_{21}PO_2SSe$, Found P 7.89, S 8.18 IR ν (cm^{-1}) $1587_{(C=C)}$, $1256_{(P=O)}$, $960_{(P\text{-}O\text{-}C)}$; ^{1}H-NMR(100MHz, $CDCl_3$) δ/ppm 5.87 (d $^{2}J_{HP}$ 24.0 Hz, 1H), 1.72 (m cyclohexyl, 12H), 4.15 (m SCH_2CH_3, 2H), 1.58 (s SCH_2CH_3, 3H), 7.24 (m arom., 5H), ^{31}P NMR($CDCl_3$) δ/ppm: ^{31}P 24.9

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