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# SELENIUM SUBSTITUTED SPIRO PHOSPHORUS HETEROCYCLES

Christo M. Angelov
Department of Chemistry, Higher Pedagogical Institute,
9700 Shoumen, BULGARIA

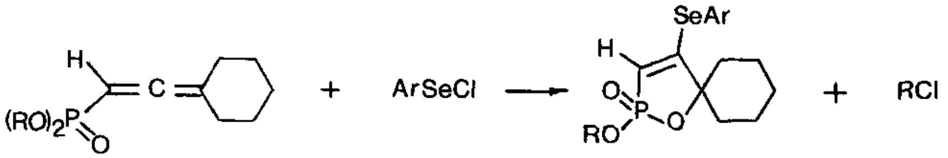
ABSTRACT - The reaction of cyclohexylideneethenylphosphonic acid and its esters with arylselenenyl chlorides leads to the formation of 4-arylseleno-2-oxo-1-oxa-2-phospha-spiro(4,5)-3-decene derivatives. The dichloride of this acid with the same reagents cyclized only in the presence of sulfur dioxide.

## INTRODUCTION

Although there has been published many papers on the preparation of 1,2-oxaphosphol-3-ene-2-oxides [1-10], this class of organophosphorus heterocycles is still not very well known. In particular bicyclic compounds are rare [6-9]. One of the methods for preparation of 1,2-oxaphosphol-3-ene derivatives is the reaction of phosphorylated allenes with electrophiles. It was shown recently that the cyclization in this case depends on the substituents at the $C^3$ atom of the allenic bond and the P-atom [10]. The reaction of selenenyl chlorides as electrophilic reagents with 1,2-alkadienylphosphonates, except for one preliminary communication [11], has not been studied. This paper presents our results on the reactions of cyclohexylideneethenylphosphonic acid and some of its derivatives with these reagents which give rise to spiro 1,2-oxaphosphol-3-ene-2-oxides.

## RESULTS and DISCUSSION

The reaction of benzene- or p-chlorobenzeneselenenyl chlorides with cyclohexylideneethenylphosphonic acid (1a) and four of its esters ( 1b-e ) gave products which were assigned the spiro cyclic structure ( 2a-e, 3c-e ):



1a-e

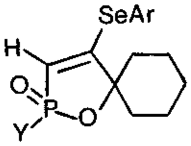
2a-e, 3c-e

| 1-3 | a | b | c | d | e |
|---|---|---|---|---|---|
| R | H | Me | Et | $Pr^n$ | $Pr^i$ |

| | 2 | 3 |
|---|---|---|
| Ar | $C_6H_5$ | $p\text{-}ClC_6H_4$ |

The reactions was conducted in chloroform with heating for 1a, or at room temperature for 1b-e. The compounds obtained after removal of the solvent were viscous oils which soon crystallized. The structure of the products was ascertained by nmr and ir spectroscopy (Table 1) and elemental analysis ( Table 2 ).

Table 1. $^1$H-nmr and ir data of spiro commpounds 2a-d, 3c-e, 5a,b



| No | Y | Ar | Chemical shifts, δ (CDCl) | | | | Spin-Spin Coupl.,J Hz | | ir absorptions, $cm^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Y | Ar | cyclo hexyl | H | Y-P | $H^3$-P | Y-P | P=O | C=C |
| 2a | HO | Ph | 9.32s | 7.40m | 1.72s | 5.18d | - | 28.0 | - | 1220 | 1542 |
| b | MeO | Ph | 3.58d | 7.40m | 1.70s | 5.14d | 12.0 | 28.0 | 1015 | 1240 | 1545 |
| c | EtO | Ph | $CH_2$ 4.02dq<br>Me 1.24t | 7.40m | 1.65s | 5.20d | 9.6 | 28.8 | 1025 | 1230 | 1535 |
| d | $Pr^nO$ | Ph | $CH_2O$ 3.84dt<br>$CH_2$ 1.60m<br>Me 0.84t | 7.30m | 1.68s | 5.14d | 8.0 | 28.0 | 1000 | 1240 | 1536 |
| 3c | EtO | p-ClPh | $CH_2$ 4.00dq<br>Me 1.26t | 7.36m | 1.73s | 5.18d | 10.0 | 27.6 | 1000 | 1250 | 1540 |
| d | $Pr^nO$ | p-ClPh | $CH_2O$ 3.90dt<br>$CH_2$ 1.52m<br>Me 0.88t | 7.36m | 1.73s | 5.21d | 8.2 | 27.6 | 1000 | 1230 | 1535 |
| e | $Pr^iO$ | p-ClPh | CH 4.56dq<br>Me 1.22d | 7.32m | 1.68s | 5.14d | 8.0 | 27.2 | 998 | 1236 | 1548 |
| 5a | Cl | Ph | - | 7.36m | 1.76s | 5.39d | - | 33.9 | - | 1240 | 1538 |
| b | Cl | p-ClPh | - | 7.38m | 1.76s | 5.36d | - | 33.6 | - | 1240 | 1536 |

s- singlet, d- doublet, t- triplet, q- quartet, dt- doublet-triplet, dq-doublet-quartet, m- multiplet

The $^1$H-nmr spectra of all spiro compounds showed a doublet from the $H^3$ of the oxaphospholene ring ( δ 5.14 - 5.40, $^2J_{HP}$ 27.0 - 33.9 Hz ) typical for 4-substituted oxaphospholenes [9,12,13]. The $^{31}$P chemical shifts ( 34.2 - 34.6 ppm ) are characteristic for heterocycles with tetracoordinate phosphorus [13,14].

When cyclohexylideneethenylphosphonic dichloride 4 was treated with arylselenenyl chlorides at 0 - 5°C no cyclic product was observed ( $^1$H-nmr ). In the presence of sulfur dioxide, however, cyclization took place with the formation of spiro 1,2-oxaphospholene-2-oxides 5a,b.

It is known that the reaction of cyclohexylideneethenylphosphonic dichloride with chlorine [11] and benzenesulfenyl chloride [12] proceeds with elimination of HCl and formation of 1,3-alkadienylphosphonic dichlorides. However, sulfuryl chloride reacted with the same allenic dichloride to give an oxaphosphol-3-ene-2-oxide [11]. Probably the sulfur dioxide which forms during the reaction in this case is responsible for the heterocyclization of allenephosphonate. Moreover, it has been shown that 3,3-disubstituted allenylphosphonic dichlorides with halogens cyclized and gave oxaphospholenes with pentavalent phosphorus which are stable in $CCl_4$ solution for several days. The latter compounds with $SO_2$ lead to formation of 1,2-oxaphosphol-3-ene-2-oxides [13]. Cyclohexylideneethenylphosphonic dichloride and selenenyl chlorides, in the presence of sulfur dioxide, probably react by a similar mechanism via an unstable intermediate ( I ) which is trapped by $SO_2$ to give 5a, 5b:

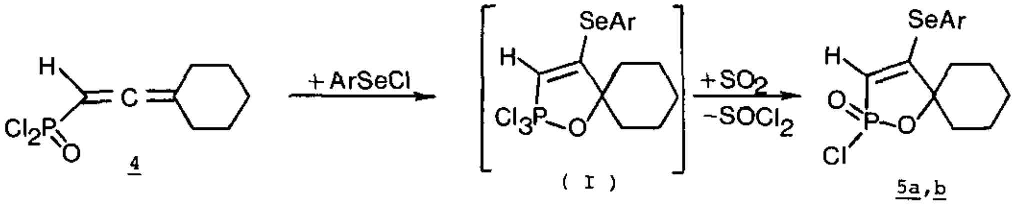
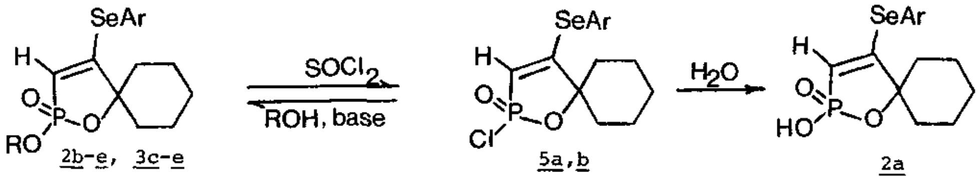


Table 2. Elemental Analysis of Oxaphospholenes 2a-e, 3c-e and 5a,b

| No | Yield % | mp °C | Found, % C | Found, % H | Found, % P | Found, % Cl | Formula | Calculated, % C | Calculated, % H | Calculated, % P | Calculated, % Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2a | 79 | 186 | 48.50 | 4.72 | 8.65 | - | $C_{14}H_{17}O_3PSe$ | 48.99 | 4.99 | 9.02 | - |
| b | 68 | 96 | 50.56 | 5.70 | 8.21 | - | $C_{15}H_{19}O_3PSe$ | 50.99 | 5.36 | 8.67 | - |
| c | 87 | 73 | 51.64 | 5.57 | 8.28 | - | $C_{16}H_{21}O_3PSe$ | 51.74 | 5.70 | 8.34 | - |
| d | 82 | 76 | 59.63 | 5.83 | 7.98 | - | $C_{17}H_{23}O_3PSe$ | 59.98 | 6.01 | 8.03 | - |
| e | 81 | 102 | 59.76 | 5.82 | 7.78 | - | $C_{17}H_{23}O_3PSe$ | 59.98 | 6.01 | 8.03 | |
| 3c | 92 | 131 | 46.92 | 5.06 | 7.76 | 8.59 | $C_{16}H_{20}ClO_3PSe$ | 47.36 | 4.96 | 7.63 | 8.74 |
| d | 88 | 130 | 48.21 | 5.35 | 6.98 | 8.22 | $C_{17}H_{22}ClO_3PSe$ | 48.64 | 5.28 | 7.38 | 8.45 |
| e | 77 | 128 | 48.25 | 5.70 | 7.06 | 8.52 | $C_{17}H_{22}ClO_3PSe$ | 48.64 | 5.28 | 7.38 | 8.45 |
| 5a | 74 | 72 | 46.10 | 4.28 | 8.17 | 9.63 | $C_{14}H_{16}ClO_3PSe$ | 46.49 | 4.46 | 8.58 | 9.85 |
| b | 76 | 121 | 42.17 | 4.01 | 7.53 | 17.55 | $C_{14}H_{15}Cl_2O_2PSe$ | 42.45 | 3.88 | 7.88 | 17.90 |

The products obtained in this work may be interconverted by standard procedures:



The compounds synthesized by both methods have identical spectroscopical data and physical constants.

## EXPERIMENTAL

The $^1$H- and $^{31}$P-nmr spectra were obtained on JEOL JNM PS 10 and FX 90 Q spectrometers using TMS and 85% $H_3PO_4$ as standards. The ir spectra were run on a IR-72 spectrophotometer ( Karl Zeis Jena, DDR ). The cyclohexylideneethenylphosphonic acid and its derivatives were synthesized according to the literature [15]. Arylselenenyl chlorides were freshly prepared from the corresponding diselenides and chlorine or sulfuryl chloride and used without purification.

4-Benzeneseleno-2-hydroxy-1-oxa-2-phospha-spiro(4,5)-3-decene-2-oxide ( 2a )

Method A

A solution of 3.85 g ( 0.02 mole ) of benzeneselenenyl chloride in 15 ml of dry chloroform was added dropwise to 3.76 g ( 0.02 mole ) of cyclohexylideneethenylphosphonic acid dissolved in 10 ml of $CHCl_3$ at 40 to 50°C. The reaction mixture was kept overnight at room temperature, then the solvent was removed and residue recrystallized from heptane. Yield 79%.

Method

0.9 g ( 0.015 mole ) of water was added dropwise to 3.62 g ( 0.01 mole ) of 5a dissolved in 50 ml of heptane at 40 - 50°C. The reaction mixture was kept at the same temperature for one hour and then the solvents were removed in vacuo to give a residue which soon became crystalline. Yield 70%.

4-Arylseleno-2-alkoxy-1-oxa-2-phospha-spiro(4,5)-3-decene-2-oxides ( 2b-e, 3c-e ).

Method

A solution of 0.02 mole of the arylselenenyl chloride in 15 ml of dry chloroform was added dropwise to 0.02 mole of the dialkyl cyclohexylideneethenylphosphonate dissolved in 10 ml of $CHCl_3$ at room temperature. The reaction mixture was kept for two hours and the solvent then removed. The crystalline residue was recrystallized from heptane. Yield 65-90%.

Method B

0.01 mole of the alcohol was added dropwise to a mixture of 0.01 mole of 5a or 5b and 0.012 mole of triethylamine dissolved in dry benzene at 40 to 50°C. The reaction mixture was stirred for one hour at the same temperature. The precipitate was filtered off and the solvent removed to give a solid residue which was recrystallized from heptane. Yield 50-60%.

4-Arylseleno-2-chloro-1-oxa-2-phospha-spiro(4,5)-3-decene-2-oxides ( 5a,b ).

Method A

Through a solution of 0.02 mole of cyclohexylideneethenylphosphonic dichloride in dry chloroform at 0 - 5°C was bubbled sulfur dioxide for 15 - 20 min. Continuing the admission of $SO_2$ with stirring, a solution of 0.02 mole of the selenenyl chloride in $CHCl_3$ was added dropwise. The reaction mixture was stirred for one hour and then the solvent was removed and the solid residue recrystallized from heptane. Yield 74-76%.

Method B

0.02 mole of 2b or 3c was added in one portion to 15 ml of thionyl chloride. The reaction mixture was boiled for 4 - 5 hours. Then, thionyl chloride was removed and the residue was recrystallized from heptane. Yield 45-50%.

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