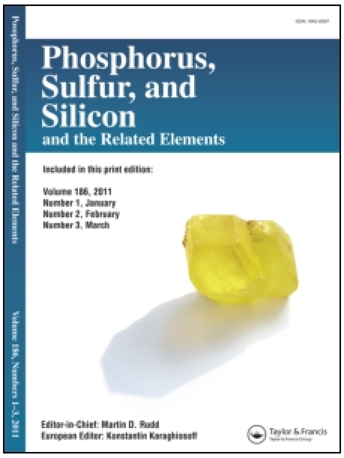

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4-Phenylsulfenyl- and 4-Phenylselenenyl-2,5-dihydro-1,2-oxaphosphole-2-oxides by the Reaction of 1,2-Alkadienephosphonic Amidoesters with Sulphenyl- and Selenenylbromides

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The reactivity of 1,2-alkadienephosphonic amidoesters towards sulphenyl- and seleneneylbromides has been investigated.

Keywords 1,2-Alkadienephosphonates; electrophilic reagents

INTRODUCTION

Phosphorylated 1,2-alkadienes provide an unusual system of reaction centers. Their syntheses as well as their reactions are subject of current interest.[1–4] There is an increasing number of publications concerning the reactivity of phosphorylated 1,2-alkadienes, as well as theoretical studies in this area.[5–18]

In continuation of our studies on phosphorus-substituted heterocycles, we now report a straight forward synthesis with high yields of 4-phenylsulphenyl- and 4-phenylselenenyl-2,5-dihydro-1,2-oxaphosphole-2-oxides.

RESULTS AND DISCUSSION

As starting compounds for our investigations we synthesized the dichlorides of 1,2-alkadienephosphonic acids following the procedure described earlier.[18] The nucleophilic displacement of the two chlorine

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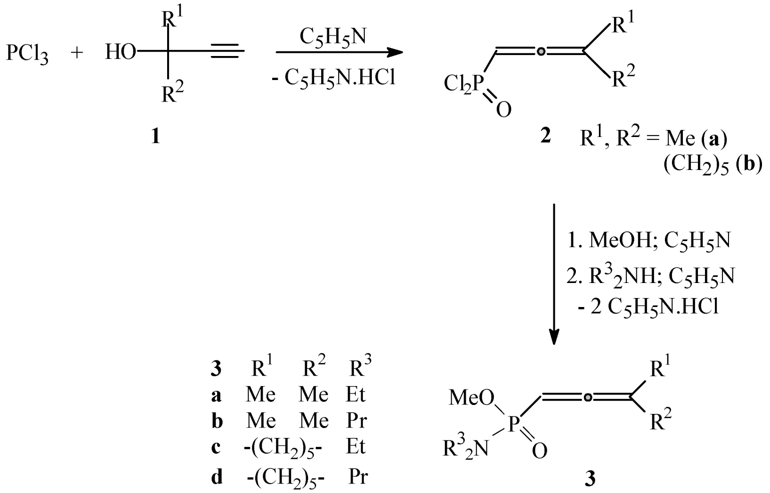
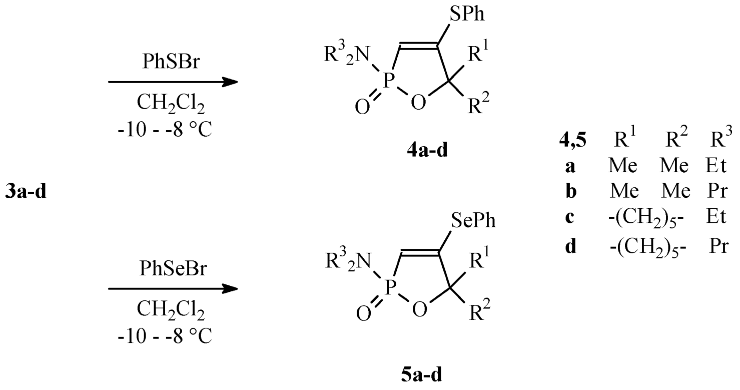
atoms at phosphorus with an alkoxy- and a dialkylamino group leads to the amidoesters of 1,2-alkadienephosphonic acids **3a–d** in very good yields.[19]



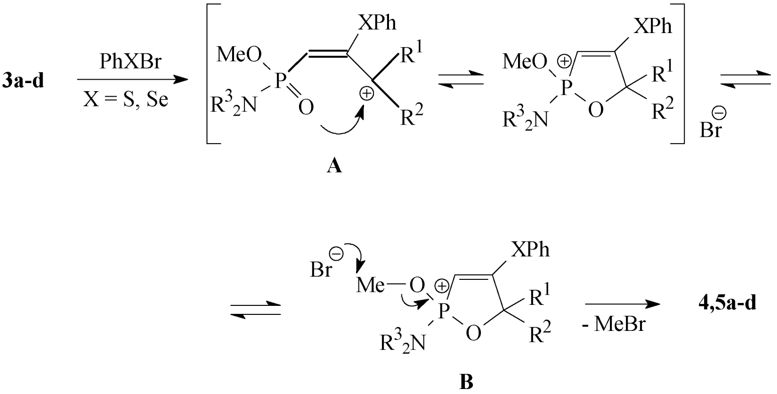
SCHEME 1

The reactions of **3a–d** with phenylsulphenyl and phenylselenenyl bromide were performed in a polar solvent at low temperature and under argon atmosphere.



SCHEME 2

The composition and structure of the 2,5-dihydro-1,2-oxaphosphole derivatives **4a–d** and **5a–d** was confirmed by their ^{1}H, ^{31}P NMR and IR spectra, as well as by elemental analyses (see EXPERIMENTAL). The results here reported confirm the direction of the reaction of amidoesters of 3,3-disubstituted-1,2-alkadienephosphonic acids with sulphenyl- and selenenyl halides: regardless of the kind of the reagent in all cases 2,5-dihydro-1,2-oxaphosphole derivatives were isolated. The driving force of the reaction is the formation of the intermediate **A**, stabilized by two methyl groups (**4a,b** and **5a,b**) or by cyclohexyl ring (**4c**,**d** and **5c,d**), which facilitates its intramolecular interaction with the phosphoryl group, acting as a nucleophile. The dealkylation of the resulting phosphonium intermediate **B** leads to the 2,5-dihydro-1,2-oxaphosphole derivatives:



SCHEME 3

EXPERIMENTAL

The ^{1}H NMR and ^{31}P NMR spectra were measured in $CDCl_3$ solution at ambient temperature on a Bruker Avance DRX 250 MHz spectrometer using TMS (^{1}H) and 85% H_3PO_4 (^{31}P) as external standards. Chemical shifts are given in ppm and are positively downfield from the standard. The IR spectra were run on an IR-72 spectrophotometer (Carl Zeiss Jena). Elemental analyses were carried out by the University of Shumen Microanalytical Service Laboratory.

Phenylselenenyl bromide is commercially available. Phenylsulfenyl bromide was synthesized according to the procedure described.[20] Compounds **3a**–**d** was synthesized according to the procedure described.[19]

The solvents were purified by standard methods. All reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purity on TLC plates.

Preparation of Compounds 4a–d and 5a–d—General Procedure

To a solution of 0.005 mol of **3a–d** in 50 mL of dry methylene chloride under argon atmosphere and stirring at –10°C to –8°C a solution of 0.005 mol of phenylsuphenyl bromide (0.094 g) or phenylselenenyl bromide (0.118 g) in 10 mL of the same solvent was added dropwise during 30 min. Then the solvent was evaporated and the residue was purified by column chromatography hexane/benzene 1:1.

(5,5-Dimethyl-2-oxo-4-phenylsulphenyl-2,5-dihydro-2λ⁵-[1,2]oxaphosphol-2-yl)diethylamine (4a)

Pale yellow oil, yield 1.32 g (85%); $C_{15}H_{21}O_2NPS$; calcd.: P, 9.98; N, 4.51; S 10.33%, Found: P, 9.95; N, 4.49; S, 10.29%; IR, ν(cm^{-1}): 1590 (C=C), 1256 (P=O). ^{1}H NMR ($CDCl_3$): δ = 7.56–7.23 (m, 5H, arom-H), 6.36 (dd, $^2J_{PH}$ = 27.8 Hz, $^3J_{HH}$ = 3.8 Hz, 1H, H—C=); 2.59 (m, 4H, CH_3CH_2N)), 1.46 (s, 3H,=CCH_3), 1.51 (s, 3H,=CCH_3), 1.02 (m, 6H, CH_3CH_2N). ^{31}P NMR ($CDCl_3$): δ = 33.1.

(5,5-Dimethyl-2-oxo-4-phenylsulphenyl-2,5-dihydro-2λ⁵-[1,2]oxaphosphol-2-yl)-dipropylamine (4b)

Pale yellow oil, yield 1.37 g (81%); $C_{17}H_{26}NO_2PS$; calcd.: P, 9.12; N, 4.12; S, 9.44%, Found: P, 9.08; N, 4.09; S, 9.40%; IR, ν(cm^{-1}): 1592 (C=C), 1259 (P=O), 1000 (P—O—C), ^{1}H NMR ($CDCl_3$); δ = 7.56–7.46 (m, 2H, arom-H), 7.29–7.23 (m, 3H, arom-H), 5.35 (dd, $^2J_{PH}$ = 27.8 Hz, $^3J_{HH}$ = 3.8 Hz, 1H, *H*—C=), 2.54–2.48 (m, 4H, $CH_3CH_2CH_2N$), 1.46 (s, 3H,=CCH_3), 1.51 (s, 3H,=CCH_3); 1.28–1.19 (m, 4H, $CH_3CH_2CH_2N$), 0.91-0.89 (m, 6H, $CH_3CH_2CH_2N$). ^{31}P NMR ($CDCl_3$): δ = 29.0.

4-(2-Oxo-4-phenylsulphenyl-1-oxo-2λ⁵-phospha-spiro[4,5]dec-3-en-2-yl)-diethylamine (4c)

Yellow oil, yield 1.28 g (71%); $C_{18}H_{26}NO_2PS$; calcd.: P, 8.81; N, 3.98; S, 9.12%; Found: P, 8.79; N, 3.95; S, 9.10%; IR ν(cm^{-1}): 1589 (C=C), 1237 (P=O). ^{1}H NMR ($CDCl_3$): δ = 7.56 – 7.46 (m, 2H, arom-H); 7.29 – 7.23 (m, 3H, arom-H); 5.35 (dd, $^2J_{PH}$ = 27.8 Hz, $^3J_{HH}$ = 3.8 Hz, 1H, *H*—C=), 2.59 (m, 4H, CH_3CH_2N), 1.90-1.43 (m, 10H, $(CH_2)_5$), 1.02 (m, 6H, CH_3CH_2N). ^{31}P ($CDCl_3$): δ = 28.9.

4-(2-Oxo-4-phenylsulphenyl-1-oxo-2λ⁵-phospha-spiro[4,5]dec-3-en-2-yl)-dipropylamine (4d)

Yellow oil, yield 1.33 g (70%); $C_{20}H_{30}NO_2PS$; calcd.: P, 8.16; N, 3.69; S, 8.45%; Found: P, 8.12; N, 3.66; S, 8.41; IR, ν(cm^{-1}): 1590 (C=C), 1253 (P=O); ^{1}H NMR ($CDCl_3$): δ =7.56-7.46 (m, 2H, arom-H);

7.29−7.23 (m, 3H, arom-H); 5.35 (dd, $^2J_{PH} = 27.8$ Hz, $^3J_{HH} = 3.8$ Hz, 1H, H—C=), 2.54−2.48 (m, 4H, $CH_3CH_2CH_2N$), 1.90−1.43 (m, 10H, $(CH_2)_5$); 1.28−1.19 (m, 4H, $CH_3CH_2CH_2N$), 0.91-0.89 (m, 6H, $CH_3CH_2CH_2N$). ^{31}P NMR (CDCl3): $\delta = 28.9$.

(5,5-Dimethyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2λ^5-[1,2]oxaphosphol-2-yl)diethylamine (5a)

Pale yellow oil, yield 1.46 g (82%); $C_{15}H_{21}O_2NPSe$; calcd.: P, 8.67; N, 3.92%, Found: P, 8.64; N, 3.89%; IR, ν(cm^{-1}): 1589 (C=C), 1258 (P=O). ^1H NMR (CDCl$_3$): $\delta =$ 7.56−7.23 (m, 5H arom-H), 6.36 (dd, $^2J_{PH} =$ 27.8 Hz, $^3J_{HH} =$ 3.8 Hz, 1H, H—C=), 2.59 (m, 4H, CH_3CH_2N), 1.46 (s, 3H,=CCH_3), 1.51 (s, 3H,=CCH_3), 1.02 (m, 6H, CH_3CH_2N). ^{31}P NMR (CDCl$_3$): $\delta = 33.1$.

(5,5-Dimethyl-2-oxo-4-phenylselenenyl-2,5-dihydro-2λ^5-[1,2]oxaphosphol-2-yl)-dipropylamine (5b)

Pale yellow oil, yield 1.54 g (80%); $C_{17}H_{26}NO_2PSe$; calcd.: P, 8.02; N, 3.62%, Found: P, 8.00; N, 3.59%; IR, ν(cm^{-1}): 1592 (C=C), 1259 (P=O), 1000 (P—O—C). ^1H NMR (CDCl$_3$): $\delta =$ 7.56−7.46 (m, 2H, arom-H), 7.29−7.23 (m, 3H, arom-H), 5.35 (dd, $^2J_{PH} =$ 27.8 Hz, $^3J_{HH} =$ 3.8 Hz, 1H, H—C=), 2.54−2.48 (m, 4H, $CH_3CH_2CH_2N$), 1.46 (s, 3H,=CCH_3), 1.51 (s, 3H,=CCH_3), 1.28−1.19 (m, 4H, $CH_3CH_2CH_2N$), 0.91-0.89 (m, 6H, $CH_3CH_2CH_2N$). ^{31}P NMR (CDCl$_3$): $\delta = 29.0$.

4-(2-Oxo-4-phenylselenenyl-1-oxo-2λ^5-phospha-spiro[4,5]dec-3-en-2-yl)-diethylamine (5c)

Yellow oil, yield 1.43 g (72%); $C_{18}H_{26}NO_2PSe$; calcd.: P, 7.77; N, 3.51%; Found: P, 7.74; N, 3.47%; IR, ν(cm^{-1}): 1593 (C=C), 1245 (P=O). ^1H NMR (CDCl$_3$): $\delta =$7.56 − 7.46 (m, 2H, arom-H), 7.29−7.23 (m, 3H, arom-H), 5.35 (dd, $^2J_{PH} =$ 27.8 Hz, $^3J_{HH} =$ 3.8 Hz, 1H, H—C=), 2.59 (q, 4H, CH_3CH_2N), 1.90-1.43 (m, 10H, $(CH_2)_5$), 1.02 (m, 6H, CH_3CH_2N). ^{31}P NMR (CDCl$_3$)$\delta = 28.9$.

4-(2-Oxo-4-phenylselenenyl-1-oxo-2λ^5-phospha-spiro[4,5]dec-3-en-2-yl)-dipropylamine (5d)

Yellow oil, yield 1.57 g (74%); $C_{20}H_{30}NO_2PSe$; calcd.: P, 7.26; N, 3.28%; Found: P, 7.22; N, 3.23%; IR, ν(cm^{-1}): 1589 (C=C), 1237 (P=O). ^1H NMR (CDCl$_3$): $\delta =$ 7.56 − 7.46 (m, 2H, arom-H), 7.29−7.23 (m, 3H, arom-H), 5.35 (dd, $^2J_{PH} =$ 27.8 Hz, $^3J_{HH} =$ 3.8 Hz, 1H, H—C=), 2.54−2.48 (m, 4H, $CH_3CH_2CH_2N$), 1.90−1.43 (m, 10H, $(CH_2)_5$), 1.28−1.19 (m, 4H, $CH_3CH_2CH_2N$), 0.91−0.89 (m, 6H, $CH_3CH_2CH_2N$). ^{31}P NMR (CDCl$_3$): $\delta = 28.9$.

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