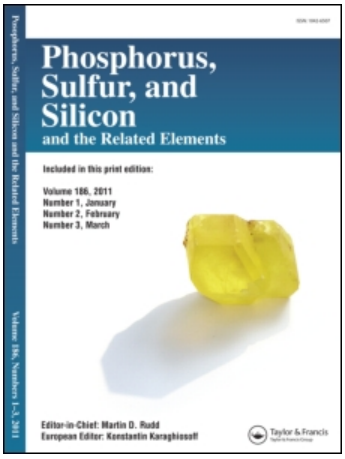

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Allene-Substituted-1,3,2-Dioxaphospholanes in the Reactions with Sulfenyl Bromides and Selenenyl Bromides

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ALLENE-SUBSTITUTED-1,3,2-DIOXAPHOSPHOLANES IN THE REACTIONS WITH SULFENYL BROMIDES AND SELENENYL BROMIDES

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The reactivity of allene-substituted-1,3,2-dioxaphospholanes towards sulfenyl bromides and selenenyl bromides has been investigated, and 2,5-dihydro-1,2-oxaphosphole derivatives have been obtained.

Keywords Allene-substituted-1,3,2-dioxaphospholanes; 2,5-dihydro-1,2-oxaphospholes; heterocyclization

INTRODUCTION

Continuing our study on the reactivity of allenephosphonates towards sulfenyl bromides and selenenyl bromides,[1–3] we have investigated the allene-substituted-1,3,2-dioxaphospholanes as substrates in the reaction with these reagents.

RESULTS AND DISCUSSION

The compounds **2a–c** have been synthesized by the procedure described,[4] i.e., by the reaction of 1,2-alkadienephosphonic dichlorides **1a–c** with 1,2-ethandiol. The reactions are shown in Scheme 1.

The obtained allene-substituted-1,3,2-dioxaphospholanes **2a–c** have been investigated in the reactions with phenylsulfenyl bromides and phenylselenenyl bromides. In all cases, regardless of the kind of the reagent employed, the 2,5-dihydro-1,2-oxaphosphole derivatives were isolated. The reactions are shown in Scheme 2.

Our results reported here, and the results of others,[5] show that regardless of the kind of electrophilic reagent used, the reaction of these substrates leads to 1,2-oxaphosphole derivatives **3a–d** and **3e**,**f**, respectively. We believe that the generation of **3a–d** and **3e,f** is due to the formation of quasiphosphonium intermediate **B** (Scheme 3), which decomposes under attack by the bromine anion. The formation of the intermediate **B** has been confirmed by others.[5]

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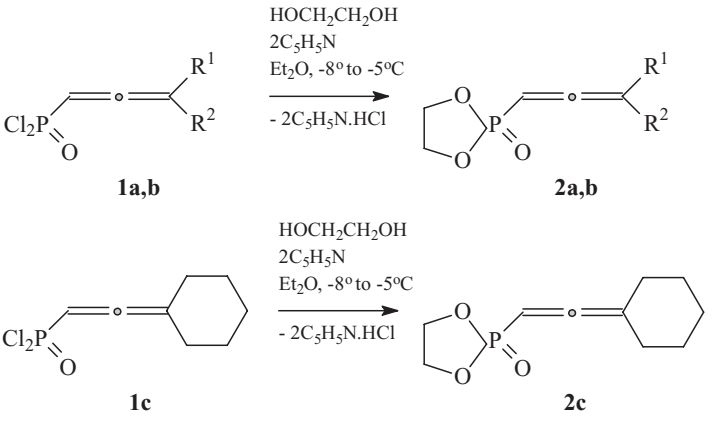
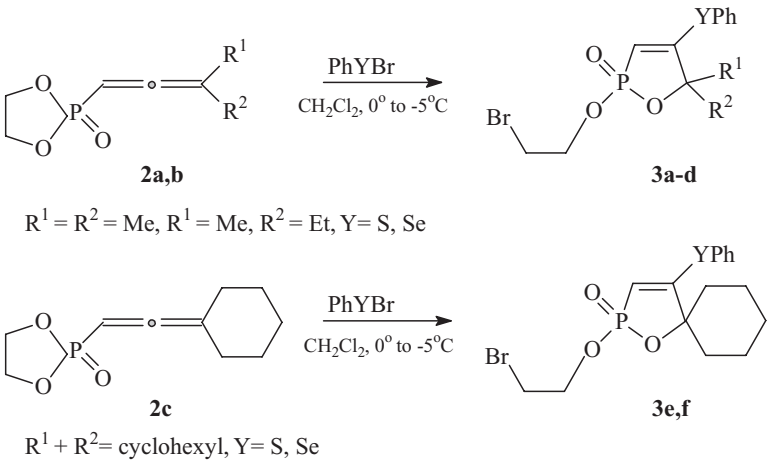


$R^1 = R^2$ =Me, R^1 = Me, R^2 = Et, $R^1 + R^2$ =cyclohexyl

Scheme 1



$R^1 = R^2$ = Me, R^1 = Me, R^2 = Et, Y= S, Se

$R^1 + R^2$= cyclohexyl, Y= S, Se

Scheme 2

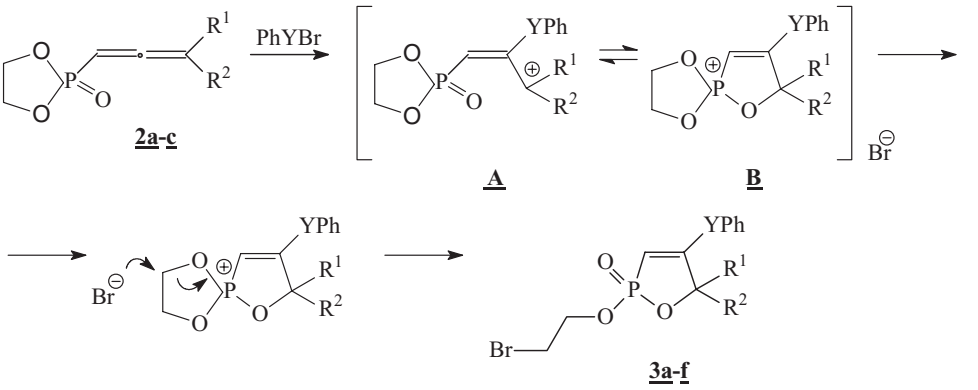
EXPERIMENTAL

The ^{1}H NMR and ^{31}P NMR spectra were measured at normal probe temperature on a Bruker Avance DRX 250 MHz spectrometer using TMS as internal reference in $CDCl_3$ solutions. Chemical shifts are given in ppm and are downfield from the internal standard. The IR spectra have been run on an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses have been carried out by the University of Shumen, Microanalytical Service Laboratory.

Phenylselenenyl bromide is commercially available. Phenylsulfenyl bromide was synthesized according to the procedure described.[6] Melting points are uncorrected.

Compounds **1a–c** were synthesized according to the procedure described.[7]

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



$R^1 = R^2 = Me$, $R^1 = Me$, $R^2 = Et$, $R^1 + R^2 =$ cyclohexyl
Y = S, Se

Scheme 3

Preparation of Compounds 2a–c

To a solution of 5 mmol of the appropriate dichloride **1a–c** in 50 mL of dry diethyl ether at –8°C to –5°C with stirring, a mixture of 5 mmol (0.32 g) of 1,2-ethandiol and 10 mmol (0.79 g) of pyridine dissolved in 50 mL of diethyl ether was added. After 1 h of stirring, the reaction mixture stood overnight. The precipitate was filtered off, the solvent was removed under reduced pressure, and the residue was purified by chromatography with ethyl acetate/hexane (1:1).

2-(3-Methylbuta-1,2-dienyl)-[1,3,2]dioxaphospholane-2-oxide 2a. Oil, 0.68 g, (79%), IR(KBr) ν_{max}/cm^{-1} 1989 (C=C=C), 1237 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$) ppm: 5.35 (d, $^2J_{HP} = 7.75$ Hz, 1 H, HC=); 4.40 (s, 4H, 2 CH_2); 2.18 (s, 6H, 2 $\underline{CH_3}$); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 17.0, Anal., Calcd. for $C_7H_{11}O_3P$ ($M_r = 174.128$): P 17.78%; Found: P 17.74%.

2-(3-Methylpenta-1,2-dienyl)-[1,3,2]dioxaphospholane-2-oxide 2b. Oil, 0.69 g, (74%), IR (KBr) ν_{max}/cm^{-1} 1990 (C=C=C), 1235 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$): ppm 5.52 (d, $^2J_{HP} = 7.74$ Hz, 1 H, HC=); 4.40 (s 4 H, 2 CH_2); 2.00 (m, 2 H, $\underline{CH_2}CH_3$); 1.70 (t, 3 H, =CCH_3); 0.99 (t, 3H, $CH_2\underline{CH_3}$); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 17.0, Anal., Calcd. for $C_8H_{13}O_3P$ ($M_r = 188.154$): P 16.46%; Found: P 16.43%.

2-(2-Cyclohelidenevinyl)-[1,3,2]dioxaphospholane-2-oxide 2c. Oil, 0.81 g, (76%), IR (KBr) ν_{max}/cm^{-1} 1990 (C=C=C), 1235 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$): ppm 5.71 (d, $^2J_{HP} = 7.68$ Hz, 1 H, HC=); 4.40 (s, 4 H, $2CH_2$); 2.09 (m, 4 H, cyclohexyl); 1.52–1.60 (m, 6 H cyclohexyl); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 17.0, Anal., Calcd. for $C_{10}H_{15}O_3P$ ($M_r = 214.19$): P 14.46%; Found: P 14.41%.

Preparation of Compounds 3a–f

To a solution of 5 mmol of **2a–c** in 50 mL of methylene chloride at 0°C to –5°C, a solution of 5 mmol (0.94 g) of phenylsulfenyl bromide or 5 mmol (1.18 g) of phenylselenenyl bromide was added with stirring. After 1 h of stirring, the solvent was removed under reduced pressure, and the residue was recrystallized in benzene/hexane (1:1).

2-(2-Bromoethoxy)-5,5-dimethyl-4-phenylsulfenyl-5H-[1,2]oxaphosphole-2-oxide 3a. Cryst., 1.39 g, (77%), mp 91–93°C, IR (KBr) ν_{max}/cm^{-1} 1589 (C=C), 1237 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$) ppm : 7.56–7.46 (m, 2 H, Ph); 7.29–7.23 (m, 3 H, Ph); 5.96 (d, $^2J_{HP}$ = 27.75 Hz, 1 H, HC=); 4.53 (q 2 H, $BrCH_2\underline{CH_2}O$); 3.74 (t, 2 H, $Br\underline{CH_2}CH_2O$); 1.28 (s, 6 H, $2\underline{CH_3}$); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 29.1, Anal., Calcd. for $C_{13}H_{16}BrO_3PS$ (M_r = 363.188): P 8.53, Br 22.00, S 8.83%; Found: P 8.50, Br 21.97, S 8.80.

2-(2-Bromoethoxy)-5-ethyl-5-methyl-4-phenylsulfenyl-5H-[1,2]oxaphosphole-2-oxide 3b. Cryst.,1.32 g, (70%), mp 95–98°C, IR (KBr) ν_{max}/cm^{-1} 1589 (C=C), 1237 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$) ppm : 7.56–7.46 (m, 2 H, Ph); 7.29–7.23 (m, 3 H, Ph); 5.96 (d, $^2J_{HP}$ = 26.75 Hz, 1 H, HC=); 4.50 (q 2 H, $BrCH_2\underline{CH_2}O$); 3.64 (t, 2 H, $Br\underline{CH_2}CH_2O$); 1.70 (q, 2 H, $\underline{CH_2}CH_3$); 1.33 (s, 3 H, $=C\underline{CH_3}$); 0.69 (t, 3 H, $CH_2\underline{CH_3}$); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 28.0, Anal., Calcd. for $C_{14}H_{18}BrO_3PS$ (M_r = 377.214): P 8.21, Br 21.18, S 8.50%; Found: P 8.19, Br 21.12, S 8.47.

2-(2-Bromoethoxy)-4-phenylsulfenyl-1-oxa-2-phosphaspyro-[4,5]dec-3-ene-2-oxide 3c. Cryst., 1.51 g, (75%), mp 101–103°C, IR (KBr) ν_{max}/cm^{-1} 1589 (C=C), 1237 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$) ppm : 7.56–7.46 (m, 2 H, Ph); 7.29–7.23 (m, 3 H, Ph); 5.61 (d, $^2J_{HP}$ = 27.70 Hz, 1 H, HC=); 4.42 (q 2 H, $BrCH_2\underline{CH_2}O$); 3.55 (t, 2 H, $Br\underline{CH_2}CH_2O$); 1.43–1.90 (m, 10 H, cyclohexyl); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 28.7, Anal., Calcd. for $C_{16}H_{20}BrO_3PS$ (M_r = 403.25): P 7.68, Br 19.81, S 7.95%; Found: P 7.66, Br 19.78, S 7.91;

2-(2-Bromoethoxy)-5,5-dimethyl-4-phenylselenenyl-5H-[1,2]oxaphosphole-2-oxide 3d. Cryst., 1.59 g, (78%), mp 90–92°C, IR (KBr) ν_{max}/cm^{-1} 1589 (C=C), 1237 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$) ppm : 7.56–7.46 (m, 2 H, Ph); 7.29–7.23 (m, 3 H, Ph); 5.96 (d, $^2J_{HP}$ = 27.75 Hz, 1 H, HC=); 4.58 (q 2 H, $BrCH_2\underline{CH_2}O$); 3.44 (t, 2 H, $Br\underline{CH_2}CH_2O$); 1.28 (s, 6 H, $2\underline{CH_3}$); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 29.0, *Anal.*, Calcd. for $C_{13}H_{16}BrO_3PSe$ (M_r = 410.088) : P 7.55, Br 19.48%; Found: P 7.50, Br 19.43.

2-(2-Bromoethoxy)-5-ethyl-5-methyl-4-phenylselenenyl-5H-[1,2]oxaphosphole-2-oxide 3e. Cryst., 1.5 g, (71%), mp 95–98°C, IR (KBr) ν_{max}/cm^{-1} 1589 (C=C), 1237 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$) ppm : 7.56–7.46 (m, 2 H, Ph); 7.29–7.23 (m, 3 H, Ph); 5.96 (d, $^2J_{HP}$ = 28.70 Hz, 1 H, HC=); 4.53 (q 2 H, $BrCH_2\underline{CH_2}O$); 3.74 (t, 2 H, $Br\underline{CH_2}CH_2O$); 1.70 (q, 2 H, $\underline{CH_2}CH_3$); 1.33 (s, 3 H, $=C\underline{CH_3}$); 0.69 (t, 3 H, $CH_2\underline{CH_3}$); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 29.0, Anal., Calcd. for $C_{14}H_{18}BrO_3PSe$ (M_r = 424.114): P 7.30, Br 18.84%; Found: P 7.26, Br 18.80.

2-(2-Bromoethoxy)-4-phenylselenenyll-1-oxa-2-phosphaspyro-[4,5]dec-3-ene-2-oxide 3f. Cryst., 1.62 g, (72%), mp 105–108°C, IR (KBr) ν_{max}/cm^{-1} 1589 (C=C), 1237 (P=O), 900 (P-O-C); ^1H NMR ($CDCl_3$) ppm : 7.56–7.46 (m, 2 H, Ph); 7.29–7.23 (m, 3 H, Ph); 5.61 (d, $^2J_{HP}$ = 26.65 Hz, 1 H, HC=); 4.50 (q 2 H, $BrCH_2\underline{CH_2}O$); 3.70 (t, 2 H, $Br\underline{CH_2}CH_2O$); 1.43–1.90 (m, 10 H, cyclohexyl); ^{31}P NMR ($CDCl_3$) ppm: ^{31}P 26.0, Anal., Calcd. for $C_{16}H_{20}BrO_3PSe$(M_r = 450.15): P 6.88, Br 17.75%; Found: P 6.86, Br 17.70.

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