SO_3-Mediated reaction of phenylselenenylamide with 1,2-alkadienylphosphonates

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SO_3-Mediated reaction of *N,N*-diethylphenylselenenylamide with 1,2-alkadienylphosphonates under conditions of generation of weak electrophilic species results in the formation of cyclization products involving phosphoryl oxygen.

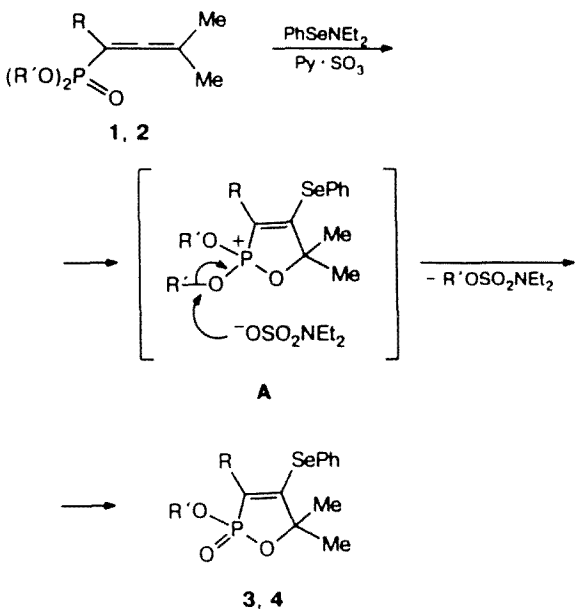
Key words: selenenylamide, sulfur trioxide, 1,2-alkadienyl phosphonate, electrophilic cyclization.

Study of reactions of phosphorylated allenes with electrophilic reagents of various polarities is necessary for solution of the problem of anomalous cyclization of functionally substituted allenylphosphonates.[1,2] The method of sulfonate activation of weak electrophilic reagents[3–6] widely used recently makes it possible to vary the polarity of reacting species over a wide range, which is clearly illustrated by the wide range of their effective electrophilicity.

At the first stage of the study, we investigated the sulfonate-activated addition of *N,N*-diethylphenylselenenylamide to allenylphosphonates under conditions in which, as shown previously,[5] weak electrophilic species are generated.

We found that under these conditions (with freshly prepared phenylselenenyl *N,N*-diethylsulfamate) the reactions of phosphorylated allenes **1** and **2** result in the formation of 1,2-oxaphosphol-3-enes **3** and **4**, respectively, *i.e.*, the cyclization involves phosphoryl oxygen, the *anti*-addition of the electrophile relative to the phosphoryl residue being observed similarly to other weakly polar reagents. It is evident that the subsequent cyclization should occur *via* the formation of quasi-phosphonium salt **A**, containing a sulfamate anion as a counterion.

It is noteworthy that similar salts with a sulfamate counterion were unknown earlier. It has been shown previously that the behavior of similar compounds strongly depends on the nature of counterion.[7,8] In this case, the nucleophilicity of the sulfamate group is evidently high enough for rapid dealkylation of the quasi-phosphonium salt, which occurs for 5 to 10 min at room temperature.



1, **3**: R = H, R' = Me
2, **4**: R = CH_2OMe, R' = Et

Experimental

^1H and ^{31}P NMR spectra were recorded on a Bruker CXP-200 spectrometer with working frequencies of 200 and 81 MHz using $SiMe_4$ and 85 % H_3PO_4 as standards, respectively. IR spectra were recorded on a Bruker IFS-113 instrument (in CCl_4).

A solution of phosphorylated allene (1 eq.) in CH_2Cl_2 was added dropwise to a solution of freshly prepared (from $PhSeNEt_2$ and $Py \cdot SO_3$) phenylselenenyl sulfamate (1 eq.) in the same solvent at ~20 °C. A white precipitate of alkyl sulfamate was observed almost immediately, and its formation was ceased in 5 to 10 min. A reaction mixture was filtered through a short column with silica gel, and a filtrate was concentrated *in vacuo*. Almost pure 4-phenylseleno-1,2-oxaphosphol-3-enes obtained were additionally purified by chromatography if necessary.

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5,5-Dimethyl-2-methoxy-2-oxo-4-phenylseleno-1,2-oxaphosphol-3-ene (3). Compound **3** (0.27 g, 85 %) as a yellowish viscous oil was obtained by the reaction of 1-dimethoxyphosphoryl-2-methyl-1,2-butadiene **1** (0.18 g), $PhSeNEt_2$, (0.23 g), and $Py \cdot SO_3$ (0.16 g). IR, ν/cm^{-1}: 1558 (C=C); 1271 (P=O). ^1H NMR ($CDCl_3$), δ: 7.6—7.4 (m, 5 H, Ph); 5.95 (d, 1 H, HC=C, J_{HP} = 26 Hz); 3.8 (d, 3 H, OMe, J_{HP} = 14 Hz); 1.6 (s, 3 H, Me); 1.55 (s, 3 H, Me). ^{31}P NMR, δ: 31.8. All spectral parameters of compound **3** coincide nearly completely with the literature data.[9]

5,5-Dimethyl-3-methoxymethyl-2-oxo-2-ethoxy-1,2-oxaphosphol-3-ene (4). Compound **4** (0.28 g, 78 %) was obtained by the reaction of 2-diethoxyphosphoryl-4-methyl-1-methoxy-2,3-pentadiene **2** (0.25 g), $PhSeNEt_2$ (0.23 g), and $Py \cdot SO_3$ (0.16 g). IR, ν/cm^{-1}: 1603 (C=C); 1267 (P=O). ^1H NMR ($CDCl_3$), δ: 7.4—7.6 (m, 5 H, Ph); 4.4 (d, 2, CH_2OMe, J_{HP} = 14 Hz); 4.3—4.0 (m, 2 H, OCH_2Me), 3.5 (s, 3 H, OMe), 1.6 (d, 6 H, Me, J_{HP} = 8 Hz), 1.4 (t, 3 H, $MeCH_2O$, J = 7 Hz). ^{31}P NMR, δ: 31.6. Found (%): C, 49.60; H, 5.53; P, 8.08. $C_{15}H_{21}O_3PSe$. Calculated (%): C, 50.01; H, 5.83; P, 8.61.

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