α-(*N*-Sulfonylamino)alkylphosphonates

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α-(*N*-Sulfonylamino)alkyl phosphites, which are intermediate products in the reactions of the corresponding hydroxy derivatives with diethyl phosphorochloridite, undergo *in situ* phosphorotropic rearrangement to give *C*-phosphorylated products.

Key words: α-(*N*-sulfonylamino)alkyl phosphites, α-(*N*-sulfonylamino)alkylphosphonates, phosphite-phosphonate rearrangement.

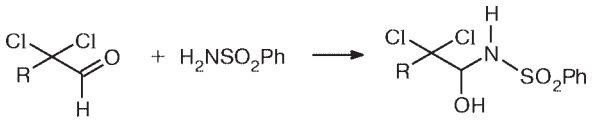
Earlier, we have obtained a broad range of substituted α-(*N*-acylamino)alkyl phosphites and found that these compounds enter into the Perkow intramolecular reaction or undergo phosphite-phosphonate rearrangement, depending on the nature of the chlorocarbonyl and amido fragments; if a phosphite contains a chloro ketone fragment, the above reactions occur concurrently.[1—3] In addition, we found that the presence of a proton at the amide N atom is a necessary condition for the phosphite-phosphonate rearrangement to occur.[4]

In continuation of these investigations, we synthesized previously unknown α-(*N*-sulfonylamino)alkyl phosphites and studied the possibility of analogous rearrangements in these compounds.

Results and Discussion

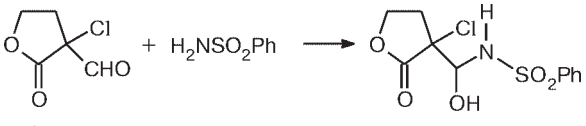
The reactions of α-chloro aldehydes **1** with benzenesulfonamide (Scheme 1) were used to obtain *N*-sulfonylhemiaminals (**2** and **3**), which served as the starting compounds in the synthesis of the target products.

Scheme 1



1a,b **2a,b**

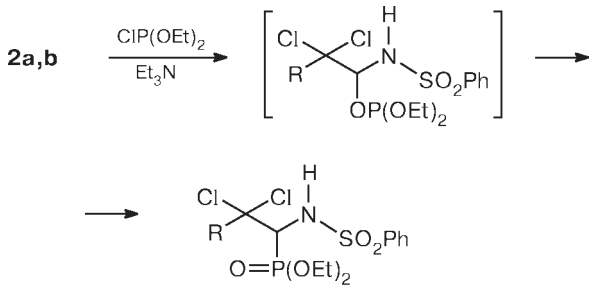
R = Cl (**a**), EtOC(O) (**b**)



1c **3**

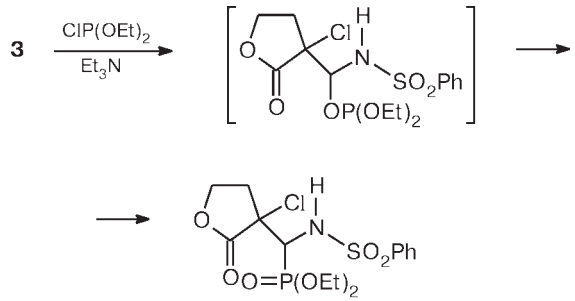
Hydroxy derivatives **2** and **3** readily react with diethyl phosphorochloridite in THF at −5 to 0 °C in the presence of Et_3N to give phosphonates **4** and **5** (Scheme 2).

Scheme 2



4a,b

R = Cl (**a**), EtOC(O) (**b**)



5

The expected intermediate phosphites were not detected by ^{31}P NMR spectroscopy; apparently, they readily undergo phosphorotropic isomerization into *C*-phosphorylated products **4** and **5**.

The structures of hydroxyalkyl amides **2** and **3** and phosphonates **4** and **5** were determined using ^1H and

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^{31}P NMR spectroscopy. Thus the ^{1}H NMR spectra of compounds **4** and **5** show a signal for the CHP proton at δ 4.6—4.9 (dd, $^{2}J_{PH}$ = 20.0 Hz, $^{3}J_{HH}$ = 7.5—10.0 Hz).

The presence of two close signals in the ^{31}P NMR spectrum of compound **5** (δ 15.35 and 15.48) suggests the formation of two diastereomers.

Hence, like α-(*N*-acylamino)- and α-(*N*-phosphorylamino)alkyl phosphites, α-(*N*-sulfonylamino)alkyl phosphites containing a proton at the amide N atom undergo phosphorotropic isomerization to give phosphonates.

Experimental

^{1}H NMR spectra were recorded on a Tesla BW spectrometer (100 MHz) with HMDS as the internal standard. ^{31}P NMR spectra were recorded on a Bruker WP-80 spectrometer with 85% H_3PO_4 as the external standard.

α-Chloro aldehydes **1a—c** were prepared according to the known procedure.[5]

***N*-(2,2,2-Trichloro-1-hydroxyethyl)benzenesulfonamide (2a)** was obtained as described in Ref. 6, m.p. 181 °C (*cf.* Ref. 6: m.p. 181 °C). ^{1}H NMR (acetone-d_6), δ: 5.40 (s, 1 H, CH); 6.50 (br.s, 1 H, NH); 7.57 (m, 3 H, Ph); 7.92 (m, 2 H, Ph).

Ethyl 2,2-dichloro-3-hydroxy-3-(phenylsulfonamido)propionate (2b). A mixture of aldehyde **1b** (18 g, 0.096 mol) and benzenesulfonamide (5.07 g, 0.032 mol) was heated at 90 °C for 1 h. The excess of the aldehyde was removed and the product was precipitated with ether. The crystals that formed were filtered off, washed with ether, and dried. The yield of compound **2b** was 65%, m.p. 100 °C. Found (%): Cl, 20.31; N, 4.25. $C_{11}H_{13}Cl_2NO_5S$. Calculated (%): Cl, 20.76; N, 4.09. ^{1}H NMR ($CDCl_3$), δ: 1.17 (m, 3 H, Me); 4.15 (m, 2 H, OCH_2); 5.43 (d, 1 H, CH, *J* = 10 Hz); 6.75 (d, 1 H, NH, *J* = 10 Hz); 7.47 (m, 3 H, Ph); 7.85 (m, 2 H, Ph).

2-Chloro-2-[phenylsulfonamido(hydroxy)methyl]butano-4-lactone (3) was obtained analogously. The yield of compound **3** was 70%, m.p. 126—130 °C. Found (%): Cl, 11.41; N, 4.67. $C_{11}H_{12}ClNO_5S$. Calculated (%): Cl, 11.62; N, 4.58. ^{1}H NMR ($CDCl_3$), δ: 2.52, 3.22 (both m, 2 H, CH_2); 4.55 (m, 2 H, OCH_2); 5.60 (d, 1 H, CH, *J* = 8.7 Hz); 6.30 (d, 1 H, NH, *J* = 8.7 Hz); 7.62 (m, 3 H, Ph); 7.90 (m, 3 H, Ph, OH).

The reactions of hemiaminals 2a,b and 3 with diethyl phosphorochloridite. Triethylamine Et_3N (0.05 mol) was added at −5 °C to a stirred solution of a mixture of hemiaminal **2a,b** or **3** (0.05 mol) and diethyl phosphorochloridite (0.05 mol) in 50 mL of anhydrous THF. The reaction mixture was kept at this temperature for 1 h and at ~20 °C for 1 h. The precipitate that formed was filtered off, the solvent was removed, and the product was precipitated with ether. The crystals that formed were filtered off, washed with ether, and dried.

Diethyl 2,2,2-trichloro-1-(phenylsulfonamido)ethylphosphonate (4a). Yield 75%, m.p. 101—104 °C. Found (%): Cl, 25.31; N, 2.95; P, 7.42. $C_{12}H_{17}Cl_3NO_5PS$. Calculated (%): Cl, 25.08; N, 2.30; P, 7.30. ^{1}H NMR (acetone-d_6), δ: 1.12 (t, 6 H, 2 Me); 4.03 (m, 4 H, 2 OCH_2); 4.66 (dd, 1 H, CH, $^{2}J_{PH}$ = 20 Hz, $^{3}J_{HH}$ = 10 Hz); 7.55 (m, 3 H, Ph); 7.90 (m, 3 H, Ph, NH). ^{31}P NMR (acetone), δ: 11.69.

Ethyl 2,2-dichloro-3-diethoxyphosphoryl-3-(phenylsulfonamido)propionate (4b). Yield 82%, m.p. 145—147 °C. Found (%): Cl, 15.41; N, 3.45; P, 6.75. $C_{15}H_{22}Cl_2NO_7PS$. Calculated (%): Cl, 15.37; N, 3.03; P, 6.71. ^{1}H NMR (acetone-d_6), δ: 1.30 (m, 9 H, 3 Me); 4.12 (m, 4 H, 2 OCH_2); 4.37 (q, 2 H, OCH_2); 4.90 (dd, 1 H, CH, $^{2}J_{PH}$ = 20 Hz, $^{3}J_{HH}$ = 7.5 Hz); 5.90 (br.s, 1 H, NH); 7.60 (m, 3 H, Ph); 8.06 (m, 2 H, Ph). ^{31}P NMR (acetone), δ: 14.40.

2-Chloro-2-[phenylsulfonamido(diethoxyphosphoryl)methyl]butano-4-lactone (5). Yield 78%, m.p. 148 °C. Found (%): Cl, 8.75; N, 3.05; P, 7.21. $C_{15}H_{21}ClNO_7PS$. Calculated (%): Cl, 8.34; N, 3.29; P, 7.28. ^{1}H NMR (acetone-d_6), δ: 1.30 (m, 6 H, 2 Me); 2.55, 3.08 (both m, 2 H, CH_2); 4.05—4.79 (m, 7 H, 3 OCH_2, CH); 7.55 (m, 4 H, Ph, NH); 8.00 (m, 2 H, Ph). ^{31}P NMR (acetone), δ: 15.35, 15.48.

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