Synthesis of novel *O*,*O*′-dialkyl α-aminoalkylphosphonothioates

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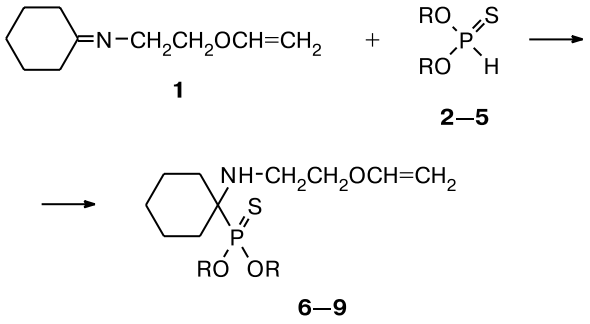
O,*O*′-Dialkyl α-amino(cyclohexyl)phosphonothioates were synthesized by the reactions of *O*,*O*′-dialkyl phosphonothioites with [2-(*N*-cyclohexylideneamino)ethyl] vinyl ether.

Key words: *O*,*O*′-dialkyl phosphonothioites, *O*,*O*′-dialkyl α-amino(cyclohexyl)phosphonothioates, Schiff′s bases.

Synthesis of aminoalkylphosphonates and -phosphinates has already been described in the literature.[1—3] One of the key routes to alkyl aminoalkylphosphonates is the Kabachnik—Fields reaction.[4,5]

Previously,[6] we have reported the reactions of dialkyl phosphites and -phosphothioites with {2-[*N*-benzylidene- and *N*-(*p*-fluorobenzylidene)amino]ethyl} vinyl ether. Aimed at further developing the methods for the synthesis of organophosphorus compounds containing cyclic and heterocyclic radicals, which can possess practically useful biological activity, we studied reactions of easily accessible [2-(*N*-cyclohexylideneamino)ethyl] vinyl ether (**1**) (obtained from cyclohexanone and 2-aminoethyl vinyl ether[7]) with *O*,*O*′-dialkyl phosphonothioites **2**—**5**.



1 **2—5** **6—9**

R = Me (**2**, **6**), Et (**3**, **7**), Pr^i (**4**, **8**), Bu^n (**5**, **9**)

The efficiency of the reaction depends significantly on temperature. The best results were obtained when the reactions were carried out at 47—50 °C for 45—50 min (the yields of the target products were 74—76%).

The structures of compounds **6**—**9** were confirmed by data from IR and ^{31}P NMR spectroscopy and elemental analysis.

The IR spectra of compounds **6**—**9** show absorption bands at 1030—1060 (P—O—C_{alkyl}), 1610—1625 (C=C), 3235—3285 (NH), and 635—660 cm^{-1} (P=S). ^{31}P NMR spectroscopic data are given in the Experimental.

Experimental

IR spectra were recorded on a UR-20 spectrometer (thin film). ^{31}P NMR spectra were recorded on a Bruker WP-200SY instrument (81.01 MHz) in C_6H_6 with 85% H_3PO_4 as the external standard.

O,*O*′-Dialkyl phosphonothioites **2**—**5** were prepared according to the known procedures.[8,9]

***O*,*O*′-Dialkyl {1-[2-(vinyloxy)ethylamino]cyclohexyl}phosphonothioates 6—9 (general procedure).** *O*,*O*′-Dialkyl phosphonothioites **2**—**5** (0.01 mol) were gradually added at ~20 °C to a solution of imine **1** (1.67 g, 0.01 mol) in benzene. The reaction mixture was heated at 47—50 °C for 50 min, the solvent was removed *in vacuo*, and the residue was chromatographed on SiO_2 (100—250 μm) in hexane—acetone (2 : 1).

Phosphonothioate 6. Yield 74.7%, n_D^{20} 1.5472. Found (%): C, 48.97; H, 8.03; N, 4.49; P, 10.37; S, 10.78. $C_{12}H_{24}NO_3PS$. Calculated (%): C, 49.13; H, 8.25; N, 4.77; P, 10.56; S, 10.93. ^{31}P NMR, δ: 108.67 (s).

Phosphonothioate 7. Yield 73.3%, n_D^{20} 1.4995. Found (%): C, 52.13; H, 8.64; N, 4.14; P, 9.37; S, 9.78. $C_{14}H_{28}NO_3PS$. Calculated (%): C, 52.32; H, 8.78; N, 4.36; P, 9.64; S, 9.98. ^{31}P NMR, δ: 104.17 (s).

Phosphonothioate 8. Yield 76.3%, n_D^{20} 1.4915. Found (%): C, 54.89; H, 9.05; N, 3.92; P, 8.69; S, 9.03. $C_{16}H_{32}NO_3PS$. Calculated (%): C, 54.99; H, 9.23; N, 4.01; P, 8.86; S, 9.17. ^{31}P NMR, δ: 99.48 (s).

Phosphonothioate 9. Yield 75.8%, n_D^{20} 1.4870. Found (%): C, 57.13; H, 9.47; N, 3.59; P, 8.07; S, 8.23. $C_{18}H_{36}NO_3PS$. Calculated (%): C, 57.27; H, 9.61; N, 3.71; P, 8.20; S, 8.49. ^{31}P NMR, δ: 104.69 (s).

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