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SHORT COMMUNICATIONS

Reaction of Seven-membered Cyclic Orthosilicates with Acetonitrile

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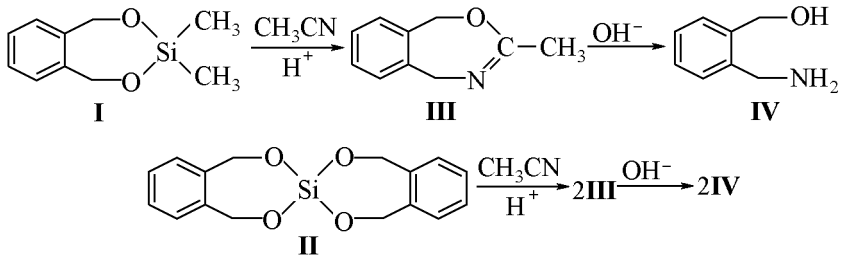
Reaction of certain heterocycles containing 2 or 3 heteroatoms in 1,2 and 1,2,3 positions respectively with nitriles may serve as a promising and sufficiently simple procedure for aminoalcohols preparation [1, 2]. We showed formerly [3,4] that methyl-substituted 1,3,2-dioxasilolanes and -dioxasilinanes reacted with acetonitrile to yield 1,3-oxazoline and 5,6-dihydro-4*H*-1,3-oxazine respectively. The latter in alkaline medium are readily hydrolyzed to 1,2- and 1,3-amino-alcohols. Here by examples of 3,3-dimethyl-1,5-dihydro-2,4,3-benzodioxasilepine (**I**) and 1,6,8,13-tetraoxa-7-siladibenzo[c,j]spiro[6,6]tridecane (**II**) we show for the first time the possibility for analogous transformation of seven-membered cyclic orthosilicates yielding 4,7-dihydro-2-methylbenzo[e]-1,3-oxazepine (**III**) and its hydrolysis product, 1-aminomethyl-2-hydroxymethylbenzene (**IV**).

Benzoxazepine **III** was isolated in both cases in 10% yield; it is a colorless crystalline compound that decomposes at heating over 185°C. Its composition and structure was confirmed by the data of mass spectrometry, and also by IR and ^{1}H NMR spectra. In the IR spectrum appear strong bands at 1665 [ν(C=N)] and 1510 cm^{-1} [ν(C↔C arom)].



In the mass spectrum is present the molecular ion peak (*m/z* 161) of relative intensity 70%, and a signal with *m/z* 119 of maximum intensity corresponding to fragmentation $M^+ - CH_3CNH$. ^{1}H NMR spectrum contains the expected signals from all proton groups (δ, ppm): 1.91 s (3H), 4.10 s (2H), 4.42 s (2H), 7.19 s (4H). The yield of aminoalcohol **IV** formed in the course of benzoxazepine **III** isolation due to hydrolysis of the latter amounts to 44%(with respect to ether I) and 49% (with respect to ether **II**). It is a viscous fluid with a characteristic amine odor. In its IR spectrum appear absorption bands at 3450–3290 cm^{-1} [ν(OH), ν(NH)], and also at 1580 and 1510 cm^{-1} [ν(C↔C arom)]. ^{1}H NMR spectrum (δ, ppm): 3.53 s (3H), 3.75 s (2H), 4.48 s (2H), 7.14 s (4H).

The reaction under study extends the possibility of chemical transformations for the seven-membered cyclic orthosilicates and opens a new approach to the synthesis of 1,3-benzoxazepines and the corresponding 1,4-aminoalcohols.

The ^{1}H NMR spectra were recorded on Tesla BS 497 spectrometer from 15% solutions of compounds under study in $CDCl_3$ with respect to TMS as internal reference. IR spectra were registered on spectrophotometer Specord 75IR from thin films or mulls in mineral oil. Mass spectrum was measured on

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MKh-1321 spectrometer, ionizing irradiation energy 70 eV.

Initial compounds **I** and **II** were synthesized according to [5, 6] in 62 and 40% yield respectively. Their physical constants and ^{1}H NMR spectra were consistent with the published data. To a solution of 0.01 mol of ester **I** in 30 ml (0.57 mol) of acetonitrile or to 0.01 mol of ester **II** in 180 ml (3.44 mol) of acetonitrile was added dropwise slowly while stirring 10.6 ml (0.2 mol) of concn. H_2SO_4, and then the mixture was refluxed at heating on a water bath for 5 h; the excess of acetonitrile was distilled off on rotary evaporator, and the viscous residue was diluted with 100 ml of water; the impurities were extracted into chloroform (2...50 ml). The remaining water phase was treated at cooling with ice with solid LiOH till pH 9–10, the separated precipitate of 1,3-benzoxazepine (**III**) was filtered off, and the water phase was extracted with chloroform (4...50 ml). On evaporating the solvent we obtained a residue containing aminoalcohol **IV** and oxazepine **III** as impurity. To isolate compound **IV** the residue was boiled for 3 h in 5-fold volume of 15% water solution of KOH, and then compound **IV** was extracted with chloroform (4...50 ml), and the solvent was distilled off on a rotary evaporator.

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