

SHORT
COMMUNICATIONS

Reaction of Seven-membered Cyclic Orthosilicates with Acetonitrile

V. V. Kuznetsov¹, S. A. Bochkor², Yu. E. Brusilovskii², and A. V. Mazepa²

¹Ufa State Oil Technical University, Ufa, Bashkortostan, 450162 Russia

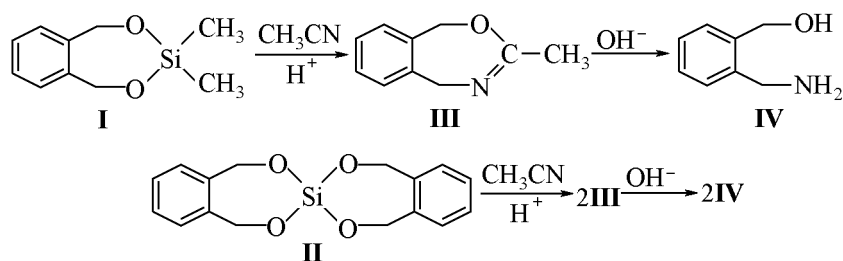
²Bogatskii Physico-chemical Institute, Ukrainian Academy of Sciences, Bogatsk, Ukraine

Received April 19, 2000

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-aminoalcohols. Here by examples of 3,3-dimethyl-1,5-dihydro-2,4,3-benzodioxasilolepine (**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-amino-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 ¹H NMR spectra. In the IR spectrum appear strong bands at 1665 [$\nu(\text{C}=\text{N})$] and 1510 cm^{-1} [$\nu(\text{C}\leftrightarrow\text{C arom})$].



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 $M^+ - \text{CH}_3\text{CNH}$. ¹H 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} [$\nu(\text{OH})$, $\nu(\text{NH})$], and also at 1580 and 1510 cm^{-1} [$\nu(\text{C}\leftrightarrow\text{C arom})$]. ¹H 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 ¹H 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

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 ^1H 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.

REFERENCES

1. Kuznetsov, V.V., Abstracts of Papers, *17th Ukrainian Conf. on Organic Chemistry*, 1995, Kharkiv, p. 191.
2. Kuznetsov, V.V., Abstracts of Papers, *12th Int. Conf. on Manufacture and Application of Chemical Reactives and Reagents "Reaktiv-99"*, Ufa–Moscow, 1999.
3. Kuznetsov, V.V. and Bochkor, S.A., *Zh. Org. Khim.*, 1998, vol. 68, no. 10, pp. 1755–1756.
4. Kuznetsov, V.V. and Bochkor, S.A., *Zh. Org. Khim.*, 1995, vol. 65, no. 8, p. 1404.
5. Birkofer, L. and Stuhl, O., *J. Organometal. Chem.*, 1979, vol. 164, no. 1, pp. C1–C5.
6. Rakhmankulov, D.L., Khekimov, Yu.K., Latypova, F.N., Nedogrei, E.P., Musavirov, R.S., Kantor, E.A., and Syrkin, A.M., *1,3-Dioxa-2-silatsikloalkany i ikh geteroanalogi* (1,3-Dioxa-2-Silacycloalcanes and Its Heteroanalogs), Ashkhabad: Minvuz TSSR, 1986.