ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 6, pp. 1008–1009. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.E. Shishkin, Yu.M. Yukhno, A.S. Ufimtsev, E.M. Baranova, S.V. Ufimtsev, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 6, pp. 1052–1053.

LETTERS TO THE EDITOR

Synthesis and Properties of 2,2,5,5-Tetramethyl-4-alkoxy-1,3,2-oxazasiloles

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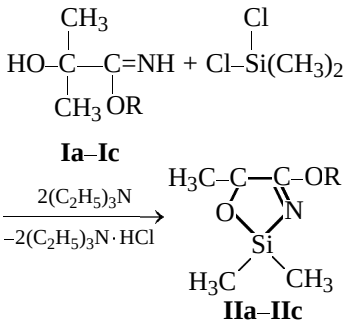
Received February 11, 2005

DOI: 10.1134/S1070363206060296

Earlier we studied reactions of C-phosphorylated imidates with organosilyl chlorides possessing one to three chlorine atoms and with tetrachlorosilanes, as well as reactions of O-phosphorylated hydroxyimidates with chlorotrimethylsilane [1, 2]. As a result, N-silylated phosphorylated imidates and hydroxyimidates that revealed a high insecticide and acaricide activity were synthesized.

Proceeding with these investigations we performed reactions of alkyl (2-hydroxy-2-methyl)propanimidates with dichlorodimethylsilane resulted in the synthesis of substituted 1,3,2-oxazasiloles. The molar ratio of isopropyl (2-hydroxy-2-methyl)propanimidate : dichlorodimethylsilane : triethylamine was 1 : 1 : 2.1. The reaction was performed in anhydrous benzene at 10–15°C for 1 h, after which the reaction mixture was kept 1–1.5 h at 25–30°C to complete reaction. The overall reaction scheme is as follows.



R = Et (**a**), *i*-Pr (**b**), Bu (**c**).

To isolate the synthesized compounds, triethylamine hydrochloride was filtered off, and benzene was removed in a vacuum. Final purification was performed by column chromatography on silica gel μLC 5/40. The purity of the products was confirmed by TLC on Silufol plates, eluent diethyl ether–methanol (1 : 3 v/v), R_f 0.39–0.42. The yields of 2,2,5,5-tetramethyl-4-alkoxy-1,3,2-oxazasiloles **II** were 65–69%.

Compounds **II** are light yellow liquids readily soluble in chloroform, benzene, dioxane, and aliphatic alcohols and poorly soluble in water and aliphatic hydrocarbons. Identification was performed by IR spectroscopy and mass spectrometry [3]. The IR spectra contain absorption bands characteristic of the following structural groups, ν, cm^{-1}: 824–810 [$Si(CH_3)_2$], 1045–1040 (C–O–Si), 1675–1670 (C=N), 1170–1160 (C–O–C), 1350–1345 [$C(CH_3)_2$]. No OH and NH absorption bands characteristic of the parent hydroxyimidates were observed in the IR spectra of the final compounds.

4-Ethoxy-2,2,5,5-tetramethyl-1,3,2-oxazasilole (IIa). A solution of 2.09 g of ethyl (2-hydroxy-2-methyl)propanimidate and 3.4 g of triethylamine in 70 ml of anhydrous benzene was added to a solution of 2.1 g of dichlorodimethylsilane in 50 ml of the same solvent. The temperature of the reaction mixture was 10–15°C, and the ethyl (2-hydroxy-2-methyl)-propanimidate : dimethyldichlorosilane : triethylamine ratio was 1 : 1 : 2.1. After 50 min the temperature was increased to 30–35°C to complete reaction. The product was purified by column chromatography. Yield 2.1 g (69%); n_D^{20} 1.4415; d_4^{20} 1.0015; MR_D 49.30, calculated 50.01; R_f 0.42. IR spectrum, ν, cm^{-1}: 810 [$Si(CH_3)_2$], 1043 (C–O–Si), 1675 (C=N), 1175 (C–O–C), 1345 [C(CH3)2]. Mass spectrum, *m/z* (I_{rel}, %): 187(12.4) $[M]^+$, 172 (31.6) $[M - CH_3]_+$, 142 (10.1) $[M - C_2H_5O]^+$, 129 (4.5) $[M - C_3H_7O]^+$.

4-Isopropoxy-2,2,5,5-tetramethyl-1,3,2-oxazasilole (IIb). A solution of 3.3 g of isopropyl (2-hyd-

roxy-2-methyl)propanimidate and 4.4 g of triethylamine in 80 ml of anhydrous benzene was added dropwise to a solution of 2.8 g of dichloro dimethylsilane in 50 ml of the same solvent. The synthesis was performed as described above. Yield 2.9 g (67%); n_D^{20} 1.4487; d_4^{20} 1.0279; MR_D 52.95, calculated 53.05; R_f 0.35. IR spectrum, ν, cm^{-1}: 825 [$Si(CH_3)_2$], 1050 (C–O–Si), 1675 (C=N), 1175 (C–O–C), 1345 [$C(CH_3)_2$]. Mass spectrum, *m/z* (I_{rel}, %): 201 (15) $[M]^+$, 186 (3.4) $[M - CH_3]^+$, 158 (9.1) $[M - C_3H_7]^+$, 145 (8.5) $[M - C_3H_7O]^+$.

1-Butoxy-2,2,5,5-tetramethyl-1,3,2-oxazasilole (IIc) was obtained by the reaction of 4.5 g of dichlorodimethylsilane with 5.1 g of butyl (2-hydroxy-2-methyl)propanimidate in the presence of 7.2 g of triethylamine. Yield 65% (4.8 g); n_D^{20} 1.4554; d_4^{20} 1.0291; MR_D 59.02, calculated 59.77; R_f 0.35. IR spectrum, ν, cm^{-1}: 824 [$Si(CH_3)_2$], 1045 (C–O–Si), 1670 (C=N), 1125 (C–O–C), 1340 [$C(CH_3)_2$]. Mass spectrum (70 eV), *m/z* (I_{rel}, %): 215 (5.08) $[M]^+$, 200 (34) $[M - CH_3]^+$, 186 (3.1) $[M - C_2H_5]^+$, 142 (18.5) $[M - C_4H_9O]^+$.

The IR spectra were registered in thin films on a Specord-82 instrument with a KBr prism. The mass spectra were obtained on a Varian MAT-11 GC–MS instrument with direct inlet, ionizing energy 70 eV.

REFERENCES

1. Shishkin, V.E., Mednikov, E.V., Isakova, E.V., and No, B.I., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 7, p. 1219.
2. Shishkin, V.E., Yukhno, Yu.M., and No, B.I., *Zh. Obshch. Khim.*, 1975, vol. 49, no. 5, p. 949.
3. Polyakova, A.A. and Khmel'niskii, R.A., *Mass-spektrometriya v organicheskoi khimii* (Mass Spectrometry in Organic Chemistry), Leningrad: Khimiya, 1972.