PREPARATION OF HETEROCYCLIC COMPOUNDS BY VAPOR-PHASE REACTIONS OF BENZOFURAN WITH TRICHLOROSILANE UNDER THE INFLUENCE OF ACCELERATED ELECTRONS

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Benzofuran reacts with trichlorosilane in the vapor phase at 250-450°C under the influence of accelerated electrons to give 2,2-dichloro-2-sila-1-oxo-1,2-dihydronaphthalene (I) or 3-trichlorosilyl-2,2-dichloro-2-sila-1-oxo-1,2,3,4-tetrahydronaphthalene (II).

Primarily II (in ~70 wt.% yield in the condensate with an ~100% degree of conversion of benzofuran) is formed at benzofuran and trichlorosilane ratios of 1:2 and higher and at 250-380°. The formation of II over the entire temperature range is observed only when the reaction is initiated with ionizing radiation. Primarily I (in up to 30 wt. % yield in the condensate with total conversion of the trichlorosilane or 60% conversion based on the converted benzofurnan) is formed at 350-450° and a benzofuran-to-trichlorosilane ratio of 1:1. Compound I is also formed by simple dehydrosilylation of II at ~ 450°, and irradiation in this case only accelerates the process.

At 340° and a molar ratio of I to trichlorosilane of 1:1 28 wt. % II is formed without irradiation, and 42 wt. % II is formed under the influence of accelerated electrons.

The above facts made it possible to establish that benzofuran is initially hydrosilylated, after which it undergoes condensation with expansion of the furan ring to give II.

A mixture of the reagents was placed in Pyrex ampuls (1-4 vol. % filling), and the ampuls were evacuated once, sealed, and irradiated in a thermostat with electrons with energies of 1.5-2.0 MeV at an electron-beam current of 50-80 μA. Chromatographic analysis and separation of all of the products in the mixtures were accomplished with LKhM-72 and Tsikloprep-2400 chromatographs. The detector was a catharometer, the carrier gas was helium, and the stationary phase was SKTFV-100 rubber on Celite C-22 (0.25-0.40-mm thick particles). The 3-m long column had a diameter of 4 mm in the case of the analytical chromatograph and 12 mm in the case of the preparative chromatograph. Compounds I and II were identified by means of their PMR, IR, and mass spectra.

A sample of II isolated with the preparative chromatograph had d_4^{20} 1.5316 and n_D^{20} 1.5408.

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