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REACTION OF 2,2,4,5-TETRAMETHYL-1,3-DIOXA-2-SILACYCLOHEXANE WITH THIONYL CHLORIDE

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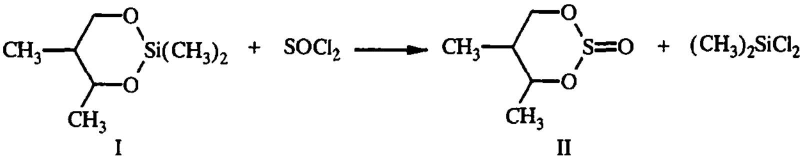
Interconversion reactions of six-membered 1,3,2-heterocycles provide a convenient means to evaluate their comparative thermodynamic stability, and allow the stereochemistry of ring formation and ring opening to be followed. We previously showed [1] that the reaction of 2,2,4,5-tetramethyl-1,3-dioxa-2-silacyclohexane (I) with acyclic boric ester leads to the dioxaborinane of the analogous stereoisomeric composition. The present communication is dedicated to studying the stereochemistry of the reaction of the ester I with thionyl chloride. It was shown by GLC that this results in the formation of 4,5-dimethyl-1,3,2-dioxathiane-2-oxide (II).



After 3 h of the mixing of the equimolar amount of the initial compounds in an inert atmosphere at room temperature, the ratio of the cyclic esters I and II was approximately 25:75, according to GLC data, and this was unchanged in the course of a further 24 h. The initial silicon ester I was synthesized by the reaction of bis(diethylamino)dimethylsilane with 2-methyl-1,3-butanediol (the 50:50 ratio of *erythro–threo* [2]) with the 50:50 ratio of *cis–trans* isomers [3]. The stereoisomeric composition of the cyclic sulfite II corresponds, within the limits of error of the measurement of peak areas on the chromatogram (±3%), to that of the ester I and the sample of compound II obtained by direct synthesis from thionyl chloride and 2-methyl-1,3-butanediol [4]. Therefore, the reaction of thionyl chloride with the silicon ester I proceeds stereospecifically, and the latter is less thermodynamically stable under conditions of the given reaction than the cyclic sulfite II.

GLC analysis was conducted on the LKhM-80 instrument with a catharometer detector, a column 4 × 2000 mm, the stationary phase of 5% DC-550 on the support Chromaton N-AW-HMDS, the gas-carrier helium, and the Tsvet-126 instrument with a flame-ionization detector, the column 4 × 3000 mm, the stationary phase of 5% OV-17 on the support Chromaton N-Super, and the gas-carrier argon. Determination of the qualitative composition of the reaction mixture was performed with the marker of the cyclic sulfite II, obtained by direct synthesis. Configurational assignment of the compounds I and II was carried out in the works [3, 4] correspondingly.

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