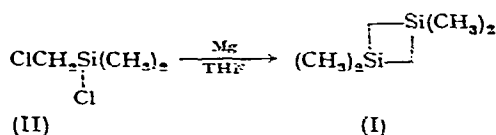


Short Communications

A preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane

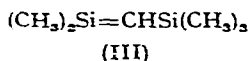
The preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) was undertaken in connection with a study concerned with the preparation and reactions of small-ring organosilicon compounds. Although a preparation of this compound has been previously described¹, that procedure involves a series of reaction steps and it did not appear attractive for our purpose.

The reaction of compounds of the general formula, $\text{ClCH}_2\text{SiR}_2\text{Cl}$, with metals has been reported² to give polymers of the type, $(\text{CH}_2\text{SiR}_2)_n$. It seemed likely that under suitable conditions, a reaction of this type could yield the desired disilacyclobutane (I). We now wish to report that reaction of (chloromethyl)dimethylchlorosilane (II) with magnesium in tetrahydrofuran (THF) gives (I) in moderate (9–20%)



yields*. The physical properties of our material were in good agreement with those previously reported¹ and the infrared spectrum was shown to be identical with that of a known sample**.

During the course of our investigation, we observed a similarity in the physical properties and chemical reactivity between (I) and an isomeric compound previously reported⁴ to be the silaolefin⁵ (III). Indeed, extensive and elegant re-examination of this problem by the original authors has shown that the compound believed to be (III) is actually 1,1,3,3-tetramethyl-1,3-disilacyclobutane^{3,6–8}.



We also observed that our material reacts slowly with bromine in carbon tetrachloride at room temperature, and rapidly reduces an ethanolic silver nitrate solution. These observations are in agreement with the high degree of reactivity previously reported¹ for (I).

The reactions of silacyclobutanes with bromine^{1,3,8,9} and silver nitrate^{9,*} are reported to proceed with ring-opening. The ability to reduce ethanolic solutions of

* A preparation of (I) employing (bromomethyl)dimethylchlorosilane and magnesium has been reported recently³.

** We wish to thank Dr. W. H. KNOTH, JR., for providing us with an infrared spectrum of this material.

silver salts is a characteristic of many four-membered silicon containing heterocycles. In addition to (I), the following compounds have been found to reduce ethanolic solutions of silver salts: 1) octaphenylcyclotetrasilane¹¹, 2) 1,1,2-triphenyl-1-silacyclobutane¹², 3) 1,1,2-triphenyl-1-silacyclobut-2-ene¹³, 4) 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene¹³, 5) 2:3-benzo-1-methyl-1-phenyl-1-silacyclobut-2-ene¹³ and 6) 1,1-dimethyl-1-silacyclobutane⁹. The qualitative test must be applied with some caution, however, since Si-H compounds¹⁴ and 1,1-dimethyl-1-silacyclopentadiene¹⁵ have also been reported to reduce silver salts under comparable conditions.

Experimental

Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride immediately before use.

Preparation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I). A solution of 30.6 g (0.2 mole) of (chloromethyl)dimethylchlorosilane in 90 ml of tetrahydrofuran was slowly added to 9.73 g (0.4 g-atom) of magnesium in 20 ml of tetrahydrofuran. The mixture was heated gently during the addition and finally refluxed for an additional 12 hours. The reaction mixture was decanted away from the excess magnesium into crushed ice acidified with 5 N hydrochloric acid. The hydrolyzed mixture was extracted with three 75-ml portions of ether, and the organic layer dried over anhydrous sodium sulfate. Subsequent to removal of the solvents, distillation of the residue gave 2.9 g (20%) of product, b.p. 115–117°, n_D^{20} 1.4422 (lit. value¹: b.p. 117–119°, n_D^{27} 1.4380).

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* A more complete examination of the reaction of (I) with silver nitrate has been carried out¹⁰ which is in agreement with the occurrence of ring-opening.