cis- and *trans*-9,10-Dimethyl-9,10-disiladecalin. Synthesis and Oxidation with Peroxides

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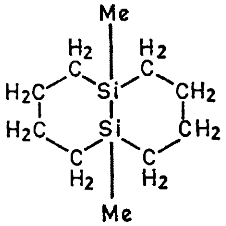
Summary The title compounds, prepared from *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane with $BrMg[CH_2]_4MgBr$, undergo oxidation with perbenzoic acid or bis(trimethylsilyl) peroxide to give *cis*-1,6-dimethyl-11-oxa-1,6-disilabicyclo[4,4,1]undecane.

IN connection with our studies on silicon–silicon containing heterocyclic compounds,[1,2] we report on the preparation of *cis*- and *trans*-9,10-dimethyl-9,10-disiladecalin (I) and their oxidation with perbenzoic acid and with bis(trimethylsilyl) peroxide.

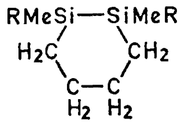
The reaction of the *cis*-isomer of (IIa)[2] with $BrMg[CH_2]_4$-MgBr in tetrahydrofuran gave the *cis*-isomer of the title compound (I) as the sole product, while a mixture of *cis* and *trans* isomers of (I) in the ratio of 1 : 0·6 was produced from *trans*-(IIa).

The structure assignment of (I) is based on the following considerations. As in the conversion of (IIa) into (IIb),[2] the replacement of the two fluorine atoms with a Grignard reagent would proceed stereospecifically, provided that no substantial amount of strain is present in the reaction product. Inspection of molecular models reveals that *trans*-(I) is fairly highly strained whereas the *cis*-isomer is not. Therefore the sole product from *cis*-(IIa) should be *cis*. The ^1H n.m.r. spectra of (I) further show that the *trans*-isomer is a rigid molecule, while the *cis*-isomer has two interchangeable limiting structures. The spectrum of *cis*-(I) shows two groups of multiplet bands due to the ring methylene hydrogens; since, because of the rapid flipping of the molecule from one form to the other, the methylene hydrogens fall into two groups and those of each group are in an average position as far as the n.m.r. spectrum is concerned.[3] The whole pattern of the spectrum is very similar to that for *cis*-(IIb), except for the peaks due to the phenyl groups. The *trans*-isomer of (I), on the other hand, shows a very complex band caused by the non-equivalent equatorial and axial hydrogens at two different kinds of positions and complicated by spin–spin coupling. The whole pattern of the spectrum resembles that of *trans*-(IIb) more closely than that of *cis*-(IIb).

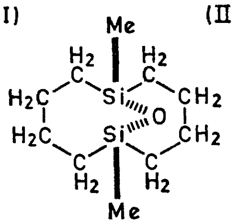
Both the *cis*- and *trans*-isomers of (I) underwent oxidation very easily when treated with perbenzoic acid at room temperature for 2 hr. to give the *cis*-isomer alone of 1,6-dimethyl-11-oxa-1,6-disilabicyclo[4,4,1]undecane (III). The yield was almost quantitative from *cis*-(I) and 83% from *trans*-(I). Elemental analysis of (III) was compatible with the molecular formula and the i.r. spectrum showed the intense absorption band (992 cm^{-1}) characteristic of the siloxane bond. The assignment to the *cis* form comes from the following reasons. Perbenzoic acid oxidation of a silicon–silicon bond[4] proceeds quite stereospecifically, as observed with the oxidation of (IIb),[2] if there is no substantial amount of ring strain and steric hindrance in the product. Inspection of molecular models reveals that the *trans*-siloxane (III) is highly strained and hindered sterically whereas the *cis*-siloxane is not. Therefore, the product obtained in quantitative yield from *cis*-(I) should be the *cis*-form, and the oxidation of *trans*-(I) must have taken place with complete stereomutation.



(I)



(IIa) R = F
(IIb) R = Ph



(III)

Oxidation with bis(trimethylsilyl) peroxide[5] at 80° for 50 hr. also converted both *cis*- and *trans*-(I) into the *cis*-siloxane (III), in *ca.* 100 and 22% yield, respectively. In the latter case, considerable amounts of nonvolatile polysiloxanes were formed as by-product.

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