

## SILICON-CONTAINING HETEROCYCLIC COMPOUNDS III\*. *cis*- AND *trans*-4a,8a-DIMETHYL-4a,8a-DISILADECALIN. SYNTHESIS AND OXIDATION WITH PEROXIDES\*\*

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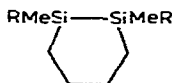
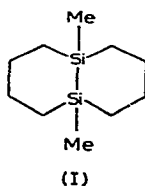
### SUMMARY

The reaction of the *cis* isomer of 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIIb) with  $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$  gave the *cis* isomer of 4a,8a-dimethyl-4a,8a-disiladecalin (I) as the sole product. On the other hand, the reaction with the *trans* isomer of (IIIb) yielded a mixture of *cis* and *trans* isomers of (I) in the ratio of 1/0.6. The structure assignment of (I) was based mainly on the NMR spectra. Both the *cis* and *trans* isomers of (I) underwent oxidation very easily when treated with perbenzoic acid, giving the *cis* isomer of 1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]undecane (IV). No *trans*-(IV) was formed at all. Oxidations with bis(trimethylsilyl) peroxide and oxygen afforded similar results. A mechanism for the formation of *cis*-(IV) from *trans*-(I) in the perbenzoic acid oxidation is proposed.

### INTRODUCTION

In the preceding paper<sup>1</sup>, we described the preparation and stereochemistry of geometric isomers of 1,2-disubstituted-1,2-dimethyl-1,2-disilacyclohexane (III). Therein, it was mentioned that the silicon-silicon bond involved in the 1,2-disilacyclohexane ring is slightly strained. The construction of molecular models reveals that in the fused ring system such as 4a,8a-disiladecalin the *trans* isomer is more strained than the *cis* isomer. It is therefore expected that the difference might be reflected in the formation and the reaction of such compounds.

In this paper, we report the stereochemistry of the formation of *cis*- and *trans*-



- a. R = Ph  
b. R = F  
c. R = Cl

\* For Part II see ref. 1.

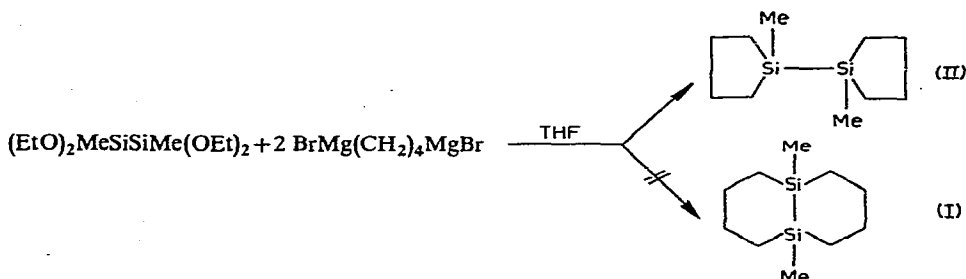
\*\* For a preliminary communication see ref. 2.

4a,8a-dimethyl-4a,8a-disiladecalin (I) from compounds (IIIb) and (IIIc), and of the oxidation of (I) with perbenzoic acid, bis(trimethylsilyl) peroxide and oxygen.

## RESULTS AND DISCUSSION

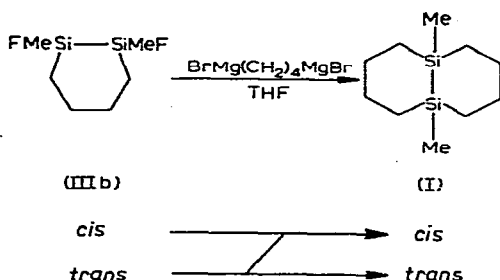
### Preparation and characterization

Attempts to prepare 4a,8a-dimethyl-4a,8a-disiladecalin (I) by the action of a di-Grignard reagent from 1,4-dibromobutane on *sym*-tetraethoxydimethyldisilane<sup>3</sup> in tetrahydrofuran (THF) resulted, as observed previously<sup>1</sup>, in the formation of its structural isomer, bi(1-methyl-1-silacyclopentyl) (II), containing five-membered rings instead of six-membered ones. The IR spectrum of (II) showed a group of bands characteristic of the silacyclopentyl ring reported by Nametkin *et al.*<sup>4</sup>.



4a,8a-Dimethyl-4a,8a-disiladecalin (I) could be obtained from 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIIb)<sup>1</sup> and from the chloro analog (IIIc)<sup>1</sup> by treating them with a di-Grignard reagent from 1,4-dibromobutane in THF. Thus, the reaction of the *cis* isomer of (IIIb) with  $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$  gave the *cis* isomer of 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*-(IIIb). From the chloro derivative (IIIc) only the *cis* isomer of (I) was obtained in 56% yield.

Each isomer was isolated by fractional distillation and subsequent preparative GLC. The *trans* isomer of (I) was purified by recrystallization from methanol under a nitrogen atmosphere because of its air-sensitivity.



The structure assignment of (I) is based on the following considerations. As in the conversion of (IIIb) into (IIIa)<sup>1</sup>, the replacement of the two fluorine atoms with a Grignard reagent would proceed stereospecifically, provided that no substantial

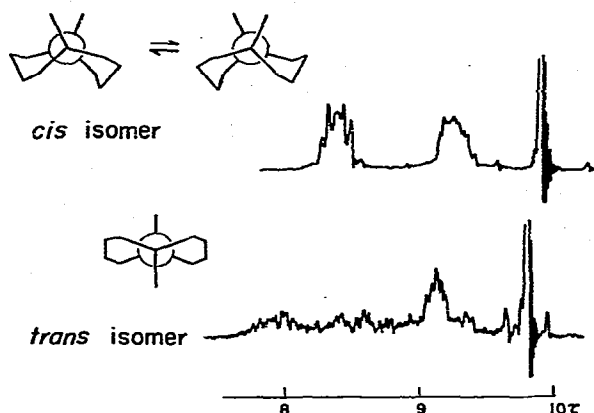


Fig. 1.  $^1\text{H}$  NMR spectra of *cis*- and *trans*-4a,8a-dimethyl-4a,8a-disiladecalin (I) in carbon tetrachloride at room temperature (60 Mc).

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*-(IIIb) should be *cis*. These relationships are in contrast with the fact that the *trans* isomer of decalin is more stable than the *cis*, and are very similar to those observed for *cis* and *trans* isomers of bicyclo [3.3.0]octane<sup>5</sup>.

It is well known that *trans*-decalin is locked, whereas *cis*-decalin has the interconvertible enantiomeric conformers<sup>5,6</sup>. Therefore it follows that the  $^1\text{H}$  NMR spectra show broad, complex signals for the former, while a sharp singlet for the latter<sup>5,7,8</sup>. Also in the present case, the  $^1\text{H}$  NMR spectra of (I) show that the *trans* isomer is a rigid molecule, while the *cis* isomer has two interchangeable limiting structures. As shown in Fig. 1, 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 NMR spectrum is concerned. The whole pattern of the spectrum is very similar to that for *cis*-(IIIa)<sup>1</sup>, 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*-(IIIa)<sup>1</sup> more closely than that of *cis*-(IIIa).

Physical properties and analytical data for compounds (I) and (II) are listed in Table 1.

#### Oxidation with peroxides

Previously<sup>9</sup>, it was reported from this laboratory that the silicon-silicon bond is oxidized with perbenzoic acid to give quantitatively the corresponding siloxane. In the preceding paper<sup>1</sup>, it has been described that the oxidation of the silicon-silicon bond with perbenzoic acid, and also with bis(trimethylsilyl) peroxide and oxygen, proceeds quite stereospecifically, unless substantial amounts of ring strain and steric hindrance are involved in the product, as observed in the oxidation of compounds (IIIa) and (IIIb). We have now investigated the oxidation of *cis*- and *trans*-(I) with

TABLE I

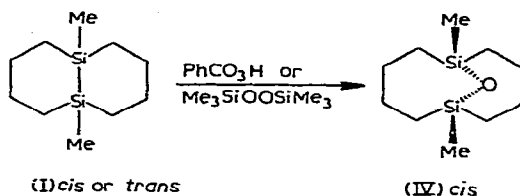
PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR COMPOUNDS (I), (II) AND (IV)

Compound	B.p. (°C/mm) or m.p. (°C)	$n_D^{20}$	$d_4^{20}$	$MR_D$	C (%) found (calcd.)	H (%) found (calcd.)	
C <sub>10</sub> H <sub>22</sub> Si <sub>2</sub> (I)	<i>cis</i>	109/17	1.5123	0.9158	65.06	60.52	11.01
	<i>trans</i>	93.5–94.5				60.71	11.26
C <sub>10</sub> H <sub>22</sub> Si <sub>2</sub> (II)	126–127/37	1.5033	0.8967	65.47 (65.32)	60.35 (60.52)	11.39 (11.17)	
C <sub>10</sub> H <sub>22</sub> OSi <sub>2</sub> (IV)					56.86 (56.00)	10.22 <sup>c</sup> (10.34)	

perbenzoic acid, bis(trimethylsilyl) peroxide<sup>10</sup> and oxygen.

Both the *cis* and *trans* isomers of (I) were found to undergo oxidation very easily when treated with perbenzoic acid at room temperature for 2 h to give the *cis* isomer alone of 1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]undecane (IV). The yield was almost quantitative from *cis*-(I) and 83% from *trans*-(I). The oxidation with bis(trimethylsilyl) peroxide at 80° for 50 h also converted both *cis*- and *trans*-(I) into the *cis*-siloxane (IV), in ca. 100 and 22% yield, respectively. In the latter case, considerable amounts of nonvolatile polysiloxanes were formed as the byproduct. The *trans*-(I) was slowly oxidized in air and more easily under an oxygen atmosphere to give *cis*-(IV), together with polysiloxanes, whilst the *cis*-(I) was stable even under the influence of oxygen.

The IR spectrum of the product (IV) showed the intense absorption band at 992 cm<sup>-1</sup> characteristic of the siloxane bond. The assignment to the *cis* form comes from the following reasons. As mentioned in the preceding paper<sup>1</sup>, the oxidation of a silicon-silicon bond with perbenzoic acid and bis(trimethylsilyl) peroxide proceeds quantitatively and in a stereospecific fashion, if there is no substantial amount of ring strain and steric hindrance in the product. As shown in Fig. 2, inspection of molecular models reveals that the *trans*-siloxane (IV) involves unfavorable, serious constellation



effects whereas the *cis*-siloxane does not. Therefore, the product obtained in quantitative yield from *cis*-(I) should be of the *cis* form, and the oxidation of *trans*-(I) must have taken place with complete stereomutation.

Perbenzoic acid is regarded as an electrophilic reagent for at least aliphatic polysilanes<sup>9</sup>. The stereomutation observed in the oxidation of the *trans*-(I) may be rationalized in terms of the inversion of a "siliconium ion" which might arise at the moment of electrophilic attack of the peracid on the silicon-silicon bond. It is interesting to compare this reaction with the rearrangement of *trans*-4a-decalyl per-

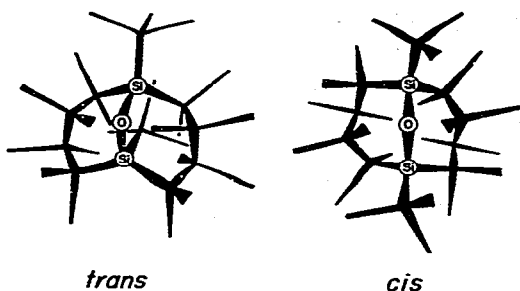
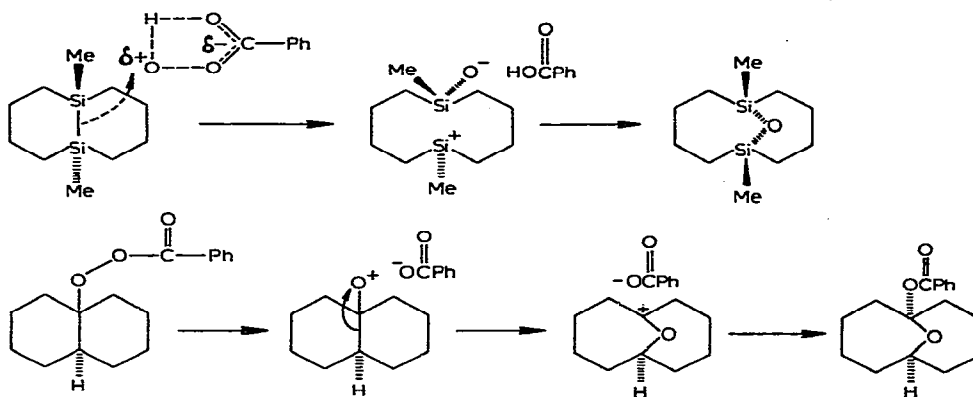


Fig. 2. Framework molecular models of *cis*- and *trans*-1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]-undecane (IV).

benzoate involving migration of carbon to positive oxygen through an intermediate of "intimate ion-pair" type<sup>11</sup>.



## EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. The reaction using 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIIb) had to be carried out within a day of its purification, for the fluoro derivative underwent *cis-trans* isomerization and was readily oxidized with oxygen<sup>1</sup>. Infrared spectra were measured on a Hitachi EPI G3 Grating spectrophotometer. NMR spectra were obtained on a JEOL Model C-60H spectrometer in carbon tetrachloride solution.

### Preparation of *cis*- and *trans*-4a,8a-dimethyl-4a,8a-disiladecalin (I)

(1). From an isomeric mixture of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIIb). A solution of 16 g (0.089 mole) of (IIIb), consisting of the *cis* and *trans* isomers (*cis/trans*  $\approx$  1/2), in 100 ml of THF was added to a Grignard solution, prepared from 28.8 g (0.133 mole) of 1,4-dibromobutane and 6.6 g (0.27 g-atom) of magnesium in 300 ml of THF, over 1 h at room temperature. The reaction mixture was heated with stirring for 5 h and then about 300 ml of THF was removed by distillation. After an additional 2-h reflux, the reaction mixture was hydrolyzed and worked

up in the usual manner. Fractional distillation gave 7.0 g (39.5% yield) of a mixture of *cis*- and *trans*-4a,8a-dimethyl-4a,8a-disiladecalin (*cis/trans*  $\approx$  1/0.47) boiling over the range of 118.5–127°/21 mm, together with 2 g of forerun and 9.0 g of residue. Each isomer was isolated by preparative GLC (230°, Apiezon-L, Varian Model 90P) and the *trans* isomer was recrystallized from methanol under nitrogen. Since the *cis* isomer had the same retention time on GLC as the siloxane (IV), it was usually contaminated with a small amount of (IV). Therefore, the *cis* isomer was purified by treatment with cold concentrated sulfuric acid and washing with saturated aqueous solution of sodium bicarbonate and water to neutral, and by redistillation. The identity was established by molecular weight determination by mass spectroscopy (Found 198, C<sub>10</sub>H<sub>22</sub>Si<sub>2</sub> calcd. 198.47), elementary analysis (Table 1) and the NMR spectra (Fig. 1).

(2). *From cis*-(IIIb). The *cis* isomer of (IIIb) (0.45 g; 2.5 mmole) was treated with the di-Grignard reagent, prepared from 1.6 g (66 mg-atom) of magnesium and 5.9 g (27.5 mmole) of 1,4-dibromobutane in 20 ml of THF, under reflux conditions for 5 h. After work-up in the usual way, the reaction mixture was flash-distilled to give 0.39 g of a viscous oil boiling over the range of 60–130°/12 mm. The presence of the *cis* isomer alone of (I) was revealed by GLC analysis of the distillate.

(3). *From trans*-(IIIb). Similarly, the freshly purified *trans* isomer of (IIIb) (2.0 g; 11.0 mmole) was allowed to react with tetramethylenedimagnesium dibromide, prepared from 10.8 g (50 mmole) of 1,4-dibromobutane and 3.0 g (123 mg-atom) of magnesium in 60 ml of THF. After work-up of the reaction mixture, distillation gave 2.0 g of a colorless liquid boiling up to 120°/15 mm. It consisted of an isomeric mixture of *cis*- and *trans*-(I) in the ratio of about 1/0.57, together with one other product in nearly equal amount to the *trans* isomer, possibly 1,2-dibutyl-1,2-dimethyl-1,2-disilacyclohexane. (Found: C, 65.40; H, 12.62. C<sub>14</sub>H<sub>32</sub>Si<sub>2</sub> calcd.: C, 65.53; H, 12.57%.)

(4). *From 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohexane* (IIIc). To a Grignard solution, prepared from 22.7 g (0.11 mole) of 1,4-dibromobutane and 5.6 g (0.23 g-atom) of magnesium in 100 ml of THF, was added a solution of 14.9 g (0.07 mole) of (IIIc)<sup>1</sup> in 100 ml of THF at room temperature with stirring over 40 min. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h and then refluxed for 6 h. About 150 ml of THF was removed by distillation. Hydrolysis of the remaining mass with dilute acid and distillation of the organic layer under reduced pressure gave 8.5 g of a liquid boiling over the range of 103–113°/20 mm, along with 4.5 g of residue. Fractionation afforded 7.8 g (56% yield) of *cis*-(I) homogeneous by GLC.

#### *Bi*(1-methyl-1-silacyclopentyl) (II)

To a di-Grignard solution, prepared from 24 g (1 g-atom) of magnesium and 105 g (0.49 mole) of 1,4-dibromobutane in 500 ml of THF, was added a solution of 50 g (0.21 mole) of *sym*-tetraethoxydimethyldisilane<sup>3</sup> in 100 ml of THF with cooling in an ice bath, over 20 min. After 8-h reflux, part of the solvent (ca. 400 ml) was removed and the residue was decomposed with saturated aqueous solution of ammonium chloride. The organic layer was worked up and then fractionally distilled to afford 26 g (62% yield) of (II). The IR spectrum showed a group of absorption bands at 1080, 1025 and 1030 cm<sup>-1</sup> characteristic of the silacyclopentyl group. The <sup>1</sup>H NMR spectrum ( $\tau$  values) exhibited 9.87 (SiCH<sub>3</sub>), 9.0–9.7 (SiCH<sub>2</sub>), and 8.2–8.5 (SiCCH<sub>2</sub>).

### Reactions of (I)

*With perbenzoic acid.* To 0.4 g (2.0 mmole) of *cis*-(I) was added a solution of perbenzoic acid (3.1 mmole) in 8 ml of methylene chloride. An exothermic, violent reaction occurred. After standing overnight the solvent was evaporated. The remainder was diluted with ether and washed repeatedly with saturated aqueous solution of sodium bicarbonate, and the solvent was removed. Preparative GLC afforded *cis*-1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]undecane (IV). The IR spectrum showed an intense band at  $992\text{ cm}^{-1}$  owing to the siloxane bond.

The reaction of *trans*-(I) with the peracid was carried out in the similar manner, but was not so exothermic. After standing overnight at room temperature, GLC analysis showed that the reaction was completed and the sole product was the *cis* isomer of the siloxane (IV) (Found: C, 56.08; H, 10.11 %). The retention time and the IR spectrum were exactly consonant with those of *cis*-(IV) obtained from *cis*-(I). The yields, estimated by GLC from runs employing a hydrocarbon added as a standard substance, were 97% from *cis*-(I) and 83% from *trans*-(I).

*With bis(trimethylsilyl) peroxide.* *cis*-(I) (0.17 g; 0.85 mmole) was heated with bis(trimethylsilyl) peroxide<sup>10</sup> (0.36 g; 2.0 mmole) in a small sealed glass tube at  $80^\circ$  for 62 h. By GLC analysis, the reaction was complete and *cis*-(IV) was the sole product, in addition to hexamethyldisiloxane having arisen from the peroxide. The former (IV) had the retention time on GLC and the IR spectrum identical with those of an authentic sample.

*trans*-(I) was similarly reacted with the peroxide to give the *cis* isomer alone of (IV), which was identified by comparison of the retention time on GLC and the IR spectrum with an authentic sample. Removal of the volatile product left a viscous liquid polysiloxane (by IR spectrum). The yield of (IV) was 98% from *cis*-(I) and 22% from *trans*-(I).

*With oxygen.* The crystals (0.1 g) of *trans*-(I) were allowed to stand under oxygen atmosphere at room temperature for 20 days. After 5 days, the crystals in part changed into an oil and after 20 days, about 20 ml of oxygen was absorbed with leaving a viscous liquid. The only product detectable by GLC was *cis*-(IV), whose IR spectrum was superimposable upon that of the authentic sample. In striking contrast, *cis*-(I) did not absorb oxygen at all, even after it was bubbled through the neat liquid at room temperature for 5 days. GLC analysis only showed the presence of the starting material.

### ACKNOWLEDGEMENTS

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