

SILICON-CONTAINING HETEROCYCLIC COMPOUNDS II*. PREPARATION, CHARACTERIZATION AND STEREOCHEMISTRY OF *cis*- AND *trans*-1,2-DISUBSTITUTED-1,2-DIMETHYL-1,2-DISILACYCLO- HEXANES**

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SUMMARY

cis- And *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia) and the 1,2-bis(*p*-chlorophenyl) analogs (Ib) have been prepared. The assignment of geometrical configuration for a pair of isomers of (Ib) has been achieved on the basis of dipole moment data, and that for isomers of (Ia) has been by correlating them with the isomers of (Ib) by reducing the latter to the former with the asymmetric silicon center intact. Fluorodephenylation of (Ia) by treatment with sulfuric acid and ammonium hydrogen fluoride always gives a 1/1.9 mixture of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIa) regardless of whether the *cis* or the *trans* isomer of (Ia) or a mixture of both is employed. The geometrical configuration of these isomers has been determined by converting them into (Ia). Chlorodephenylation of (Ia) with H₂SO₄/NH₄Cl or with HCl/AlCl₃ gives an inseparable isomeric mixture of the 1,2-dichloro analog. *cis*- And *trans*-(IIa) undergo stereomutation to form a 1/1.9 mixture of these two under the influence of sulfuric acid or ethanol in a hydrocarbon solution. A possible mechanism for this process is discussed in terms of pseudorotation of a pentacovalent, trigonal-bipyramidal silicon intermediate. (Ia) and (IIa) are oxidized stereospecifically to the corresponding cyclic siloxanes in almost quantitative yield by perbenzoic acid, bis(trimethylsilyl) peroxide, and oxygen.

INTRODUCTION

Since 1959² a considerable amount of research activity has concentrated around the stereochemistry of reactions on a silicon center, and its achievements greatly owe to Sommer and his coworkers³. In their studies, almost always optically active 1-naphthylphenylmethylsilicon compounds have been used. However, very little attention has been paid to the stereochemistry of compounds containing the silicon-silicon bond⁴. In the course of continuing investigation into the behavior of silicon-containing heterocyclic compounds⁵, we had occasion to study the stereochemistry of *cis* and *trans* isomers of 1,1,2,2-tetrasubstituted-1,2-disilacyclohexanes.

Cyclic compounds practically possess the following merits: (a) resolution of

* For Part I see ref. 5.

** For a preliminary communication see ref. 1.

cis and *trans* isomers is relatively easy; (b) there are many methods to determine the relative configuration, for which six methods have usually been used⁶; (c) it is possible to discuss the stereochemistry of reactions by using both of the epimeric isomers without optical resolution.

In this paper, we report first synthesis and identification of *cis* and *trans* isomers of 1,2-disubstituted-1,2-dimethyl-1,2-disilacyclohexanes, a facile stereomutation of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane, and the stereospecific oxidation of the silicon-silicon bond with perbenzoic acid, bis(trimethylsilyl) peroxide and oxygen.

RESULTS AND DISCUSSION

Preparation and characterization

Some physical properties and analytical data for new compounds (I)-(VII)

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR NEW COMPOUNDS (I)-(VII)

Compound		B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	MR_D found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)
C ₁₈ H ₂₄ Si ₂ (Ia)	<i>cis</i>	158/3	1.5847	1.0127	98.11	73.11	8.41
	<i>trans</i>	158/3	1.5888	1.0169	98.26 (98.73)	72.71 (72.90)	8.01 (8.16)
C ₁₈ H ₂₂ Cl ₂ Si ₂ (Ib)	<i>cis</i>	43.0-43.5				59.52	6.17
	<i>trans</i>	202-206/2	1.6002	1.1511	108.64 (108.41)	59.39 (59.16)	6.16 (6.07)
C ₆ H ₁₄ F ₂ Si ₂ (IIa)	<i>cis</i>	^a	1.4390	1.0282	46.14	39.96	7.95 ^b
	<i>trans</i>	^a	1.4410	1.0331	46.10 (46.51)	39.90 (39.96)	8.00 (7.82) ^c
C ₆ H ₁₄ Cl ₂ Si ₂ (IIb) ^d		90/18	1.4991	1.0931	57.30 (57.54)	34.24 (33.78)	6.76 (6.62) ^c
C ₁₄ H ₁₆ Cl ₂ Si ₂ (IIIa)		141-145/2 67.5-71.0 ^e				54.44 (54.00)	5.24 (5.18) ^f
C ₁₄ H ₁₄ Cl ₄ Si ₂ (IIIb)		179-183/1.5 85.0-89.5 ^e				44.61 (44.22)	3.90 (3.71) ^h
C ₁₀ H ₂₄ O ₂ Si ₂ (IV)		117-118/38	1.4534	0.9078	69.27 (69.35)	51.73 (51.66)	10.53 (10.41)
C ₆ H ₁₄ F ₂ Si ₂ (V)		147-148	1.4282	1.0013	46.36 (46.72)		
C ₁₈ H ₂₄ Si ₂ (VI)		161/4	1.5820	1.0030	98.68 (98.73)	73.14 (72.90)	8.13 (8.16)
C ₁₈ H ₂₄ OSi ₂ (VIIa)	<i>cis</i>	ca. 158-160/3	1.5473			59.74	7.80
	<i>trans</i>	ca. 160-164/3	1.5479			69.38 (69.17)	7.71 (7.74)
C ₆ H ₁₄ F ₂ OSi ₂ (VIIb)	<i>cis</i>		1.4035				
	<i>trans</i>		1.4020				

^a B.p. of a mixture of the *cis* and *trans* isomer, 90-95°/100 mm. ^b F%: 20.98 (21.07). ^c F%: 21.27 (21.07).

^d Obtained from the H₂SO₄/NH₄Cl method (see *Experimental*). ^e Cl%: 33.77 (33.25). ^f Cl%: 22.71 (22.78).

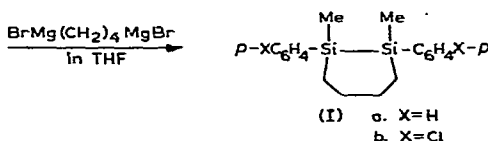
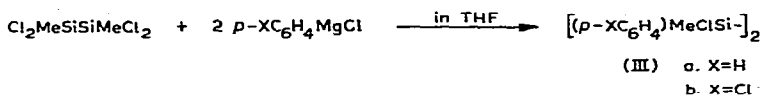
^g The m.p. reported here is the highest value obtained, since it varies with each crop of crystallization.

^h Hydrolyzable Cl%: 18.30 (18.65). ⁱ F%: 21.42 (21.07). ^j F%: 19.58 (19.35). ^k F%: 19.47 (19.35).

are summarized in Table 1, and the ^1H NMR data, except for (V), in Table 2.

1,2-Diaryl-1,2-dimethyl-1,2-disilacyclohexane

A mixture of *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia) was successfully prepared in 75% yield by the reaction of tetramethylenedimagnesium dibromide with 1,2-dichloro-1,2-diphenyl-1,2-dimethyldisilane (IIIa) in tetrahydrofuran (THF). The latter was obtained as a mixture of *meso* and DL compounds in 50% yield through the action of two equivalents of phenylmagnesium chloride on *sym*-tetrachlorodimethyldisilane⁷ followed by the crystallization from *n*-hexane.



Either of the isomers of compound (Ia) could be separated pure by several repeated fractional distillations through a spinning band column and/or by preparative GLC. The configurational assignment for the isomeric (Ia) is necessary before any conclusions can be drawn regarding the stereochemistry on silicon atoms. In general, dipole moment measurements provide a very convenient means to characterize geometric isomers of cyclic compounds. In aid of measurements, the cyclic compounds involving some electronegative groups are desired. Accordingly, a mixture of *cis* and *trans* isomers of the *p*-chlorophenyl derivative (Ib) was analogously prepared (70% yield) from the corresponding dichlorodisilane (IIIb). Each of *cis* and *trans* isomers of (Ib) could be isolated by fractional distillation and recrystallization from ethanol. One isomer having a shorter retention time on GLC melts at 43° and another is an oily liquid.

The geometrical configuration of the *p*-chlorophenyl compound (Ib) was established on the basis of the dipole moment data, which were evaluated from measurements of dielectric constants and densities of benzene solutions of each isomer at 25° and from their molar refractions. Thus, one isomer having a shorter retention time on GLC had a higher value, 3.0₂ D*, than the other, 2.2₃ D*, the results indicating that the former is *cis* and the latter is *trans*.

The assignment of the phenyl derivative (Ia) to *cis*- and *trans*-configuration could be achieved by correlation with the known configuration of the *p*-chlorophenyl derivative (Ib) after Summerbell and co-workers' techniques⁸. Thus the action of ethyl bromide and magnesium on both the *cis* and *trans* isomer of the *p*-chlorophenyl derivative (Ib) in tetrahydrofuran, followed by hydrolysis, converted them, with the asymmetric silicon centers intact, into the *cis* and *trans* isomer, respectively, of the phenyl derivative in an excellent yield.

* In a preliminary account, the values of 2.9₂ D and 2.1₂ D were reported¹.

pentane (VI). GLC analysis of (VI) showed a homogeneous peak different from the peaks corresponding to the *cis* and *trans* isomers of (Ia). The IR spectra of compounds (IV) and (VI) showed a group of absorption bands characteristic of the silacyclopentyl group, reported by Nametkin *et al.*¹⁰.

For both cyclic systems (I), the *cis* isomers have lower physical constants (see Table 1) and shorter retention times on GLC (Apiezon-L and SE 301) than do the *trans* isomers. The proton NMR spectroscopy (see Table 2) showed that the methyl protons in *cis* isomers of both the phenyl and *p*-chlorophenyl derivatives absorb at about 0.07 ppm lower field than those in the *trans* isomers. This is consistent with the above assignments because a somewhat larger effect of magnetic anisotropy of the benzene ring can be expected for the *trans* isomers from inspection of molecular models. The spectrum of *cis*-(Ia) shows two groups of multiplets due to the ring methylene hydrogens, while those in the *trans*-(Ia) occur in a more complex, but rather characteristic pattern (Fig. 1). The small differences in the chemical shifts of the

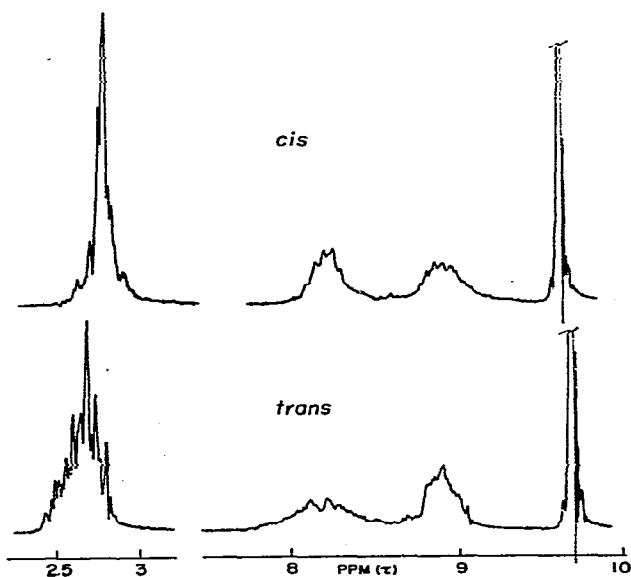


Fig. 1. ¹H NMR spectra of *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia) in carbon tetrachloride at room temperature (60 Mc).

methyl protons observed in both the dichlorodisilanes (IIIa) and (IIIb) possibly originate from *meso* and DL compounds. The similar observations have been reported for a number of *meso* and DL compounds^{11,12}. Attempts to resolve *meso* and DL compounds of (IIIa) by fractional crystallization from *n*-hexane were unrewarding.

1,2-Dihalo-1,2-dimethyl-1,2-disilacyclohexane

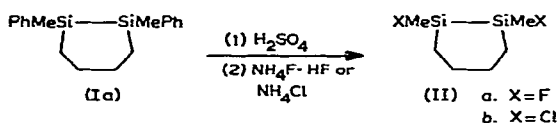
When the phenyl derivative (Ia) was fluorodephenylated by dissolving it in concentrated sulfuric acid in the cold and then treating the resulting solution with

TABLE 3

FLUORODEPHENYLATION OF (Ia)

Isomer ratio of starting (Ia) <i>cis/trans</i>	Isomer ratio in produced (IIa) <i>cis/trans</i>
1/0	1/1.7
0/1	1/1.9
1/1.7	1/1.8
1/2.1	1/1.9
1/4.7	1/1.95

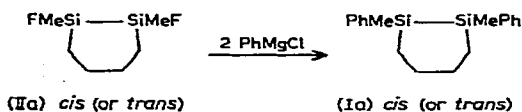
ammonium hydrogen fluoride, always a mixture of *cis* and *trans* isomers of 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIa) in a molar ratio of about 1/1.9 was obtained regardless of whether the pure *cis* or *trans* isomer of (Ia) or a mixture of both was employed (Table 3). The total yields were almost quantitative.



This reaction is in contrast with the exclusive cleavage of the silicon-silicon bond observed in the action of sulfuric acid on 1,1,2,2-tetramethyl-1,2-disilacyclohexane¹. The result demonstrates that dephenylation of compound (Ia) by sulfuric acid takes place in preference to the cleavage of a slightly strained silicon-silicon bond involved in the 1,2-disilacyclohexane. Furthermore, the silicon-silicon bond linked to some electronegative group(s), in the present case probably hydrogen sulfate group, seems to be reluctant to further attack by sulfuric acid.

These isomers could be separated by preparative GLC. The Silicone DC 550 was the most suitable column packing for the separation of the isomers. The greatest care had to be taken to prevent air oxidation by use of a collecting tube filled with nitrogen, since the fluoro derivative (IIa) was readily oxidized with oxygen even at room temperature. Therefore, measurements of their physical constants and all reactions using them had to be carried out within a day of their purification.

The geometrical identification could be achieved by converting them back into the phenyl derivative (Ia), whose geometrical configuration had been established. Thus, one isomer of (IIa) having a shorter retention time on GLC exclusively gave rise to the *trans*-(Ia), while the other having a longer retention time resulted in predominant formation of the *cis*-(Ia), in excellent yields, upon treatment with phenylmagnesium chloride in tetrahydrofuran. Since the overall results of this phenylation involved no stereomutation, unambiguous correlation of configuration between (Ia) and (IIa) was thus achieved¹³. A small amount of *trans* isomer of (Ia) was produced from *cis*-(IIa), possibly due to the isomerization of the latter (*vide infra*).



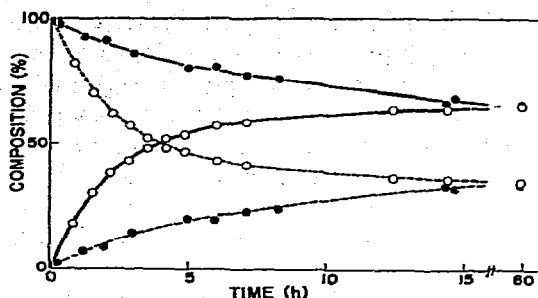
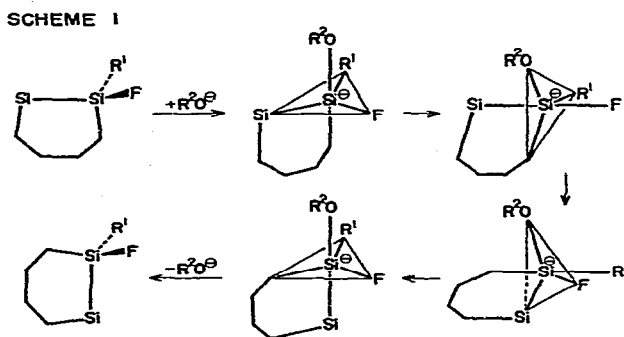


Fig. 2. Equilibration of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIa) by EtOH in benzene solution at 30.0°. Concentrations: (IIa), 0.15 M; EtOH, 1.00 M. —, *trans*; — —, *cis*. ○, from *cis*; ●, from *trans*.

being apical. Such an intermediate could return to R_3Si^*F with retention or inversion of configuration, depending upon which pair of *trans* groups moves toward the methoxy group as it leaves*.

The isomerization of *cis* and *trans* isomer of (IIa) might also proceed via a similar intermediate. However, in the present case, the compound under consideration is cyclic. Therefore a more attractive mechanism seems to involve pseudorotation¹⁷ between trigonal-bipyramidal silicon intermediates (Scheme 1). Pseudorotation for



compounds of pentacovalent elements has recently been successfully employed for interpretation of isomerization or racemization of various organophosphorus compounds (for leading reviews, see *e.g.* ref. 18). Examination of models reveals that if all skeletal atoms are tetrahedral, namely in sp^3 hybridization, our six-membered ring is found to be slightly strained. However, if at least one of the internal bond angles Si-Si-CH₂ deviates from the tetrahedral angle to 90°, the angle strain appears to be reduced. Consequently, if one assumes that a pentacoordinate silicon linked to the alkoxy group is involved in the stereomutation of (IIa), the concept of *I* strain may recommend a trigonal-bipyramidal structure rather than a tetragonal-pyramid for structure of the intermediate, since in the trigonal-bipyramidal configuration where

* In their recent report, Sommer *et al.*¹⁶ have discussed a mechanism involving the pseudorotation process for this racemization.

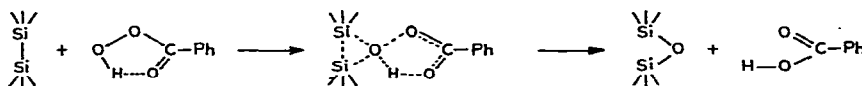
the ring occupies one apical and one equatorial position the Si-Si-CH₂ angle can become 90°, whilst in a tetragonal pyramid where the ring spans two basal positions that angle may be smaller than 90° and when the ring spans one apical and one basal position it may become about 105° (ref. 3). Moreover, it has been shown by theoretical calculations that, in general, the trigonal-bipyramidal configuration is, though slightly, more probable than the tetragonal-pyramid^{19,20}. In fact, almost all compounds of which structures have been determined by X-ray diffraction possess the trigonal- or near trigonal-bipyramidal arrangement²¹.

Scheme 1 illustrates the epimerization of the cyclic compound (IIa) involving pseudorotation. Three times repeated operations of the process followed by leaving of the alkoxy group from the apical position lead to the opposite configuration to that of the starting material, resulting in the stereomutation owing to inversion of one of two asymmetric silicons. Therein, the entering of the alkoxy group as well as leaving may take place at the apical position¹⁸, and the ring spans one apical and one equatorial position all the time to keep the Si-Si-CH₂ bond angle 90°. Although more electronegative groups are known to tend to occupy apical positions in at least phosphorus compounds^{18,21a}, we believe that in the present case the steric requirements, *i.e.* the angular requirements described above, exceed the generalization. In fact, recent X-ray structural determinations for pentacoordinate silicon compounds, such as PhSi(OCH₂CH₂)₃N²² and RSi(*o*-O₂C₆H₄)₂²³, show that they have a slightly distorted trigonal-bipyramidal structure with electronegative groups (oxygen atoms) at the equatorial positions owing to steric constraints.

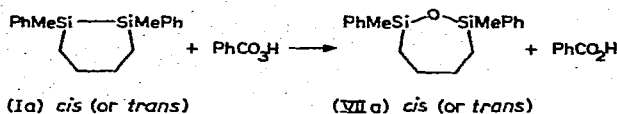
It has recently been reported that pseudorotation is observed by NMR for SiF₅⁻ and RSiF₄⁻ but not for Ph₂SiF₃⁻, and that R₃SiF₂⁻ can not exist as a ground state species owing to its instability²⁴. Furthermore, as pointed out by Sommer and Bauman¹⁶, a rapid stereomutation of alkoxy silanes formed from alcoholysis of fluorosilane suggests the possibility of mechanisms other than the pseudorotation route. From these considerations, it should be recognized that the exact mechanism of stereomutation of (IIa) remains rather obscure.

Stereospecific oxidation of (Ia) and (IIa)

Previously, it was reported from this Laboratory that the silicon-silicon bond is oxidized with perbenzoic acid to form quantitatively the corresponding siloxane bond and, on the basis of kinetic data, a molecular mechanism involving electrophilic attack of the oxygen atom was proposed as follows²⁵:



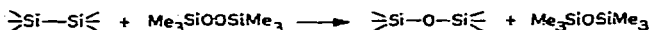
We have now found that the oxidation proceeds in a stereospecific fashion. Thus, both the *cis* and the *trans* isomer of the phenyl derivative (Ia) reacted with perbenzoic acid in dichloromethane at room temperature to afford quantitatively *cis*- and *trans*-2,7-dimethyl-2,7-diphenyl-1-oxa-2,7-disilacycloheptane (VIIa), respectively. Since both the starting isomers gave the different products, it is obvious that no equilibration is involved during the reaction⁶. Consequently, it follows that the isomer of (VIIa) formed from *cis*-(Ia) must be *cis* and the other *trans*. This very high



stereospecificity of reaction supports the above molecular mechanism.

As briefly mentioned earlier, the fluoro derivative (IIa) is air-sensitive. When oxygen was passed through the neat liquid at room temperature, both the *cis*- and the *trans*-(IIa) absorbed the gas to give *cis*- and *trans*-2,7-dimethyl-2,7-difluoro-1-oxa-2,7-disilacycloheptane (VIIb), respectively, in about 50% yield, leaving nonvolatile residue. For the initial several hours the reaction proceeded exothermally and, after about 50 hours, about 0.8 equivalent of oxygen was absorbed. The results indicate the stereospecific insertion of oxygen into the silicon-silicon bond. The facile aerobic oxidation of (IIa) is in good contrast with the behavior of compound (Ia) and 1,1,2,2-tetramethyl-1,2-disilacyclohexane⁵ which are little affected by oxygen, and suggests the acceleration effects by fluorine substitutions.

In connection with the aerobic oxidation, we have investigated the reaction of (Ia) and (IIa) with bis(trimethylsilyl) peroxide (BSPO)²⁶, and found that the reactions also proceed in the stereospecific fashion to yield the corresponding cyclic siloxane, while BSPO is converted to hexamethyldisiloxane:



Here again, the fluorine derivative (IIa) is much more reactive than the phenyl derivative (Ia), as shown in Table 4. The "fluorine effects" and the detailed discussion for these oxidations will be reported elsewhere.

TABLE 4

OXIDATION OF (Ia) AND (IIa) WITH BIS(TRIMETHYLSILYL) PEROXIDE

Compound (mmole)	BSPO ^a (mmole)	Conditions	Product yield (%)
$ \begin{array}{c} \text{RMeSi} \text{---} \text{SiMeR} \\ \text{[Cyclohexane ring]} \end{array} $			$ \begin{array}{c} \text{RMeSi} \text{---} \text{O} \text{---} \text{SiMeR} \\ \text{[Cyclohexane ring]} \end{array} $
(Ia), R = Ph			(VIIa), R = Ph
<i>cis</i> 0.354	0.846	80°, 55 h	<i>cis</i> 97.7
<i>trans</i> 0.446	0.947	80°, 55 h	<i>trans</i> 91.9 ^b
(IIa), R = F			(VIIb), R = F
<i>cis</i> 0.355	0.537	r.t., 1.5 h	<i>cis</i> 96.0
<i>trans</i> 0.238	0.356	r.t., 1.5 h	<i>trans</i> 96.3

^a Bis(trimethylsilyl) peroxide. ^b Conversion, ca. 92%.

EXPERIMENTAL

cis- And *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia)

To a di-Grignard reagent from 1,4-dibromobutane, prepared from 6 g (0.25

g-atom) of magnesium and 32 g (0.14 mole) of 1,4-dibromobutane in 250 ml of THF, a solution of 32 g (0.10 mole) of compound (IIIa) in 50 ml of THF was added with cooling in an ice bath over a period of 10 min. After 5-h reflux and removal of solvent by distillation, the remaining mass was hydrolyzed with saturated aqueous solution of ammonium chloride. The organic layer and the extracts were washed with water, sodium bicarbonate and then water, and dried over potassium carbonate. Distillation under reduced pressure gave 25 g of a liquid boiling over the range of 45–148°/2 mm, along with 6 g of residue. Fractionation through a column packed with glass helices yielded 20 g (74% yield) of (Ia) boiling at 157–159°/4 mm as a mixture of *cis* and *trans* isomer (*cis/trans* \approx 1/1.54), n_D^{20} 1.5848. Each isomer was isolated by repeated fractional distillation through a spinning band column. Purification was also possible by preparative GLC (Apiezon-L, 280°).

cis- And trans-1,2-bis(p-chlorophenyl)-1,2-dimethyl-1,2-disilacyclohexane (Ib)

Compound (IIIb) (38.0 g, 0.10 mole) diluted with 50 ml of THF was allowed to react with a di-Grignard reagent prepared from 32.6 g (0.15 mole) of 1,4-dibromobutane and 6.8 g (0.28 g-atom) of magnesium in 150 ml of THF. The reaction mixture was worked up in the same manner as described above. Simple distillation gave 34 g of a distillate boiling over the range of 60–205°/1.5 mm, in which the ratio of *cis* to *trans* lay in about unity. Fractional distillation through a short column packed with glass helices afforded the following two fractions: (1) 19 g, b.p. 196–201°/2 mm, consisting of *ca.* 60% of *cis* and 40% of *trans*, and (2) 7.5 g, b.p. 201°/2 mm, *trans* > 90%. Total yield of (Ib) was 72%. The *trans* isomer was readily isolated by fractional distillation through a spinning band column, whilst several repeated fractionations and recrystallization from ethanol were required for the purification of the *cis* isomer.

1,2-Dichloro-1,2-diphenyl-1,2-dimethyldisilane (IIIa)

To a solution of 228 g (1.0 mole) of *sym*-tetrachlorodimethyldisilane⁷ in 200 ml of THF was added a phenyl Grignard solution, prepared from 51.0 g (2.1 g-atom) of magnesium and 270 g (2.4 mole) of chlorobenzene in 800 ml of THF over a 2 h-period. The mixture was then refluxed for 10 h. After removal of THF by distillation, the remaining solid was filtered by using 600 ml of ether. The organic layer was distilled to give 272 g of a liquid boiling over the range of 110–200°/3 mm, along with 20 g of residue. Fractionation through a column packed with glass helices gave 161 g (52% yield) of a crystallizable material boiling at 141–146°/2 mm, m.p. 65.0–68.5° (in a sealed tube), which was contaminated with a small amount of 1,1-dichloro-2,2-diphenyl-1,2-dimethyldisilane. The above fraction was, however, used for the preparation of the compound (Ia) without recrystallization. A pure sample of (IIIa) could be obtained by recrystallization from dry *n*-hexane in about 30% yield. The highest melting point of those examined was 67.5–71.0°.

1,2-Bis(p-chlorophenyl)-1,2-dichloro-1,2-dimethyldisilane (IIIb)

The reaction was carried out in essentially the same way as described above, except for use of 294 g (2.0 mole) of *p*-dichlorobenzene instead of chlorobenzene. Distillation gave 230 g of a liquid boiling over the range of 120–225°/3 mm, together with 95 g of residue. Fractional distillation of the above distillate afforded 133 g (36% yield) of a crystallizable material boiling at 170–183°/1.5 mm (mainly 179–183°/

1.5 mm). Recrystallization from dry n-hexane gave pure (IIIb) in about 19% yield, melting at 85.0–89.5° (in a sealed tube).

Reduction of p-chlorophenyl (Ib) to phenyl derivative (Ia)

From trans-(Ib). To a mixture of 3.65 g (0.01 mole) of *trans*-(Ib), 6.8 g (0.30 g-atom) of magnesium and 100 ml of THF was added dropwise 31.8 g (0.20 mole) of ethyl bromide in the cold. The mixture was then heated to reflux with stirring for 35 h. A second portion of magnesium (3.4 g, 0.15 g-atom) and ethyl bromide (10.9 g, 0.10 mole) was added to the mixture, which was heated for an additional 16 h. The progress of the reaction was monitored by GLC of a small, extracted and hydrolyzed, sample. The reaction mixture was hydrolyzed and the organic layer and ether extracts were combined, and then distilled to give 3.3 g of an oily liquid boiling over the range of 110–180°/2 mm. Redistillation of this fraction gave 2.5 g (83% yield) of the phenyl derivative (Ia) boiling mainly at 139–141°/1 mm, being almost homogeneous by GLC. The retention time on GLC and NMR spectrum were exactly identical with those of an isomer of (Ia) having a longer retention time. A sample purified by preparative GLC had n_D^{20} 1.5873. (Found: C, 73.10; H, 8.19%.)

From cis-(Ib). *cis*-(Ib) was treated with ethyl bromide and magnesium in THF in essentially the same manner as described above. The reduced phenyl derivative (Ia) was purified by distillation and by preparative GLC, whose retention time on GLC and NMR spectrum were consonant with those of an isomer of (Ia) having a shorter retention time; n_D^{20} 1.5819. (Found: C, 73.15; H, 8.25%.)

Measurement of dipole moment of compound (Ib)²⁷

Solvent. Benzene was refluxed with anhydrous aluminum chloride (5–10%) for 2 h and distilled, washed to neutral, dried by refluxing over sodium wire and then carefully distilled through a Widmer column.

Apparatus. The dielectric constants were measured by the resonance method by using an apparatus built by Dr. K. Kimura, Osaka City University. The circuit diagram had been given by Le Fèvre *et al.*²⁸. The dielectric constant cell of a Higashi type²⁹, equipped with three concentric nickel electrodes, had the capacity of about 100 pF and a volume of ca. 10 ml. The densities of the solutions were measured in a pycnometer of a modified Lipkin type.

Procedure. Three or four solutions of each isomer in benzene were used with weight fractions between 0.002 and 0.02. They were prepared in glass-stoppered Erlenmeyer flask and stored in a desiccator. The measurements were made in a large thermostat maintained at 25.0°, filled with an oil which was stirred well. The dielectric cell was calibrated with air and with pure benzene, and the pycnometer with benzene.

Results. The dipole moments were obtained from the Debye equation:

$$\mu = 0.0128 \sqrt{(P_2 - 1.05MR_D) \cdot T} \text{ (D)}$$

The MR_D value was obtained by addition of bond refractions. The value of P_2 is given by the formula:

$$P_2 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M_2}{d_1} \cdot \left[1 + \frac{3a}{(\epsilon_1 - 1) \cdot (\epsilon_1 + 2)} - \frac{b}{d_1} \right]$$

TABLE 5

COMPOUND (Ib) WITH A SHORTER RETENTION TIME (*cis*)

$\omega_2 \times 100$	ϵ_{12}	$\omega_2 \times 100$	d_{12}
0	(2.2710) ^a	0	0.87283
0.2343	2.2785	0.3221	0.87352
0.5616	2.2875	1.527	0.87596
1.2088	2.3071	1.909	0.87673
1.8440	2.3258		

$a=2.97$ $b=0.205$
 $\mu=3.0_2$ D

^a Intercept.

TABLE 6

COMPOUND (Ib) WITH A LONGER RETENTION TIME (*trans*)

$\omega_2 \times 100$	ϵ_{12}	$\omega_2 \times 100$	d_{12}
0	(2.2712) ^a	0	0.87283
0.2959	2.2767	0.2485	0.87336
0.6926	2.2832	0.6006	0.87405
1.236	2.2930	1.415	0.87573
1.929	2.3048		

$a=1.75$ $b=0.205$
 $\mu=2.2_3$ D

^a Intercept.

The coefficients a and b , defined by the equations,

$$\epsilon_{12} = \epsilon_1 - a \cdot \omega_2$$

$$d_{12} = d_1 - b \cdot \omega_2$$

were determined from the plot of ϵ_{12} and d_{12} versus ω_2 , which are recorded in Tables 5 and 6.

The notations used here are: ϵ_1 and d_1 , dielectric constant and density of solvent; ϵ_{12} and d_{12} , those of solution; ω_2 , weight fraction of solute; M_2 , molecular weight of solute; P_2 , molar polarization of solute at infinite dilution.

Reaction of *sym*-tetraethoxydimethyldisilane with tetramethylenedimagnesium dibromide

To a Grignard reagent, prepared from 22 g (0.92 g-atom) of magnesium and 110 g (0.51 mole) of 1,4-dibromobutane in 500 ml of ether, was added a solution of 100 g (0.38 mole) of *sym*-tetraethoxydimethyldisilane⁹ in 200 ml of ether in the cold over a period of 20 min. The reaction mixture was stirred at room temperature for 2 h and then refluxed for 4 h. After removal of about 400 ml of ether, the remainder was heated for an additional 20 h. The resulting mass was filtered by use of about 200 ml of ether and the salt was washed with several 100 ml portions of ether. The filtrate was distilled to give, together with 41 g of residue, 24 g (27% yield) of 1-(diethoxy-

methylsilyl)-1-methyl-1-silacyclopentane (IV) as a colorless liquid homogeneous by GLC. The IR spectrum showed a group of bands at 1080, 1027 and 1033 cm^{-1} characteristic of the silacyclopentyl ring¹⁰.

1-(Difluoromethylsilyl)-1-methyl-1-silacyclopentane (V)

With cooling in an ice bath, to vigorously stirred concentrated sulfuric acid (200 g) was added dropwise 30 g (0.13 mole) of 1-(diethoxymethylsilyl)-1-methyl-1-silacyclopentane over a period of 30 min. After the addition was completed, 28 g (0.5 mole) of ammonium hydrogen fluoride was added in several portions at the same temperature. The resulting organic layer was flash-distilled under reduced pressure and the subsequent fractional distillation gave 16 g (68% yield) of compound (V).

1-(Diphenylmethylsilyl)-1-methyl-1-silacyclopentane (VI)

To a phenyl Grignard reagent, prepared from 5 g (0.20 g-atom) of magnesium and 35 g (0.22 mole) of bromobenzene in 50 ml of ether, was added 15 g (0.083 mole) of 1-(difluoromethylsilyl)-1-methyl-1-silacyclopentane over 10 min, and the mixture was then refluxed for 15 h. Work-up and fractional distillation gave 18 g (55% yield) of 1-(diphenylmethylsilyl)-1-methyl-1-silacyclopentane (VI). The IR spectrum showed a group of absorption bands at 1080, 1027 and 1035 cm^{-1} characteristic of the silacyclopentyl ring¹⁰. The product was homogeneous by GLC and had a shorter retention time than both the *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia).

cis- And *trans*-1,2-dimethyl-1,2-difluoro-1,2-disilacyclohexane (IIa)

In a typical run, to a stirred concentrated sulfuric acid (98 g; 1.0 mole) was added 29.7 g (0.1 mole) of compound (Ia) (*cis/trans* $\approx 1/1.66$) in the cold (below 3°) over a period of 1.5 h and the mixture was then stirred for an additional 2 h at the same temperature. With cooling, 13 g (0.228 mole) of ammonium hydrogen fluoride was then added in several portions. Distillation of an organic layer under a nitrogen stream gave 16.5 g (92% yield) of the fluoro derivative (IIa), as an isomeric mixture in the ratio of *cis/trans* $\approx 1/1.82$, boiling over the range of 90–95°/100 mm. Each isomer was isolated by preparative GLC (Silicone DC 550, 110°). A collecting tube had to be equipped for a nitrogen atmosphere, since the fluoro derivative (IIa) was readily oxidized with oxygen even at room temperature.

Analogously, 1 g of the pure *cis*-(Ia) was treated with 2 g of H_2SO_4 and then with ammonium hydrogen fluoride (1 g) with cooling. An isomeric mixture of (IIa) in the ratio of *cis/trans* $\approx 1/1.69$ was formed. The ratio of *cis* to *trans* isomer of (IIa) formed from the pure *trans*-(Ia) also lay in about 1/1.86. These data are collected in Table 3.

Phenylation of (IIa)

From an isomer having the shorter retention time. An isomer (0.15 g) having the shorter retention time on GLC, freshly isolated, was treated with phenylmagnesium chloride in THF. Predominant formation of *trans* isomer of (Ia), *cis/trans* $\approx 3/97$, was shown by GLC analysis of a hydrolyzed sample of the reaction mixture. The ¹H NMR spectrum of the product isolated by preparative GLC was superimposable with that of the authentic sample of *trans*-(Ia). In another run, essentially the same result was obtained.

From an isomer having the longer retention time. Similarly, an isomer (0.14 g) of (IIa) having the longer retention time was phenylated, resulting in the predominant formation of *cis* isomer of (Ia), *cis/trans* \approx 91/9. The retention time on GLC and the ^1H NMR spectrum of the products were coincident with those of the authentic samples. In another run, essentially the same result was obtained.

1,2-Dichloro-1,2-dimethyl-1,2-disilacyclohexane (IIb)

(a). To cold concentrated sulfuric acid (98 g; 1 mole) was added dropwise 14.8 g (0.05 mole) of (Ia) (*cis/trans* \approx 1/1.7) with vigorous stirring over a period of $1\frac{1}{2}$ h. After an additional 2 h stirring, 16 g (0.3 mole) of ammonium chloride was added in several portions with cooling. Flash distillation and subsequent fractionation of the separated organic layer gave 8.2 g (77% yield) of (IIb) boiling at $90^\circ/18$ mm.

(b). To a solution of 15 g (0.051 mole) of *cis*-(Ia) in 100 ml of chloroform was added 0.8 g of freshly sublimed aluminum chloride. Dry hydrogen chloride was passed through the above mixture in the cold (an ice bath) for the first 1 h and then at room temperature for 14 h. Evaporation of chloroform under reduced pressure was followed by fractional distillation through a short column packed with glass helices to afford 5.5 g (51% yield) of (IIb) having b.p. $107\text{--}108^\circ/35$ mm, n_D^{20} 1.4972, d_4^{20} 1.0904; MR_D 57.25. (Found: C, 34.31; H, 6.90; Cl, 32.70%.)

The similar reaction using 21 g (0.071 mole) of *trans*-(Ia), 1 g of aluminum chloride and 150 ml of chloroform yielded 8.5 g (56% yield) of (IIb); b.p. $102^\circ/27$ mm, n_D^{20} 1.4973, d_4^{20} 1.0915; MR_D 57.21. (Found: C, 33.76; H, 6.78; Cl, 33.34%.)

The NMR spectra of (IIb) obtained from all the above methods revealed that the methyl group protons absorb at 9.43τ as a singlet. Compound (IIb) was almost homogeneous by GLC on all packing materials examined (Silicone DC550, Apiezon-L and SE30).

Phenylation of (IIb)

By the method (a) described above, the pure *cis*-(Ia) was treated with sulfuric acid (10 g) and subsequently with ammonium chloride (3 g). The organic layer was phenylated with excess phenylmagnesium chloride in THF to form, after hydrolysis, an isomeric mixture of (Ia) in the ratio of *cis/trans* \approx 1/2.3. With *trans*-(Ia), the similar result (*cis/trans* \approx 1/2.5) was obtained.

Compound (IIb) obtained from *cis*-(Ia) by the method (b) above was treated with excess phenylmagnesium chloride to give a mixture of *cis*- and *trans*-(Ia) in the ratio of about 1/2.8. Phenylation of (IIb) from *trans*-(Ia) also resulted in the formation of an isomeric mixture of (Ia) in the ratio of *cis/trans* \approx 1/3.2.

Stereomutation of *cis*- and *trans*-(IIa)

By the action of H_2SO_4 . A pure sample of the *cis* isomer of (IIa) (ca. 0.05 g), benzene (1 ml) and concentrated H_2SO_4 (1 ml) were shaken at room temperature. The progress of the isomerization was followed by GLC. The equilibration was already accomplished after about 1 h. Addition of ammonium hydrogen fluoride did not change the isomeric ratio of *cis/trans* \approx 1/1.82.

Similarly, the *trans* isomer (0.1 g), benzene (1 ml) and H_2SO_4 (2 g) were combined and shaken at room temperature. Equilibration was achieved after about 3 h. The ratio of *cis* to *trans* lay in about 1/1.83.

By the action of EtOH. The *cis* isomer (35 μ l), EtOH (20 μ l) and n-hexane (1 ml) were combined and allowed to stand at room temperature. The progress of the isomerization was followed by GLC. The relatively slow isomerization was observed. After overnight, the ratio of *cis* to *trans* was about 1/2.21.

A solution of the *trans* isomer (30 μ l) and EtOH (30 μ l) in 1 ml of benzene was allowed to stand at room temperature. The isomerization was much slower than that under the influence of H₂SO₄. After 45 h, the ratio of *cis* to *trans* was 1/1.99.

The progress of the isomerization of *cis* and *trans* isomer of compound (IIa) under the influence of ethanol in benzene solution was measured. Each isomer was used within a day of purification, because the compound is readily oxidized by air and isomerized to each other even by moisture. All vessels used here (measuring flasks, pipettes and reaction vessels) were filled with nitrogen. The reaction vessel was a glass-stoppered 10-ml test tube. To carry out a rate experiment, a solution of the sample (2.0 ml) was placed in the test tube, which was immersed in a thermostat bath (30.0 \pm 0.1 $^{\circ}$), and the solution of ethanol (2.0 ml) was then added rapidly. The decrease in amounts of one isomer and the increase of another were analyzed at intervals through the course of the reaction by GLC (Silicone DC550, 89 $^{\circ}$, He flow rate 12–13 ml/min). The results are plotted against time in Fig. 2.

Reaction of (Ia) with perbenzoic acid

To compound (Ia) (1.5 g; 5 mmole) was added a solution of perbenzoic acid (13.5 mmole) in methylene chloride (25 ml) and the mixture was allowed to stand overnight at room temperature. GLC analysis showed that the starting material was completely consumed, while a new homogeneous product formed quantitatively. After washing with saturated aqueous solution of sodium bicarbonate to remove benzoic acid formed and excess of the peracid, the product was isolated by preparative GLC. *cis*-(Ia) formed the *cis* isomer of the corresponding cyclic disiloxane, 2,7-diphenyl-2,7-dimethyl-1-oxa-2,7-disilacycloheptane (VIIa).

Similarly, *trans*-(Ia) yielded *trans*-(VIIa).

The IR spectrum showed the absorption band characteristic of the siloxane bond at 1013 cm⁻¹ for both the *cis*- and *trans*-(VIIa). The retention time on GLC of the *cis*-(VIIa) was shorter than that of the *trans* isomer.

Oxidation of (IIa) with oxygen

Oxygen was passed through 1.8 g (10 mmole) of *cis*-(IIa) at room temperature. Slightly exothermic reaction occurred for the initial several hours. After 59 h, 205 ml of oxygen was absorbed and GLC analysis revealed that the starting material was no longer present. The volatile product was distilled under reduced pressure (boiling up to 55 $^{\circ}$ /15 mm) to give 1.2 g of *cis*-2,7-difluoro-2,7-dimethyl-1-oxa-2,7-disilacycloheptane (VIIb), leaving 0.5 g of residue. The product was almost homogeneous by GLC and the stereospecificity was over 97%. Preparative GLC (Silicone DC550, 135 $^{\circ}$) afforded a pure sample of the siloxane (VIIb).

trans-(IIa) was allowed to react with oxygen for 40 h in essentially the same manner as described above. Distillation yielded 1.1 g of *trans*-(VIIb), together with 0.5 g of residue. After purification by preparative GLC, the siloxane showed n_D^{20} 1.4020. (Found: F, 19.47%.) The stereospecificity was again over 97%. The IR spectrum showed a strong band at 1045 cm⁻¹ due to ν (Si-O) for both the *cis*- and *trans*-(VIIb).

Reaction of (Ia) and (IIa) with bis(trimethylsilyl) peroxide

Bis(trimethylsilyl) peroxide was prepared in essentially the same manner reported by Hahn and Metzinger²⁶, except using 90% hydrogen peroxide in place of anhydrous peroxide. Moreover, to remove hydrogen chloride formed, ammonia was used in place of pyridine.

The reactions were carried out in a small, sealed glass tube. The GLC analysis revealed that the reaction proceeded in a stereospecific fashion to form the corresponding cyclic siloxane, as well as hexamethyldisiloxane arising from the peroxide. The product was isolated by preparative GLC and their IR spectra were compared with those of authentic samples. The yield was estimated by GLC by comparison of the peak areas with the area of a standard substance added. For the reaction of (Ia) it was necessary to heat for a prolonged period of time, whilst the reaction of (IIa) was slightly exothermic. The results are collected in Table 4.

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REFERENCES

- 1 K. TAMAO, M. ISHIKAWA AND M. KUMADA, *J. Chem. Soc. D*, (1969) 73.
- 2 L. H. SOMMER AND C. L. FRYE, *J. Amer. Chem. Soc.*, 81 (1959) 1013.
- 3 L. H. SOMMER, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill, New York, 1965.
- 4 (a) L. H. SOMMER AND R. MASON, *J. Amer. Chem. Soc.*, 87 (1965) 1619;
(b) L. H. SOMMER AND K. T. ROSBOROUGH, *J. Amer. Chem. Soc.*, 89 (1967) 1756; 91 (1969) 7067.
- 5 M. KUMADA, K. TAMAO, T. TAKUBO AND M. ISHIKAWA, *J. Organometal. Chem.*, 9 (1967) 43.
- 6 E. L. ELIEL, *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York, 1962, Chapter 7.
- 7 H. SAKURAI, T. WATANABE AND M. KUMADA, *J. Organometal. Chem.*, 7 (1967) P15.
- 8 R. K. SUMMERBELL, B. S. SOKOLSKI, J. P. BAYS, D. J. GODFREY AND A. S. HUSSEY, *J. Org. Chem.*, 32 (1967) 946.
- 9 M. KUMADA, M. YAMAGUCHI, Y. YAMAMOTO, J. NAKAJIMA AND K. SHIINA, *J. Org. Chem.*, 21 (1956) 1264.
- 10 N. S. NAMETKIN, V. D. OPPENGEIM, V. I. ZAV'YALOV, K. S. PUSHCHEVAYA AND V. M. VDOVIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1965) 1547.
- 11 J. W. EMSLEY, J. FEENEY AND L. H. SUTCLIFFE, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 1, Pergamon Press, Oxford, 1965, pp. 559-573.
- 12 F. FÉHER, P. PLICHTA AND R. GUILLERY, *Tetrahedron Lett.*, (1970) 2889.
- 13 C. EABORN, *J. Chem. Soc.*, (1952) 2846.
- 14 Ref. 3, Chapter 8.
- 15 L. H. SOMMER AND P. G. RODEWALD, *J. Amer. Chem. Soc.*, 85 (1963) 3898.
- 16 L. H. SOMMER AND D. L. BAUMAN, *J. Amer. Chem. Soc.*, 91 (1969) 7045.
- 17 R. S. BERRY, *J. Chem. Phys.*, 32 (1960) 933.
- 18 (a) F. H. WESTHEIMER, *Accounts Chem. Res.*, 1 (1968) 70;
(b) E. L. MUETTERTIES, *Accounts Chem. Res.*, 3 (1970) 266;
(c) K. MISLOW, *Accounts Chem. Res.*, 3 (1970) 321;
(d) F. RAMIREZ, *Bull. Soc. Chim. Fr.*, (1970) 3492.
- 19 J. W. LINNETT AND C. E. MELLISH, *Trans. Faraday Soc.*, 50 (1954) 665.
- 20 J. ZEMANN, *Z. Anorg. Allg. Chem.*, 324 (1963) 241.

- 21 (a) E. L. MUETTERTIES AND R. A. SCHUNN, *Quart. Rev.*, 20 (1966) 245; (b) B. J. AYLETT, *Progr. Stereochem.*, 4 (1969) 213.
- 22 F. P. BOER, J. W. TURLEY AND J. J. FLYNN, *J. Amer. Chem. Soc.*, 90 (1968) 5102.
- 23 F. P. BOER, J. J. FLYNN AND J. W. TURLEY, *J. Amer. Chem. Soc.*, 90 (1968) 6973.
- 24 F. KLANBERG AND E. L. MUETTERTIES, *Inorg. Chem.*, 7 (1968) 155.
- 25 H. SAKURAI, T. IMOTO, N. HAYASHI AND M. KUMADA, *J. Amer. Chem. Soc.*, 87 (1965) 4001.
- 26 W. HAHN AND L. METZINGER, *Makromol. Chem.*, 21 (1956) 113.
- 27 F. DANIELS, J. H. MATHEWS, J. W. WILLIAMS, P. BENDER AND R. A. ALBERTY, *Experimental Physical Chemistry*, McGraw-Hill, New York, 6th ed., 1962, pp. 212-231.
- 28 R. J. W. LE FÉVRE, I. G. ROSS AND B. M. SMYTHE, *J. Chem. Soc.*, (1950) 276.
- 29 Y. MORINO AND I. MIYAGAWA, *Kagaku ho Ryoiki, Extra Ed.*, No. 8 (1953) p. 1 ff.

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