Synthesis, resolution, and absolute configuration of 1-phenyl-1-methyl-1-silacyclohexanone-2^{1,2}

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The synthesis and resolution of 1-phenyl-1-methyl-1-silacyclohexanone-2 by oxidative hydroboration of the related silacyclohexene to the silacyclohexanol, resolution of this via the strychnine salt of the phthalate half-ester, and subsequent oxidation of the silacyclohexanol to the silacyclohexanone is described. The carbon analog 1-phenyl-1-methylcyclohexanone-2 was also synthesized in optically active form. The (+)-enantiomers of the two ketones had similar optical rotatory dispersion curves, presenting convincing evidence for the identity of their configurations, and the carbon compound could be degraded without affecting the asymmetric center to (-)-(R)-2-phenyl-2-methylhexandioic acid, thereby establishing the absolute configurations of both compounds.

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As part of our continuing interest in the chemistry of acylsilanes (1) we have resolved and determined the absolute configuration of 1-phenyl-1methyl-1-silacyclohexanone-2 (1). At the time that this research was initiated only two cyclic systems containing an asymmetric silicon center in the ring were known. These were 2(2), and 3(3). In these latter systems, the resolving agent,



an optically active amino acid for 2, and l-menthol for 3 were bonded directly to the asymmetric silicon center through reactive Si-O and Si-N bonds. These methods did not appear to be suitable for the resolution of cyclic acylsilanes; however, certain developments discussed below suggested that a resolution might be effected through the carbinol precursor to the ketone 1, 1-phenyl-1-methyl-1-silacyclohexanol-2 (8).

It has been shown previously that hydroboration of cyclic silvalkenes such as 1,1-diphenylsilacyclohexene-2 (4) results in the formation of the α -silylcarbinol, 5, as the only isolated product (see Scheme 1) (4). The carbinol can then be oxidized in reasonable yield using the DMSO/



dicyclohexylcarbodiimide (DCC) reagent to the corresponding acylsilane 6.

Upon investigating such a synthetic route to the ketone, 1, it was found that treatment of racemic 1-phenyl-1-methyl-1-silacyclohexene-2 (7) with excess diborane resulted after oxidative workup in the carbinol 8, whose gas-liquid phase chromatography (g.l.p.c.) analysis showed that it consisted of the two possible diastereomeric carbinols in the proportions of about 95:5 (Scheme 2).

That the diastereomeric carbinols had indeed



¹Taken in part from the M.Sc. thesis of H. W. Kucera, University of Toronto, 1968.

Part of this material was presented at the Second International Symposium on Organosilicon Chemistry, Bordeaux, France, July, 1968, Abstracts Page 26. ³Holder of an NRCC Bursary, 1966–1967.

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been separated on the column was shown by reducing the racemic acylsilane 1, with diisopinocamphenylborane (R_2BH) (5). A g.l.p.c. analysis of the crude reduction product indicated that approximately equal amounts of the diastereomeric carbinols had been produced.

Thus, although the reaction of R_2BH with the ketone exhibits low stereoselectivity, the reaction of B_2H_6 with the alkene 7, is highly stereoselective. This remarkable fact makes it possible to introduce a second reactive asymmetric center into the molecule, whose configuration is directly related to the configuration at the silicon center. We are attempting to establish the configuration at the carbinol center of the predominant diastereomer.

It seemed feasible to resolve this system through its new asymmetric carbinol center, and a successful resolution was achieved through the phthalic acid-ester of the α -silylcarbinol 8. This material could be crystallized to diastereomeric purity since the carbinol isolated from the hydrolysis of the crystalline acid-ester showed only one peak by g.l.p.c. analysis, corresponding to the more abundant diastereomer.

On preparing the strychnine salt of the acidester in chloroform-acetone, the less soluble diastereomer precipitated and could be recrystallized readily to a constant melting point and rotation. Reisolation of the carbinol ($[\alpha]_D^{25}$ -73.5°) and oxidation with DMSO using the method reported by Brook and Pierce (4) gave the optically pure ketone, $[\alpha]_D^{24} - 160^\circ$. Isolation of the carbinol from the more soluble strychnine salt followed by oxidation gave (+)-1 of lower optical purity, $[\alpha]_D^{24} + 73.5^\circ$. The optical rotatory dispersion (o.r.d.) spectrum of (+)-1 showed a positive Cotton effect with a maximum at 400 mµ⁵ as shown in Fig. 1.

A considerable amount of effort was expended in trying to devise a workable scheme whereby the absolute configuration of 1 could be determined by degradative reactions. However, the stereochemistry to be expected in displacement reactions at silicon in a new cyclic silicon system is uncertain, since the rules found to apply to Sommer's acyclic 1-naphthylphenylmethylsilyl system (6) are not always applicable to Corriu's cyclic 2-(1-naphthylsila)-1,2,3,4-tetrahydronaph-



FIG. 1. Optical rotatory dispersion curves obtained in cyclohexane for the analogous carbon and silicon cyclohexanones. *The amplitude of the curve for the carbon ketone is not on an absolute scale since the optical purity of this material is unknown.

thalene system (3) (3, 7). Therefore, chemical degradation to compounds of known absolute configuration was considered to be a hazardous and unreliable approach.

The possibility of relating the configurations of the silicon ketone, **1** and its carbon analog **9**, was considered. The relation of the configuration at the silicon and carbon centers could be based upon the reasonable assumption that analogous silicon and carbon compounds with similar o.r.d. curves and Cotton effects of the same sign have the same absolute configuration, as was proposed and confirmed in earlier studies (8).

The resolution of 1-phenyl-1-methylcyclohexanone-2 (9) (9), has not been previously reported. Thus, a method for resolving this ketone had to be found. The method used for the analogous silicon ketone was not considered practical, since hydroboration of the alkene 10 would be expected to give rise to a mixture of products bearing the carbinol function at the 2 and 3 positions (10).

Instead it was decided to reduce selectively one enantiomer of the ketone 9 (Scheme 3), using 1/2mole-equivalent of optically active diisopinocamphenylborane (R₂BH) (5). Selective reduction

⁵The interpretation of the o.r.d. spectra in these systems is currently under study in these laboratories.



was carried out at 0 °C in diglyme to yield after separation of the carbinol, **12**, residual ketone **9**, $[\alpha]_D^{25} + 35.4^\circ$. The optical purity of this ketone has not been determined; however, this is not important for the work that follows.

The recent work of Cram and Hoffman (11) in which they report the absolute configuration of (-)-(R)-2-phenyl-2-methylhexandioic acid 14, greatly simplified the approach to the determination of the absolute configuration of 9. The degradation used was as follows (Scheme 4):



The ketone, (+)-9, was converted to its tosylhydrazone, 13, in absolute ethanol in the presence of a few drops of glacial acetic acid and this in turn was converted directly to the alkene (-)-10 by treatment with 2 mole-equivalents of *n*butyllithium in ether (12). The alkene was then oxidized with sodium periodate in the presence of a catalytic amount of potassium permanganate (13) to the diacid (-)-14. The spectral characteristics and mixed melting point with authentic material prepared by an alternate route (14) confirmed the identity of this compound.

Since (+)-9 gave rise to (-)-14 via a series of reactions not involving the asymmetric center, it is possible to assign the absolute configuration of (+)-9 as R, as shown.

Furthermore, since (+)-(R)-9 has a positive Cotton effect, it is reasonable to assign the same absolute configuration to the cyclic acylsilane (+)-(R)-1 as shown since it also exhibits a positive Cotton effect having a similar character.

This work represents the first assignment of

absolute configuration to a cyclic organosilicon compound, asymmetric at silicon. Furthermore, it prepares the way for the assignment of absolute configurations to a number of other compounds. For example, treatment of (+)-(R)-1 with diazomethane (15) (Scheme 5), gives rise to (-)-(S)-1-phenyl-1-methyl-1-silacycloheptanone-3 (15) as the major product whose configuration must be as shown since this reaction has been demonstrated to proceed with retention of configuration at silicon (16). Minor amounts of material presumed to be 16 on the basis of nuclear magnetic resonance (n.m.r.) data were detected.



Hopefully, it will be possible to relate the stereochemistry of this system to other systems such as Corriu's naphthylsilatetralene compounds (3) whose absolute configurations have not yet been established.

Experimental

General

Nuclear magnetic resonance spectra were run on either a Varian A-60 or A-56/60 instrument using carbon tetrachloride or deuterochloroform as specified. Infrared (i.r.) spectra were obtained on a Perkin-Elmer model 237-B grating i.r. spectrophotometer in carbon tetrachloride or as a liquid film as specified. Ultraviolet (u.v.) spectra were obtained on a Perkin-Elmer model 350 spectrophotometer in the solvent specified.

Optical rotations were obtained on a Galileo manual polarimeter at the Sodium D line using a 1 dm cell. Optical rotatory dispersion spectra were obtained on a Jasco Model ORD/UV-5 spectrophotometer.

Boiling points and melting points are uncorrected.

Preparation of 1-Phenyl-1-methyl-1-silacyclohexene-2 (7) To 34.0 g (0.204 mole) of 1,1-dichloro-1-silacyclohexene-2 (17) in 125 ml anhydrous ether were added 145 ml (0.213 mole) of phenyllithium solution, over a period of 30 min. The mixture was left at ambient temperature for 22 h and then the clear solution was decanted off leaving a precipitate of lithium chloride. The ether was removed on a rotary evaporator and the residue was distilled under vacuum. Three fractions were isolated. The first consisted of 6.7 g (20%) of unreacted 1,1-dichloro-1-silacyclohexene-2, the third of 4.5 g (9%) of 1,1-diphenyl-1-silacyclohexene-2.

The central fraction consisted of 24.1 g (57%) of 1-chloro-1-phenyl-1-silacyclohexene-2, b.p. 120–125° (4.5 mm). This was not characterized but methylated directly with methylmagnesium bromide.

To a solution of 19.4 g (0.093 mole) of 1-chloro-1phenyl-1-silacyclohexene-2 in 100 ml anhydrous tetrahydrofuran (THF) was added 0.21 mole of methylmagnesium bromide solution (1.5 M in ether). Most of the diethyl ether was distilled off and the residual THF solution was refluxed overnight. The mixture was acidified with 10% HCl solution and extracted 3 times with diethyl ether. The combined ether extracts were washed with dilute sodium bicarbonate solution and were dried over anhydrous magnesium sulfate. Removal of the ether on a rotary evaporator followed by distillation of the high boiling residue gave 16.1 g (93%) of the desired alkene, b.p. 80–84° (0.8 mm); i.r. (film) λ_{max} 6.29 (C=C), 7.0, 9.0 (SiPh), 8.0 (SiMe) μ; n.m.r. (CCl₄) δ 7.2-7.6 (Ar, complex, 5), 6.9 (olefinic, doublet (J = 14 c.p.s.) of triplets (J = 4 c.p.s.), 1), 5.8 (olefinic, d, J = 14 c.p.s., 1), 1.7-2.4 (aliph, m, 4) 0.7-1.1 (aliph, m, 2), 0.35 (SiMe, s, 3) p.p.m.

Anal. Calcd. for $C_{12}H_{16}Si: C, 76.52; H, 8.57$. Found: C, 76.35; H, 8.38.

Preparation of 1-Phenyl-1-methyl-1-silacyclohexanol-2 (8)

To a solution of 16.5 g (0.088 mole) of 1-phenyl-1methyl-1-silacyclohexene-2 in 40 ml of anhydrous THF cooled with an ice bath were added 100 ml of diborane solution (1.0 M in THF) over 30 min. After the addition was complete, the mixture was left at 0° for an additional 4 h and then the solvents were removed on a rotary evaporator. The residual oil was carefully acidified with 5% HCl solution and was extracted 3 times with ether. Removal of the ether from the combined extracts on a rotary evaporator left a viscous oil which was dissolved in 175 ml of THF. This solution was cooled on an ice bath and a solution of 2.5 g of sodium hydroxide (0.063 mole) in 45 ml water was added, followed by 35 ml of 30% hydrogen peroxide solution. The mixture was left at room temperature for 18 h and then was acidified with 10% HCl solution. The organic products were isolated by 3 ether extractions. After drying the combined extracts over anhydrous magnesium sulfate, the ether was removed on a rotary evaporator and the residue was distilled. The desired carbinol, 15.0 g (84%) was isolated as a constant boiling fraction, b.p. 117° (0.4 mm); i.r. (film) λ_{max} 2.8–3.1 (OH), 7.0, 9.0 (SiPh), 8.0 (SiMe) μ ; n.m.r. (CCl₄) & 7.2-7.6 (Ar, m, 5), 3.35-3.7 (CHOH, m, 1), 0.5-2.0 (aliph, m, 8), 0.25 (SiMe, s, 3) p.p.m.

Anal. Calcd. for C₁₂H₁₈SiO: C, 69.84; H, 8.79. Found: C, 69.49; H, 8.88.

An n.m.r. spectrum in DMSO showed a doublet at δ 4.2 p.p.m. $J_{AB} = 4.5$ c.p.s., which disappeared on the addition of D₂O. This is consistent with the secondary carbinol function.

The g.l.p.c. analysis of this carbinol using a 10 ft, 10% neopentylglycol sebacate column at 225 °C indicated a 95:5 ratio of the two possible diastereometric carbinols.

Resolution of 1-Phenyl-1-methyl-1-silacyclohexanone-2 (1)

(a) Preparation of the Phthalic Acid-ester of 1-Phenyl-1-methyl-1-silacyclohexanol-2

A solution containing 68 g (0.33 mole) of 1-phenyl-1methyl-1-silacyclohexanol-2, 49 g (0.33 mole) of phthalic anhydride, and 50 ml of pyridine in 300 ml of dry benzene was refluxed for 3 h. The solvent was then removed on a rotary evaporator and the residue was extracted with dilute sodium bicarbonate solution. The aqueous phase was washed with ether to remove any non-acidic organic residues. Acidification of the aqueous phase with 10% HCl precipitated the acid-ester as an oil which was extracted with chloroform. The chloroform solution was then dried over anhydrous sodium sulfate and the solvent was removed on a rotary evaporator. The residual oil was taken up in approximately 300 ml of carbon tetrachloride and 700 ml of petroleum ether (b.p. $60-70^\circ$) were added. On cooling to 5° the acid-ester crystallized in hemispherical clusters, over a period of 4 days.

The crude crystals were filtered and recrystallized 3 times from the same mixed solvent system (2:3, CCl₄: petroleum ether (60–70 °C)) to yield 68 g (57%) of pure acid-ester, m.p. 116–118 °C.

Anal. Calcd. for $C_{20}H_{22}O_4Si$: C, 67.76; H, 6.26. Found: C, 67.55; H, 6.15.

(b) Resolution of the Phthalic Acid-Ester of 1-Phenyl-1methyl-1-silacyclohexanol-2

To 15 g (0.042 mole) of the acid-ester in 400 ml of acetone at reflux, were added 14 g (0.042 mole) of strychnine partially dissolved in 50 ml chloroform. This mixture was left at reflux for 10 min and then cooled to 5 °C. The less soluble diastereomer crystallized from the solution overnight, yielding 10.9 g (38%) of colorless crystals, m.p. 225–230 °C (decomposition).

The strychnine salt was recrystallized to constant melting point and optical rotation using the following procedure. The salt was dissolved in excess chloroform (50 ml CHCl₃ for every 10 g of salt) and the solution was then concentrated to approximately half its volume on a rotary evaporator. To this solution at reflux was added hot acetone (150 ml acetone per 10 g of salt). Crystallization commenced almost immediately and after approximately 1 h the solution was filtered and the crystals were washed with acetone. Table 1 summarizes the relevant recrystallization data.

TABLE 1

Resolution of silacyclohexanol acid phthalate

Recrystallization no.	Yield (g)	[α] _D ²³ (°)	Melting point (°C)
1	8.3	- 61	225-230
2	5.5	- 58	228-230
3	4.8	- 59	230-231
4	4.2	- 59	229-230

(c) Reisolation of the Acid-Ester

To a suspension of 4.0 g (0.0057 mole) of the strychnine salt of the acid-ester ($[\alpha]_{D}^{25} - 59^{\circ}$) in 50 ml of ether were added 50 ml of 10% HCl and the mixture was stirred vigorously for 15 min. To this were added 100 ml water and the suspension was filtered to remove the precipitated strychnine hydrochloride. This precipitate was then washed well with ether and the ether phase was isolated and was extracted with dilute sodium bicarbonate solution. Acidification of the bicarbonate phase with 10% HCl precipitated the acid-ester as an oil which was isolated by ether extraction in the normal fashion. The residue, on removing the ether on a rotary evaporator, was crystallized from 20 ml of *n*-hexane and sufficient carbon tetrachloride such that the acid-ester did not oil out on cooling to -20 °C. After a few weeks at this temperature the acid-ester had precipitated to yield 1.5 g (75%) of the crystalline acid-ester, $[\alpha]_D^{24} + 150^\circ$ (CHCl₃), m.p. 84–86 °C. A second recrystallization did not alter the optical rotation although the melting point range was changed to 85–86 °C. An i.r. spectrum of this material in carbon tetrachloride was identical to that of the racemic acid-ester.

(d) Hydrolysis of the Acid-ester

To 17 g (0.048 mole) of the resolved acid-ester (from the strychnine salt having $[\alpha]_D^{24} - 59^\circ$, m.p. 230–231 °C) in 30 ml THF were added 100 ml of 1.5 N sodium hydroxide solution. The mixture was then heated on a steam bath for 15 min and then was extracted with ether. The aqueous phase was again heated on a steam bath for an additional 15 min and then was extracted with ether. This cycle was repeated 2 more times. In the last cycle the aqueous phase was heated for 1 h on the steam bath. The carbinol was isolated from the ether extracts in the normal manner. Distillation of the residue gave 7.4 g (75%) of the desired optically active carbinol, b.p. 85– 95 °C (0.2 mm). This material solidified on standing to a waxy solid m.p. 32.5–33°, $[\alpha]_D^{22} - 73.5^\circ$. The n.m.r. and i.r. spectra of this material were identical to those of an authentic sample of racemic carbinol.

(e) The Oxidation of 1-Phenyl-1-methyl-1silacyclohexanol-2 (8)

To a solution of 7.43 g (0.0361 mole) of the resolved 1-phenyl-1-methyl-1-silacyclohexanol-2 and 12.4 g (0.062 mole) of dicyclohexylcarbodiimide in a solvent mixture of 30 ml anhydrous ether and 100 ml dry DMSO (distilled from calcium hydride) were added slowly 7.0 g (0.036 mole) of pyridinium trifluoroacetate in 50 ml dry DMSO. This mixture was left overnight, under nitrogen, at room temperature. It was then filtered to remove the precipitated dicyclohexylurea and the precipitate was washed well with ether. The filtrate was extracted with 100 ml of water and the aqueous phase in turn was reextracted with ether. The combined ether phases were then washed well with water to remove any DMSO and then were dried over anhydrous magnesium sulfate. Removal of the ether on a rotary evaporator left a residue which was distilled on a spinning band column to yield 4.20 g (57%) of the desired ketone, b.p. 85° (0.02 mm) $n_{\rm D}^{21}$ 1.5448, $[\alpha]_{\rm D}^{24}$ -160° (c, 2.15, cyclohexane); i.r. (film) λ_{max} 6.08 (C=O) μ ; n.m.r. (CCl₄) δ 7.4 (Ar, m, 5) 2.4 (COCH₂, t, (J = 6 c.p.s.), 2), 1.0–2.0 (aliph, m, 6), 0.4 (SiMe, s, 3) p.p.m.; u.v. λ_{max} (ϵ) (cyclohexane) 336 (157), 361 (217), 390 (204) mµ.

Anal. Calcd. for C₁₂H₁₆OSi: C, 70.53; H, 7.89. Found: C, 70.54; H, 7.84.

1-Phenyl-1-methylcyclohexanone-2 (9)

The ketone, **9**, was prepared according to the literature procedure (9). However, g.l.p.c. analysis of the product indicated presence of a small amount of material tentatively identified as 1-methyl-3-phenylcyclohexanone-2. This could be removed by chromatography on neutral alumina with carbon tetrachloride, or by preparative g.l.p.c. on 20% SE-30 on Chromosorb W. Boiling point 98° (1.5 mm) $n_D^{25} = 1.5327$; i.r. (carbon tetrachloride) $\lambda_{max} 5.84$ (C=O) μ ; n.m.r. (CCl₄) δ 7.0–7.5 (Ar, m, 5), 2.7, 2.25, 1.8 (aliph, 3m, 8), 1.2 (CMe, s, 3).

Selective Asymmetric Reduction of 1-Phenyl-1-methylcyclohexanone-2 (9)

To a solution of 7.9 g (0.0584 mole) of α -pinene, $[\alpha]_{D}^{25}$ +40.8° (neat), in 75 ml of dry diglyme were added 21.9 ml of a 1.0 M solution of sodium borohydride in diglyme (0.0219 mole). While cooling in an ice bath, 4.15 g (0.0292 mole) of boron trifluoride etherate were added dropwise with stirring. Following the above addition, the mixture was stirred overnight at 0 °C. A thick white precipitate formed in the mixture to which 10.0 g (0.053 mole) of (rac)-1-phenyl-1-methylcyclohexanone-2 (9) were added all at once in 20 ml of dry diglyme. The reaction mixture was stirred at 0 °C until all of the precipitate had disappeared (approximately 20 h). Stirring at room temperature was continued overnight and the reaction was worked-up by pouring the clear solution into 30 ml of 30% NaOH. Exactly 30 ml of 30% H2O2 solution were added dropwise over 15 min and the mixture was stirred for 1 h. The reaction mixture was extracted with diethyl ether, washed with water, and the ether layer dried over anhydrous magnesium sulfate.

The solvent was removed and the mixture was distilled under vacuum. Following removal of residual diglyme and isopinocamphenol, the product was distilled over a range of 94-115 °C (0.9 mm). Three fractions were collected, the first 2 of which consisted of approximately equal amounts of ketone and carbinol. The third consisted of a small amount of almost pure carbinol. The ketone was separated from the carbinol by column chromatography on neutral alumina (Woelm) using 2:1 benzene-chloroform. Analysis by g.l.p.c. $(3/8 \text{ in.} \times 20 \text{ ft},$ 20% SE-30 on Chromosorb W) showed the presence of pure ketone whose spectral data were identical to those of the racemic material. The ketone was isolated in 50% yield after distillation, b.p. 98° (1.5 mm), $[\alpha]_D^{25} + 35.4$ ° (c, 9.32 cyclohexane). An o.r.d. spectrum showed a positive Cotton effect with the first maximum at 321 mu in cyclohexane.⁵ Further elution of the alumina column with chloroform yielded the carbinol (+)-12, b.p. 116– 118° (1.0 mm), $n_{\rm D}^{20} = 1.5467$; $[\alpha]_{\rm D}^{25} + 4.45^{\circ}$ (c, 9.41, cyclohexane).

Anal. Calcd. for C₁₃H₁₈O: C, 82.06; H, 9.59. Found: C, 82.07; H, 9.41.

Conversion of (+)-(R)-9 to (-)-(S)-1-Phenyl-1-

methylcyclohexene-2((-)-(S)-10)

Treatment of 1.48 g (0.0078 mole) of the ketone (+)-(R)-1-phenyl-1-methylcyclohexanone-2 with 1.5 g (0.0080 mole) of tosylhydrazine in absolute ethanol in the presence of a few drops of glacial acetic acid yielded after work-up a white crystalline tosylhydrazone, 13, that was not purified further. The tosylhydrazone was treated with slightly more than 2 mole-equivalents of *n*-butyllithium in ether at room temperature. The mixture was extracted with ether and water, the ether layer was dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporator. The yellow oil was introduced onto a basic alumina column and eluted with pentane. Removal of the pentane and distillation of the

oil yielded 0.6 g (45%) of (-)-(S)-3-phenyl-3-methylcyclohexene 10, b.p. 71° (2.5 mm), $n_{\rm p}^{25}$ 1.5349; $[\alpha]_{\rm p}^{25}$ -16.6°; (c, 9.37, cyclohexane); n.m.r. (CCl₄) δ 1.35 (CMe, s, 3) 5.5-6.0 (vinyl, m, 2), 7.0-7.3 (Ar, m, 5), 1.3-2.2 (aliph, m, 6) p.p.m., i.r. (carbon tetrachloride) λ_{max} 6.05 (weak) (C=C) μ.

Anal. Calcd. for C13H10: C, 90.60; H, 9.40. Found: C, 90.61; H, 9.42.

Oxidation of alkene (-)-(S)-10 to (-)-(R)-2-

Phenyl-2-methylhexandioic Acid ((-)-(R)-14)

To 50 ml of an aqueous solution containing 4.0 g (0.019 mole) of sodium periodate, 0.25 g potassium permanganate, and 5.0 g potassium carbonate were added, 0.5 g (0.0029 mole) of (-)-(R)-10. The mixture was stirred vigorously for 48 h at room temperature. The mixture was extracted with diethyl ether to remove any unreacted alkene and then the aqueous layer was acidified. The aqueous layer was extracted a second time with diethylether and the ether layer was dried over anhydrous magnesium sulfate. The solvents were removed and the gummy material after pumping under vacuum at 100 °C for 15 h had $[\alpha]_{D^{25}} - 7.90^{\circ}$ (c, 6.98, ethanol). A small amount of racemic material crystallized from benzene petroleum ether (b.p. $60-70^\circ$) m.p. $75-78^\circ$. When this was heated under vacuum to 80° the melt resolidified m.p. 113-114°, mixed m.p. 113-115° with authentic material (14). Crystals were obtained from the residue dissolved in carbon tetrachloride, m.p. 111-119 °C; $[\alpha]_{D}^{25} - 10.3^{\circ}$ (c, 4.53, ethanol); lit. (11) m.p. 126.3– 127.5°, $[\alpha]_{546}^{25} - 25.65^{\circ}$ for optically pure material. The i.r. and n.m.r. spectra confirmed identity of this compound.

Preparation of (-)-(S)-1-Phenyl-1-methyl-1silacycloheptanone-3 ((-)-(S)-15)

The acylsilane (+)-(R)-1-phenyl-1-methyl-1-silacyclohexanone-2, $[\alpha]_D^{25}$ +73.5°, (containing 73% of one enantiomer) was treated with diazomethane according to the published method (15).

Examination of the n.m.r. spectrum of the crude reaction product revealed 2 singlets δ 3.81 and 4.05 p.p.m. These were assigned to the cyclic siloxyalkene 16, whose yield, while not isolated, was estimated at 5-10% by

integration. Distillation of the oil yielded 76% of (-)-(S)-1-phenyl-1-methyl-1-silacycloheptanone-3, $[\alpha]_D^{25}$ -47.2° (c, 3.18, cyclohexane), b.p. 105–106° (0.1 mm); n.m.r. (neat with external TMS standard) δ -0.05 (SiMe, s, 3), 2.02, 2.37 (SiCH₂CO, 2d, J = 10 c.p.s., 2), 1.98, 1.30, 0.55 (aliph, 3m, 8), 7.0 (Ar, m, 5) p.p.m.; i.r. (film) λ_{max} 5.93 (C=O) μ ; u.v. λ_{max} (ϵ) (cyclohexane), 248 (358), 253 (418), 259 (470), 263 (425), 266 (480), 271 (342), 296 (100), 305 (65) mµ; o.r.d. (cyclohexane) negative Cotton effect, first maximum 308 mu.

Anal. Calcd. for C₁₃H₁₈SiO: C, 71.50; H, 8.31. Found: C, 71.25; H, 8.17.

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