Journal of Organometallic Chemistry, 154 (1978) 187—201
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STEREOCHEMISTRY OF REACTIONS IN THE 1,2-DIMETHYLSILACYCLOPENTANE RING SYSTEMS. I. STEREOSPECIFIC TRANSFORMATIONS.*

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(Received November 8th, 1977)

SUMMARY

Preparations, separations of geometric isomers, and structural assignments based on nmr and on chemical evidence are described for a number of 1-substituted 1,2-dimethylsilacyclopentanes. A number of stereospecific reactions have been observed, and the stereochemistry is in all cases the same as that observed for acyclic silanes. A discussion of the role of ring strain in determining stereochemical outcome and reaction rates is presented.

INTRODUCTION

Comparative studies among different ring systems and between cyclic and acyclic species have made major contributions to understanding reaction mechanisms. Particularly elegant work has been done over the past decade correlating rates, stereochemistry and mechanism in displacement reactions at 4-coordinate phosphorus in cyclic and acyclic examples. We have attempted in the last few years to bring comparable clarity to the organosilicon area [1-8]. Among the questions to which

*Preliminary communications of portions of this work have appeared (Refs. 3a and 7).

we have addressed ourselves are the following: (1) Are extracoordinate intermediates to be found in organosilicon reactions and are they more commonly found in reactions of strained ring species? (2) What is the nature of such intermediates? (3) Is there a rate acceleration associated with reactions of the strained ring species as has been amply documented in the case of phosphorus heterocycles? (4) Is there a stereochemical crossover in the small ring species as compared to larger rings or acyclics, and if so where does it occur? (5) Can evidence be adduced that extracoordinate species undergo pseudorotations and is the rate of pseudorotation dependent on the ring size and on the nature of substituents? We now wish to report significant new information bearing on these questions which is derived from the first systematic study of stereochemistry in the silacyclopentane series.

RESULTS

A number of 2-methylsilacyclopentane derivatives are readily obtainable through ring closure using 1,4-dibromopentane, a dihalosilane and magnesium in ether (Reaction 1), and further derivatives are available through a variety of

(1)

I, R = H

II, R = Cl

transformations, namely, reactions which result in substitution at Si without competition from ring-opening processes, to be described in this and the following paper. Yields of pure product from the ring closure reactions are generally in the range of 50% to 70% with comparable yields being obtained by mixing all the reactants in one pot or by initial formation of the di-Grignard reagent from the dibromide. Recently an alternative route into the 2-methylsilacyclopentane series involving a hydrosilylation reaction has been reported [9].

In the Grignard-type ring closure reactions employed in the present work, the mixture of geometric isomers obtained has always been near to 50/50. It is perhaps surprising that that should be the case, because ring closure to 1,2-

dimethylsilacyclobutanes gives a product mixture substantially enriched in one isomer [4b]. For the purpose of carrying out stereochemical studies, separate geometric isomers are required, and a number of routes to separated isomers have been developed. In the cases of the silicon hydride (I) and fluoride (IV) isomers, spinning band distillation served to separate the mixture into fractions of greater than 98% isomeric purity. Considerable effort was expended in attempts to separate the geometric isomers of the chloride (II) by distillation or preparative gas chromatography, but unsuccessfully. Nevertheless, the chloride isomers, and those of other derivatives, could be obtained in near isomeric purity by using the SiH (I) or SiF (IV) isomers, and carrying out one of a number of stereospecific reactions (Table 1). Thus, essentially pure E-1-bromo-1,2-dimethylsilacyclopentane (III) was obtained by free radical bromination of Z-1,2-dimethylsilacyclopentane using $CHBr_3$. In addition to the reactions shown in Table 1, metal-catalyzed alcoholysis of the hydride (I) is stereospecific when carried out with relatively bulky alcohols (isopropyl or cyclohexyl). Alternative routes for obtaining a number of derivatives enriched in one geometric isomer are offered by several reactions which are stereoselective, and which will be discussed in detail in the accompanying paper. Thus, alcoholysis of the chloride (II) catalyzed by a variety of amines gives a mixture of alkoxysilanes in which the E-isomer normally predominates, sometimes to the extent of 90% or more.

Structural Assignments. The assignment of structures to the E- and Z-isomers was routinely made on the basis of nmr spectra, and the assignments are in agreement with reasonable stereochemical outcomes for the reactions investigated. The basis that could be consistently used for nmr assignments in all derivatives is the mutual shielding effect of the methyl groups on Si and on C_2 when they are cis to one another. These data are shown in Table 2, and there are no exceptions to the generalization just stated. Thus, in both silacyclopentanes and silacyclobutanes [1,4] the steric shielding effect is a dependable criterion. In some cases the chemical shift differences are quite small, and it is reassuring to have additional data with which to confirm assignments. In the fluoride isomers (IV) the ^{19}F chemical shift is substantially upfield when F is cis to the C_2-methyl. In the aryl derivatives (V, VI) there is a much larger difference in

TABLE 1. STEREOCHEMISTRY OF REACTIONS OF 1-SUBSTITUTED 1,2-DIMETHYLSILACYCLOPENTANES

Reaction	Compound	Z/E*	Reagent	Product	Z/E Ratio	Predominant Stereochemistry
2	Si-Cl	70/30	$LiAlH_4/Et_2O$	Si-H	66/34	Inversion
	Si-Cl	26/74	"	"	24/76	"
3	Si-Cl	55/45	p-$CH_3OC_6H_4Li/Et_2O$	Si-$C_6H_4OCH_3$-p	45/55	Inversion
4	Si-Cl	55/45	p-$CH_3OC_6H_4MgBr/Et_2O$-THF	Si-$C_6H_4OCH_3$-p	7/93	Stereoselective
	Si-Cl	86/14	"	"	10/90	"
5	Si-H	75/25	C_6H_5Li/Et_2O	Si-C_6H_5	25/75	Retention
	Si-H	30/70	"	"	70/30	"
6	Si-C_6H_5	25/75	Br_2/CCl_4	Si-Br	65/35	Inversion
	Si-C_6H_5	70/30	"	"	40/60	"
7	Si-$C_6H_4OCH_3$-p	7/93	Br_2/CCl_4	Si-Br	87/13	Inversion
	Si-$C_6H_4OCH_3$-p	53/47	"	"	48/52	"
8	Si-H	71/29	CCl_4/Bz_2O_2	Si-Cl	30/70	Retention
	Si-H	9/91	"	"	90/10	"
9	Si-H	100/0	$CHBr_3/Bz_2O_2$	Si-Br	0/100	Retention
	Si-H	33/67	"	"	70/30	"
10	Si-H	97/3	Br_2/CCl_4	Si-Br	8/92	Retention
	Si-H	31/69	"	"	61/39	"

*Z and E are defined using the Cahn-Ingold-Prelog sequence rules. If the group on Si, other than methyl, has higher priority than the methyl group, then the isomer is Z when that group is cis to the methyl on C_2. Among the compounds reported in this paper, the Z isomers have methyls on Si and C_2 trans to one another, except in the case of the silicon hydride (I).

TABLE 2. NMR SPECTRA OF 1-SUBSTITUTED 1,2-DIMETHYLSILACYCLOPENTANES*

COMPOUND	δ^1H (Si-CH_3)	δ^1H (C_2-CH_3)	$\delta^{13}C$(Si-CH_3)
E-SiH (I)	0.13	1.07	-5.0
Z-SiH (I)	0.06	1.04	-7.6
E-SiCl (II)	0.38	1.00	
Z-SiCl (II)	0.42	1.09	
E-SiBr (III)	0.62		
Z-SiBr (III)	0.66		
E-SiF (IV)	0.21	0.96	
Z-SiF (IV)	0.23	1.11	
E-SiC_6H_5 (V)	0.27		
Z-SiC_6H_5 (V)	0.33		
E-$SiC_6H_4OCH_3$-p (VI)	0.25	0.82	
Z-$SiC_6H_4OCH_3$-p (VI)	0.32	1.05	

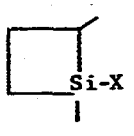
*Chemical shifts measured in ppm downfield from either TMS or benzene as internal standard. Complete spectra are presented in the experimental section.

chemical shift between C_2-methyls in Z- and E- isomers as a result of the diamagnetic anisotropic shielding of the aryl rings when they are cis to the C_2-methyl. Such diamagnetic anisotropic shifts have previously been observed in phenyl-substituted cyclic silanes [4b, 10]. There is an almost 0.2 ppm difference in the positions of the Si-H protons in E-I and Z-I occasioned by shielding from a cis C_2-methyl group. Moreover, as with methylcyclopentanes [11], the reciprocal shielding due to methyl groups in the Z-1,2-dimethylsila (or germa) cyclopentanes as compared to the E-isomers is much more evident in the ^{13}C nmr spectra [12]. Particularly in the cases of the silyl chloride (II) and bromide (III) there is compelling chemical evidence that the free radical halogenations [13] producing them occur with retention stereochemistry. This argument has been elaborated in detail for the corresponding reactions in other Si systems [4a, 14].

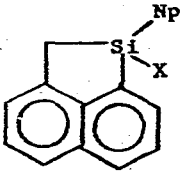
Reaction Stereochemistries. The stereochemical outcomes of a number of reactions of 1-substituted 1,2-dimethylsilacyclopentanes are given in Table 1. All except

Reaction 4 are clearly stereospecific, with the possible additional exception of the displacement of chloride by aryllithium (Reaction 3) for which only one experiment has been performed. Inversion would be a logical outcome for that reaction, although the possibility that it is stereoselective and not stereospecific cannot be eliminated. All of the reactions studied are ones that are also stereospecific with acyclic or six-membered ring cyclic silanes, and in all cases the stereochemistry observed is the same as that previously noted for the relatively unstrained silanes. There are some striking differences, however, between these results and those for the corresponding silacyclobutanes. The $LiAlH_4$ reduction of SiCl proceeds with retention in the latter system, as does displacement of SiCl by aryl Grignard [4]. The closest analogy to the latter reaction is the inversion observed with aryllithium in Reaction 3.

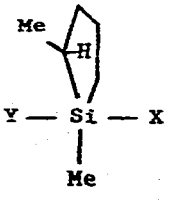
It thus appears that with Si heterocycles, in contrast to P analogs [15], the effect of ring strain in determining the stereochemistry of stereospecific reactions in simple monocyclic ring systems [16] is first seen in 4- and not in membered rings. Despite the fact that C-Si-C bond angles in silacyclopentanes l been measured to be substantially smaller than the tetrahedral angle (92° to 96' and to be even comparable to the angle in ring system XV (93.4°) [18], a transi state or intermediate leading to inversion of configuration at Si can be accomm without prohibitive increase in angle strain. That presumably means that a spe as XVI in which two of the ring bonds span equatorial positions in a trigonal b



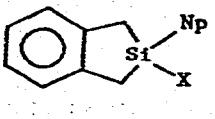
XIV



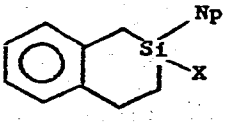
XV



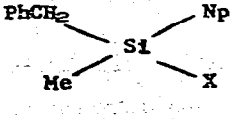
XVI



XVII



XVIII



XIX

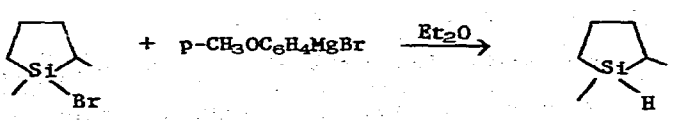
is readily accessible energetically. If formation of a pentacoordinate intermediate with one ring bond axial were to occur and be followed by pseudorotations, as is proposed in phosphorus examples, then retention or isomerization leading to a stereoselective reaction would be more logical stereochemical outcomes. There is some indication [6b,8] that silacyclopentanes give isomerization, probably via a route involving pseudorotation of a pentacoordinate intermediate, with more facility than acyclic (or even than more strained cyclic) species, but stereospecific reactions have not yet shown a bias toward retention, such as that shown by XIV and XV.

Relative Reactivities. Augmented reactivities apparently associated with ring strain have been observed for a number of reactions of organosilicon species [5,19-22] as is also the case for phosphorus heterocycles. The generalization has been made [22] that increased ring strain can be expected to lead to increased reactivity in substitution reactions at Si. We would like to suggest that the situation may be more complex than that. Qualitatively, and in one case quantitatively [6b], we have found reactions of the silacyclopentanes which are much slower than silacyclobutanes, and at least similar to the reactivities expected for acyclic silanes (see the Grignard reactions discussed below). It is difficult at this time to make direct comparisons since our silacyclopentane system presumably has much different steric requirements for reaction than the acyclic systems previously studied. The most thorough investigation of the reactivity of a 5-membered silicon ring system in comparison to other silanes is a recently published study of reactions of ethylmagnesium bromide, allylmagnesium bromide and n-butyllithium with XVII, XVIII and XIX, in which Cl, F and OCH_3 act as leaving groups [22]. In no case was the stereochemistry of the reactions of XVII determined, but at least in some cases retention seems to be the only reasonable proposal. In all cases XVII is the most reactive of the three compounds, but sometimes the spread in rates is $> 10^5$ and in other cases < 10. In general, the larger rate differences occur when all of the reactions are retentions, and the smaller rate differences occur when at least some of the reactions are inversions. In the only certain case in which a crossover in stereochemistry is known to occur, XIX (X = Cl) reacts with n-BuLi by inversion faster than does the more strained XVIII (X = Cl), which reacts by retention. An earlier quantitative comparison of rates of base-catalyzed hydrolysis of 1-methylsilacyclopentane, 1-methylsilacyclohexane and

diethylmethylsilanes shows the cyclopentane to be most reactive [23]. Here also stereochemical studies are lacking but front-side attack seems likely.

We would like to suggest that only small acceleration, if indeed any at all, can be expected when rate comparisons are made between acyclic and 5-membered cyclic silanes undergoing inversion reactions, since transition state XVI will frequently be more strained than the corresponding one for an inversion reaction in an acyclic silane. On the other hand, retention reactions will not require the ring bonds to equatorially placed in a trigonal bipyramid, and they should show rate acceleration due to ring strain. This argument has been made for a few phosphorus reactions by Haake [24]. It appears from presently available information that with silanes there is frequently a substantial energetic bias toward inversion, so that the inversion pathway will be followed unless there is some very compelling reason for front-side attack, as there is in, for instance, the S_Ni-Si mechanism of Sommer [25] in which entering and leaving groups are coordinated to each other. Consequently, we can expect the effects of ring strain on reaction rates to be complex and perhaps to vary from substantial acceleration to substantial retardation. Considerable additional work on comparable cyclic and acyclic systems will be required to clarify the situation.

Grignard Reactions. A number of attempts were made to effect reaction of silacyclic derivatives with aryl Grignards. Addition of p-anisylmagnesium bromide to silyl chloride (II) in ether failed to give reaction even with prolonged heating. Addition of THF to the reaction mixture and further heating gave anisylderivative in poor yield (31%, Reaction 4) and in a stereoselective manner. Some possible mechanisms for stereoselective reactions in the silacyclopentane series will be discussed in accompanying paper, but at the moment we have no evidence as to how Reaction 4 should be classified mechanistically. When silyl bromide (III) was reacted with p-anisyl bromide in ether a rapid reaction occurred, but the predominant product (50%) was derivative, and no anisyl product could be isolated.



Reductions of silyl halides by Grignards have been observed [26], but these have apparently been associated with the presence in the Grignard of a reactive β-hydrogen. Other kinds of reduction products in Grignard reactions have been associated with the production of magnesium hydride in the course of Grignard preparation [27], but the yield of reduced product in the present case seems too high to have been formed exclusively by that route, and furthermore, reduction is not observed with SiCl. The reduction of a silyl bromide in low yield by Mg has been previously reported [28], and a silyl Grignard reagent was proposed to account for the reduction. Formation of silyl Grignard by halogen-metal interconversion is a possible route for formation of SiH in the present case. In addition to the silyl halide experiments, attempts were made to react alkoxysilacyclopentanes with allylmagnesium bromide and benzylmagnesium chloride, and all attempts failed even using reflux in benzene. In marked contrast to these results of sluggish reactivity in the silacyclopentane series, both silyl halides and alkoxides readily react with Grignards in the silacyclobutane series.

Acknowledgement. We wish to thank the National Science Foundation and the Centre National de la Recherche Scientifique for financial assistance.

EXPERIMENTAL

General. Unless otherwise stated, all Grignard and lithium reagents were prepared in three-neck round-bottom flasks equipped with a reflux condenser, a magnetic stirrer, and an addition funnel. The glassware was oven dried, assembled hot, and flushed with nitrogen prior to conducting the reaction under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried by distilling from calcium hydride and then shaking with Linde 5A molecular sieves. Carbon tetrachloride and bromoform were dried by shaking with Linde 4A molecular sieves. ^{1}H nmr spectra were run on a Brucker WH90 or Varian HA-100, A60A or T60 spectrometers. ^{13}C nmr spectra were run on a Brucker EP60 at 15.08 MHz with complete decoupling. Chemical shifts were measured relative to internal TMS unless otherwise noted. Infrared spectra were obtained using a Perkin-Elmer 137 Infracord spectrophotometer. Mass Spectra were recorded on a Hitachi-Perkin-Elmer RMS-4 Mass Spectrometer operating at 70 eV ionization potential and data are reported as m/e

(relative intensity). GLPC-Mass Spectra were obtained on a Perkin-Elmer 990 Gas Chromatograph interfaced through a Biemann-Watson separator to a Hitachi-Perkin-Elmer RMS-4 Mass Spectrometer. The spinning band distillations were done on a Nester-Paust auto annular still.

Preparation of 1,2-dimethylsilacyclopentane (I). A solution of 100 g (0.44 mole) of 1,4-dibromopentane and 600 ml of anhydrous ether was added dropwise to a flask containing 500 ml of anhydrous ether and 45 g (1.8 g. atoms) of magnesium turnings. After addition was complete, the reaction mixture was refluxed for 2 h and then added dropwise to a solution of 50.7 g (0.44 mole) of methyldichlorosilane in 300 ml of ether. The reaction mixture was stirred overnight and then washed with a solution of 75 g of ammonium chloride in 500 ml of cold water. The organic solution was dried over anhydrous magnesium sulfate and distilled at 112°C to yield 24.3 g (48%) of a 50:50 mixture of Z- and E- 1,2-dimethylsilacyclopentane. The isomers were separated by spinning band distillation. Z-I. ^{1}H nmr (CCl_4): δ 0.055 (d, J = 3.5 Hz, 3H), 0.15-1.95 (m, 10H), 1.04 (s, contained in previous multiplet), 4.01 (m, 1H); ^{13}C nmr (C_6D_6): δ-7.6 ($SiCH_3$), 15.0 (CCH_3), 17.3 (C_2), 37.3 (C_3), 25.4 (C_4), 11.0 (C_5); IR (film): 2890(s), 2800(s), 2100(s), 1240(s), 1080(w), 790(w), 728(w) cm^{-1}. E-I. ^{1}H nmr (CCl_4): δ 0.13 (d, J = 3.5 Hz, 3H), 0.2-2.0 (m, 10H), 1.07 (s, contained in previous multiplet), 3.83 (m, 1H); ^{13}C nmr: δ-5.0 ($SiCH_3$), 16.9 (CCH_3), 20.3 (C_2), 37.3 (C_3), 25.7 (C_4), 10.9 (C_5); IR (film): 2830(s), 2740(s), 2090(s), 1260(m), 1100(m), 891(w), 875(w), 840(w), 810(w), 770(w), 723(w) cm^{-1}. Anal. Calcd. for $C_6H_{14}Si$: C, 63.07; H, 12.35; Si, 24.58. Found: C, 62.98; H, 12.35; Si, 24.74%. On a gas chromatography column (20' x 1/4" 20% SE 30 on Chromosorb W) operating at 95° relative retention times of the two isomers was: t_Z/t_E = 1.10.

Preparation of 1-Chloro-1,2-dimethylsilacyclopentane (II). A solution of 102 g (0.44 mole) of 1,4-dibromopentane and 66 g (0.44 mole) of methyltrichlorosilane in 700 ml of anhydrous ether was added dropwise to a flask containing 45 g (1.8 g. atoms) of magnesium turnings and 500 ml of ether. The reaction mixture was refluxed for 2 days and then filtered under nitrogen. The ether was removed by distillation and the residue distilled under vacuum to yield 36 g (55%) of a

45/55 mixture of E- and Z- 1-chloro-1,2-dimethylsilacyclopentane, bp 95-96° (142 mm). Anal. Calcd. for $C_6H_{13}SiCl$: C, 48.46; H, 8.81; Si, 18.89. Found: C, 48.50; H, 8.78; Si, 18.97%. ms: 148(69), 122(84), 120(40), 117(56), 116(85), 115(100), 94(40), 93(56), 79(70), 78(91), 63(55).

Various ratios of isomers E-II and Z-II were obtained by chlorinating (Reaction 8) the appropriate mixture of I isomers as illustrated by the following example. A 29/71 mixture of Z-I and E-I (5.86 g, 0.05 mole) was placed in a flask containing 0.1 g (0.0005 mole) of benzoyl peroxide and 15 ml dry CCl_4. The reaction mixture was heated at 82° for 1.5 h. The solvent was removed by distillation and the residue distilled under vacuum to yield 7.62 g (54.6%) of a 30/70 mixture of E-II and Z-II, bp 65° (44 mm). E-II. ^1H nmr (CCl_4): δ 0.38 (s, 3H), 0.4-2.04 (m, 10H), 1.00 (s, contained in previous multiplet). Z-II. ^1H nmr (CCl_4): δ 0.42 (s, 3H), 0.54-2.05 (m, 10H), 1.09 (d, J = 6.8 Hz, contained in previous multiplet).

Reduction of II (Reaction 2). A mixture containing 0.38 g (0.0026 mole) of a 30/70 ratio of E- and Z-II, 0.0302 g (0.0008 mole) of lithium aluminum hydride and 2 ml dry ether was placed in a vial equipped with a septum. GLPC analysis (16' x 1/8" 15% Apiezon L on 60-80 mesh Chromosorb W; 115° isothermal) immediately after mixing showed that two products had formed with retention times (min) (measured from the ether signal) of 2.82 (33.8%) and 3.44 (66.2%). GC-MS analysis and comparison of the retention times identified the products as E- and Z-I, respectively. GLPC analysis showed that the silyl hydride (I) formed in the reaction slowly isomerized with time under the reaction condition such that after 1 day the isomerization was complete. The reaction was repeated as shown in Table 1.

Preparation of 1-Bromo-1,2-dimethylsilacyclopentane (III). (Reaction 9). A solution of 0.102 g (9×10^{-4} mole) of E-I in 0.5 ml bromoform was placed in a nmr tube with a small amount of benzoyl peroxide. The reaction mixture was heated at 80° for 10 min. An nmr spectrum showed exclusive formation of Z-III. ^1H nmr (CCl_4): δ 0.66 (s, 3H), 0.8-2.0 (m, 10H), 1.04 (broad d, contained in previous multiplet). The reaction was repeated (Table 1) to give predominantly

E-III. ^{1}H nmr (CCl_4): δ 0.62 (s, 3H), 0.7-2.0 (m, 10H), 1.07 (broad d, contained in previous multiplet).

(Reaction 10) A solution of 12 g (0.11 mole) of I (Z/E = 33/67) in 25 ml. of CCl_4 was placed in a flask cooled by an ice bath. A solution of 16.89 g of bromine (0.11 moles) in 20 ml CCl_4 was added slowly to the reaction mixture. After removing the solvent, the residue was distilled under vacuum to yield 13.7 g (67%) of the desired product, bp 63° (15 mm). ^{1}H nmr analysis showed a Z/E isomer ratio of 70/30. Ms: 194(41), 192(42), 166(100), 164(100), 151(44), 125(55), 123(56). Anal. Calcd. for $C_6H_{13}BrSi$: C, 37.31; H, 6.78; Si, 14.54. Found: C, 37.26; H, 6.72; Si, 14.56%.

(Reaction 6) Cleavage of the Si-Ph bond in V by Br_2 was carried out in CCl_4 at the temperature of the nmr probe (ca. 35°) by adding Br_2 to a solution of V. Decoloration of the Br_2 is slow, and as Br_2 is added the stereochemistry of the reaction can be followed from the appearance of the ^{1}H nmr signals in III and V (Table 2). Two such runs were conducted, as shown in Table 1. In order to obtain III in pure form, a solution of 15.8 g (0.083 mole) of V (Z/E = 50/50) in CCl_4 was prepared and treated with 13.26 g (0.083 mole) of Br_2 at room temperature. After allowing the reaction mixture to stand for 48 h protected from light, the solution was distilled to afford 12.8 g (80%) of III (Z/E = 50/50 as determined by nmr), bp 90-95° (20 mm).

(Reaction 7) Cleavage of the p-anisyl group from Si was carried out by placing a solution of 0.0716 g (3×10^{-4} mole) of a 53/47 mixture of Z-VI and E-VI in 0.1 ml of CCl_4 in an nmr tube and adding 0.2 ml of a 1 M solution of Br_2 in CCl_4. A nmr spectrum recorded immediately after addition showed formation of a 48/52 mixture of Z-III and E-III. The reaction was repeated as indicated in Table 1.

Preparation of 1-Phenyl-1,2-dimethylsilacyclopentane (V). (Reaction 5) To 35.7 g of a 2 M ether solution of phenyllithium was added 2.70 g (0.023 mole) of a 75/25 mixture of Z-I and E-I in 20 ml of ether under Ar atmosphere and with constant stirring. After 16 h of reflux, hydrolysis and extractions, the organic solution was distilled to obtain 3 g (65%) of V as a 25/75 mixture of Z and E isomers, bp 120-5° (15 mm). Anal. Calcd. for $C_{12}H_{18}Si$: C, 75.7; H, 9.5. Found: C,

75.7; H, 9.5%. The reaction was repeated as shown in Table 1.

Preparation of 1-(p-anisyl)-1,2-dimethylsilacyclopentane (VI). (Reaction 3) A solution of 18.8 g (0.1 mole) p-bromoanisole in 60 ml of ether was added slowly to a flask containing 1.4 g (0.2 g. atom) of lithium wire and 160 ml of ether. After the reaction was complete, a solution of 10 g (0.07 mole) of a 55/45 mixture of Z-II and E-II in 50 ml of ether was added slowly to the lithium reagent. The reaction mixture was hydrolyzed with an aqueous solution of NH_4Cl, the ether was removed, and the residue was distilled under vacuum to give 9 g (61%) of a 45/55 mixture of Z-VI and E-VI, bp 86-7° (0.25 mm). ^1H nmr (CCl_4): δ 0.25 (s, 3H), 0.32 (s, 3H), 0.5-2.1 (m, 20H), 0.8 (s), 3.65 (s, 6H), 6.8-7.6 (m, 8H). Anal. Calcd. for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15; Si, 12.75. Found: C, 70.59; H, 8.98; Si, 13.01%.

(Reaction 4) A solution of 43 g (0.23 mole) of p-bromoanisole in 150 ml of ether was added slowly to a flask containing 10 g (0.4 g.-atom) of Mg turnings and 300 ml of ether. After addition was complete, the reaction mixture was stirred for 1 h. The Grignard reagent was then added to a solution of 27 g (0.2 mole) of a 50/50 mixture of E- and Z-II in 150 ml of ether. After the reaction mixture was refluxed for approximately 18 h, 200 ml THF was added and refluxing was continued overnight. The reaction mixture was hydrolyzed with an aqueous solution of NH_4Cl, the ether was removed and the residue was vacuum distilled to give 14 g (31%) of a 95/7 mixture (as determined by nmr) of E- and Z-VI, bp 96° (0.9 mm). The reaction was repeated as indicated in Table 1.

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