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METHYL NMR CHEMICAL SHIFT-STRUCTURE CORRELATIONS IN CYCLOPOLYMETHYLPHENYLSILOXANES

DWIGHT E. WILLIAMS, GARY M. RONK and DAVID E. SPIELVOGEL
Dow Corning Corporation, Midland, Michigan 48640 (U.S.A.)

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Summary

The methyl ^1H NMR chemical shifts of various isomers of the title compounds are reported, as is the synthesis of several new compounds. A reliable correlation is shown between chemical shift and structure which is useful for structure confirmation. A statistical approach to isomer identification by use of these shift-structure correlations is given which often affords unambiguous identifications.

Introduction

^1H NMR spectroscopy provides a useful means for the structural analysis of cyclopolydialkylsiloxanes of the type $(RR'SiO)_x$. Often, the identity of R and R′ and their relative amounts can be determined. In addition, various isomers of the following types can sometimes be identified simply from the number and intensity of the NMR bands [1,2]:

1. Substitutional isomers, e.g., $(Me_2SiOPh_2SiO)_2$ vs. $(PhMeSiO)_4$.

2. Positional isomers, e.g., the head-to-head vs. head-to-tail isomer of $(Me_2SiOPh_2SiO)(Me_2SiOMePhSiO)$.

3. Stereoisomers, e.g., the *cis* vs. *trans* isomer of $(MePhSiO)_3$.

Often, however, time-consuming physical separations and chemical manipulations such as stereospecific synthesis must be combined with the NMR data in order to determine the structure. The number of NMR-distinguishable isomers can be very large. For example, there are 34 such structures for cyclic tetramers and 78 such structures for cyclic pentamers containing methyl and phenyl groups. Since biological properties [3] of such compounds are strongly structure dependent, more rapid methods of structure determination would be of real value.

Hickton et al. [1] have suggested that the methyl chemical shift may be correlated with structure in certain cyclopolymethylphenylsiloxanes and have shown [4] that the shift is dominated by the magnetic anisotropy of neighboring phenyl groups. However, their work did not include sufficient compounds to fully test the usefulness of this suggestion. Furthermore, they felt that a shift-structure correlation would not be reliable since it would seem to require an invariant distribution of cyclic conformations.

We report here a study of the derivation, reliability, and usefulness of such correlations by use of a multiple linear regression analysis applied to data for a large variety of trimer, tetramer, and pentamer cyclosiloxanes containing phenyl and methyl groups. We found an excellent shift-structure correlation which facilitates structure determinations and which often affords unambiguous isomer identifications.

Results and discussion

The chemical shift data and structures we studied are shown in Tables 1 - 3. Data for each group of positional and stereo isomers are divided by horizontal lines in these tables. Each vertex represents Si and each edge represents O in the structural formulae. Unambiguous (sure) band assignments are marked by an asterisk. These sure assignments were based primarily upon band integrals. However, it soon became clear that the NMR band of SiMe*Ph-type groups are invariably far downfield (by about 0.25 ppm) from those for $SiMe_2$-type groups. Some sure assignments were based upon this consideration. The remainder of the NMR bands of each compound were assigned to best fit the shift-structure correlations, as described below.

1. Derivation of shift-structure correlation

Our working hypothesis was that the methyl chemical shift depended upon the cyclic size and upon the position and orientation of neighboring phenyl groups, as expressed by the following equation:

$$\tau = a_0 + a_1 x_1 + a_{2c} x_{2c} + a_{2t} x_{2t} + a_{3c} x_{3c} + a_{3t} x_{3t} \qquad (1)$$

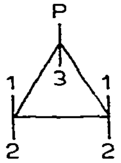
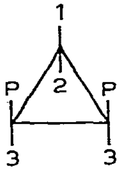
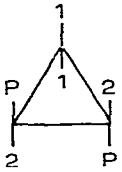
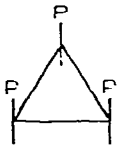
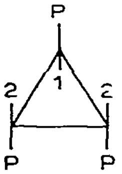
where the a_i are regression parameters that depend upon cyclic size and where the x_i are structural variables specified as follows: x_1 is unity when the silicon which bears the observed methyl group also bears a phenyl group and is zero otherwise; x_{2c} and x_{2t} are the number of adjacent phenyl groups oriented *cis* and *trans*, respectively, to the observed methyl group; x_{3c} and x_{3t} are the number of remote phenyl groups oriented *cis* and *trans*, respectively, to the observed methyl group.

Several multiple linear regression analyses [6] were done with the aid of a computer using the data in Tables 1 - 3 in order to determine the regression parameters of eqn. (1). The trimer, tetramer, and pentamer data were analyzed as separate groups since this separation greatly improved the correlation. Initially, only the data for the sure bands were analyzed. These correlations were remarkably good, as shown by the small standard deviations of the regression parameters and of the shift difference (between calculated and observed shift) given in Table 4. However, the pentamer-sure data were not redundant so that standard deviations could not be obtained in that case.

In order to test the correlations more thoroughly, regression analyses were done using all of the chemical shift data rather than just the sure data. The

(continued on p. 74)

TABLE 1
TRIMER DATA

Compund[a]	Compound notation	Assignment	Observed shift (τ)	Calculated shift[b]	Difference
$(Me_2SiO)_3$	A	^{c}	9.879	9.878	0.001
	B	1 2 3^c	9.875 9.786 9.636	9.876 9.801 9.638	−0.001 −0.015 −0.002
$(Ph_2SiO)(Me_2SiO)_2$	C	^{c}	9.792	9.800	−0.008
$(PhMeSiO)_2(Me_2SiO)$ isomers					
	D	1 2 3^c	9.879 9.726 9.566	9.875 9.724 9.561	0.004 0.002 0.005
	E	1 2	9.817 9.648	9.800 9.636	0.017 0.012
$(PhMeSiO)_3$ isomers					
	F	^{c}	9.484	9.484	0.000
	G	1^c 2^c	9.622 9.557	9.635 9.559	−0.013 −0.002

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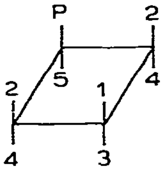
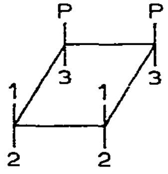
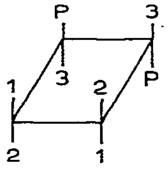
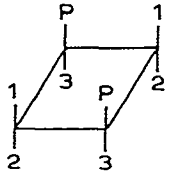
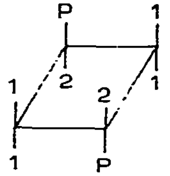
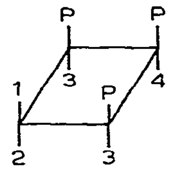
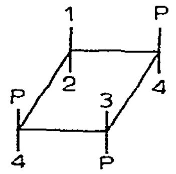
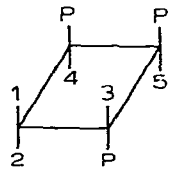
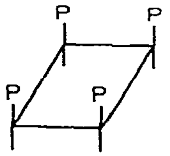
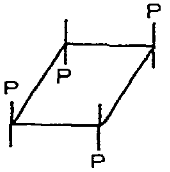
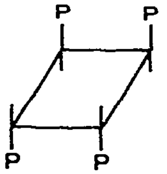
[a] P denotes phenyl and the numerals denote specific methyl groups in these structural formulae. [b] Based on the total data set correlation. [c] Sure assignment.

TABLE 2
TETRAMER DATA

Compound[a]	Compound notation	Assign-ment	Observed shift (τ)	Calculated shift[b]	Difference
$(Me_2SiO)_4$	H	[c]	9.930	9.904	0.026
	I	1	9.949	9.948	0.001
		2	9.949	9.958	—0.009
		3	9.887	9.873	0.014
		4	9.844	9.835	0.009
		5[c]	9.688	9.680	0.008
$(PhMeSiO)_2(Me_2SiO)_2$ isomers					
	J	1	9.993	10.002	—0.009
		2	9.820	9.804	0.016
		3[c]	9.615	9.611	0.004
	K	1	9.896	9.917	—0.021
		2	9.879	9.889	—0.010
		3[c]	9.707	9.725	—0.018
	L	1	9.980	9.992	—0.012
		2	9.762	9.766	—0.004
		3[c]	9.637	9.649	—0.012
	M	1[c]	9.870	9.879	—0.009
		2[c]	9.725	9.735	—0.010

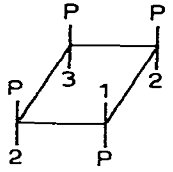
(continued)

TABLE 2 (continued)

Compound[a]	Compound notation	Assignment	Observed shift (τ)	Calculated shift[b]	Difference
$(PhMeSiO)_3(Me_2SiO)$ isomers					
	N	1	10.054	10.047	0.007
		2	9.758	9.735	0.023
		3	9.578	9.580	—0.002
		4	9.534	9.543	—0.009
	O	1	9.959	9.961	—0.002
		2	9.803	9.820	—0.017
		3	9.782	9.769	0.013
		4	9.693	9.693	—0.011
	P	1	9.935	9.933	0.002
		2	9.844	9.848	—0.004
		3	9.782	9.779	0.003
		4	9.670	9.666	0.004
		5	9.648	9.656	—0.008
$(PhMeSiO)_4$ isomers					
	Q	[c]	9.519	9.511	0.008
	R	[c]	9.743	9.737	0.006
	S	[c]	9.719	9.710	0.009

(continued)

TABLE 2 (continued)

Compound[a]	Compound notation	Assignment	Observed shift (τ)	Calculated shift[b]	Difference
(PhMeSiO)$_4$ isomers (continued)					
	T	1 2[c] 3	9.852 9.608 9.598	9.823 9.624 9.597	0.029 −0.016 0.001

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[a] P denotes phenyl and the numerals denote specific methyl groups in the structural formulae. [b] Based on the total data set correlation. [c] Sure assignment.

required additional peak assignments were obtained by adjusting the assignments to attain maximum consistency between observed chemical shifts and shifts calculated from the sure data correlations. The resultant assignments appeared to be reliable since the shift differences were quite small and did not exceed two standard deviations (based on sure data correlations). Alternate peak assignments were not very likely: The most probable case is the assignment reversal of pairs of peaks. All such reversals were less probable than 5% based upon the u and $F_{1,10}$ tests [6], and only eight reversals were more probable than 0.01%. It is very unlikely that many of these reversals were valid, and hence, it is unlikely that such assignment errors significantly affected the regression analyses.

The regression analyses which include all data continue to reveal excellent shift-structure correlations, as shown by the correlation coefficients (which are unity for a perfect correlation) and by the standard deviations of the shift difference and of the regression parameters shown in Table 4. It is important to note that the regression parameters obtained from the total data are not significantly different from those obtained from the much smaller sure data. In addition, data for all of the compounds show a good fit to the regression analyses, as judged by the fact that none of the shift differences given in Tables 1 - 3 exceed two standard deviations. All of these facts indicate that the effect which a phenyl group exerts on the chemical shift of a neighboring methyl group is independent of the particular compound examined provided the cyclic size is constant. Hence, major changes in the distribution of molecular conformations apparently do not occur between compounds of the same cyclic size. However, there does appear to be a significant difference between the regression parameters of trimer, tetramer, and pentamer cyclics, perhaps due to a change in molecular geometry and in available conformations as the cyclic size increases.

The total data correlations appear to be as reliable as the sure data correlations. The regression parameters and standard deviations should be more clearly defined in the former case due to the much larger data set. Accordingly, we feel

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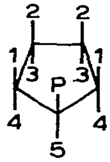
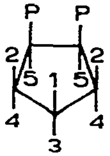
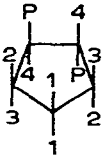
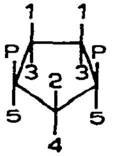
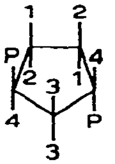
TABLE 3
PENTAMER DATA

Compound[a]	Compound notation	Assignment	Observed shift (τ)	Calculated shift[b]	Difference
$(Me_2SiO)_5$	U	[c]	9.935	9.908	0.027
	V	1	9.939	9.968	—0.029
		2	9.939	9.950	—0.011
		3	9.881	9.900	—0.019
		4	9.848	9.853	—0.005
		5[c]	9.691	9.681	0.010
$(PhMeSiO)_2(Me_2SiO)_3$ isomers					
	W	1	10.027	10.027	0.000
		2	10.004	10.009	—0.005
		3	9.895	9.892	0.003
		4	9.846	9.844	0.002
		5[c]	9.613	9.626	—0.013
	X	1	9.977	9.959	0.018
		2	9.959	9.941	0.018
		3	9.929	9.912	0.017
		4[c]	9.727	9.723	0.004
	Y	1	10.009	10.009	0.000
		2	9.999	9.991	0.008
		3	9.848	9.844	0.004
		4	9.803	9.797	0.006
		5[c]	9.662	9.673	—0.011
	Z	1	9.924	9.941	—0.017
		2	9.900	9.912	—0.012
		3	9.889	9.894	—0.005
		4[c]	9.750	9.740	0.010

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[a] P denotes phenyl and the numerals denote specific methyl groups in the structural formulae. [b] Based on the total data set correlation. [c] Sure assignment.

TABLE 4

SHIFT-STRUCTURE CORRELATIONS

Data set	Regression parameters[a]						Standard[b] error	No. of assignments	No. of compounds	Correlation coefficients
	a_0	a_1	a_{2c}	a_{2t}	a_{3c}	a_{3t}				
Trimer sure	9.878	−0.239	−0.008	−0.076			±0.003	7	6	0.9998
		±0.003	±0.002	±0.002						
Trimer total	9.878	−0.240	−0.001	−0.077			±0.010	13	7	0.998
		±0.006	±0.004	±0.004						
Tetramer sure	9.914	−0.235	0.040	−0.068	0.057	−0.032	±0.018	11	8	0.994
		±0.016	±0.008	±0.008	±0.016	±0.014				
Tetramer total	9.904	−0.224	0.044	−0.069	0.054	−0.031	±0.014	36	13	0.996
		±0.005	±0.003	±0.003	±0.006	±0.006				
Pentamer sure	9.935	−0.244	0.036	−0.078	0.059	−0.029		6	6	
Pentamer total	9.908	−0.277	0.041	−0.056	0.059	−0.008	±0.016	24	6	0.992
		±0.010	±0.008	±0.008	±0.008	±0.008				

[a] See eqn. (1). All error limits are ±1 standard deviation. [b] Standard deviation of the calculated shift *vs.* observed shift.

that isomer identifications should ordinarily be based upon the total data correlations.

2. *Structure identification by shift-structure correlations*

The correlations can be used to determine if the chemical shifts of a newly synthesized compound of the types included in our correlations are consistent with some postulated structure. This determination can be made quantitative by a statistical analysis of the differences between the calculated and observed shifts. If individual shift differences or if the average or the standard deviation of the shift differences depart too greatly from expected values, then the postulated structure should be rejected. These decisions may be based upon the *u-distribution* or the *F-distribution* tests [6] by using expected values obtained from the shift-structure correlations.

The rejection of a postulated structure can be made unambiguous by adopting a low *significant level* for rejection. We recommend a *significance level* of 0.1%, meaning that the probability that a rejected structure is correct is only 0.1%. Conversely, in some instances an incorrect structure may be accepted. When several structures are accepted, their relative probabilities may differ appreciably so that one structure is "preferred", but this decision does not constitute a positive identification. However, other information will often allow such incorrect structures to be excluded from consideration.

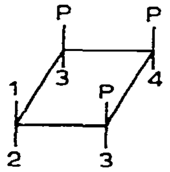
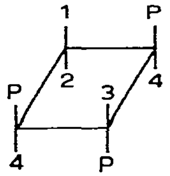
The two isomers of $(MePhSiO)_3(Me_2SiO)$ shown in Table 5 provide a good example of the use of the shift-structure correlations. A statistical analysis was done to determine if the methyl chemical shifts of an unknown compound were consistent with Structure (I), based upon the correlation obtained from the tetramer sure data. (The tetramer total data included data for the above isomers.) The average ($\bar{X}$) and the standard deviation (S_x) of the shift differences are also given in Table 5. The probabilities that these values for $\bar{X}$ and S_x would occur are far larger than 0.1%, as shown in Table 5, and hence Structure (I) was accepted.

Similarly computed probabilities were obtained for Structure (II). These probabilities were much less than 0.1%, as shown in Table 5 and, hence, Structure (II) was rejected. The number and intensity of the NMR peaks and the derived methyl/phenyl ratio of the unknown compound clearly showed it to be one of the isomers shown in Table 5. This conclusion was also consistent with the IR and mass spectra and the method of synthesis, as discussed in the experimental section. Therefore the shift-structure correlation allowed us to unambiguously assign Structure (I) to the unknown compound.

In a similar way, we were able to show that a second unknown compound separated from the same reaction mixture possessed Structure (II). A final compound separated from the same reaction mixture was shown to possess the third possible structure by means of the number and intensity of its NMR peaks. The chemical shifts were also consistent with that structure. Hence the shift-structure correlations allowed us to correctly identify all of the isomers of $(MePhSiO)_3(Me_2SiO)$.

There are 97 cyclopolysiloxanes in the trimer, tetramer, and pentamer series containing solely phenyl and methyl groups whose synthesis has not yet been reported. It is clear that the shift-structure correlations can be used to

TABLE 5
A STRUCTURE IDENTIFICATION BASED UPON THE SHIFT-STRUCTURE CORRELATION

Structure[a]	Methyl	Calculated shift (τ)[b]	Best assignment		Alternate assignment	
			Observed shift	Diff = X	Observed shift	Diff = X
(I) 	1	10.051	10.054	0.003		
	2	9.746	9.758	0.012		
	3	9.579	9.578	−0.001		
	4	9.543	9.534	−0.009		
(II) 	1	9.962			10.054	0.092
	2	9.835			9.758	−0.077
	3	9.759			9.578	−0.181
	4	9.687			9.534	−0.153

Probability parameters[c]	Best assignment	Alternate assignment
$\bar{X}$	0.001	−0.080
s_x	0.009	0.116
U	0.11	8.9
Probability of U	91%	$<10^{-10}$%
$F_{3,10}$	0.25	41
Probability of $F_{3,10}$	10%	<<0.01%

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[a] P denotes phenyl and the numerals denote specific methyl groups in the structural formulae. [b] Calculation based on sure tetramer data set correlation. [c] Defined in statistical analysis texts, e.g., in ref. [6], Chapt. 3.

identify these compounds. Furthermore, we believe that the identification of related types of compounds (e.g., the cyclic hexamers) may be handled in the same way when the need arises by studying a small number of additional model compounds.

Experimental

The chemical shift data were obtained at ambient probe temperature (30 to 38°) using dilute solutions in carbon tetrachloride and TMS as the internal reference. Data for $(MePhSiO)_x$ were taken from the literature [1]. All other data were obtained by us using a Varian Associates A-60 spectrometer and a 50 Hz calibrated [5] sweep width. We estimate our data to be accurate within ± 0.008 ppm. Our data for $(Me_2SiO)_4$ and for $(Me_2SiO)_3(MePhSiO)$ also agreed with literature values [1] to within the above estimated error.

Compounds A, H, and U were prepared as described by Hunter et al. [7].

Compound C was prepared as described by Sporck and Coleman [10]. Compound (I) was prepared as described by Hickton et al. [1]. Compounds B, D, E, and V were prepared and isolated using the procedures indicated by Kuznetsova et al. [8] and Andrianov et al. [9]. In each case, physical properties such as b.p. and n_D^{25} agreed with published values. The IR and NMR spectra also agreed with the structures.

The preparation, isolation, and identification of compounds J, K, L, M, N, O, P, W, X, Y, and Z have not appeared previously in the literature, although compounds J, L, and M are described by Hyde and Spielvogel [3]. These were prepared and characterized as described below and shown in Scheme 1.

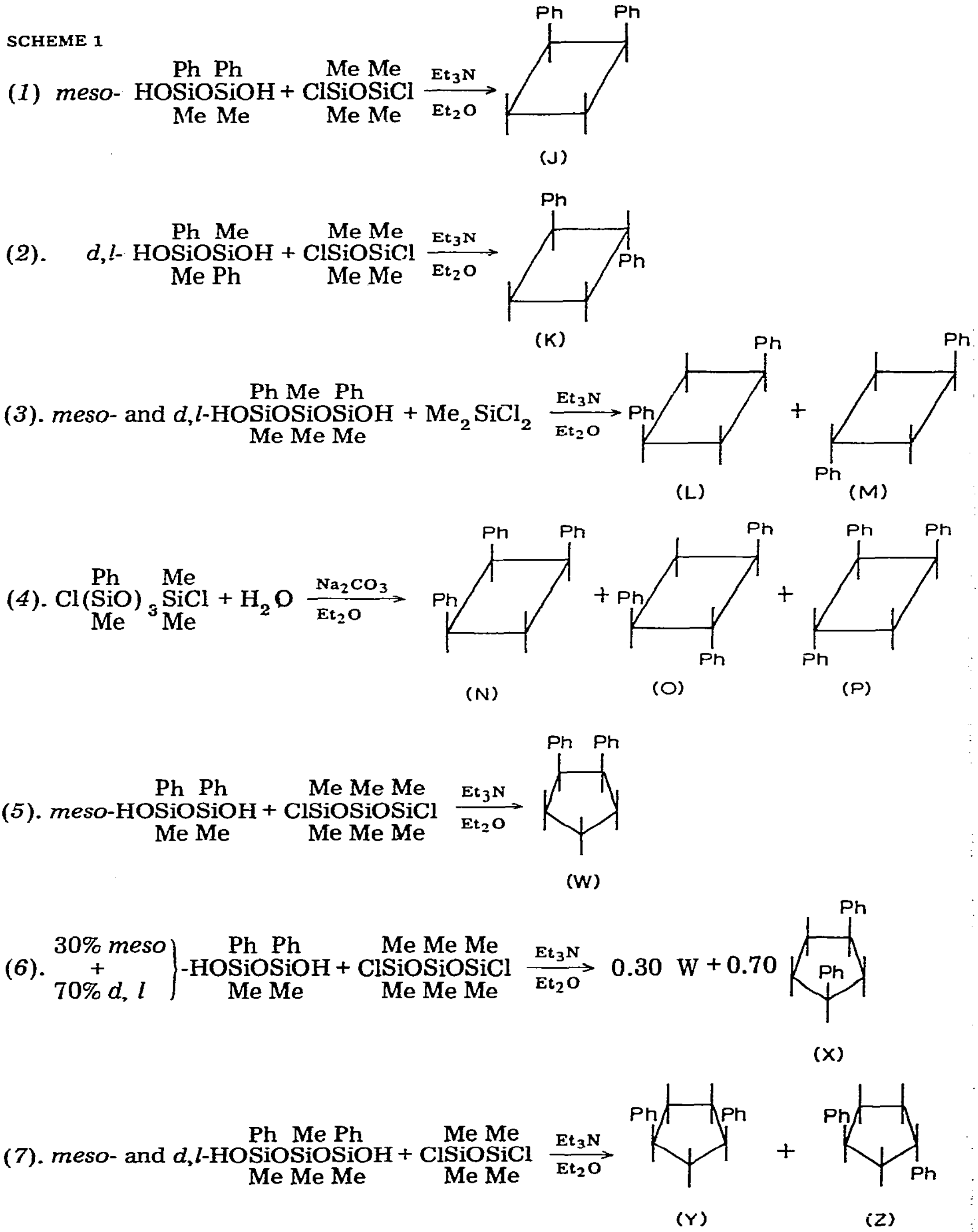
cis-2,4-Diphenylhexamethylcyclotetrasiloxane (J). A solution of *meso*-1,3-dimethyl-1,3-diphenyldisiloxanediol [11] (36.2 g) and triethylamine (25.2 g) in diethyl ether (355 g) was cooled in an ice bath. A solution of tetramethyl-1,3-dichlorodisiloxane [12] (25.4 g) in ether (25 g) was added dropwise with stirring over a period of two hours. The $Et_3N\cdot HCl$ salt was filtered off and the ether solution was washed with water and separated. The ether was removed under reduced pressure giving a concentrate which weighed 42.9 g (theory 52.5 g). This material was vacuum distilled to provide 30.4 g (58% yield) of *cis*-2,4-diphenylhexamethylcyclotetrasiloxane, b.p. 102° at 0.10 mm, n_D^{25} 1.4870, d_4^{25} 1.067, MR_D 114.41 (calcd. MR_D 114.67). GLC analysis indicated an isomeric purity of $\geq$ 99%. The infrared and mass spectra agree with the structure. The ^1H NMR spectrum exhibits absorptions at 9.993 τ (CH_3, 6.0 protons), 9.820 τ (CH_3, 6.0 protons), 9.615 τ (CH_3, 6.0 protons), 2.3 to 2.9 τ (C_6H_5, 10.0 protons), confirming that *meso* reagent leads to *cis* product, as expected.

trans-2,4-Diphenylhexamethylcyclotetrasiloxane (K). The reaction with *racemic*-1,3-dimethyl-1,3-diphenyldisiloxanediol [11] was carried out in a similar manner. Vacuum distillation provided a 66% yield of *trans*-2,4-diphenylhexamethylcyclotetrasiloxane, b.p. 101 - 102° at 0.10 mm, n_D^{25} 1.4875, d_4^{25} 1.065, MR_D 114.73 (calcd. MR_D 114.67). GLC analysis indicated an isomeric purity $\geq$ 97%. The infrared and mass spectra agree with the structure. The ^1H NMR spectrum exhibits absorptions at 9.896 τ (CH_3, 6.0 protons), 9.879 τ (CH_3, 6.0 protons), 9.707 τ (CH_3, 6.0 protons), 2.3 - 2.9 τ (C_6H_5, 10.0 protons), confirming that *racemic* reagent leads to *trans* product, as expected.

cis-2,6-Diphenylhexamethylcyclotetrasiloxane (L). The reaction of *meso* and *d,l*-1,3,3,5-tetramethyl-1,5-diphenyltrisiloxanediol [3] with dimethyldichlorosilane was carried out in the manner described above. Vacuum distillation provided a 58% yield of *cis* and *trans*-2,6-diphenylhexamethylcyclotetrasiloxane, b.p. 101 - 102° at 0.10 mm, n_D^{25} 1.4868 (supercooled). The ^1H NMR and infrared spectra agree with the structure. Repeated fractional distillation afforded small quantities of the *cis* isomer, m.p. 43.5°. GLC analysis indicated an isomeric purity $\geq$ 99%. The infrared and mass spectra agree with the structure. The ^1H NMR spectrum exhibits absorptions at 9.980 τ (CH_3, 6.0 protons), 9.762 τ (CH_3, 6.0 protons), 9.637 τ (CH_3, 6.0 protons), 2.3 - 2.9 τ (C_6H_5, 10.0 protons), as expected for the *cis* isomer.

trans-2,6-Diphenylhexamethylcyclotetrasiloxane (M). M was obtained from the above distillation, m.p. 55°. GLC analysis indicated an isomeric purity

SCHEME 1



Each vertex represents Si and each connecting edge represents O in the above formulae. Each vertical line from a vertex represents an Si—Ph (phenyl) or an Si—Me (methyl) group if Ph is not specified.

$\geqslant$ 99%. The infrared and mass spectra agree with the structure. The ^{1}H NMR spectrum exhibits absorptions at 9.870 τ (CH_3, 12.0 protons), 9.725 τ (CH_3, 6.0 protons), 2.3 - 2.9 τ (C_6H_5, 10.0 protons), as expected for the *trans* isomer.

2,4,6-Triphenylpentamethylcyclotetrasiloxane (N, O, P). A solution of 1,1,3,5,7-pentamethyl-3,5,7-triphenyl-1,7-dichlorotetrasiloxane [13] (180.8 g) in diethyl ether (180.8 g) was stirred with sodium carbonate (37.2 g). Water (12.6 g) was added dropwise to the stirred mixture over a period of two days. The combined salts were filtered off and the material was concentrated by solvent removal to leave the product as clear fluid which weighed 140.1 g (theory 163.9 g). This material was vacuum distilled to provide a 68% yield of the mixed cyclotetrasiloxane isomers, b.p. 167 - 171° at 0.05 mm, n_D^{25} 1.5195, d_4^{25} 1.093, MR_D 134.17 (calculated MR_D 134.50). The infrared spectrum agrees with the structure. The ^{1}H NMR spectrum and the phenyl-to-methyl proton ratio also agree with the structure. The above isomer mixture was carefully redistilled. Three distillation fractions were obtained which GLC indicated had isomer ratios of 81%/19%, 0%/100%, and 0%/100%. (Two isomers were not separated by GLC.) Infrared, mass, and ^{1}H NMR spectra of these fractions agreed with the structure. Isomer ratios obtained by NMR were as follows: 81%/7%/12%, 0%/42%/58%, and 0%/68%/32% for N/O/P, in agreement with the GLC analyses. Examination of the ^{1}H NMR spectra of these three fractions, which were successively rich in each isomer, allowed each set of absorptions to be assigned to the proper isomer. Isomer P was positively identified from the number and intensity of the methyl NMR absorptions. Isomers N and O were positively identified from the methyl chemical shifts as described in the Discussion section.

cis-2,4-Diphenyloctamethylcyclopentasiloxane (W). A solution of *meso*-1,3-dimethyl-1,3-diphenyldisiloxanediol [11] (2.90 g) and triethylamine (2.1 g) in diethyl ether (72 ml) was cooled in an ice bath. Hexamethyl-1,5-dichlorotrisiloxane [12] (2.77 g) was added dropwise with stirring. After stirring for 1 h, the slurry was added to water to dissolve the triethylamine hydrochloride. The ether layer was washed with water until neutral, dried over anhydrous sodium sulfate, filtered, and devolatilized to leave the product as a fluid which weighed 2.7 g (theory 4.94 g). GLC analysis indicated an isomeric purity of $\geqslant$ 99%. The ^{1}H NMR spectrum exhibits absorptions at 10.027 τ (CH_3, 3.0 protons), 10.004 τ (CH_3, 6.0 protons), 9.895 τ (CH_3, 3.0 protons), 9.846 τ (CH_3, 6.0 protons), 9.613 τ (CH_3, 6.0 protons), 2.3 - 2.9 τ (C_6H_5, 10.0 protons), confirming that *meso* reagent leads to *cis* product, as expected.

trans-2,4-Diphenyloctamethylcyclopentasiloxane (X). The reaction of *meso*- and *racemic*-1,3-dimethyl-1,3-diphenyldisiloxanediol [11] (*meso/d,l* 0.3/0.70) with hexamethyl-1,5-dichlorotrisiloxane [12] was carried out as described above. The product was obtained as a clear fluid which weighed 3.2 g (theory 4.94 g). GLC analysis indicated a 30% *cis*-, 70% *trans* distribution. The ^{1}H NMR spectrum exhibits absorptions at 9.977 τ (CH_3, 6.0 protons), 9.959 τ (CH_3, 6.0 protons), 9.929 τ (CH_3, 6.0 protons), 9.727 τ (CH_3, 6.0 protons), 2.3 - 2.9 τ (C_6H_5, 10 protons) due to the *trans* isomer and also exhibits the above listed absorptions of the *cis* isomer in an intensity ratio which agrees with the isomer ratio indicated by GLC.

cis- and trans-2,6-Diphenyloctamethylcyclopentasiloxane (Y and Z). The reaction of *meso* and *d,l*-1,3,3,5-tetramethyl-1,5-diphenyltrisiloxanediol [3] with tetramethyl-1-3-dichlorodisiloxane [12] was carried out as described above. Vacuum distillation provided a 12% yield of *cis* and *trans*-2,6-diphenyloctamethylcyclopentasiloxane b.p. 110 - 112°/0.075 mm, n_D^{25} 1.4758, d_4^{25} 1.045, MR$_D$ 133.59 (calculated MR$_D$ 133.28). The infrared and mass spectra agree with the proposed structure.

Examination of the ^{1}H NMR spectra of two of the fractions, which are successively rich in each isomer, allowed each set of NMR absorptions to be assigned to the proper isomer. Isomer ratios obtained by NMR agreed with those obtained by GLC. The isomers were positively identified by the number and intensity of the methyl NMR absorptions. The *cis* isomer exhibits NMR absorptions at 10.009 (CH_3, 6.0 protons), 9.999 τ (CH_3, 3.0 protons), 9.848 τ (CH_3, 6.0 protons), 9.803 τ (CH_3, 3.0 protons), 9.662 τ (CH_3, 6.0 protons), 2.3 - 2.9 τ (C_6H_5, 10.0 protons). The *trans* isomer exhibits absorptions at 9.924 τ (CH_3, 6.0 protons), 9.900 τ (CH_3, 6.0 protons), 9.889 τ (CH_3, 6.0 protons), 9.750 τ (CH_3, 6.0 protons), and 2.3 - 2.9 τ (C_6H_5, 10.0 protons).

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