

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MO.]

## Exchange of Parts between Molecules at Equilibrium. I. $\alpha,\omega$ -Disubstituted Polydimethylsiloxanes

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The systems  $(\text{CH}_3)_2\text{SiCl}_2-[(\text{CH}_3)_2\text{SiO}]$ ,  $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2-[(\text{CH}_3)_2\text{SiO}]$ , and  $(\text{CH}_3)_2\text{Si}[\text{N}(\text{CH}_3)_2]_2-[(\text{CH}_3)_2\text{SiO}]$  have been studied by proton nuclear magnetic resonance (n.m.r.). Through redistribution of bridging oxygen atoms with the monofunctional chloro, methoxyl, and dimethylamino groups, an equilibrium between the *meso* molecules and the end and middle groups is set up in the families of compounds making up these systems. The equilibrium constants for the interaction of two end groups to give a middle group plus a *meso* molecule are, respectively,  $0.110 \pm 0.004$ ,  $0.24 \pm 0.02$ , and  $0.50 \pm 0.05$ .

### Introduction

**General.**—An outstanding challenge in chemistry is the preparation and characterization of families of compounds (ranging from the smallest molecule of the series—the *meso* molecule—to infinite macromolecules) based on atoms other than carbon in the spine of the molecule. From the present literature, one can surmise that about three-fourths of the hundred-odd elements may be put together, often in alternation with other atoms, to form molecular backbones, and that very many families of compounds based on such molecule-backbone atoms from various regions of the periodic table are awaiting discovery and/or clarification. Although kinetically controlled reactions rule in organic chemistry where C–C catenation predominates, it will be shown in this series of papers that either chemical equilibration or diffusion control is pre-eminent in the chemistry of molecules held together by other than C–C chains. Indeed, the present lack of information about reasonably complicated molecules not based on the C–C backbone is due in great part to their lability when present in fluid form.

The laborious classical method of demonstrating the existence and molecular structure of new families of compounds (e.g., the hydrocarbons or the sugars) was to separate and identify each member of the sequence of smaller molecules and to prove the existence of the larger ones by synthesis and degradation reactions. However, in the case of molecules which readily exchange parts with each other, attempts<sup>2</sup> at separation may cause molecular rearrangements while synthesis or degradation reactions may involve extensive rearrangements<sup>3</sup> and hence be unsuitable for a classical structure proof.

In the work described in this series of papers, we shall employ physical and mathematical tools which obviate the need for separation of the individual compounds making up a family and yet afford ample proof that such compounds exist and have the assigned molecular structure. Of course, this means that different characteristic properties (such as nuclear magnetic resonance [n.m.r.] chemical shifts) will be reported in place of the constants (such as index of refraction or boiling point) used classically to identify a new molecule.

The first two papers in this series deal with families of molecules. Paper I is concerned with compounds which are sufficiently labile so that equilibrium with respect to exchange of parts between the molecules

can be achieved and, at the same time, are sufficiently stable so that separation of the individual species can be achieved by distillation. Paper I, therefore, serves as an introduction to families of compounds such as are described in paper II, where the individual compounds cannot be separated by the usual application of existing separation techniques.

**The Polydimethylsiloxanes.**—Although reorganization based on making and breaking of the Si–O–Si linkage to give equilibria<sup>4</sup> between the  $\alpha,\omega$ -dimethyl-*in*apolydimethylsiloxanes<sup>5</sup> and between these and the various cyclopolydimethylsiloxanes have been carefully studied, the literature<sup>6,7</sup> concerning other  $\alpha,\omega$ -disubstituted polydimethylsiloxanes is much less complete and the reorganization equilibria exhibited by these systems are seen "through a glass darkly." One purpose of this paper is to clarify the reorganization of polydimethylsiloxanes having readily exchangeable end groups and to show that there is an equilibrium between the *meso*, end, and middle structure-building units similar to that which we have described previously<sup>8</sup> for compounds of phosphorus. The second purpose is to show the extent to which high-resolution nuclear magnetic resonance at a sufficiently large magnetic-field strength can be employed to establish the detailed position of a given structure-building unit, such as a middle group, in a complex molecule present only in mixtures and perhaps not isolable.

### Experimental Highlights

**Reagents.**—Dichlorodimethylsilane, dimethoxydimethylsilane, and hexamethyldisiloxane were carefully purified by redistillation from commercial preparations purchased from the Anderson Chemical Co. The octamethylcyclotetrasiloxane purchased from K and K Laboratories contained about 0.5% of the Si as other siloxanes, according to the proton n.m.r. However, the crystalline hexamethylcyclotrisiloxane purchased from Chemical Procurement Laboratories was essentially free of impurities. These ring compounds were used without purification. The bis-(dimethylamino)-dimethylsilane was prepared<sup>9</sup> from the dichlorodimethylsilane and was carefully purified by redistillation. The aluminum chloride catalyst used in these studies was an anhydrous analytical grade reagent.

A sample of the  $\alpha,\omega$ -dimethyl-*in*apolydimethylsiloxane having a number-average number of silicon atoms of 100 was made from the hexamethylcyclotrisiloxane plus a very small amount of hexamethyldisiloxane, according to the catalytic-rearrangement tech-

(4) D. F. Wilcock, *ibid.*, **69**, 477 (1947); D. W. Scott, *ibid.*, **68**, 356, 2294 (1946); and W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

(5) The prefixes *in* for chain, *cyclo* for ring, and *meso* for simple molecules, the latter being based in these systems on a single silicon atom, are used throughout this paper. See J. R. Van Wazer, "Phosphorus and Its Compounds, Volume I: Chemistry," Interscience Publishers, Inc., New York, N. Y., 1958, p. 89.

(6) *E.g.*, for the chloro compounds see W. I. Patnode, U. S. Patent 2,381,366 (1945); R. O. Sauer, U. S. Patent 2,421,653 (1947); K. A. Andrianov, D. B. Severnyi, and B. G. Savin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1456 (1961).

(7) N. N. Sokolov and K. A. Andrianov, *ibid.*, 806 (1957) (p. 827 in English translation).

(8) *E.g.*, J. R. Van Wazer, ref. 5, Chapter 12; L. C. D. Groenweghe, J. H. Payne, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **82**, 5305 (1960), and E. Schwarzmann and J. R. Van Wazer, *ibid.*, **82**, 6009 (1960).

(9) H. Breederveld and H. I. Waterman, *Research (London)*, **5**, 537 (1952).

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(2) *E.g.*, see the difficulties encountered by G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **66**, 931 (1944), as compared to G. Calingaert and H. A. Beatty, *ibid.*, **61**, 2748 (1939). The existence of the mixed species which Forbes and Anderson could not separate has been demonstrated spectrographically by M. L. DeWaulle and F. Francois, *Compt. rend.*, **219**, 64 (1914); **227**, 1229 (1948).

(3) *E.g.*, see E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **83**, 365 (1961), concerning the work of H. Tolkmith, *ibid.*, **76**, 5270 (1953).

nique of Patnode and Wilcock.<sup>4</sup> Several  $\alpha,\omega$ -dichloropolydimethylsiloxanes were prepared according to the method of Sokolov and Andrianov.<sup>7</sup> Although a still having 20–30 theoretical plates was used for separation of these dichloro compounds and their observed boiling points were the same as those reported,<sup>7</sup> it was found that the best fractions of the di-, tri-, and tetra-chain molecules contained only about 78% of the total silicon as these particular molecules. Although good separation was not effected in our distillation, the purity was high enough so as to cause no problem in making proper n.m.r. peak assignments for these  $\alpha,\omega$ -dichloropolydimethylsiloxanes.

**Thermal Equilibration.**—On the basis of a number of exploratory experiments, it was found that mixtures of either dichlorodimethylsilane or bis-(dimethylamino)-dimethylsilane with octamethylcyclotetrasiloxane reached equilibrium with respect to structural reorganization in about 1 day at 200°, using 2% by weight of  $AlCl_3$  as catalyst (*viz.* Reorganization Kinetics following). Mixtures of dimethoxydimethylsilane with octamethylcyclotetrasiloxane took approximately twice as long to reach equilibrium under the same conditions. Therefore, the equilibrium measurements reported here correspond to 3 days at 200°, using 2 wt. % of anhydrous aluminum chloride as catalyst. Without added catalyst, the methoxyl system seemed to approach equilibrium more quickly than the chloro system which was somewhat faster than the dimethylamino system.

All equilibrations, as well as the kinetic studies, were carried out by sealing the reagents, generally the *neso* compound with octamethylcyclotetrasiloxane, in Pyrex tubes which were contained in capped pieces of iron pipe in a furnace. For the kinetic studies, the samples were quenched by dropping the iron pipes into a pail of iced water immediately upon removal from the furnace. Thus, a different sample was used for each set of points corresponding to a given time in a rate study.

**N.m.r. Measurements.**—A Varian A-60 analytical spectrometer running at a frequency of 60 Mc. was employed for the  $H^1$  n.m.r. determination, generally using the smallest available sweep width (50 c.p.s. for the entire scale). The chemical shifts are all measured in p.p.m. of the magnetic field with respect to tetramethylsilane, with negative shifts being downfield. The samples were carefully poured in a dry atmosphere into the precision glass tubes used with the spectrometer, after breaking the end off the reaction tubes.

In the case of the  $\alpha,\omega$ -dichloro family of compounds, the protons on the two methyl groups bonded directly to the silicon atoms were used for analysis, with the n.m.r. measurements being carried out in a 1:1 carbon tetrachloride solution in order to achieve the optimum in peak resolution *vs.* peak area. Under these conditions, the known references for assigning the peaks in the spectrum were the *neso* molecule at  $-0.777$  p.p.m.; the di-chain molecule (consisting of two ends bonded to each other) at  $-0.485$ ; the two ends of the tri-chain at  $-0.445$ ; and the middle group of this chain at  $-0.172$  p.p.m. The tetra-chain showed two equal resonance peaks, one due to ends at  $-0.434$  and the other to middles at  $-0.134$  p.p.m. The tri- and tetra-rings gave single peaks at  $-0.100$  and  $-0.075$  p.p.m., respectively. Middles in very long chains were found to resonate at  $-0.067$  p.p.m., as determined from a 1:1 carbon tetrachloride solution of the long-chain  $\alpha,\omega$ -dimethylpolydimethylsiloxane having a degree of polymerization of 100. The data in this  $(CH_3)_2SiCl_2-[(CH_3)_2SiO]$  system have been corrected for a small peak due to an impurity, chlorotrimethylsilane, occurring at  $-0.406$  p.p.m. This impurity was present in a roughly constant amount of *ca.* 1% of the total  $CH_3$  groups.

Analysis for the various species present in the  $\alpha,\omega$ -dimethoxy family was also carried out by measuring the areas of the peaks corresponding to the two methyl groups directly bonded to the silicon atoms. As was done for the chloro system, relatively pure fractions of the di- through penta-chains were obtained by fractionation. These showed that the pair of n.m.r. peaks at  $-0.028$  and  $-0.02$  p.p.m. is due to end groups and the one at  $-0.038$  p.p.m. to any middle group, with the peak at  $-0.005$  p.p.m. due to the *neso* molecule—dimethoxydimethylsilane. These four peaks are seen in the spectrum of the dimethylsilicon moiety. The proton resonances for the methoxyl groups are not resolvable for the *neso* and end structures, although at highest resolution a shoulder would sometimes show on this peak. All samples were measured in 1:1 carbon tetrachloride solution. However, in this case, dimethyl ether (at  $-3.27$  p.p.m.) was formed as a by-product. Therefore, the over-all compositions (expressed for this system in terms of *R*-values, equal to the over-all  $CH_3O/Si$  mole ratios) were corrected for the dimethyl ether from the ratio of twice the methoxyl peaks appearing in the n.m.r. spectrum to the peaks owing to the two methyl groups bonded to the silicon atoms; 24% of the total methyl groups bonded to oxygen atoms was found to be present as dimethyl ether for  $R = 0.2$ . This value dropped off to 2% for *R*-values in the range of 1.3 to 1.8.

In the  $\alpha,\omega$ -bis-(dimethylamino) family, there was also a by-product problem, owing to formation of some trimethylamine. Corrections to the over-all composition similar to those used for the methoxyl system were employed. It was found that 11%

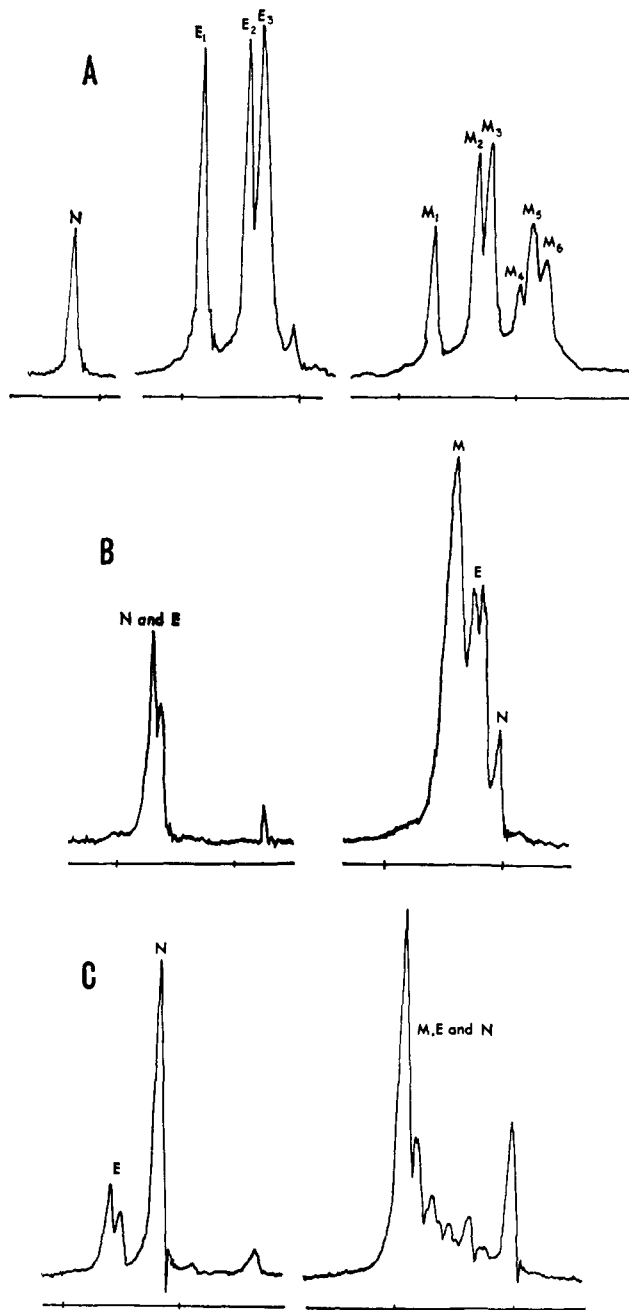


Fig. 1.—Proton n.m.r. traces for the (A)  $\alpha,\omega$ -dichloro-, (B)  $\alpha,\omega$ -dimethoxy-, and (C)  $\alpha,\omega$ -bis-(dimethylamino)-polydimethylsiloxane equilibrium mixtures corresponding to  $R = 0.60$ . The symbols are N for the *neso* molecule, E for end groups, and M for middle groups. The entire A spectrum and the right sides of the B and C spectra refer to the methyl groups directly bonded to the silicon atoms. The left spectrum under B is due to the methoxyl group and the left one under C to the dimethylamino group.

of the methyl groups bonded to nitrogen atoms were present in the form of trimethylamine for  $R = 0.2$ , and that this decreased to 0.5% of the methyl groups for  $R = 1.8$ . The area of the proton resonances corresponding to the methyl groups bonded to nitrogen atoms was used to determine the relative amounts of the *neso* and end structure units, with the middle units being obtained by difference between the areas of the methyl groups bonded to nitrogen and those bonded to silicon. In this way, we overcame the problem of making assignments in the rather complex and crowded proton spectra of the  $CH_3-Si$  moieties.

The relative areas corresponding to the various proton u.m.r. resonances were obtained from the integrator on the spectrometer and also by cutting out the peaks and weighing them. Good agreement was observed between the two methods even though, in some cases, there was overlap between neighboring resonance peaks.

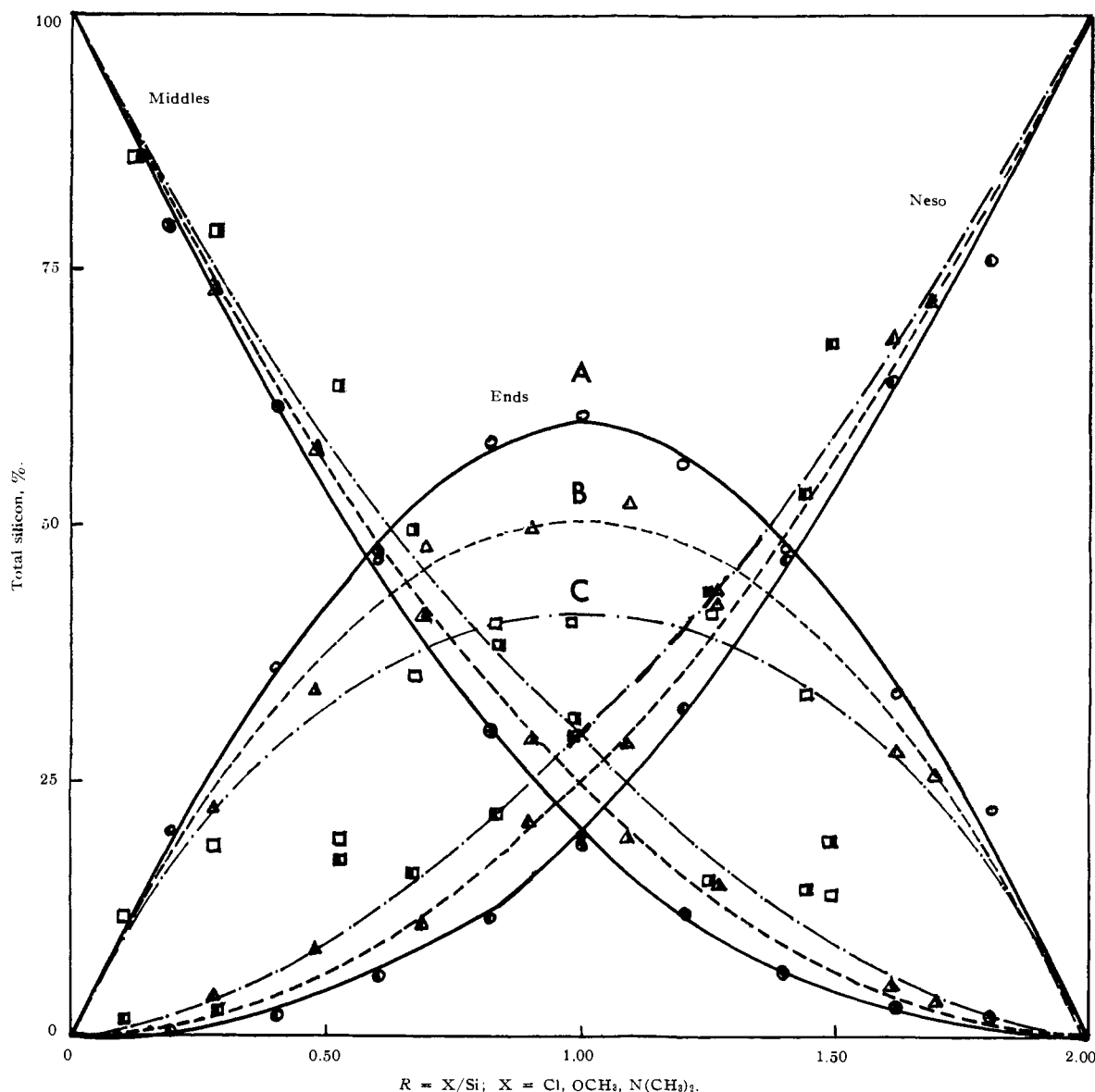
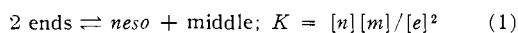


Fig. 2.—Equilibrium at 200° between *nesos*, *ends*, and *middles* in (A)  $\alpha,\omega$ -dichloro, (B)  $\alpha,\omega$ -dimethoxy, and (C)  $\alpha,\omega$ -bis-(dimethylamino)-polydimethylsiloxanes.

### Results and Conclusions

**Reorganization Equilibria.**—Typical spectra with peak assignments are shown in Fig. 1 for the three systems studied here. For the  $\alpha,\omega$ -dichloropolydimethylsiloxanes, the resonances at  $-0.485$ ,  $-0.445$ , and  $-0.434$  were assigned to end groups, with the six resonances in the range of  $-0.172$  to  $-0.075$  being assigned to middle groups on the basis of the n.m.r. data on the separated molecules. The variation of the amount of total silicon in *neso*, end, and middle structure-building units as a function of  $R = \text{Cl}/\text{Si}$  is shown in Fig. 2, from which it can be seen that the end units occur to a somewhat greater extent than would be expected for random redistribution of chlorines with bridging oxygen atoms on the two readily exchangeable sites of the dimethylsilicon moiety. The experimental data and the smoothed curves for the equilibrium between *neso*, end, and middle structure-building units for the methoxyl system and for the dimethylamino system are also presented in Fig. 2. For all three systems, the interaction between structure-building units may be discussed in terms of equilibrium constants for the reaction



For completely random redistribution of substituents on the dimethylsilicon moiety, the equilibrium constant for this equation would equal 0.250. For the chloro system, it has been found to be  $0.110 \pm 0.004$ . For the methoxyl system, it is  $0.24 \pm 0.02$ , and for the dimethylamino system, it is  $0.50 \pm 0.05$ , where the value following the  $\pm$  sign is the standard deviation.<sup>10</sup> This means that the heat of formation<sup>11</sup> of the end group from the *neso* compound and the middle group is  $-0.36$  kcal. for the  $(\text{CH}_3)_2\text{SiCl}_2-[(\text{CH}_3)_2\text{SiO}]$  system, and is  $+0.33$  kcal. for the  $(\text{CH}_3)_2\text{Si}[\text{N}(\text{CH}_3)_2]_2-[(\text{CH}_3)_2\text{SiO}]$  system.

The equilibrium constant for the chloro system exhibits less error than that for the other two systems. This is due to the fact that the various shifts are spread farther apart in the spectrum for this system than for the other two systems, as can be seen in Fig. 1. We attribute this to a greater change in chemical shift when

(10) The statistics used in the error calculation is given by L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

(11) This calculation is made on the assumption that the difference in free energy between the observed and ideally random equilibria is attributable wholly to its  $\Delta H$  component, i.e., the  $\Delta S$  contribution is solely equal to the "entropy of mixing" of the exchangeable ligands.

substituting a chlorine for a siloxyl group than is found when substituting either a methoxyl or a dimethylamino group for a siloxyl group on the silicon atom, which is separated from the proton used in the n.m.r. measurements by an intermediate carbon atom. This is in line with the idea<sup>12</sup> of a roughly additive shift contribution for each substituent.

**Interpretation of N.m.r. Spectral Details.**—Since nuclear magnetic resonance gives information concerning the neighboring structure-building units around the unit to which the resonance peak is attributable, methods are needed for calculating the number of arrangements of all structure-building units which might occur around a given unit and the relative probabilities of these arrangements. A given unit and its immediate neighbors within a molecule represent a third-order environment. It follows that  $\theta$  of a  $\theta$ -order environment is a measure in terms of building units of the diameter of the environmental sphere. The first-order environment will denote the given structure building unit itself.

When only *neso*, end, and middle units are present, the number,  $\phi$ , of combinatorially distinct configurations (hence excluding consideration of spatial asymmetry or restricted rotation) is given as a function of the order of environment,  $\theta$ , by

$$\phi_0 = 1; \phi_1 = (\theta + 1)/2; \text{ and } \phi_2 = (\theta + 1)(\theta + 3)/8 \quad (2)$$

where the subscripts 0, 1, and 2 on the  $\phi$  refer to the *neso* (zero functional), end, and middle (difunctional) units, respectively.

The fraction,  $\mathfrak{Z}_i(X_\theta)$ , of the total structure-building units present as units of functionality  $i$  having a prescribed  $\theta$ -order environment,  $X_\theta$ , may be calculated from probability considerations.<sup>13</sup> For the case under consideration here

$$\mathfrak{Z}_1(\psi_a') = [e] \left( \frac{2[m]}{[e] + 2[m]} \right)^{a-1} \left( \frac{[e]}{[e] + 2[m]} \right) \quad \text{for } 1 \leq a \leq (\theta - 1)/2 \quad (3)$$

$$\mathfrak{Z}_1(\psi_a) = [e] \left( \frac{2[m]}{[e] + 2[m]} \right)^a \quad \text{for } a = (\theta - 1)/2 \quad (4)$$

$$\mathfrak{Z}_2(\psi_a', \psi_b') = \epsilon [m] \left( \frac{2[m]}{[e] + 2[m]} \right)^{a+b-2} \left( \frac{[e]}{[e] + 2[m]} \right)^2 \quad \text{for } 1 \leq a \leq b \leq (\theta - 1)/2 \quad (5)$$

$$\mathfrak{Z}_2(\psi_a', \psi_b) = 2[m] \left( \frac{2[m]}{[e] + 2[m]} \right)^{a+b-1} \left( \frac{[e]}{[e] + 2[m]} \right) \quad \text{for } 1 \leq a \leq (\theta - 1)/2, b = (\theta - 1)/2 \quad (6)$$

$$\mathfrak{Z}_2(\psi_a, \psi_a) = [m] \left( \frac{2[m]}{[e] + 2[m]} \right)^{2a} \quad \text{for } a = (\theta - 1)/2 \quad (7)$$

where  $[n] + [e] + [m] = 1$ ,  $\psi_a$  is a chain segment of  $a$  middles,  $\psi_a'$  is a chain segment of  $a - 1$  middles followed by an end, and  $\epsilon$  is a parameter which equals 1 when  $a = b$  and 2 when  $a \neq b$ ; *i.e.*,  $\mathfrak{Z}_2(\psi_a', \psi_b)$  refers to a middle unit connected to a chain segment of  $a - 1$  middles and an end on one side and a chain segment of  $b$  middles on the other side.

**Detailed N.m.r. Assignments.**—In the chloro system, sufficiently good resolution was achieved between each of the three peaks assigned to end groups and the six peaks assigned to middle groups that it seems worthwhile to discover what special placement in the molecules corresponds to each of these nine n.m.r. resonances. In doing this, the peaks will be captioned as shown in Fig. 1; *i.e.*, the one at  $-0.485$  p.p.m. will be called  $E_1$ ;  $-0.445$ ,  $E_2$ ;  $-0.434$ ,  $E_3$ ;  $-0.172$ ,  $M_1$ ;

(12) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

(13) For calculations which are consistent mathematically with our equations, see W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944); P. J. Flory, *J. Am. Chem. Soc.*, **74**, 2718 (1952).

TABLE I

PERCENTAGE OF TOTAL SILICON IN THE VARIOUS ARRANGEMENTS CORRESPONDING TO A FIFTH-ORDER ENVIRONMENT OF THE ENDS AND MIDDLES AS COMPARED TO THE N.M.R. PEAK AREAS

R	$e^1 e^1$			$e^1 m$			$e^1 m m$			$e^1 m m m$			$e^1 m m m m$			$m^4$		
	$\mathfrak{Z}_1(\psi_1')$	$E_1$	$\mathfrak{Z}_1(\psi_2)$	$\mathfrak{Z}_1(\psi_2')$	$E_2$	$E_3$	$\mathfrak{Z}_2(\psi_1', \psi_1')$	$M_1$	$\mathfrak{Z}_2(\psi_1', \psi_2')$	$M_2$	$M_3$	$\mathfrak{Z}_2(\psi_2', \psi_2')$	$M_4$	$\mathfrak{Z}_3(\psi_2', \psi_2)$	$M_5$	$\mathfrak{Z}_3(\psi_2, \psi_2)$	$M_6$	
0.192	1.85	2.4	1.66	0.83	2.9	14.8	1.50	1.4	13.29	3.1	13.1	0.67	3.0	11.95	12.6	55.03	46.2	
.403	8.01	7.7	6.21	3.11	7.7	21.1	4.82	3.8	16.70	7.9	15.3	1.87	3.7	12.96	11.5	22.48	19.8	
.592	16.48	13.4	10.84	5.42	14.3	19.8	7.13	6.4	13.71	10.2	11.5	2.35	4.3	9.03	7.9	8.68	5.5	
.819	28.17	28.3	14.41	7.21	17.3	15.10	7.37	9.2	7.72	9.4	5.2	1.89	2.2	3.96	2.3	2.07	1.3	
.999	36.11	36.5	14.42	7.21	17.4	9.56	5.76	10.8	3.83	5.0	1.9	1.15	0.7	1.54	0.6	0.51	0.4	
1.203	40.84	40.1	11.61	5.80	13.1	4.61	3.30	7.9	1.32	3.4	0.3	0.47	.2	0.38	.2	.07	0	
1.403	39.33	38.7	7.41	3.70	8.9	1.72	1.40	4.3	0.52	1.0	0	.13	.2	.01	0	.00	0	
1.614	30.80	30.7	3.29	1.64	2.8	0.39	0.35	2.3	.04	0	0	.02	0	.00	0	.00	0	
1.798	18.23	20.0	0.91	0.46	1.4	0.05	0.05	1.0	.00	0.5	0	.00	0	.00	0	.00	0	

<sup>a</sup> The building unit corresponding to the observed n.m.r. peak is given in bold-face type, with the neighboring building units that affect the position of the peak also being shown.

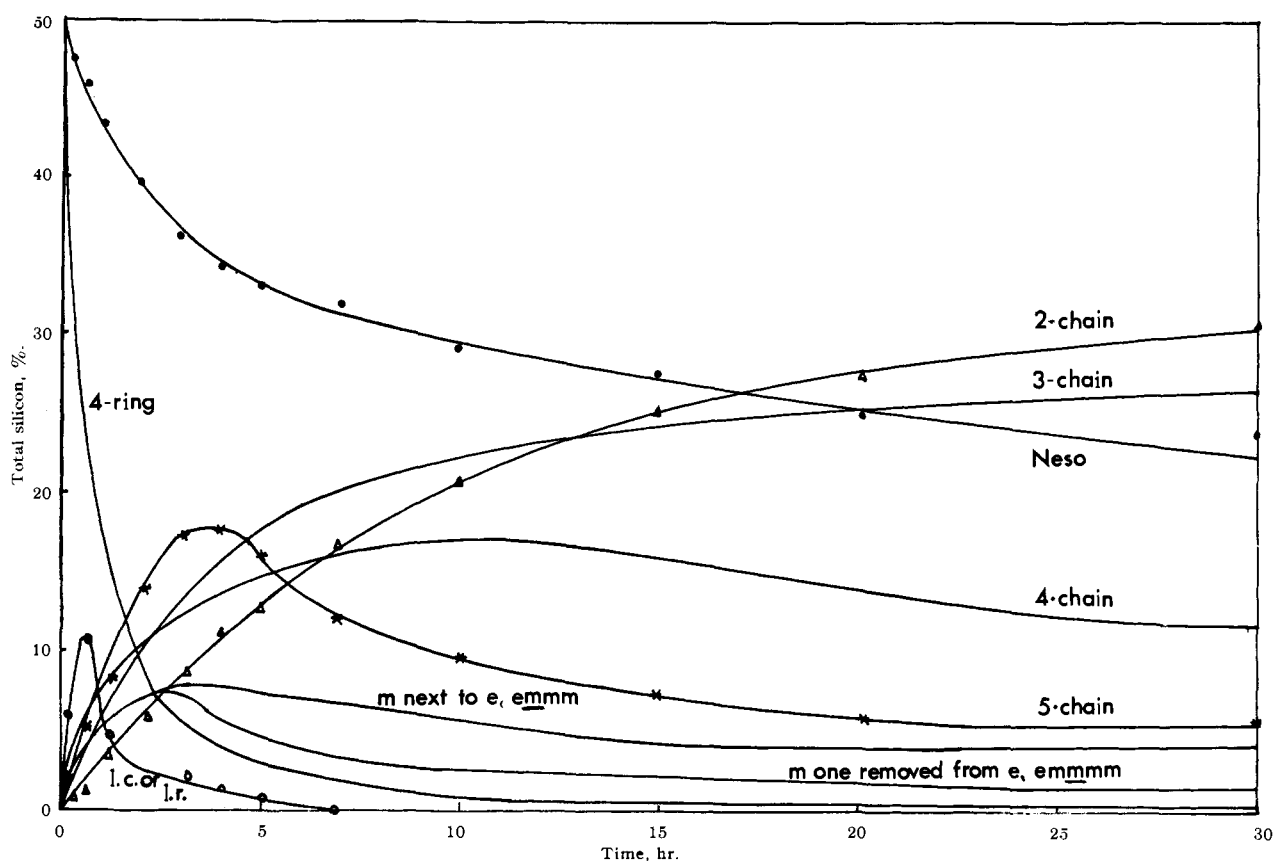


Fig. 3.—Variation with time of the percentage of total silicon present in certain molecules and molecular building units during equilibration at 200° of a mixture of dichlorodimethylsilane (1 mole) and octamethylcyclotetrasiloxane (0.25 mole) with 0.5 wt. %  $\text{AlCl}_3$ . To avoid confusion, experimental points are shown only for the *neso* compound, ●; the di-chain, Δ; the penta-chain, \*; and the long chains on large rings, O. [l.c. denotes long chains and l.r. large rings.]

−0.134,  $M_2$ ; −0.125,  $M_3$ ; −0.097,  $M_4$ ; −0.087,  $M_5$ ; and −0.067,  $M_6$ .

Since there are 3 end- and 6 middle-group resonances, we can tentatively conclude that a fifth-order environment of the structure-building units has been covered in these measurements (*i.e.*, for  $\theta = 5$ ,  $\phi_1 = 3$  and  $\phi_2 = 6$ , according to eq. 2). From the fact that the di-chain exhibits only the  $E_1$  peak, the tri-chain the  $E_2$  peak, and the tetra-chain the  $E_3$  peak, we assign  $E_1$  to an end bonded to another end,  $E_2$  to an end bonded to a middle which in turn is attached directly to an end, and  $E_3$  to the ends of all chains containing four or more silicon atoms.

From the spectra on the reasonably purified tri- and tetra-chains, we clearly assign  $M_1$  to the middle between two ends, and  $M_2$  to each of the two middles found between the two ends of the tetra-chain. The next sure assignment is for  $M_6$ , which was observed for the middles in long chains. In other words,  $M_6$  corresponds in a fifth-order environment of building units to those middle groups having two middle groups on either side of them. This leaves  $M_3$ ,  $M_4$ , and  $M_5$  to be assigned to the remaining three configurations of a second-order environment, namely middles with an end-middle sequence on one side and either an end, an end-middle, or a middle-middle on the other.

In Table I, the areas of the n.m.r. resonance peaks corresponding to the three end- and six middle-group assignments are compared with the relative amounts of end and middle groups having a fifth-order environment as calculated with an IBM-704 computer from eq. 1 and 3–7 using  $K = 0.110$  for eq. 1. The generally good agreement between the observed and calculated values shows that (a) the assignments of peaks  $M_3$ ,  $M_4$ , and  $M_5$  are properly made in Table I;

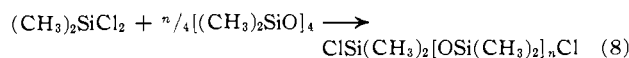
(b) hence the assumption of a fifth-order environment is correct, and (c) the sorting of end and middle groups into molecules is essentially random.

Now that all peaks have been assigned, we can roughly estimate how many rings are present. First off, since there was no resonance maximum at −0.100 p.p.m., it appears that the amount of trimeric rings in equilibrium in the reorganization product corresponds to less than *ca.* 0.3% of the total Si. This finding is in accord with the work<sup>4</sup> on the polysiloxanes terminated with methyl groups. Those studies<sup>4</sup> also showed that there is an appreciable amount (*ca.* 5% of the total Si for small  $R$ -values) of tetra-rings in the system of methyl-terminated polydimethylsiloxanes. In the work reported here, a tetrameric ring at −0.075 p.p.m. was not observed. If it were assumed that this peak was submerged in the near-neighbor peak at −0.067 p.p.m., we would then expect the measured value for  $M_6$  would be larger than the calculated value for middles with a pair of middles on either side of them in ring-free systems. As shown in Table I, this does not seem to be the case for the  $\alpha,\omega$ -dichloropolydimethylsiloxanes since the measured values for  $M_6$  were always somewhat smaller than the calculated ones. Furthermore, in the kinetic studies reported in Fig. 3, the tetra-ring could be distinguished from peak  $M_6$  so that we must conclude that there is little, if any, tetra-ring at equilibrium.

Some computer runs were made assuming various amounts of rings at the chosen  $R$ -values. These calculations demonstrated that, if there were more than 2–5% of the total Si present as rings, an unacceptably poor fit between experiment and theory would have been found for the *ee* and *eme* molecules. The fact that the intensities of the  $E_1$  resonance in Table I were

not consistently larger than the calculated values indicated that, except for  $R < ca. 0.3$ , there was less than 2–5% of the total Si in rings. For  $R = 0.192$ , there may be anywhere from 0 to 10% of the total Si in rings.

**Reorganization Kinetics in the Chloro System.**—The variation in the n.m.r. resonance peaks with time was measured on a mixture of dichlorodimethylsilane with octamethylcyclotetrasiloxane, proportioned so that equimolar amounts of silicon were derived from each species.

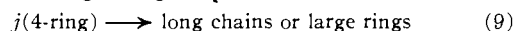


At 200° with 0.5 wt. % of  $AlCl_3$  as catalyst, it was found that the diminution of the *neso* molecules and of the total middle groups with time, as well as the increase of total end groups with time, gave a first-order plot over the period of time corresponding to the first half-life with a rather rapid switchover to a succeeding first-order plot for the remainder of the reaction (at least the next two half-lives). The half-life for the pseudo-first-order initial rate was found to equal 2.8 hr. and for the remainder of the process 7.8 hr. A similar experiment was carried out for a period of somewhat less than one half-life on the same mixture with no catalyst at the same temperature. In this case, first-order kinetics were again simulated and the measured half-life was 7560 hr. Even though there was undoubtedly a trace of HCl catalyst in the "uncatalyzed" system, it is seen that addition of only 0.5 wt. % of anhydrous aluminum chloride caused the reaction to go forty thousand times faster.

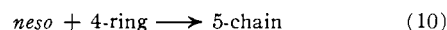
The variation of the change of the various measurable molecular species with time, as shown in Fig. 3, for this system at 200° with 0.5 wt. % aluminum chloride was calculated from the various resonance peaks as discussed in the previous section. Two prominent features of Fig. 3 are that the amount of tetra-rings decreases rapidly, the curves corresponding to the four- and five-membered chains go through broad maxima, and there is a sharp maximum for the middles in long chains or large rings as determined from n.m.r. peak  $M_6$  at

–0.067 p.p.m. A material balance, as well as subtraction of  $(M_3 + 2M_4)$  from  $E_3$ , shows that there are essentially no ends available for the middles in the long chains or large rings corresponding to  $M_6$  so that this curve in Fig. 3 truly corresponds to rings or macromolecular chains, including few if any chains shorter than the 20-membered molecule. By the way, it should be noted here that the resonance at –0.075 p.p.m. corresponding to tetrameric rings was reasonably well resolved from the one at –0.067 corresponding to middle groups not near the ends of chains so that, with good resolution, n.m.r. can be used to distinguish these two very similar types of middle groups.

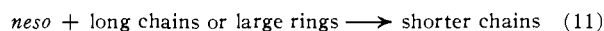
From the fact that the resonance corresponding to middle groups in long chains was the first to maximize, it is apparent that we have the following process occurring at the beginning of the reaction



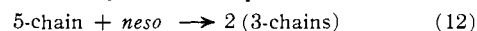
The early and prominent maximum noted for the five-membered chains shows that the following reaction is also initially prominent



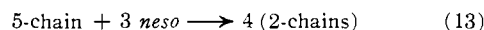
The rapid diminution in the long chains or large rings after they have maximized is most probably attributable to



Somewhat later on, it appears that the observed diminution of the five-membered chains is caused by the following mechanistically more complex over-all reactions



or, perhaps



After about 15 hr. under the experimental conditions of Fig. 3, it is apparent that all of the different species of molecules are in the process of exchanging parts with each other so that any theoretical explanation of the latter end of the curves of Fig. 3 must involve reactions between many different molecules, as must be the case at the final dynamic equilibrium.

[CONTRIBUTION FROM MONSANTO CHEMICAL CO., CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MO.]

## Exchange of Parts between Molecules at Equilibrium. II. Polyarsenous Oxyhalides

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Dissolution of arsenous oxide in either arsenic trifluoride or trichloride gives homogeneous liquids, the viscosity of which increases greatly with increasing arsenous oxide content. Thus, for a liquid made by combining 5 moles of  $AsX_3$  with 6 moles of  $As_2O_3$ , the viscosity at 20° is about  $10^5$  poises as compared to a value near  $10^{-2}$  poise for the pure trihalide.  $F^{19}$  nuclear magnetic resonance (n.m.r.) shows that the oxide and fluoride react to give a nearly statistically random mixture of end, middle, and branch molecular structure building units, along with the equilibrium amount of the trifluoride molecule. These structure building units are combined together in various ways to form molecules based on As–O–As linkages, with each arsenic exhibiting an unshared pair of electrons. The fine structure in the n.m.r. spectra was interpreted in terms of the various arrangements of ends, middles, and/or branches around either an end or middle group. The coalescence of separate n.m.r. peaks as the temperature is raised, distillation at 0° of more  $AsF_3$  from a mixture than the amount originally present at equilibrium, and n.m.r. experiments based on mixing liquids exhibiting various proportions of  $AsF_3$  and  $As_2O_3$  show that structural reorganization in these molecules is very rapid even at 0°. For a composition made by combining 10 moles of  $AsF_3$  with 7 moles of  $As_2O_3$ , the average lifetime of the structure building units with respect to reorganization is *ca.* 0.5 sec. at 20° and *ca.*  $10^{-2}$  sec. at 100°, with an activation energy for the reorganization process of 9.5 kcal.

Although there appears to be no *a priori* reason that arsenic should not exhibit as rich and replete a chemistry as that of phosphorus, few arsenic-based families of

compounds have been described. A reasonable explanation for this may well be that the majority of arsenic compounds undergo structural reorganization so readily that classical methods of separation and identification are inapplicable. This paper is one of

(1) Member of the Computer Center Staff of the University of California, Berkeley.