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REDISTRIBUTION STUDIES WITH ORGANOPOLYSILANES
I. METHOXY-SUBSTITUTED POLYSILANES*

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INTRODUCTION

The redistribution of a variety of substituents on the silicon atoms of monosilanes has been the subject of numerous publications**[1,2]. Related redistributions have also been studied, although to a considerably lesser degree, with polysilanes. A particularly interesting and synthetically useful type of redistribution in polysilanes is the silicon–silicon (Si–Si) and silicon–ligand (Si–L) exchange illustrated by the general equation (1).

$$\text{-SiSi-} + \text{-SiSiL} \rightarrow \text{-SiSiSi-} + \text{-SiL} \qquad (1)$$

Redistribution reactions of this latter type have been reported for halogen[3–8], hydrogen[9,10], cyano[8] and methoxy[11] ligands. While the majority of these reactions are base-catalyzed, thermally induced redistributions have been described[3,9].

In the case of methoxy ligands, only one example of the Si–Si/Si–L redistribution has been reported. Thus, heating 1,2-dimethyltetramethoxydisilane (I) in the presence of a catalytic amount of sodium gave methyltrimethoxysilane and an unidentified polysilane residue (2)[11].

$$(MeO)_2MeSi\text{-}SiMe(OMe)_2 (I) \rightarrow MeSi(OMe)_3 + \text{“Polysilane residue”} \qquad (2)$$

We now wish to report that this redistribution (2) is applicable to polysilanes containing two alkyl groups per silicon and that, because the exchange involves primarily the terminal silicon–silicon bonds, this reaction offers some unique advantages in the synthesis of methoxy-substituted polydimethylsilanes.

RESULTS AND DISCUSSION

In order to study the reaction products resulting from the Si–Si/Si–OMe redistribution, it seemed advisable to begin with mono- or di-functional derivatives rather than the tetra-functional compound (I). The homologous series, $MeO\cdot(SiMe_2)_nOMe$ (where $n=2$–4) was prepared by treatment of the corresponding silanes, $H(SiMe_2)_nH$***, with methanol in the presence of catalytic amounts of li-

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[*] Presented in part at the Division of Organic Chemistry, 150th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September 13–17, 1965, Abstracts, p. 76S.

[**] For a recent review of this subject see ref. 1.

[***] Prepared from a mixed sodium coupling of Me_2HSiCl and Me_2SiCl_2[12].

$$H(SiMe_2)_nH+2\,MeOH \xrightarrow{LiOMe} MeO(SiMe_2)_nOMe+2\,H_2 \tag{3}$$

thium methoxide* (3). In all cases a small amount of silicon–silicon bond cleavage was observed as evidenced by the formation of dimethyldimethoxysilane. The physical properties and pertinent analytical data for the $MeO(SiMe_2)_nOMe$ series are given in Table 1. Further structural confirmation of this series was obtained from the infrared, NMR (see Table 2), UV (see Table 3) and mass spectral data**.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR THE $MeO(SiMe_2)_nOMe$ SERIES

n	*B.p.* [°C(mm.)]	n_D^{26}	*Mol. wt.*[a]	*Analysis (%)*[b] *C*	*H*	*Si*
2	84	1.4207	178	39.8	9.82	31.5
	(90)			39.8	9.95	31.4
				(40.4)[b]	(10.1)	(31.5)
3	79	1.4569	236	41.4	10.4	35.1
	(10)			41.7	10.2	35.3
				(40.6)	(10.2)	(35.6)
4	116	1.4809	294	40.8	9.49	37.9
	(10)			41.4	9.48	38.3
				(40.8)	(10.2)	(38.1)
5	125	1.4974	352	40.9	10.1	
	(3)			41.0	10.1	
				(40.9)	(10.2)	

[a] Calculated and observed values by mass spectroscopy. [b] Calculated values are in parentheses.

TABLE 2

NMR DATA FOR THE $MeO(SiMe_2)_nOMe$ SERIES (τ VALUES)

n	*Assignment*[a] *MeO-*	$-OSiMe_2-$	$-OSiSiMe_2-$	$-OSiSiSiMe_2-$
2	6.61	9.81		
3	6.63	9.80	9.85[b]	
4	6.63	9.80	9.84[b]	
5	6.62	9.80	9.83	9.825[b]

[a] All peaks were singlets and gave the correct proton ratios. [b] Spectrum run at 50 cps.

In view of recent observations that the ultraviolet absorption of polysilanes is characteristic of the chain length[14–18] it is instructive to compare the ultraviolet properties of the $H(SiMe_2)_nH$ and $MeO(SiMe_2)_nOMe$ series with those previously reported for the $Me(SiMe_2)_nMe$ series[14] (see Table 3). Examination of Table 3 shows that in these series the λ_{max} is relatively independent of the end group. Thus, the band position is of considerable value in determining the length of the polysilane chain.

We observed that 1,2-dimethoxytetramethyldisilane (II) undergoes the

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* This reaction has been previously[13] employed for the preparation of alkoxy-substituted monosilanes.

** The mass spectra of these and numerous other polysilane derivatives have been determined and the results will be the subject of a later report.

TABLE 3

UV SPECTRAL DATA FOR THE R(SiMe$_2$)$_n$R SERIES

n	*R*	*Band position* λ_{max} *(mμ)*	*Molar absorbtivity* ε
2	H	below 200	
	OMe	below 200	
	Me[a]	below 200	
3	H	218	7,400
	OMe	222	6,300
	Me	215	9,000
4	H	236	12,600
	OMe	238	12,000
	Me	235	14,700
5	H	248	22,000
	OMe	251	13,200
	Me	250	18,400

[a] The values for R=Me were determined previously[14-16].

SiSi/SiOMe redistribution on heating in the presence of a lithium alkoxide catalyst. The sequential conversion of (II) to the higher molecular weight methoxypolysilanes by heating at 100° with lithium methoxide is shown in Fig. 1. The amount of (II) decreased sharply within a ten-hour period to give, via reaction (4), a high yield of

$$2\,\mathrm{MeO(SiMe_2)_2OMe(II)} \rightarrow \mathrm{Me_2Si(OMe)_2} + \mathrm{MeO(SiMe_2)_3OMe(III)} \qquad (4)$$

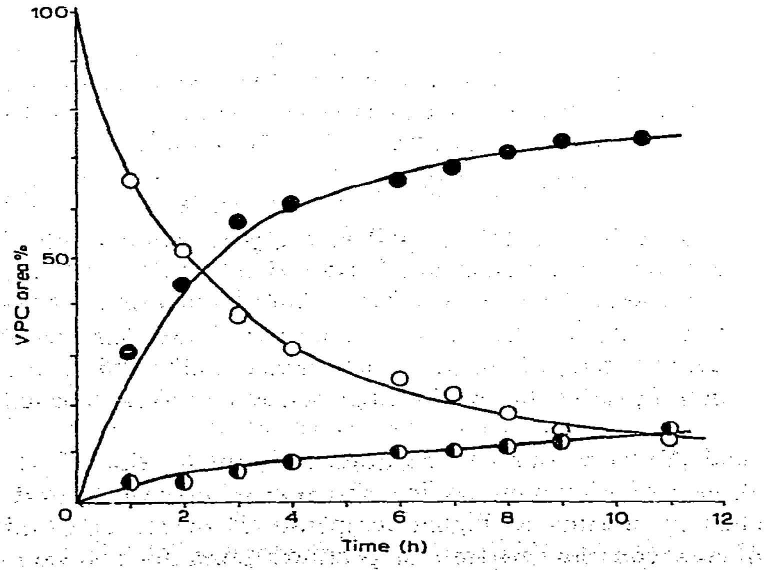


Fig. 1. Observed MeO(SiMe$_2$)$_n$OMe distribution *vs.* time for the reaction of MeO(SiMe$_2$)$_2$OMe in the presence of 1% MeOLi at 100±5°; ○, *n*=2; ●, *n*=3; ◐, *n*=4.

trisilane (III). The small amount of tetrasilane (IV) present at this time was presumably formed by the competitive reaction (5). When the reaction was carried out on a preparative scale, 55–60% of the trisilane (III) was obtained.

$$\text{(II)} + \text{(III)} \rightarrow Me_2Si(OMe)_2 + MeO(SiMe_2)_4OMe\ \text{(IV)} \qquad (5)$$

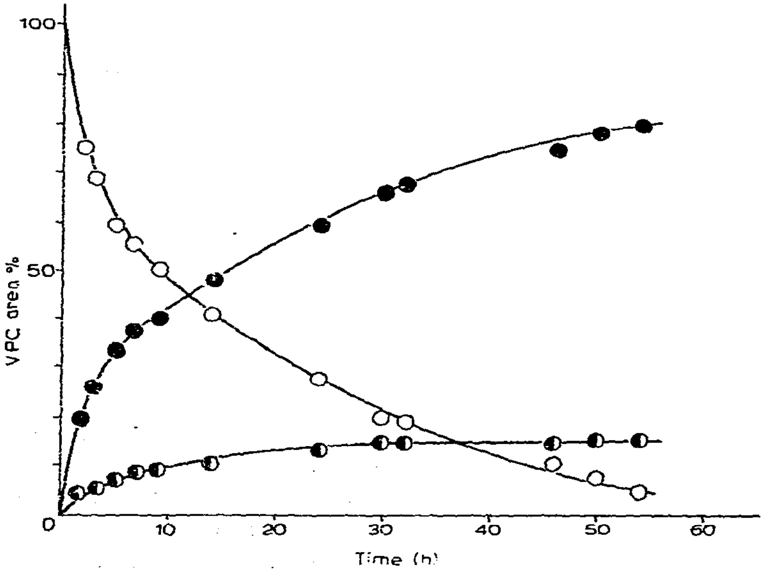


Fig. 2. Observed $MeO(SiMe_2)_nOMe$ distribution *vs.* time for the reaction of $MeO(SiMe_2)_3OMe$ in the presence of 1% MeOLi at 185±5°; ○, $n=3$; ◐, $n=4$; ●, $n=5$.

When (III) was heated at 185° in the presence of lithium methoxide (see Fig. 2), the major product was the pentasilane (V) suggesting that the predominant reaction was (6). The tetrasilane (IV) was again observed as a minor product. In preparative scale reactions, 40–50% of the pentasilane (V) was obtained.

$$2\ \text{III} \rightarrow Me_2Si(OMe)_2 + MeO(SiMe_2)_5OMe\ \text{(V)} \qquad (6)$$

At no time during the redistribution of (II) or (III) were appreciable amounts of materials of chain length greater than the pentasilane (V) detected by VPC. Also, the results obtained in Figs. 1 and 2 were the same whether or not dimethyldimethoxysilane was removed continuously during the reaction. The partial vaporization of dimethyldimethoxysilane during the redistribution experiments resulted in erratic trends in the concentration of this product upon VPC analyses, and it was not plotted in Figs. 1 and 2.

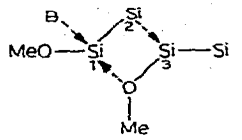
Compounds (IV) and (V) were found to be quite resistant to SiSi/SiOMe exchange at 185° in the presence of lithium methoxide. Attempts to force the redistribution of these compounds by heating at higher temperatures or for extended periods of time resulted in a complex mixture of products containing silicon–hydrogen bonds. Apparently a base-catalyzed rearrangement competes with the ligand exchange under these conditions, since these compounds are thermally stable at 185° in the absence of added base. Similarly, no redistribution was observed when methoxypentamethyldisilane was heated at 185° in the presence of lithium methoxide.

A reinvestigation of the first reported SiSi/SiOMe redistribution, that of 1,2-dimethyltetramethoxydisilane (I), confirmed the previous[11] findings. The lithium methoxide-catalyzed redistribution of (I) was extremely rapid at 130°, and within five minutes 98% of the theoretical amounts of methyltrimethoxysilane was obtained, based on the stoichiometry in equation (7). The application of the redistribution of (I) for the synthesis of $[(MeO)SiMe]_n$ and $(MeSi)_n$ materials is currently under investigation.

$$(MeO)_2MeSi{-}SiMe(OMe)_2\ (I) \rightarrow MeSi(OMe)_3 + [(MeO)SiMe]_n \qquad (7)$$

The above results on the SiSi/SiOMe redistributions in the $MeO(SiMe_2)_nOMe$ series demonstrates that these reactions proceed primarily by exchange of the SiOMe group and the terminal Si–Si bond to give dimethyldimethoxysilane and a methoxy-ended polysilane containing $(2n-1)$ silicons. Also, the reactivity of the series decreases rather dramatically with increasing chain length; *i.e.*, (II) > (III) > (IV) or (V). The combination of these two factors allows the conversion of (II) and (III) into the higher homologues in good yields. Finally, our initial studies with 1,2-dimethyltetramethoxydisilane (I) indicate that this material undergoes a similar redistribution reaction. The greater reactivity of (I) relative to 1,2-dimethoxytetramethyldisilane (II) and methoxypentamethyldisilane shows that the ease of SiSi/SiOMe redistribution increases with increasing methoxy substitution, and again suggests a reaction scheme involving nucleophilic attack at the terminal silicon atom.

The above data are consistent with a mechanism involving nucleophilic assistance in a four-centered transition state of the type:



Attack by the base (B) on acceptor 1-Si should weaken the 1-Si–2-Si bond thus favoring the formation of the incipient silanion, Si_2. Simultaneous attack of this incipient silanion on 3-Si and transfer of the methoxy group to 1-Si completes the exchange. An alternative mechanism involving stepwise formation of the silanion 2-Si, followed by attack of this species at 3-Si is also consistent with these data. The formation of the tetrasilane (IV) from the trisilane (III) and MeOLi (see Fig. 2) suggests that base attack at a non-methoxy bearing silicon atom (*e.g.*, 2-Si) also occurs, although to a lesser degree.

We are continuing our studies of the general redistribution (1), as applied to related methoxy-substituted polysilanes and other SiSi–L groupings, in an attempt to determine the scope, mechanism and synthetic utility of these reactions.

EXPERIMENTAL

All VPC analyses were obtained with an F and M Model 300 Gas Chromatograph using an 8′ × 0.25″ column packed with a mixture of Dow Corning® FS-1265 Fluid on Chromsorb W (30%) and 25% Dow Corning® 200 Fluid on Chromsorb

W (20%). Ultraviolet spectra were obtained with a Cary Model 15 Spectrophotometer. Nuclear magnetic resonance spectra were determined with a Varian A60 Spectrometer as *ca.* 10% solutions in carbon tetrachloride using tetramethylsilane as internal standard. The n-butyllithium (15% in hexane) was purchased from Foote Mineral.

A. Reaction of the $H(SiMe_2)_nH$ series with methanol

The reactions were carried out in the same manner for all $H(SiMe_2)_nH$ ($n = 2$–4) compounds and will be described in detail for the disilane.

To a 500-ml three-necked, round-bottomed flask, fitted with a stirrer, thermometer, condenser and a wet test gas meter, was added 59 g (0.5 mole) of sym-tetramethyldisilane[12] and 200 ml of anhydrous methanol. To this rapidly stirred mixture was added 2 ml of n-butyllithium. The evolution of hydrogen occurred almost immediately and the reaction became exothermic. External cooling was applied so that the reaction temperature did not exceed 40°. After 3–4 h the evolution of hydrogen ceased and 2–3 ml of allyl bromide was added to destroy the catalyst. The methanol was removed by distillation under a nitrogen atmosphere and the residue distilled to give 62 g (81%) of 1,2-dimethoxytetramethyldisilane (II).

The same experimental procedure, although on a smaller scale, gave 1,3-dimethoxyhexamethyltrisilane (64%) and 1,4-dimethoxyoctamethyltetrasilane (55.5%).

B. Redistribution of the $MeO(SiMe_2)_nOMe$ series with MeOLi

The data in Figs. 1 and 2 were obtained by mixing a small amount of the $MeO(SiMe_2)_nOMe$ compound with 1% n-butyllithium (generating 1% MeOLi) in a 25-ml flask equipped with a condenser, septum cap and nitrogen inlet. The desired temperature was maintained at 185 ± 5° using a constant temperature bath.

In the case of $MeO(SiMe_2)_4OMe$ (IV), VPC analyses showed a complex mixture of products, and strong absorptions at 4.7 μ characteristic of SiH bonds were present in the infrared spectrum.

C. Preparation of $MeO(SiMe_2)_3OMe$ (III)

To a 100-ml flask, equipped with a septum cap inlet and attached to an 18-inch Nester Faust spinning band column, was added 3 ml of dimethyldimethoxysilane and 4.4 ml of n-butyllithium (1%). Following the resultant exothermic reaction, 44.6 g (0.24 mole) of 1,2-dimethoxytetramethyldisilane (II) was added. The flask was heated using a 100° constant temperature bath. After 10 to 11 h 15 g of dimethyldimethoxysilane was collected. The reaction residue was cooled, quenched with 2 ml of allyl bromide and distilled to give 18.1 g (61%) of 1,3-dimethoxyhexamethyltrisilane (III). Vapor-phase chromatographic analyses of the residue (5 g) indicated that it was 90% 1,4-dimethoxyoctamethyltetrasilane (IV).

D. Preparation of $MeO(SiMe_2)_5OMe$ (V)

To a 50-ml flask, equipped with a septum cap inlet and attached to an 18-inch Nester Faust spinning band column, was added 3 ml of dimethyldimethoxysilane and 3 ml of n-butyllithium (1%). Following the resultant exothermic reaction, 26.2 g (0.092 mole) of 1,3-dimethoxyhexamethyltrisilane (III) was added. The reaction mixture was heated to 185° using a constant temperature bath. After 48 h, 4.6 g of dimethyldimethoxysilane was collected. The reaction residue was cooled, quenched with 2 ml of allyl bromide and distilled to give 8.1 g (50%) of 1,5-dimethoxydecamethylpentasilane (V).

E. Thermal stability of the $MeO(SiMe_2)_nOMe$ *series*

These compounds were shown to be thermally stable at their respective redistribution temperatures by heating for 16 h in sealed glass tubes ($n=2$, 150°; $n=3$, 185°; $n=4$, 185°; $n=5$, 185°) followed by VPC analyses.

F. Preparation of methoxypentamethyldisilane

A solution of 20.2 g (0.2 mole) of triethylamine and 6.4 g (0.2 mole) of anhydrous methanol was added slowly beneath the surface of a solution of chloropentamethyldisilane[19] (25 g, 0.1 mole) and 250 ml of dry hexane. Subsequent to stirring for 3 h, the mixture was filtered under nitrogen to remove the hydrochloride and distilled to give 8.8 g (35.6%) of methoxypentamethyldisilane, b.p. 129–130°; n_D^{26} 1.4225. (Found: C, 44.5, 44.7; H, 10.6, 10.5; Si, 34.7; Mol. Wt. by mass spectroscopy, 162. $C_8H_{18}OSi_2$ calcd.: C, 44.4; H, 11.1; Si, 34.6%; Mol. Wt., 162.

The NMR spectrum of this compound showed singlets at 6.62 9.85 and 9.92 τ in a 1:2:3 ratio, characteristic of the SiOMe, Me_2Si and Me_3Si protons.

Methoxypentamethyldisilane did not undergo the SiSi/SiOMe redistribution when heated at 185° with 1% MeOLi for 16 h.

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SUMMARY

The first detailed study of the base-catalyzed redistribution of silicon–silicon and silicon–methoxy groups has been carried out. Subsequent to the preparation of the previously unreported series, $MeO(SiMe_2)_nOMe$ ($n=2-5$), it was observed that the lower members ($n=2$ and 3) undergo a facile base-catalyzed SiSi/SiOMe redistribution. Because this redistribution involves primarily the terminal silicon–silicon bonds, this reaction offers some unique advantages in the synthesis of methoxy-substituted polydimethylsilanes.

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