

sym-DIMETHOXYTETRAMETHYLDISILAZANE

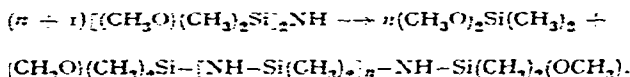
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INTRODUCTION

In an investigation of the properties of some alkoxydisilazanes, Buerger and Wannagat¹ found that pyrolysis of hexamethoxydisilazane at 200° in a sealed tube led to the formation of crosslinked polymers, accompanied by the evolution of tetramethoxysilane. This observation led to the thought that if a partially methoxylated methyl-disilazane could be prepared, then it might be possible to achieve a condensation to give a linear silicon-nitrogen framework rather than a crosslinked one:



With one methoxy group per silicon atom, dimethoxytetramethyldisilazane could not lead to a crosslinked structure if the reaction mechanism merely involved the splitting out of dimethyldimethoxysilane, as shown here.

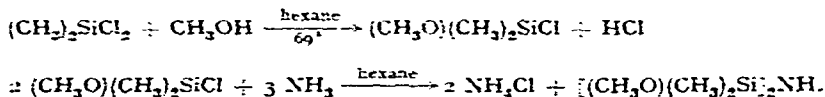
EXPERIMENTAL

Materials

Dimethyldichlorosilane was kindly supplied by the Silicone Products Department of the General Electric Company and was used without further purification. All solvents were dried over sodium wire.

Analytical methods and apparatus

Standard methods of analysis for carbon, hydrogen, nitrogen and silicon were employed. Infrared spectra were obtained on pure liquid films using a Perkin Elmer 137 Spectrophotometer. The NMR spectra were taken in carbon tetrachloride as solvent with tetramethylsilane as the reference, using a Varian A-60 Spectrometer.

Preparation of dimethoxytetramethyldisilazane

In a typical experiment 5 moles of dimethyldichlorosilane was added to 1.5

of dry *n*-hexane in a 3-l, 3-necked flask equipped with a stirrer, reflux condenser and dropping funnel. Five moles of methanol was added dropwise, and HCl evolution began immediately. After all the methanol had been added the reaction mixture was refluxed for 2 h and the apparatus flushed with dry nitrogen to remove traces of hydrogen chloride. The products of this reaction were not isolated; ammonia gas was added directly to the hexane solution, and ammonium chloride was precipitated immediately. The reaction was highly exothermic. Ammonia addition was continued for 4 h until the reaction mixture began to cool.

The hexane solution was separated from the ammonium chloride by suction filtration. The precipitate was then washed with 2 l of hexane, and the two hexane fractions were combined and distilled. The liquid boiling above 95° weighed 312 grams, a 66% yield of crude *syn*-dimethoxytetramethyldisilazane. This was fractionally distilled at atmospheric pressure, 740 mm, using a short column packed with glass helices. Since the normal boiling points of hexamethyldisilazane and hexamethoxydisilazane are 126° and 220°, respectively, the boiling point expected for dimethoxytetramethyldisilazane should have been approximately $126^\circ + (220^\circ - 126^\circ)/3 = 157^\circ$; Fraction (I), the desired material, boiled at 162–164°, n_D^{20} 1.4148, d_4^{20} 0.923, yield 37%. (Found: C, 36.82; H, 9.90, 9.82; N, 7.33; Si, 30.25; mol. wt., 205. $C_6H_{19}NO_2Si_2$ calcd.: C, 37.25; H, 9.90; N, 7.24; Si, 29.04; mol. wt., 193.) Fraction (II), b.p. 178–182°, n_D^{20} 1.4315, d_4^{20} 0.941, yield 13%. (Found: C, 34.93; H, 9.41; N, 10.82; Si, 30.99; mol. wt., 290. $C_8H_{26}N_2O_2Si_3$ calcd.: C, 36.02; H, 9.83; N, 10.50; Si, 31.60%; mol. wt., 267.) (Fraction (III), b.p. 210–225°, yield 11%. Fraction (IV), b.p. 255–265°, yield 5%. There was also 10 g of a higher-boiling oily material, liquid at room temperature.

Infrared spectra of compounds (I) through (IV)

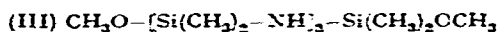
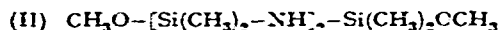
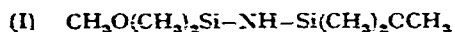
All of the spectra were identical except for the appearance of an additional absorption at 1025 cm^{-1} in the spectrum of compound (IV), probably due to Si–O bonds from hydrolysis. Most of the peaks in the spectrum of compound (I) could be assigned by comparison with values reported by Smith² for some alkoxy silicon compounds and also the infrared absorption frequencies of hexamethylcyclotrisilazane discussed by Kriegsmann³. The infrared absorption frequencies of compound (I) and their relative intensities are entirely consistent with that expected for dimethoxytetramethyldisilazane.

NMR spectra of compounds (I) through (IV)

The spectrum of compound (I) showed only 2 peaks, one of which was assigned to methyl protons at δ 0.06 upfield from TMS and the other, due to methoxy protons, at δ 3.4. Integration gave a ratio of methyl to methoxy protons of 2.1/1. Since there was only one methyl and one methoxy peak, all of the methyl groups and all of the methoxy groups in compound (I) are in the same respective environments.

The spectra of compounds (II), (III), and (IV) all contained three peaks. The single methoxy peak was in the same place as for compound (I), but the methyl peak was split, one part at δ 0.06 upfield from TMS (as in compound I) while the second was at δ 0.04 downfield. Furthermore, this second methyl peak became progressively larger in going from compound (II) to (III) to (IV). This illustrates that while all of these compounds contain only one type of methoxy group, structurally, there are two

distinct types of methyl group. The methyl-to-methoxy ratios were 3.08/1, 3.9/1 and 5.4/1, respectively. From the NMR data as well as the results of the elemental analyses and the infrared spectra, the following structures can be written:



(IV) A mixture of straight chain compounds composed largely of penta- and hexa-silazanes

Effect of various acids and bases on the Si-N bond in sym-dimethoxytetramethyldisilazane

The following series of experiments was performed to test the catalytic effect of various nonaqueous acids and bases on the polymerization of *sym*-dimethoxytetramethyldisilazane. Advantage was taken of the greater polarity of the silicon-nitrogen bond with respect to the silicon-carbon bond, and it was thought that cleavage of the silicon-nitrogen bonds under conditions where silicon-carbon bonds remain intact could lead to the formation of some novel polymeric silicon-nitrogen frameworks.

These experiments were all carried out in the absence of a solvent. The disilazane and the catalyst under examination were mixed and heated to the reflux temperature of the disilazane, 162°. When a sample of dimethoxytetramethyldisilazane was refluxed under nitrogen for 24 h in a 100 ml flask equipped with condenser and drying

TABLE I

RESULTS OF THE INFLUENCE OF VARIOUS CATALYSTS ON THE POLYMERIZATION OF *sym*-DIMETHOXY-TETRAMETHYLDISILAZANE

<i>Catalyst</i>	<i>Duration of the experiment</i>	<i>Products</i>	<i>Experimental evidence</i>
<i>Acid and base catalysis</i>			
Ammonium chloride	24 hours	unchanged disilazane	NMR and infrared spectra, b.p.
Ammonium bromide	24 hours	unchanged disilazane	NMR and infrared spectra, b.p.
Ammonium bromide	7 days	unchanged disilazane + 2-3 g of dimethyl-dimethoxysilane ^a	NMR and infrared spectra, b.p. NMR and infrared spectra, b.p., elemental analysis
Potassium cyanide	7 days	unchanged disilazane	NMR and infrared spectra, b.p.
<i>Alkoxide catalysis</i>			
Aluminum isopropoxide	24 hours	unchanged disilazane + 8-10 g of dimethyl-dimethoxysilane + mixture of tri- and tetra-silazanes	NMR and infrared spectra, b.p. NMR spectrum, b.p. NMR and infrared spectra, b.p. of the two constituents
Aluminum methoxide	24 hours	unchanged disilazane + dimethyldimethoxysilane + dimethoxyhexamethyltrisilazane	NMR and infrared spectra, b.p. NMR spectrum, b.p. NMR spectrum, b.p.

^a This compound caused severe conjunctivitis in two individuals.

tube, no change resulted. Any changes in the nature of the disilazane in the presence of a foreign substance must, then, be due to the so-called catalyst and not simply the prolonged heating in the experiments described below. One hundred g of the disilazane and 1 g of catalyst were used, and the products were separated by fractional distillation. The results of these studies are shown in Table I. Only sodium methoxide and potassium *tert*-butoxide entered into reaction with the disilazane, and these two reactions are discussed separately because of their complexity.

Reaction of sym-dimethoxytetramethyldisilazane with sodium methoxide

A mixture of 0.44 mole of disilazane with 0.1 mole of sodium methoxide was refluxed for 24 h as described above. Ammonia was given off and the insoluble sodium methoxide disappeared. At reflux temperature there was only a clear, slightly yellow liquid left at the end of the reaction. Upon cooling and standing for several hours, a crystalline solid, $[\text{CH}_3\text{O}(\text{CH}_3)_2\text{Si}]_2\text{N}^\ominus\text{Na}^\oplus$, (very sensitive to hydrolysis) separated from the liquid. A flame test indicated sodium. A sample was recrystallized from hexane, in which it was moderately soluble, and samples were hydrolyzed in aqueous methanol. The resulting alkaline solution was acidified with excess standard HCl and back-titrated with standard NaOH to determine the amount of sodium as sodium hydroxide. Standard Kjeldahl procedures were followed to determine the amount of nitrogen. (Found: N, 4.69; Na, 10.47. $\text{C}_{12}\text{H}_{32}\text{NNaO}_2\text{Si}_2$ calcd.: N, 4.65; Na, 10.05 %.) The NMR spectrum of this solid, taken in benzene, was identical with that of the disilazane in benzene except that the methyl protons were shifted 0.24 ppm upfield in the case of the solid. This shows the carbon (and, therefore, the nitrogen) to be less electronegative in the somewhat ionic sodium compound than they are in the disilazane itself. This is taken as further evidence for the identity of the solid reaction product.

The liquid fraction was distilled at atmospheric pressure and boiled at 78–82°. The NMR spectrum of this liquid showed it to be pure dimethyldimethoxysilane. Thirty-three grams of a solid residue which had been dissolved in the dimethyldimethoxysilane remained.

The polymeric material was insoluble in hexane, carbon tetrachloride, water and dilute acids. Concentrated sulfuric acid decomposed it easily. It was slightly soluble in benzene but could not be reprecipitated from this solvent. Therefore, the solid was not purified and no consistent analyses could be obtained. The NMR spectrum of the unpurified solid in benzene showed no methoxy protons and two very broad methyl proton peaks at 0.17 and 0.33 ppm, both upfield from TMS. The infrared spectrum of this material showed a rather weak absorption corresponding to the N–H stretching frequency. The average molecular weight of all of the constituents of this solid mixture, taken in ether, was 2420.

Reaction of sym-dimethoxytetramethyldisilazane with potassium tert-butoxide

If the methoxide ion of sodium methoxide had attacked the silicon–nitrogen bond in the disilazane, the product would still have been dimethyldimethoxysilane. To determine whether or not the alkoxide ion was in fact involved in the reaction in this way, the reaction of the disilazane with potassium *tert*-butoxide was studied. The general procedure was the same as that described above, but the reflux condenser was connected through two Leiden gas-washing bottles to a reservoir of concentrated

hydrochloric acid. Any ammonia generated during the course of the reaction was trapped in this way, and its amount determined by standard Kjeldahl procedures. It was found that in different experiments in which the amount of disilazane was kept constant and the amount of potassium *tert*-butoxide was varied, the moles of ammonia liberated per mole of potassium *tert*-butoxide was essentially constant.

The potassium *tert*-butoxide appeared to dissolve in the disilazane. After cooling, the reaction mixture consisted of a colorless crystalline solid which contained potassium and nitrogen (as determined by qualitative tests) and a slightly yellow liquid. The crystalline material was presumably the potassium salt of the disilazane. Analytical data were not obtained, but the solubility characteristics, sensitivity to moisture and presence of potassium, as well as the NMR spectrum taken in benzene, all argue in favor of the potassium salt. No potassium *tert*-butoxide could be isolated from the reaction mixture.

The liquid portion was separated from the crystals by filtration and distilled under vacuum.

Fraction A, b.p. 25–27° at 11 mm, was collected in a trap at –78°. The infrared spectrum, taken as a pure liquid film between sodium chloride plates, agrees in all respects with that of a known sample of dimethyldimethoxysilane. The NMR spectrum of $(\text{CH}_3)_2\text{Si}(\text{CH}_3\text{O})_2$ should contain just one methyl and one methoxy proton peak, and the experimental results are in agreement with this. There was, however, one other much smaller peak which has been assigned to the protons of the *tert*-butoxy group present in the impurity $(\text{CH}_3)_2\text{Si}(\text{CH}_3\text{O})(\text{C}_4\text{H}_9\text{O})$. The calculated methoxy-to-*tert*-butoxy proton ratio, if all of the potassium *tert*-butoxide reacted with the disilazane, is 2.4/1. The found value was 23/1. The methyl-to-methoxy ratio in the dimethyldimethoxysilane was found to be 1.06/1 and 1.1/1, compared to the calculated value to 1/1. (Found: C, 40.10; H, 10.61; Si, 23.35. $\text{C}_4\text{H}_{12}\text{O}_2\text{Si}$ calcd.: C, 39.92; H, 10.50; Si, 23.37 %.) There can be no doubt that fraction A is dimethyldimethoxysilane. The presence of the calculated amount of methoxy-*tert*-butoxydimethylsilane impurity gives credence to the notion that the aluminium *tert*-butoxide is not merely a catalyst, but actually takes part in the formation of products.

Fraction B, b.p. 64–70° at 11 mm, was unreacted *sym*-dimethoxytetramethyl-disilazane, as shown both by its infrared and NMR spectra. The calculated methyl-to-methoxy ratio for this compound is 2/1, while the values found were 2.1/1 and 2.08/1. (Found: C, 37.58; H, 9.90; N, 7.46; Si, 30.25. $\text{C}_6\text{H}_{19}\text{NO}_2\text{Si}_2$ calcd.: C, 37.25; H, 9.90; N, 7.24; Si, 29.04 %.)

Fraction C, b.p. 62–65° at 0.1 mm, had an NMR spectrum which contained 5 methyl peaks and one methoxy peak. They were in the ratio 4.0/1 and 4.2/1. The presence of only one methoxy peak is reasonable and shows that all of the methoxy groups are in the same environment. They are most likely attached to terminal silicon atoms, as they are in the starting material. The infrared spectrum was typical of a polysilazane in its general features and did show that there was a significant amount of N-H in the molecule. The relatively low boiling point of this compound suggests that it is probably not of high molecular weight. The analytical data do not correspond to the calculated values for any linear polysilazane, and no speculation as to its structure has been made.

The distillation residue was composed of a small amount of the potassium compound of the disilazane which had been dissolved in fractions A through C, and

also several grams of a colorless oily liquid. The NMR spectrum of this oil showed one type of methoxy group and a broad resonance for the methyl protons, composed of a large singlet and two smaller doublets. The methyl to methoxy ratio was 6.02/1. From the analytical data it was obvious that this oil was not strictly a linear polysilazane, for the nitrogen percentage was too low for that. The number of methyl peaks in the NMR spectrum also suggests a more complicated structure; n_D^{20} 1.4651. [Found: C, 34.71; H, 8.79; N, 11.90; Si, 42.50. $(C_2H_7NSi)_x$ calcd.: C, 32.84; H, 9.45; N, 19.15; Si, 38.37%.]

DISCUSSION

This study has shown that it is possible to prepare symmetrically methoxylated di-, tri- and tetrasilazanes in satisfactory yields from readily available starting materials with ease. Reaction of sodium methoxide and potassium *tert*-butoxide with the disilazane clearly leads to the formation of low molecular weight linear polymers. If these low polymers are pyrolyzed in the presence of a small amount of dissolved sodium or potassium salt of the disilazane, higher molecular weight solid polymeric materials are obtained. These are undoubtedly mixtures of compounds, some of which are somewhat crosslinked, as evidenced by the evolution of ammonia during the polymerization process. This *sym*-dimethoxytetramethyldisilazane system provides another example of cleavage of the N-H bonds under conditions at which rearrangement of Si-O and Si-N bonds occur.

ACKNOWLEDGEMENT

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SUMMARY

sym-Dimethoxytetramethyldisilazane and the corresponding tri- and tetrasilazanes have been prepared by the reaction of dimethyldichlorosilane with methanol, followed by treatment with anhydrous ammonia. The infrared and NMR spectra of these compounds have been examined. Prolonged heating of the disilazane in the presence of sodium methoxide or potassium *tert*-butoxide led to the formation of low-molecular-weight linear silicon-nitrogen polymers, as well as to some other silicon-nitrogen substances of a more complicated nature.

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