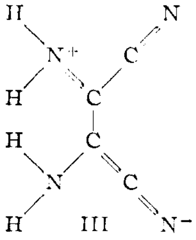
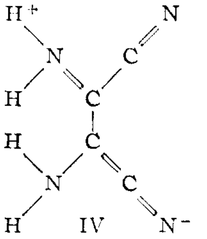
An extreme configuration of the amino groups in the *trans* derivative (where the cyano dipoles cancel) leads to an estimated moment of 2.2 *D* while a centro-symmetric configuration leads to zero moment.

In the *cis* derivative, the powerful cyano dipoles no longer cancel and an estimated moment of 4.2 or 5.2 *D* results (depending on the rotation of the amino groups).

The large moment found for the tetramer thus is incompatible with the *trans* configuration. While the estimated moments for the *cis* compound fall short of the observed moment, a favorable situation exists for participation by a number of highly polar resonance forms, III (2 forms), and IV (4 forms) which would increase the estimated moment.


III


IV

Heretofore the structure of the tetramer has been argued on the basis of its chemical reaction products. However, these reactions can be explained on the basis of either structure I or II since the possibility always exists that either structure may be converted to the other under the influence of any of the chemical reagents employed. It is important therefore to decide such a question by physical methods which would not be likely to alter the structure of the molecule. It is believed that the foregoing physical evidence supports the view that HCN tetramer exists as diaminomaleonitrile, both in the crystalline state and in dilute solutions in neutral solvents at ordinary temperature.

The assistance of the following members of the Stamford Laboratories is gratefully acknowledged: Dr. R. C. Hirt and Mr. F. T. King in the preparation and interpretation of the ultraviolet spectra; Dr. R. C. Gore, Mr. N. B. Colthup and Dr. J. E. Lancaster in the preparation and interpretation of the infrared spectra; Mr. R. McFarlane, Jr., in the determination of the dipole moment.

STAMFORD, CONNECTICUT

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Amination of Chloromethylsiloxanes

BY P. D. GEORGE AND J. R. ELLIOTT

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The amination of chloromethylpentamethyldisiloxane was studied in detail in order to develop a general procedure for aminating chloromethylsiloxanes without siloxane rearrangement. Application of the method to chloromethylheptamethylcyclotetrasiloxane gave the corresponding amines in 35–60% yields. Several (trimethylsilylmethyl)-amines also were synthesized. The alkylamine-substituted dimethylsiloxanes exhibited an extraordinary order of siloxane bond lability inasmuch as they polymerized on standing at room temperature and depolymerized on standing in solution. The physical properties and infrared spectra of the aminomethylsilicon compounds were determined and are discussed.

Previous publications on aminoalkyl silicon compounds have dealt principally with aminoalkylsilanes[1,2] and with aminoalkylsiloxanes[1,3] derived from them by hydrolysis or by sulfuric acid cleavage of methyl groups. Few aminomethylsiloxanes have been prepared by the amination of the corresponding chloromethylsiloxanes,[4,5] and no amine-substituted dimethylsiloxanes have been obtained in this way. We wish to describe the reaction of chloromethylpentamethyldisiloxane (MM'Cl)[6] and chloromethylheptamethylcyclotetrasiloxane ($D_3D'Cl$) with ammonia and amines, and we wish to report the properties of a number of novel compositions, particularly the amine-substituted dimethylsiloxanes, obtained in this way.

Studies aimed at developing a general procedure for amination of chloromethylsiloxanes were based on MM'Cl as a model compound because its structural features would permit ready detection of any siloxane rearrangement or silicon–carbon cleavage which might occur. The following was found to be a satisfactory procedure. Anhydrous liquid ammonia and MM'Cl in a 50:1 mole ratio were stirred for ten hours at 70° in a glass-lined autoclave. The ammonia was evaporated and the product slurry was filtered. Fractional distillation of the filtrate gave a 55% yield of pure aminomethylpentamethyldisiloxane ($MM'NH_2$). Important process vari-

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[1] (a) J. E. Noll, J. L. Spier and B. F. Daubert, THIS JOURNAL, **73**, 3867 (1951); (b) J. E. Noll, B. F. Daubert and J. L. Speier, *ibid.*, **73**, 3871 (1951).

[2] L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

[3] L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, **75**, 2932 (1953).

[4] J. L. Speier, U. S. Patent 2,567,131, September 4, 1951.

[5] Dow Corning Ltd., British Patent 697,684, September 30, 1953.

[6] For the sake of conciseness and clarity the carbon-functional siloxanes are designated by a short-hand system which is an extension of a system frequently used in the past. M signifies the $Me_3SiO_{0.5}$ group and D designates the $-SiMe_2O-$ group. The application of a prime to these symbols serves to indicate the presence of a substituent other than a methyl group; for example D' and D'' have served to designate $-SiMePhO-$ and $SiPh_2O-$, respectively. In the present case the prime indicates the presence of a methylene group thus:

$$Me_3SiOSiMe_2CH_2-$$
$$MM'$$
$$\underbrace{OSiMe_2OSiMe_2OSiMe_2OSiMeCH_2-}$$
$$D_3D'$$

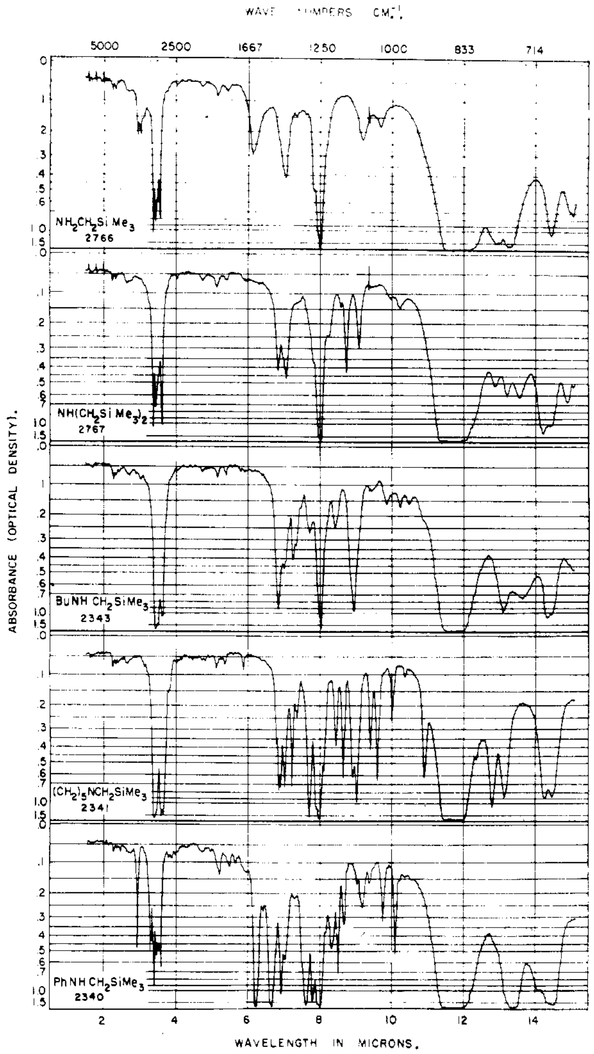


Fig. 1.—Infrared spectra of aminomethylmonosilanes.

ables whose rigid control were essential were reaction time and temperature, molar proportions, use of glass-lined equipment to exclude iron, and avoidance of aqueous washes.

Attention to the above details is much more critical than would at first be suspected. For example it was essential that reaction time and temperature be such as to ensure completeness of reaction, inasmuch as no convenient way was available for separating the starting material from the desired product. Chloromethylpentamethyldisiloxane and MM'NH$_2$ boil at very nearly the same temperature; even if this were not so, separation by distillation would be unattractive because further reaction would occur on heating, thus consuming product and clogging the still with solid amine hydrochlorides. The fact that MM'NH$_2$ decomposes in aqueous solution precluded use of the time-honored procedure for purifying amines, *i.e.*, solution in aqueous acid followed by removal of the insoluble neutral compounds and subsequent liberation of the amine with alkali.

Another ordinarily unimportant process variable that assumed importance in the amination of chloromethylsiloxanes was the use of a glass-lined reactor or other suitable means to exclude iron from the medium. The presence of iron seemed to affect the reaction adversely, perhaps by siloxane rearrangement or by silicon–carbon cleavage. Iron also was exceptionally troublesome because steam distillation from aqueous alkali could not be used to remove it.

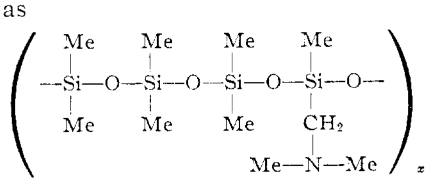
Even an aqueous sodium bicarbonate wash, commonly used to free amines of dissolved hydrochlorides, adversely affected the quality of MM'NH$_2$ obtained. This was demonstrated clearly in a run in which half of the crude product was washed and half was not washed prior to distillation. The product from the washed material contained appreciable amounts of a close-boiling impurity having a lower nitrogen content. The unwashed material gave a good yield of pure MM'NH$_2$.

Reaction of D$_3$D'Cl with anhydrous amines gave the corresponding aminomethylsiloxanes in 35–60% yields under process conditions selected with due regard for the variables shown to be important by the MM'Cl amination study. The reaction of D$_3$D'Cl with liquid ammonia proved to be an exception in that the product obtained was a benzene-soluble aminomethylsiloxane gum which lost nitrogen and became cross-linked on standing. Obtained as distilled liquids were: D$_3$D'NMe$_2$, D$_3$D'NEt$_2$, D$_3$D'NHBu, D$_3$D'NHPh and D$_3$D'NMePh.

While the amination of chloromethylsiloxanes with excess amine was satisfactory, the use of the theoretical amount of amine with an inert diluent also was investigated. The reaction of D$_3$D'Cl with amines in toluene and in isoöctane proceeded satisfactorily with formation of good yields of the corresponding aminomethylsiloxanes.

A number of aminomethylsilanes were prepared by the amination of chloromethylsilanes during the investigation of the aminomethylsiloxanes. Reaction of ClCH$_2$SiMe$_3$ with the appropriate amines gave BuNHCH$_2$SiMe$_3$, Et$_2$NCH$_2$SiMe$_3$, (CH$_2$)$_5$NCH$_2$SiMe$_3$, C$_6$H$_5$NHCH$_2$SiMe$_3$,[2] NH$_2$CH$_2$SiMe$_3$[1,2] and NH(CH$_2$SiMe$_3$)$_2$.[1,2] From the reaction of ClCH$_2$SiMe$_2$Cl with BuNH$_2$ there was obtained, apparently through the presence of moisture in the reagents, the cyclic aminomethylsiloxane, BuN(CH$_2$SiMe$_2$)$_2$O.

Most of the D$_3$D' amine compounds, which were initially obtained as distillable liquids, underwent polymerization on standing at room temperature. D$_3$D'NHC$_6$H$_5$ showed no change on prolonged standing; however, D$_3$D'NMe$_2$, D$_3$D'NEt$_2$, D$_3$D'NHBu and D$_3$D'NMeC$_6$H$_5$ gradually increased in viscosity and formed benzene-soluble sirups and gums. The polymerization occurred in tightly closed containers with little, if any, formation of volatile nitrogen compounds and was therefore apparently primarily a manifestation of siloxane rearrangement involving the formation of such compositions as



$$\left(\begin{array}{cccccccc} \text{Me} & & \text{Me} & & \text{Me} & & \text{Me} & \\ | & & | & & | & & | & \\ -\text{Si}- & \text{O} & -\text{Si}- & \text{O} & -\text{Si}- & \text{O} & -\text{Si}- & \text{O}- \\ | & & | & & | & & | & \\ \text{Me} & & \text{Me} & & \text{Me} & & \text{CH}_2 & \\ & & & & & & | & \\ & & & & & & \text{Me}-\text{N}-\text{Me} & \end{array}\right)_x$$

The molecular weights of (D$_3$D'NMe$_2$)$_x$ and (D$_3$D'-

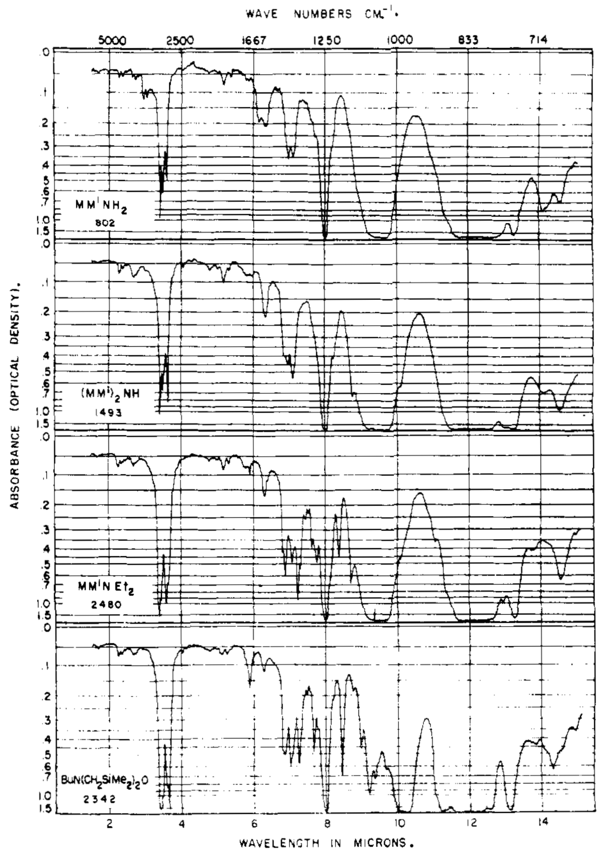


Fig. 2.—Infrared spectra of aminomethyldisiloxanes.

$NEt_2)_x$ determined cryoscopically at an early stage of their polymerization were found to be about three times the monomeric value. These aminomethylsiloxanes depolymerized on standing in 1% cyclohexane solution. The cryoscopic molecular weights dropped precipitously during the first few days, and during the next several days they began to level off at close to the tetrasiloxane value.

Densities and viscosities at three temperatures were determined for a number of the aminomethylsiloxanes. The specific refractions showed satisfactory agreement with the calculated values. The viscosity–temperature coefficients of aminomethylsiloxanes were significantly higher than those of the corresponding methylsiloxanes; this is indicative of enhanced intermolecular forces, attainment of which was one of the goals of this investigation.

The infrared spectra of fourteen aminomethyl silicon compounds were determined and the curves are given in Figs. 1, 2 and 3. (Trimethylsilylmethyl)-amine, $NH_2CH_2SiMe(OEt)_2$, (curve not shown) and $MM'NH_2$ exhibited definite absorption bands in the 2.9 and 6.3 μ regions, which are characteristic NH_2 group frequencies, although the bands were weaker than those found in the spectra of ordinary organic amines. All the secondary aminomethyl silicon compounds showed absorption bands in the 3.0 μ region, which are characteristic NH group frequencies; except for the medium bands in $C_6H_5NHSiMe_3$ and $D_3D'NHC_6H_5$, the bands were extremely weak (overtone intensity), but the absorption was consistently present in the spectra of the secondary amines and consistently absent from the spectra of the tertiary amines.[7,8] All the spectra exhibited an unusual, strong, single or double band in the 3.5–3.6 μ region; the location of these bands and the fact that they appeared in the spectra of all fourteen aminomethyl silicon compounds suggested that they are characteristic C–H stretching vibrations for a methylene group between silicon and nitrogen in aminomethyl silicon compounds.

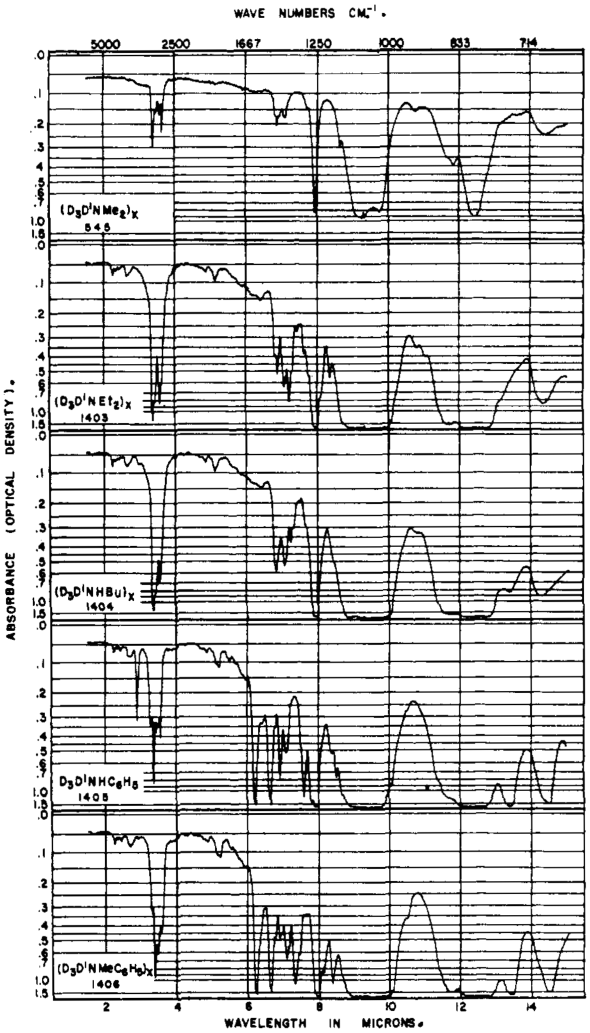


Fig. 3.—Infrared spectra of aminomethyldimethylpolysiloxanes.

Experimental

Amination of Chloromethylpentamethyldisiloxane.—A total of fifteen runs of the reaction of MM'Cl[9] with liquid ammonia was carried out. The most successful of these is described in detail below, and this is followed by the general features of the reaction established by the other runs.

In a glass-lined two-gallon autoclave was placed 482 g., 2.46 moles, of MM'Cl. The autoclave was sealed, partially evacuated and charged with 3460 ml., 2080 g., 122 moles, of anhydrous liquid ammonia. The reaction mixture was stirred vigorously for ten hours at 75° and 300 lb. per sq.

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(7) Reëxamination of the infrared spectra mentioned in ref. 1b showed that they also exhibited the characteristic NH_2 group frequencies. 8

(8) Since learned through Dr. J. L. Speier, Jr.,

(9) R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945).

in.; then the reaction mixture was cooled and the ammonia was allowed to evaporate.

The crude product consisted of a white slurry. Filtration followed by ether washing and drying to constant weight gave 150 g. of white solid—theory for NH_4Cl, 132 g. The 368-g. total liquid product, including 44 g. from ether washings, deposited several grams of white crystals on standing.

In order to determine the effect of washing the crude product, one-half was washed prior to distillation and the other was distilled directly. A 180-g. portion obtained by decantation was washed thoroughly with aqueous sodium bicarbonate and with distilled water and was dried over anhydrous potassium carbonate. A 186-g. portion for direct distillation also was obtained by decantation. The data for the two distillations are given in Table I.

Table I

Cut	Temp., °C. at 21 mm.	$n^{20}D$	Wt., g.	Neut. equiv.
	Distillation of Washed Portion			
1	47	1.4090	12.8	226
2	52	1.4103	12.6	212
3	52	1.4115	35.3	180
4	53	1.4110	14.1	177
5	54	1.4108	13.3	177
6	128	1.4138	5.5	
7	129	1.4168	4.2	
8	129	1.4158	12.9	
9	125	1.4140	14.8	
10	Residue	1.4259	9.5	
11	Trap	1.3881	15.2	
	Distillation of Unwashed Portion			
	at 16 mm.			
1	47	1.4100	30.9	178
2	47	1.4105	31.5	178
3	47	1.4105	31.3	178
4	51	1.4105	24.7	177
5	114	1.4180	11.3	
6	117	1.4178	4.6	
7	113	1.4170	13.7[a]	
8	Residue	....	18.0[a]	
9	Trap	1.3852	12.7	

[a] Cuts 7–8 contained much solid. The fact that no solid hydrochloride was obtained from the washed portion, whereas a relatively large amount was obtained from the unwashed portion, suggests that the hydrochloride did not arise from unreacted MM′Cl but that it was present as solute in the crude. In one case the white crystalline solid was filtered and washed with ether; it was a water-soluble, silicon-containing substance melting at 175°. Found: Cl, 17.2. Calcd. for $MM'NH_2 \cdot HCl$; Cl, 16.6.

The data from the first distillation clearly demonstrated the adverse influence of washing the product prior to distillation. The first four fractions in the second distillation represented 118 g., 0.67 mole, 54% yield of aminomethylpentamethyldisiloxane. The next three fractions represented 30 g., 0.09 mole, 15% yield of bis-(pentamethyldisiloxanylmethyl)-amine.

Anal. Calcd. for $C_6H_{19}ONSi_2$: C, 40.63; H, 10.80; Si, 31.65; neut. equiv., 177. Found for cut 2: C, 40.8; H, 10.9; Si, 31.6; neut. equiv., 177. Found for cut 3: C, 40.5; H, 10.7; neut. equiv., 177. Found for cut 4: C, 40.8; H, 10.8; Si, 32.4; neut. equiv., 176.

The secondary amine, $(MM')_2NH$, which was used for analysis, had b.p. 127° at 18 mm. and $n^{20}D$ 1.4161 and had been obtained in 22% yield in another run.

Anal. Calcd. for $C_{12}H_{35}O_2NSi_4$: C, 42.68; H, 10.45; Si, 33.24; neut. equiv., 338. Found for one cut: C, 42.7; H, 10.3; neut. equiv., 329. Found for another cut: C, 43.0; H, 10.6; Si, 32.6; neut. equiv., 333.

The above results with the unwashed portion were duplicated in another run. In this case there was obtained a 56% yield of $MM'NH_2$, b.p. 51° at 18 mm., $n^{20}D$ 1.4108.

The freezing point of $MM'NH_2$ was found to be −70.8°. This value was obtained from the melting curve of a 10-g. sample having a maximum 1.2° melting range. The material used had been prepared several months previously. The freezing point apparatus consisted of an N.B.S.-calibrated platinum resistance thermometer and a glass-metal cell immersed in a pre-cooled large brass block suspended in a Dewar flask. This apparatus was designed and constructed by Dr. J. D. Hoffman, and we are grateful to him for its use.

A number of other observations were made in connection with the amination of MM′Cl. The room temperature reaction of 1 mole of MM′Cl with 25–50 moles of NH_3 went to the extent of about 50% in ten hours and was substantially complete in 50 hours. The reaction at 70° was just about complete in four hours, but a ten-hour reaction time was used in our best runs to ensure completeness of reaction. Varying the molar excess of ammonia between 25:1 and 50:1 did not influence the yields of primary and secondary amines in the room temperature reaction. Yields of primary amine were much higher when the reaction was carried out at 70° than at room temperature. Some siloxane cleavage occurred during the amination, inasmuch as hexamethyldisiloxane was found in distillation foreruns and also was identified in the vented ammonia by mass spectrometric analysis.

In a number of the runs, particularly those which were not carried to completion, the solid by-products weighed more than the expected amount of ammonium chloride. This indicated the presence of amine hydrochlorides. In one case 275 g. of solid by-product was dissolved in water and steam distilled. There was obtained 40 g. of water-immiscible liquid which was identified by its infrared spectrum as trimethylsilanol, b.p. 98.5° (752 mm.) and $n^{20}D$ 1.3891.

Amination of Chloromethylheptamethylcyclotetrasiloxane.—In a two-gallon, glass-lined autoclave was placed 200 g., 0.60 mole, of $D_3D'Cl$.[10] The bomb was sealed, freed of air by evacuation, and charged with 900 ml., 540 g., 32 moles, of anhydrous liquid ammonia. The reaction mixture was stirred at 70° for ten hours and, after cooling, the ammonia was vented. The crude reaction product consisted of 209 g. of white, crumbly, dry gum having a strong ammoniacal odor.

The polymeric product was dissolved in about a liter of benzene. Considerable difficulty was encountered in separating the ammonium chloride; vacuum filtration failed due to excessive frothing, and gravity filtration proved inconveniently slow even when coarse paper and Filter-aid were used. Centrifugation finally gave 1460 ml. of a clear benzene solution of product. Removal of the benzene from a 250-ml. aliquot by evaporation to constant weight *in vacuo* left 25 g. of a slightly opalescent gum. The calculated total yield of polymeric product was 146 g. This material, apparently a condensation product of $D_3D'NH_2$, contained: C, 31.3; H, 8.1; N, 2.1; Si, 32.6. For comparison the values calculated for $D_3D'NH_2$ are: C, 30.84; H, 8.09; N, 4.50; Si, 36.03.

The polymeric product had a strong ammoniacal odor. Its already low nitrogen content became lower on standing for six months in a screw-cap closed container (Found: N, 0.8), and the polymer was no longer benzene-soluble. On the other hand, the 10% benzene solution of product remained clear upon standing one year; this benzene solution had an ammoniacal odor, and methylamine was detected by mass spectrometric analysis of the vapors over its surface.

(Dimethylaminomethyl)-heptamethylcyclotetrasiloxane $D_3D'NMe_2$.—Into an autoclave glass liner containing 49 g., 0.15 mole, of $D_3D'Cl$[10] was distilled 300 ml. (at 8°) of anhydrous dimethylamine. After having been wiped free of condensed atmospheric moisture, the reaction vessel was sealed into a one-liter Aminco autoclave and rocked at room temperature for 60 hours. The excess dimethylamine was vented, and the crude reaction product consisted of a white granular solid suspended in a colorless liquid.

The ether-washed and dried white solid weighed 11.7 g. and contained 40.6% ionic chlorine. Since theory for $Me_2NH \cdot HCl$ was 12.4 g. containing 43.5% ionic chlorine, the solid accounted for 90% of the chlorine in the starting material.

The liquid product gave a negative Beilstein test for halo-

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(10) R. H. Krieble and J. R. Elliott, This Journal, **68**, 2291 (1946).

gen. Rapid vacuum fractional distillation of 36 g. of the liquid product gave 17.3 g., 0.051 mole, 34% yield of $D_3D'NMe_2$ in two fractions, b.p. 92–4° at 9 mm., $n^{20}\mathrm{D}$ 1.4131–2.

Anal. Calcd. for $C_{10}H_{29}O_4NSi_4$: C, 35.37; H, 8.61; N, 4.13; neut. equiv., 340. Found for cut 2: C, 35.3; 35.2; H, 8.5, 8.6; N, 4.2, 4.2; neut. equiv., 353. Found for cut 3: C, 35.5, 35.6; H, 8.7, 8.8; N, 4.0, 4.1; neut. equiv., 340.

After standing for 2–3 months, the product had increased in viscosity and had $n^{20}\mathrm{D}$ 1.4209. Molecular weights determined cryoscopically in benzene and in cyclohexane were approximately three times the monomeric value. The product polymerized to a clear gum on standing for two years in a bottle closed with a lubricated ground-glass stopper.

(Diethylaminomethyl)-heptamethylcyclotetrasiloxane D_3-$D'NEt_2$.—In a five-liter, round-bottom flask fitted with a reflux condenser protected by a drying tube was placed 467 g., 144 moles of $D_3D'Cl$,[10] 3.15 g., 4.32 moles, of anhydrous diethylamine, and 800 ml. of isoöctane. The reaction mixture was refluxed for 64 hours, and then the precipitate which had generally formed was filtered from the chilled reaction mixture. The washed and dried white solid corresponded in weight to the theoretical amount of diethylamine hydrochloride. Rapid vacuum distillation of the filtrate and washings gave 316 g., 0.86 mole, 60% yield of $D_3D'NEt_2$ in four cuts, b.p. 80–100° at 1.5 mm., $n^{20}\mathrm{D}$ 1.4180–2.

Anal. Calcd. for $C_{12}H_{33}O_4NSi_4$: C, 39.20; H, 9.05; N, 3.81; Si, 30.53. Found for cut 3: C, 39.2; H, 9.1; N, 3.8; Si, 31.0. Found for combined cuts 2, 4, 5: C, 38.9; H, 9.1; N, 3.9.

This product exhibited an increase in refractive index on standing at room temperature; in four days the value reached about $n^{20}\mathrm{D}$ 1.423 where it remained constant for months. Refrigeration retarded but did not eliminate the refractive index increase. The product also increased somewhat in viscosity, turned yellow, and deposited a very small amount of brown tar.

Two other runs were made prior to the one described in detail above. In the first the reactants were refluxed for only 33 hours; the reaction was 78% complete and a 35% yield of product b.p. 80–87° at 1.5 mm., $n^{20}\mathrm{D}$ 1.4180, was obtained. In the second run the amine hydrochloride was filtered periodically to determine the extent of reaction, and it was established that about 60 hours was required for complete reaction; there was obtained a 58% yield of product b.p. 80–90° at 1.0–1.5 mm., $n^{20}\mathrm{D}$ 1.4180. The combined products from these two runs had the following percentage analyses: C, 38.0; H, 8.7; N, 3.7. The residue from the second run combined with that from the run described in detail above had the following percentage analyses: C, 36.5; H, 8.7; N, 3.0.

(*n*-Butylaminomethyl)-heptamethylcyclotetrasiloxane D_3-$D'NHBu$.—In a five-liter, round-bottom flask fitted with a reflux condenser protected with a drying tube was placed 467 g., 1.44 moles, of $D_3D'Cl$,[10] 296 g., 4.04 moles, of anhydrous *n*-butylamine and 800 ml. of isoöctane. The reaction mixture was refluxed for 64 hours, and the white solid which precipitated during this period was filtered from the chilled mixture, washed thoroughly with isoöctane and dried *in vacuo*. There was obtained 174 g. of solid; theoretical for *n*-butylamine hydrochloride was 158 g. Vacuum distillation of the filtrate and washings gave 192 g., 0.52 mole, 36% yield of $D_3D'NHBu$ in two cuts, b.p. 75–94° at 0.5 mm., $n^{20}\mathrm{D}$ 1.4195–6.

Anal. Calcd. for $C_{12}H_{33}O_4NSi$: C, 39.20; H, 9.05; N, 3.81. Found for cut 1: N, 3.9. Found for cut 2: C, 38.7; H, 8.7; N, 4.0. Found for 218 g. distillation residue: C, 36.9; H, 7.9; N, 3.2.

On standing for several months fraction 1 polymerized to a gum. A year later this gum still flowed when its container was laid on its side. The distillation residue remained a viscous, yellow liquid a year after it was prepared.

Two preparations, in which un-dried *n*-butylamine was used, were made prior to the run described above. In the first there was obtained 88 g., 17% yield, of material b.p. 120–130° at 2 mm., $n^{20}\mathrm{D}$ 1.4186 (Found: N, 3.4) together with a large viscous residue (Found: C, 36.4; H, 8.7; N, 2.7) that set to a non-flowing gum on standing several months. In the second run there was obtained 50 g., 14% yield, of material, b.p. 87–99° at 1 mm., $n^{20}\mathrm{D}$ 1.4185 (Found: N, 3.8).

(Phenylaminomethyl)-heptamethylcyclotetrasiloxane D_3-$D'NHC_6H_5$.—In a three-liter, round-bottom flask fitted with a reflux condenser protected with a drying tube was placed 331 g., 1.0 mole, of $D_3D'Cl$,[10] 214 g., 2.3 moles of anhydrous aniline and 500 ml. of toluene. The reaction mixture was refluxed for 70 hours, and then it was cooled in an ice-bath. The 117 g. of aniline hydrochloride (recovered by filtration, washing with toluene and drying *in vacuo*) indicated that reaction was 90% complete. Further refluxing for 95 hours more with an additional 19 g., 0.2 mole, of aniline resulted in the formation of 6 g. of white solid, thus bringing the total yield of aniline hydrochloride to 96%.

Vacuum distillation of the toluene solution of crude product gave 244 g., b.p. 129–49° at 0.5 mm., $n^{20}\mathrm{D}$ 1.4703–10 together with a little white solid, presumably aniline hydrochloride, and a 62-g. viscous residue (Found: C, 40.2; H, 7.5; N, 2.6). Redistillation of the crude product gave 222 g., 0.57 mole, 57% yield of $D_3D'NHC_6H_5$ in five cuts, b.p. 122–127° at 0.5 mm., $n^{20}\mathrm{D}$ 1.4698–1.4706.

Anal. Calcd. for $C_{14}H_{29}O_4NSi_4$: C, 43.38; H, 7.54; N, 3.61; Si, 28.96. Found for cut 6: C, 43.9; H, 7.9; N, 3.7; Si, 28.5, 29.1, 29.4. Found for cuts 3, 4, 5, 7: C, 43.9; H, 7.5; N, 3.7.

The product exhibited no tendency to polymerize on standing. Its viscosity did not noticeably increase after almost two years, and its $n^{25}\mathrm{D}$ was 1.4682.

(N,N-Methylphenylaminomethyl)-heptamethylcyclotetrasiloxane $D_3D'NCH_3C_6H_5$.—In a three-liter round-bottom flask fitted with a reflux condenser protected by a drying tube was placed 331 g., 1.0 mole, of $D_3D'Cl$,[10] 237 g., 2.2 moles, of N-methylaniline and 500 ml. of toluene. The reaction mixture was refluxed for 90 hours, whereupon a lower liquid layer separated and solidified on cooling. The solid weighed 131 g. after being washed with toluene and dried *in vacuo;* the theoretical weight of methylaniline hydrochloride was 144 g.

Vacuum distillation of the toluene solution of product gave 225 g., b.p. 134–144° at 1 mm. Redistillation of this material gave 211 g., 0.53 mole, 53% yield of $D_3D'NCH_3$-C_6H_5, b.p. 126–136° at 1 mm., $n^{20}\mathrm{D}$ 1.4741–3.

Anal. Calcd. for $C_{15}H_{31}O_4NSi_4$: C, 44.85; H, 7.78; N, 3.49. Found: C, 44.9; H, 7.6; N, 3.7, 3.8.

Upon standing several weeks the product increased in viscosity and its $n^{20}\mathrm{D}$ rose to 1.4760. After about a year the material had reached the consistency of a thick sirup.

$BuN(CH_2SiMe_2)_2O$.—Dropwise addition of 83 g., 0.58 mole, of *n*-butylamine to a stirred solution of 25 g., 0.19 mole, of $ClCH_2SiMe_2Cl$[9] in 100 ml. of toluene resulted in the formation of a white solid with evolution of heat. The reaction mixture was refluxed for ten hours, and the white solid was filtered. There was isolated by distillation 15 g., 0.07 mole, 12% yield of $BuN(CH_2SiMe_2)_2O$, b.p. 98° at 11 mm., $n^{20}\mathrm{D}$ 1.4360. Its infrared spectrum confirmed the identity of this product, which apparently arose through the presence of water in the reagents.

Anal. Calcd. for $C_{10}H_{25}ONSi_2$: neut. equiv., 231; N, 6.05. Found: neut. equiv., 235; N, 6.1.

Aminomethylsilanes.—During our investigation of the amination of chloromethylsiloxanes a number of aminomethylsilanes were prepared. These were obtained by the reaction of amines with $ClCH_2SiMe_3$[11] under conditions similar to those described above for chloromethylsiloxanes. Their properties are summarized in Table II.

TABLE II

Compound	B.p. °C.	B.p. Mm.	$n^{20}\mathrm{D}$	Neut. equiv. Calcd.	Neut. equiv. Found	Nitrogen, % Calcd.	Nitrogen, % Found
$BuNHCH_2SiMe_3$	165 90	Atm. 62	1.4238	159	163	8.79	8.8
$Et_2NCH_2SiMe_3$	145–150	Atm.	1.4231	159	163	..	..
$(CH_2)_5NCH_2SiMe_3$	59	9	1.4519	171	172	8.18	8.3
$C_6H_5NHCH_2SiMe_3$	119	12	1.5241	..	..	7.81	7.7
$NH_2CH_2SiMe_3$[1,2]	94	Atm.	1.4170				
$NH(CH_2SiMe_3)_2$[1,2]	87	50	1.4252				

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[11] F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946).

Densities and Viscosities of Aminomethylsiloxanes.—The densities and viscosities of the aminomethylsiloxanes were determined by conventional methods. In the case of the self-polymerizing compounds the densities, refractive indexes and viscosities were determined during the same week several months after the compounds were prepared. The viscosities offer some measure of the extent to which polymerization had occurred; in the case of $(D_3D'NEt_2)$ cryoscopic molecular weight determinations indicated that x was approximately three. The properties together with values calculated from them are listed in Table I.

TABLE III

	MM'-NH_2	$(MM')_2$-NH	D_3D'-NHC_6-H_5	$(D_3D'$-$NHBu)x$	$(D_3D'$-$NEt_2)x$	$(D_3D'$-NCH_3-$C_6H_5)x$
d^{15}	0.850	0.857	1.045	0.975	0.977	1.045
d^{20}	.846	.852	1.042	.971	.971	1.040
d^{25}	.842	.848	1.038	.967	.968	1.037
$n^{20}D$	1.4105	1.4143	1.4710	1.4241	1.4249	1.4780
R_D(found)	0.2931	0.2934	0.2682	0.2629	0.2632	0.2721
R(calcd.)[a]	.2953	.2941	.2646	.2631	.2703	.2673
$\eta_{100°F.}$[b]	1.147	1.88	7.59	584	119	87.0
$\eta_{150°F.}$[b]	0.820	1.29	3.80	255	55.0	42.0
$\eta_{210°F.}$[b]	.596	0.92	2.14	117	26.6	21.8
VTC[c]	.48	.51	0.73	0.80	0.78	0.75
E_{vis}[d]	2.7	3.1	4.7	6.3	5.9	5.4

[a] Calculated with bond refractions given by K. G. Denbigh, *Trans. Faraday Soc.*, **36,** 936 (1940), and by E. L. Warrick, THIS JOURNAL, **68,** 2455 (1946). Similar results may be obtained by the method of R. O. Sauer, *ibid.*, **68,** 954 (1946). [b] In centistokes. [c] $1 - (\eta_{210°F.}/\eta_{100°F.})$. [d] Energy of activation for viscous flow, *i.e.* the energy term in the exponential for the equation relating viscosity and temperature: $\eta = Ae^{-\Delta H/RT}$.

Solution Depolymerization of Aminomethylsiloxanes.—Cryoscopic molecular weight determinations of $(D_3D'NMe_2)_x$ and $(D_3D'NEt_2)_x$ in cyclohexane were performed in the usual way. The molecular weights were found to be dependent upon time in solution and therefore values were obtained at various time intervals. In the $(D_3D'NMe_2)_x$ series two 1% solutions in cyclohexane were allowed to stand in the cryoscopic apparatus slightly open to the atmosphere through the stirrer bearing. The $(D_3D'NEt_2)_x$ values were obtained on four separate solutions (1.3, 0.7, 0.6, 0.9%) in cyclohexane which were allowed to stand for the stated time intervals in bottles closed with lubricated ground joints. The changes in molecular weight with time are shown in Table IV.

TABLE IV

$(D_3D'NMe_2)x$				$(D_3D'NEt_2)x$	
Solution 1		Solution 2			
Days	Mol. wt.	Days	Mol. wt.	Hours	Mol. wt.
0	1270	0	1277	2	901
3	384	1	659	26	508
7	358	4	384	92	463
10	336	8	357	140	393

Molecular weights of $(D_3D'NMe_2)_x$ in benzene at "zero" time were 1002, 943, 817 and 890 at concentrations of 1.5 to 5%. These values were obtained before the variability of molecular weight with time was recognized, and hence the solutions probably stood for varying periods (perhaps of several hours) prior to the determinations.

Infrared Spectra.—These were determined by C. A. Hirt with a Perkin-Elmer recording infrared spectrophotometer, model 21. The cell thicknesses were 0.024 to 0.031 mm. except for No. 545 in which no spacer was used. The curves presented are tracings of photographic reductions. We are grateful to Dr. J. F. Brown, Jr., and Dr. R. S. MacDonald for assistance with interpretations of the spectra.

Nitrogen Analysis in Aminomethyl Silicon Compounds.—In the simpler aminomethyl silicon compounds nitrogen was determined readily by running neutral equivalents in the manner standard for simple aliphatic amines. In some cases in order to attain complete reaction it was necessary to use an aqueous alcohol solution and to allow the samples to stand overnight in excess acid and then back-titrate with base to a phenolphthalein end-point.

For polymeric aminomethylsiloxanes the sealed tube Kjeldahl method was found to be the best; limits for a single determination were ±0.14 in the percentage nitrogen (std. dev., $s = 0.047$; $3s = 0.14$).[12] The Dumas procedure also was applicable to polymeric aminomethylsiloxanes, but it was necessary to use an oxidizing agent, *e.g.*, $KClO_3$, else erratic results, usually too high, were obtained. With an oxidizing agent, the usual ±0.4 or 0.5 in the percentage nitrogen as determined by the Dumas method was found to apply.[13] It is possible that methane, produced by pyrolysis of some siloxanes, led to high Dumas results when no oxidizing agent was added, just as occurs with some organic compounds.[14]

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(12) The sealed tube Kjeldahl determinations were made by E. W. D. Huffman Microanalytical Laboratories, Denver, Colo.

(13) H. A. Liebhafsky, H. G. Pfeiffer and E. W. Balis, *Anal. Chem.*, **23**, 1531 (1951).

(14) Al Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., New York, N. Y., 1951, p. 57.