rather than the five observed. The sharp absorption bands are also characteristic of f–f transitions; d–d bands are ordinarily much broader than those observed.

The qualitative differences between U(V) spectra in [U(OC$_2$H$_5$)$_5$]$_2$ and in UCl$_5$·SOCl$_2$ indicate a stronger crystal field in [U(OC$_2$H$_5$)$_5$]$_2$. In [U(OC$_2$H$_5$)$_5$]$_2$ all absorption bands are shifted to shorter wave lengths and spaced over a 1600 cm.$^{-1}$ wider energy range. The directions of the energy shifts are as predicted in Fig. 2 for an increased crystal field in [U(OC$_2$H$_5$)$_5$]$_2$. The energy change between the Γ_7* levels is small, but the Γ_8, Γ_8*, and Γ_6 levels are shifted upward in [U(OC$_2$H$_5$)$_5$]$_2$ by 1190, 1525, and 2690 cm.$^{-1}$, respectively. Taking $Q/(Q + \zeta)$ as a measure of field strength, the field on the U(V) ion in [U(OC$_2$H$_5$)$_5$]$_2$ is about 30% stronger than the field in UCl$_5$·SOCl$_2$. The magnitude of this change is surprising, but it should be noted that no other data on a 5f^1 configuration are available for comparison. The increase in field strength conforms to a greater strength for a U–O bond than for a U–Cl bond, as would be expected from a comparison of the electronegativities of oxygen and chlorine.

The effect of the field on the U(V) ion is in marked contrast to the effect of crystal field on U(IV)[22,23] where only minor shifts in the energy levels have been observed. The field effect on the U(V) ion indicates that the f orbitals extend near the region of bonding; f orbitals in the U(IV) ion are still well shielded from bond effects, and thus a sharp decrease in the spatial extension of the 5f orbitals must occur when a second f electron is added. A similar, but smaller, decrease in the spatial extension of the 4f orbitals has been noted by comparison of the field parameters for Ce^{3+} and Pr^{3+}.[24] Further investigations of the spectra of 5f^1 ions in different fields would be of interest in defining both the field effect and the changes between 5f^1 and 5f^2 ions.

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The Synthesis and Properties of N-Substituted Cyclotrisilazanes

By L. W. BREED and R. L. ELLIOTT

N-Substituted cyclotrisilazanes are obtained when bis(alkylamino)diorganosilanes are heated in the presence of ammonium sulfate. Good yields are reported for the methylamino and the ethylamino derivatives, but lower yields are obtained when bulkier groups are substituted on nitrogen. In the series Si-substituted groups include methyl, ethyl, vinyl, phenyl, and *p*-anisyl. The ease of hydrolysis of various silicon–nitrogen compounds is compared to show the steric effects on hydrolytic stability. *cis* and *trans* isomers of hexamethyl-2,4,6-triphenylcyclotrisilazane and hexamethyl-2,4,6-tri-*p*-anisylcyclotrisilazane were separated, and the configuration of both isomers was assigned on the basis of their n.m.r. spectra. Infrared spectra are discussed.

Introduction

Although ≡SiNH$_2$ compounds condense readily to ≡SiNHSi≡ derivatives, ≡SiNHR compounds, where R is an alkyl or aryl group, exhibit little tendency to condense because of the marked steric effect exhibited by groups that are substituted on nitrogen. As a consequence, only a few N-substituted cyclotrisilazanes are described in the literature and little is known of their properties.

When dichlorodiorganosilanes are treated with primary amines, the products are generally disubstituted alkylamino or arylamino diorganosilanes rather than the N-alkyl or N-aryl cyclotrisilazanes that might be expected. Reported exceptions are the formation of a small quantity (3%) of hexamethyl-1,3,5-triphenylcyclotrisilazane from the reaction of dichlorodimethylsilane with aniline, and the partial condensation to bis(dimethylmethylaminosilyl)methylamine of a part of the dimethylbis(methylamino)silane obtained on treating dichlorodimethylsilane with methylamine.[1] The disubstituted compounds are usually sufficiently stable against self-condensation that they can be recovered in high yields by distillation at moderate temperatures.

Indirect methods have been described for preparing several N-substituted cyclotrisilazanes, but no general method has been reported that is useful in preparing compounds with varied structures. Andrianov prepared hexamethyl-1,3,5-triphenylcyclotrisilazane and hexamethyl-1,3,5-tripentylcyclotrisilazane from hexamethylcyclotrisilazane and the appropriate amines, but the yields were not reported.[2] An approach recently described for preparing nonamethylcyclotrisilazane is to treat the dilithium derivative of bis(dimethyl-

(1) E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949).
(2) K. A. Andrianov and G. Rumba, *Zh. Obshch. Khim.*, **32**, 1993 (1962).

TABLE I: PREPARATION AND PROPERTIES OF N-SUBSTITUTED CYCLOTRISILAZANES

$$3\,RR'Si(NHR'')_2 \xrightarrow{(NH_4)_2SO_4} (RR'SiNR'')_3 + 3\,R''NH_2$$

R	R'	R''	Yield, %	B.p., °C (mm.)	M.p., °C	n_D^t (°C.)	Mol. wt. Calcd.	Mol. wt. Found[a]	Calcd. N	Calcd. Si	Found N	Found Si
CH_3	CH_3	CH_3	87–93	96–97 (10)	33–34		261	262	16.06	32.21	15.91	32.22
CH_3	$CH{:}CH_2$	CH_3	76	110–113 (4)		1.4783 (27°)			14.12	28.31	13.82	28.40
C_2H_5	C_2H_5	CH_3	50		167–169		346	322	12.15	24.37	12.11	24.31
CH_3	CH_3	C_2H_5	66	95–97 (6)		1.4619 (25°)	304	261	13.84	27.75	13.75	27.90
CH_3	CH_3	$CH_2CH{:}CH_2$	21	82–85 (0.1)		1.4795 (27°)			12.37	24.81	12.34	25.11
CH_3	CH_3	$CH_2C_6H_5$	19		57–60[b]				8.57	17.21	8.27	16.80
CH_3	CH_3	C_6H_5	15–25		251–252[c]		447	286[d]	9.38	18.81	9.51	18.52
C_6H_5	C_6H_5	CH_3	52–57		219–221[c]		634	578	6.63	13.29	6.50	13.17
$p\text{-}CH_3OC_6H_4$	$p\text{-}CH_3OC_6H_4$	CH_3	20		280–285[c]				5.16	10.35	5.26	10.26
CH_3	C_6H_5	CH_3	17		153–154[c]		447	420	9.38	18.82	9.42	18.96
CH_3	C_6H_5	CH_3	63		84–88[e]		447	416	9.38	18.82	9.52	18.95
CH_3	$p\text{-}CH_3OC_6H_4$	CH_3	6		176–177[c]		538	508	7.81	15.67	7.75	15.76
CH_3	CH_3	$p\text{-}CH_3OC_6H_4$	45		114–116[c]		538	502	7.81	15.67	7.96	15.56

[a] Determined cryoscopically in benzene. [b] From petroleum ether (b.p. 35–60°). [c] From acetonitrile. [d] Calcd. for $((CH_3)_2SiNC_6H_5)_2$, 298. This compound was apparently a cyclodisilazane. [e] From petroleum ether (b.p. 60–90°).

TABLE II: PREPARATION AND PROPERTIES OF BIS(ALKYLAMINO)DIORGANOSILANES

Reactants	Products	Yield, %	B.p., °C (mm.)	n_D^t (°C.)	Lit. ref.[a]	Calcd. N	Calcd. Si	Found N	Found Si
$(CH_3)_2SiCl_2 + CH_3NH_2$	$(CH_3)_2Si(NHCH_3)_2$	23–44	107–108	1.4393 (27°)	a				
	$CH_3N(Si(CH_3)_2NHCH_3)_2$	26–31	78 (11)	1.4318 (27°)	a	20.45	27.34	20.50	27.18
$CH_3(CH_2{:}CH)SiCl_2 + CH_3NH_2$	$CH_3(CH_2{:}CH)Si(NHCH_3)_2$	21	65–66 (78)	1.4571 (24°)					
	$CH_3N(SiCH_3(CH{:}CH_2)NHCH_3)_2$	11	86 (11)	1.4308 (26°)	b	18.31	24.48	18.11	24.66
$(C_2H_5)_2SiCl_2 + CH_3NH_2$	$(C_2H_5)_2Si(NHCH_3)_2$	77	73 (39)	1.4121 (26°)	a				
$(CH_3)_2SiCl_2 + C_2H_5NH_2$	$(CH_3)_2Si(NHC_2H_5)_2$	74	135–141	1.4433 (28°)					
$(CH_3)_2SiCl_2 + CH_2{:}CHCH_2NH_2$	$(CH_3)_2Si(NHCH_2CH{:}CH_2)_2$	76	87–88 (30)	1.4270 (28°)		16.45	16.49	16.48	16.56
$(CH_3)_2SiCl_2 + n\text{-}C_4H_9NH_2$	$(CH_3)_2Si(NH\text{-}n\text{-}C_4H_9)_2$	72	103 (16)			13.84	13.88	13.60	14.08
$(CH_3)_2SiCl_2 + C_6H_5CH_2NH_2$	$(CH_3)_2Si(NHCH_2C_6H_5)_2$	52	127 (0.1)	1.5410 (27°)	a	10.36	10.39	10.51	10.14
$(CH_3)_2SiCl_2 + C_6H_5NH_2$	$(CH_3)_2Si(NHC_6H_5)_2$	72	166–170 (2)[e]		c				
$(C_6H_5)_2SiCl_2 + CH_3NH_2$	$(C_6H_5)_2Si(NHCH_3)_2$	84	108–112 (0.1)	1.5690 (28°)					
$(p\text{-}CH_3OC_6H_4)_2SiCl_2 + CH_3NH_2$	$(p\text{-}CH_3OC_6H_4)_2Si(NHCH_3)_2$	d							
$CH_3(p\text{-}CH_3OC_6H_4)SiCl_2 + MeNH_2$	$CH_3(p\text{-}CH_3OC_6H_4)Si(NHCH_3)_2$	63	124–126 (4)	1.5177 (28°)		13.32	13.35	13.49	13.27
$CH_3(C_6H_5)SiCl_2 + CH_3NH_2$	$CH_3(C_6H_5)Si(NHCH_3)_2$	70–77	95–96 (6)	1.5090 (25°)		15.53	15.58	15.25	15.51
	$CH_3N(SiCH_3(C_6H_5)NH(CH_3))_2$	9	125–127 (0.1)	1.5446 (25°)		11.75	23.56	11.74	23.20

[a] Ref. 1. [b] E. A. Semenova, D. Ya. Zhinkin, and K. A. Andrianov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2036 (1962); Chem. Abstr., **58**, 9114 (1963). [c] S. J. Groszos and J. A. Hall, U. S. Patent 2,885,370 (May 5, 1959). [d] The crude compound was converted directly to the cyclic trimer without purification. [e] M.p. 56°.

methylaminosilyl)methylamine with dichlorodimethylsilane.[3]

It has been found that N-substituted cyclotrisilazanes can be prepared directly by the acid-catalyzed self-condensation of alkylamino and arylamino diorganosilanes. Ammonium sulfate is known to catalyze transamination reactions between amines and silylamines.[4] The self-condensation of an aminosilane under similar conditions can be expected, and indeed the condensation of allylaminotrimethylsilane to the disilazane, 2-allylhexamethyldisilazane, in the presence of ammonium sulfate has been reported.[5]

Results and Discussion

Synthesis Procedures.—All bis(methylamino)diorganosilanes were converted to the cyclotrisilazanes in good yield when they were heated in the presence of ammonium sulfate. The preparation and properties of the cyclotrisilazanes are summarized in Table I. The condensations were usually carried out at 150–200°, and the mixtures were heated until the stoichiometric quantity of amine had distilled out. Reaction time was 2–24 hr. depending on the rate of condensation.

Although good yields were obtained for all N-methyl compounds, and the one N-ethyl compound, the yields were lower for N-allyl, N-benzyl, and N-phenyl compounds. The severe steric restriction on the size of the group substituted on nitrogen was demonstrated by the recovery of 27% of the starting material and no cyclosilazane when bis(*n*-butylamino)dimethylsilane was heated 28 hr. at 170–190°. The substitution of bulky groups on silicon, however, did not appear to interfere with the condensation reaction. The cyclic derivatives were obtained from bis(methylamino)diethylsilane and from bis(methylamino)diphenylsilane in yields of about 50%.

As starting materials for the preparation of cyclosilazanes, a number of bis(alkylamino)diorganosilanes were prepared. The preparation and properties of these compounds are given in Table II.

Hydrolytic Stability.—Because the silicon–nitrogen bond is subject to hydrolytic cleavage, it is of considerable interest to correlate changes in chemical structures in the cyclosilazane series with hydrolytic stability. The interpretation of data reported in the literature is often complicated by the insolubility of silazanes in water, and no systematic studies are reported.

The rate of ammonia or amine formation from the cyclosilazanes in solution with water in a toluene–methanol mixture was taken as an index of the hydrolytic stability of the silicon–nitrogen bond in the silazanes. Although both hydrolysis and methanolysis occurred in these mixtures, the compound stabilities were limited by the presence of water.

The relative stabilities of several silazanes and silylamines are reported in Table III. Comparative stabilities were determined for the four bis(alkylamino)-

diorganosilanes because the corresponding cyclotrisilazanes were not sufficiently hydrolyzed under the experimental conditions.

Table III
RELATIVE HYDROLYTIC STABILITIES OF CYCLOTRISILAZANES AND BIS(ALKYLAMINO)DIORGANOSILANES

Silazane or silylamine	% ammonia or amine evolved after 2 hr. in methanol–toluene–water soln. at 65°
2,4,6-Trimethyl-2,4,6-triphenyl-cyclotrisilazane	69.0
Hexamethylcyclotrisilazane	56.8, 57.6
Octamethylcyclotetrasilazane	44.8
Nonamethylcyclotrisilazane	7.12
Hexamethyl-2,4,6-triphenyl-cyclotrisilazane	1.01
Hexamethyl-2,4,6-tri-*p*-anisyl-cyclotrisilazane	1.09
Hexaphenyl-1,3,5-trimethyl-cyclotrisilazane	0.20
Hexaethyl-1,3,5-trimethyltri-silazane	0.27
Hexamethyl-1,3,5-triethylcyclo-trisilazane	0.41
Bis(methylamino)methylphenyl-silane	7.47
Bis(methylamino)-*p*-anisyl-methylsilane	5.98
Bis(methylamino)diphenyl-silane	6.80
Bis(methylamino)diethylsilane	1.73

Steric factors appear to determine the hydrolytic stability of silazanes, and significant effects can be observed for relatively small groups. For example, replacement of the =NH groups by =NCH$_3$ groups in hexamethylcyclotrisilazane gave a substantial increase in hydrolytic stability even though ammonia is less basic than methylamine. Ethyl-substituted derivatives were more stable than the methyl-substituted cyclotrisilazane. Phenyl substitution on silicon appeared to decrease hydrolytic stability, but this effect could not be observed in the cyclic derivatives containing methyl-substituted nitrogen. 2,4,6-Trimethyl-2,4,-6-triphenylcyclotrisilazane was decomposed more rapidly than hexamethylcyclotrisilazane, probably because of the competition of the aromatic π-electrons with the nitrogen π-electrons for the d-orbitals of silicon. Under these circumstances, the dative π-bonding between silicon and nitrogen would be weakened and increased susceptibility to hydrolysis would result. Similarly, bis-(methylamino)diphenylsilane was less stable than bis-(methylamino)diethylsilane.

Cyclotrisilazane Stereoisomers.—It was of considerable interest that when two different groups were attached to each silicon atom in certain cyclotrisilazanes, two stereoisomers could be isolated. 2,4,6-Trimethyl-2,4,6-triphenylcyclotrisiloxane has been reported to exist in two isomeric forms for which configurations were assigned on the basis of symmetry considerations.[6,7] Ring isomerism in the carbon series is well

(3) K. Lienhard and E. G. Rochow, *Angew. Chem.*, **75**, 638 (1963).

(4) R. Fessenden and D. F. Crowe, *J. Org. Chem.*, **26**, 4638 (1961).

(5) J. L. Speier, R. Zimmerman, and J. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956).

(6) R. N. Lewis, *ibid.*, **70**, 1115 (1948).

(7) V. Chvalovsky and V. Bazant, *Chem. Listy*, **49**, 894 (1955).

known and the structures of the isomers have been studied by means of their n.m.r. spectra, as for example the *cis* and *trans* isomers of 2,4,6-trimethyl-1,3,5-tri-thiane.[8]

Structural assignments were possible from the n.m.r. spectra for the two isomers of hexamethyl-2,4,6-tri-phenylcyclotrisilazane and hexamethyl-2,4,6-tri-*p*-anisylcyclotrisilazane that were isolated. A satisfactory model for the cyclic trimers is a rapidly interconverting chair. Such a model allows equatorial N–CH$_3$ bonds in both isomers of hexamethyl-2,4,6-triphenylcyclotrisila-zane. The limiting structures for the rapidly inter-converting forms of the two isomers can be differen-tiated by the *cis* structure having all axial Si–CH$_3$ bonds and the *trans* structure having two axial Si–CH$_3$ bonds and one equatorial Si–CH$_3$ bond.

Unfilled valences = CH$_3$

cis-Hexamethyl-2,4,6-tri-   *trans*-Hexamethyl-2,4,6-tri-
phenylcyclotrisilazane   phenylcyclotrisilazane
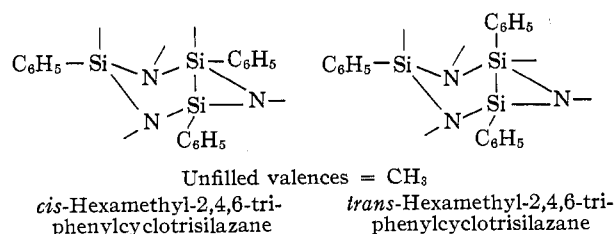
Symmetrically substituted cyclotrisilazanes have spectra that are consistent with a rapidly interconvert-ing chair structure. Hexamethylcyclotrisilazane ex-hibits a single sharp peak at δ 0.07 p.p.m. (=Si(CH$_3$)$_2$) and nonamethylcyclotrisilazane two sharp peaks, one at δ 0.03 p.p.m. (=Si(CH$_3$)$_2$) and one at δ 2.43 p.p.m. (=N(CH$_3$)).

The isomer of hexamethyl-2,4,6-triphenylcyclotri-silazane that melted at 153–154° gave an n.m.r. spec-trum containing a sharp peak at δ 0.48 p.p.m. (≡SiCH$_3$), a sharp peak at δ 2.27 p.p.m. (=NCH$_3$), and a complex series of peaks at δ 7.21–7.66 p.p.m. (≡SiC$_6$H$_5$). The isomer that melted at 84–88° gave two sharp peaks at δ 0.49 and 0.52 p.p.m. with an area ratio of 2.08:1 (≡SiCH$_3$), two sharp peaks at δ 2.23 and 2.24 p.p.m. (=NCH$_3$) (an additional weak peak at δ 2.27 p.p.m.), and a complex series of peaks at δ 7.23–7.73 p.p.m. (≡SiC$_6$H$_5$). Both spectra are shown in Fig. 1. The *cis* isomer, in which all the silicon-attached methyl groups are axial, would be expected to show single sharp peaks for ≡SiCH$_3$ and =NCH$_3$. The *trans*, however, should exhibit two peaks for each ≡SiCH$_3$ and =NCH$_3$ with integrated area ratios of 2:1. Thus, the low-melting isomer can be assigned the *trans* configuration and the high-melting isomer the *cis* configuration.

Structures of the two isomers of hexamethyl-2,4,6-tri-*p*-anisylcyclotrisilazane were similarly assigned. The *cis* isomer, which melted at 176–177°, gave the following n.m.r. peaks: δ 0.43 (≡SiCH$_3$), 2.25 (=NCH$_3$), 3.80 (—OCH$_3$), and 6.76–7.55 p.p.m. (≡SiC$_6$H$_5$). The *trans* isomer, which melted at 114–116°, gave the following n.m.r. peaks: δ 0.40 and 0.43 p.p.m. (≡Si-CH$_3$) with an area ratio of 2.02:1, δ 2.18 (=NCH$_3$), 3.80 (—OCH$_3$), and 6.76–7.55 p.p.m. (≡SiC$_6$H$_5$).

It was felt that isomer pairs should also be isolated from cyclotrisilazanes that do not contain methyl-sub-stituted nitrogen. Hizawa reported obtaining a single product melting at 115–116° by the ammonolysis of dichloromethylphenylsilane. The compound was ob-tained in a 24% yield and characterized as 2,4,6-tri-methyl-2,4,6-triphenylcyclotrisilazane. Repetition of his procedure gave an 11% yield of the same compound melting at 114–116°, but 1.5% of a second isomer melt-ing at 202–205° was also isolated. The latter compound gave a satisfactory elemental analysis and molecular weight for the cyclic trimer. However, no separation of the Si–CH$_3$ proton resonance could be detected in the n.m.r. spectrum of either isomer, both isomers showing a single strong peak for ≡SiCH$_3$ and a broad peak for =NH. The ≡SiCH$_3$ peak for the low-melting isomer was found at δ 0.47 p.p.m. and for the high-melting iso-mer at δ 0.34 p.p.m. The area ratio of the (≡SiCH$_3$): (NH):(≡SiC$_6$H$_5$) protons was 8.7:3.0:13.5 for the low-melting isomer and 9.2:3.0:15.0 for the high-melting isomer. Although the assignment configuration could not be made from the n.m.r. spectra, it is reasonable to assume that the higher melting isomer has the *cis* structure.

Infrared Spectra.—Absorption bands of the silazanes in the infrared were consistent with band assignments recorded in the literature.[9] A shift to higher frequen-cies for the asymmetric SiNSi stretch was observed in passing from the linear dimers to the cyclic trimers. In the dimers, CH$_3$N(SiRCH$_3$NHCH$_3$)$_2$, where R was methyl, phenyl, or vinyl, absorption was observed at 905–900 cm.$^{-1}$, but in the corresponding cyclic trimers (SiRCH$_3$NCH$_3$)$_3$, where R was methyl, phenyl, or vinyl, this absorption had shifted to 940–935 cm.$^{-1}$, indicating a bond shortening in the cyclic derivatives.

A strong band that could not be correlated with known frequency assignments was observed in the 1050 cm.$^{-1}$ region. This band was present in the N-sub-stituted cyclotrisilazanes (SiRCH$_3$NCH$_3$)$_3$ where R was methyl, vinyl, or phenyl, and also in (Si(C$_2$H$_5$)$_2$-NCH$_3$)$_3$ and (Si(C$_6$H$_5$)$_2$NCH$_3$)$_3$ with strong absorption occurring at 1055–1045 cm.$^{-1}$. The band was absent when no alkyl groups were substituted on nitrogen, for example in (SiRCH$_3$NH)$_3$ compounds where R was methyl, vinyl, or phenyl. The absorption is apparently not associated with the cyclotrisilazane ring, however, since the same band at about 1060 cm.$^{-1}$ was found in the linear dimers, CH$_3$N(SiRCH$_3$NHCH$_3$)$_2$, where R was methyl, vinyl, or phenyl.

Experimental

Aminolysis of Dichlorodiorganosilanes.—The compounds in Table II were prepared by treating the diorganodichlorosilanes with the appropriate amines. Dichlorodimethylsilane, dichloro-diethylsilane, and dichloromethylvinylsilane were treated with excess methylamine by introducing the methylamine above the surface of a stirred solution cooled to 5–10°. Approximately 1.25 l. of petroleum ether (b.p. 35–60°) per mole of silane were em-ployed as the solvent. After the addition was complete, the

(8) E. Campaigne, N. F. Chamberlain, and B. E. Edwards, *J. Org. Chem.*, **27**, 135 (1962).

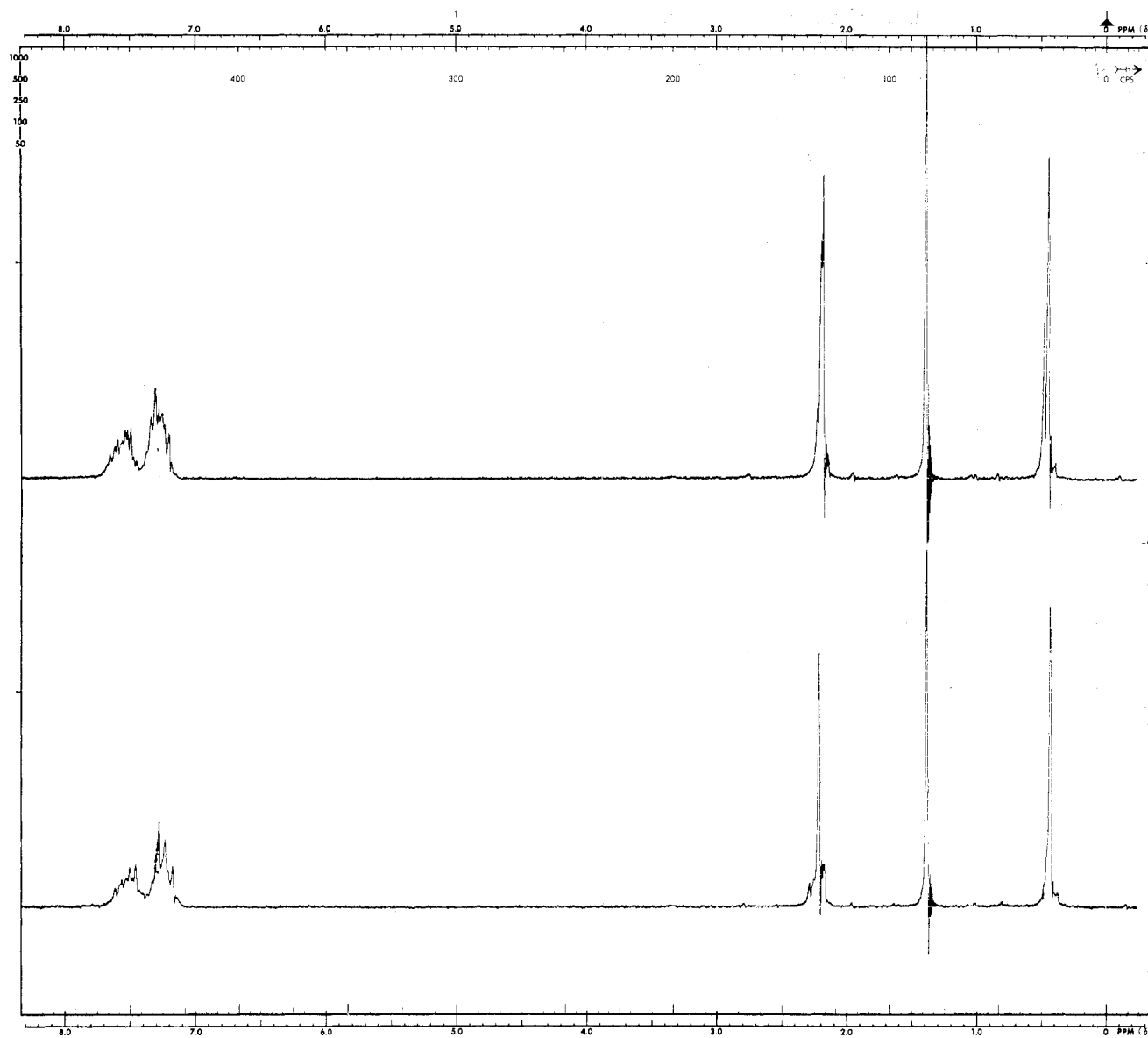(9) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

Fig. 1.—N.m.r. spectra of hexamethyl-2,4,6-triphenylcyclotrisilazane isomer.

mixture was heated at reflux for 1 hr., cooled, and filtered; the solvent was distilled off and the residue was fractionally distilled. The preparations in which dichlorodimethylsilane was treated with allylamine, butylamine, or benzylamine were carried out by adding 0.5 mole of the silane in 200 ml. of diethyl ether to a stirred solution of 2.2 moles of the amine in 200 ml. of ether. The products were purified in the same manner as the methylamine derivatives. Dibenzylaminodimethylsilane was prepared by Larsson's procedure by treating bis(diethylamino)dimethylsilane with benzylamine and distilling out diethylamine.[1] The bis(methylamino) derivatives of diphenyldichlorosilane, methylphenyldichlorosilane, di-*p*-anisyldimethylsilane, and *p*-anisylmethyldichlorosilane and the bis(ethylamino)derivative of dichlorodimethylsilane were prepared in a manner similar to the bis(methylamino) derivative of dichlorodimethylsilane except that petroleum ether (b.p. 60–90°) was employed as the solvent. About 1 l. of solvent per mole of silane was used, the mixture was maintained at 5–10° during the addition of the amine, and the product mixture was refluxed 1 hr. before purification.

Nonamethylcyclotrisilazane.—A mixture of 71.5 g. (0.60 mole) of dimethylbis(methylamino)silane and 0.7 g. of ammonium sulfate was heated to 155° in 2 hr. and subsequently maintained at 155° for 3 hr. Methylamine was evolved continuously during the heating. The product was isolated by fractional distillation.

The properties and elemental analyses for this and the following compounds are reported in Table I.

Hexamethyl-2,4,6-trivinylcyclotrisilazane.—Methylbis(methylamino)vinylsilane (17.0 g., 0.14 mole) and 0.18 g. of ammonium sulfate were heated to 180° over a 80-min. period, and the product was purified by fractional distillation.

Hexamethyl-1,3,5-triethylcyclotrisilazane.—Bis(ethylamino)-dimethylsilane (79.2 g., 0.54 mole) and 0.8 g. of ammonium sulfate were heated to a maximum temperature of 190° over a 10-hr. period, and the product was fractionally distilled.

Hexamethyl-1,3,5-triallylcyclotrisilazane.—After 20 g. (0.12 mole) of dimethylbis(allylamino)silane and 0.2 g. of ammonium sulfate were heated 2 hr. to a maximum temperature of 160°, the product was fractionally distilled.

Hexaethyl-1,3,5-trimethylcyclotrisilazane.—A mixture of 13.1 g. (0.09 mole) of diethylbis(methylamino)silane and 0.13 g. of ammonium sulfate was heated for 27 hr. to a maximum temperature of 160° when the calculated quantity of methylamine had distilled out. The residue was cooled and recrystallized from acetonitrile.

Hexamethyl-1,3,5-tribenzylcyclotrisilazane.—A mixture of 40.5 g. (0.15 mole) of bis(benzylamino)dimethylsilane and 0.4 g. of ammonium sulfate was heated 2 hr. to a maximum temperature of 190–200°, at a pressure of 10 mm., and 89% of the expected

benzylamine was collected as a distillate. Distillation of the product gave 4.5 g. of a fraction boiling at 170–200° at 0.1 mm. Recrystallization of this fraction from petroleum ether (b.p. 35–60°) gave the product.

1,3-Diphenyltetramethylcyclodisilazane.—When 36.6 g. (0.15 mole) of dianilinodimethylsilane and 0.4 g. of ammonium sulfate were heated 4 hr. to a maximum temperature of 190–200° at a pressure of 10 mm., 70% of the expected aniline was collected as a distillate. The cooled product was treated with 50 ml. of petroleum ether (b.p. 60–90°) and filtered to yield the crude product which was recrystallized from petroleum ether (b.p. 60–90°).

Hexaphenyl-1,3,5-trimethylcyclotrisilazane.—A mixture of 48.4 g. (0.20 mole) of bis(methylamino)diphenylsilane and 0.5 g. of ammonium sulfate was heated 56 hr. to a maximum temperature of 190–205°. Titration of the evolved methylamine, which was collected in an acid trap, indicated that the reaction was 98% complete. The product was dissolved in a refluxing petroleum ether (b.p. 60–90°)–toluene mixture and filtered. On cooling, the product crystallized.

Hexa-*p*-anisyl-1,3,5-trimethylcyclotrisilazane.—When 14.2 g. (0.047 mole) of di-*p*-anisylbis(methylamino)silane and 0.2 g. of ammonium sulfate were heated to 185° in 2 hr., 107% of the expected methylamine was collected. The product was recrystallized from a 4:1 mixture of toluene and petroleum ether (b.p. 60–90°).

Hexamethyl-2,4,6-triphenylcyclotrisilazane.—A mixture of 148.0 g. (0.82 mole) of methylbis(methylamino)phenylsilane and 1.5 g. of ammonium sulfate was heated for 12 hr. to a maximum temperature of 173°. During the heating period 97% of the calculated quantity of methylamine was evolved. The product was dissolved in 50 ml. of hot petroleum ether (b.p. 60–90°) and filtered. One isomer (21.2 g., 17% yield) separated from the filtrate on cooling and was recrystallized from petroleum ether (b.p. 60–90°). The other isomer (77.6 g., 63% yield) was obtained when the soluble portion was concentrated and recrystallized from acetonitrile.

Hexamethyl-2,4,6-tri-*p*-anisylcyclotrisilazane.—When 25.0 g. (0.12 mole) of *p*-anisylbis(methylamino)methylsilane and 0.5 g. of ammonium sulfate were heated at 130–146° for 4 hr., 99% of the expected methylamine was obtained. The two isomers were separated by the difference in their solubility in petroleum ether (b.p. 60–90°) in the manner described for hexamethyl-2,4,6-triphenylcyclotrisilazane.

Product from Bis(*n*-butylamino)dimethylsilane.—A mixture of 40 g. (0.2 mole) of bis(*n*-butylamino)dimethylsilane and 0.4 g. of ammonium sulfate was heated at 170–190° for 28 hr. and 6.0 g. of butylamine was collected (calcd., 14.6 g.). On fractional distillation, 10.8 g. (27%) of unchanged starting material was recovered and 6.7 g. of an unidentified fraction boiling at 175–190° (17 mm.) was obtained.

Anal. Calcd. for $C_{13}H_{33}N_3Si_2$: C, 54.29; H, 11.55; N, 14.61; Si, 19.55. Found: C, 54.59; H, 11.51; N, 14.31; Si, 19.35.

2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilazane.—Excess am-

monia was added during 2.5 hr. to a stirred solution of 95.5 g. (0.5 mole) of dichloromethylphenylsilane in 500 ml. of petroleum ether (b.p. 60–90°) maintained at 10°. The mixture was refluxed 2 hr. and filtered. After the solvents were distilled off, 1 g. of ammonium sulfate was added and the mixture was heated 3 hr. at 100–145°. When the cooled mixture was treated with 50 ml. of petroleum ether (b.p. 60–90°), 7.3 g. (11.0%) of the cyclic trimer separated and was collected by filtration. The compound melted at 114–116° (lit.[10] 115–116°) after recrystallization from petroleum ether (b.p. 60–90°) and had a molecular weight of 391 (cryoscopically in benzene). Evaporation of the filtrate gave 1.0 g. (1.5%) of a second isomer, m.p. 202–205°, after recrystallization from acetonitrile.

Anal. Calcd. for $C_{21}H_{27}N_3Si_3$: N, 10.36; Si, 20.77; mol. wt., 406. Found: N, 10.28; Si, 20.60; mol. wt., 400 (cryoscopically in benzene).

Hydrolytic Stabilities.—The method employed to determine the relative hydrolytic stabilities of the silazanes and silylamines was a modification of Pike's procedure for determining the rate of reaction of silylamines and silanols.[11] The following is a typical experiment.

A solution of 0.0997 g. (0.000455 mole) of hexamethylcyclotrisilazane in 10 ml. of toluene (dried over calcium chloride) was introduced into a 100-ml. thermowell flask equipped with a 12-in. water-cooled condenser. After the mixture was heated to 65°, 20 ml. of a 2.5% solution of water in methanol was added from the top of the condenser (zero time). Nitrogen was introduced through a tube extending through the condenser to the bottom of the flask, and effluent gases were passed through 20 ml. of a freshly prepared 2% boric acid solution. A nitrogen flow of 30 ml./min. and a temperature of 65° were maintained throughout the run. At intervals of 15, 30, 60, 90, and 120 min. the boric acid-containing traps were replaced, and the ammonia, evolved during each time period, was titrated with 0.01 N hydrochloric acid using a brom cresol green and methyl red mixed indicator.

After 120 min., 57% of the ammonia required for the complete decomposition of the hexamethylcyclotrisilazane had been collected. A similar experiment in which water was omitted gave 45% of the required ammonia.

Infrared and N.m.r. Spectra.—Infrared spectra were prepared with a Perkin-Elmer Infracord spectrophotometer. The n.m.r. spectra were determined with a Varian Associates Model A-60 n.m.r. spectrometer with cyclohexane as an internal standard. Chemical shifts are reported as Δ tetramethylsilane (c.p.s.) × 10^6/oscillator frequency (c.p.s.).

(10) K. Hizawa and E. Nojimoto, *Kogyo Kagaku Zasshi*, **59**, 1445 (1956); *Chem. Abstr.*, **53**, 4176 (1959).

(11) R. M. Pike, *J. Org. Chem.*, **26**, 236 (1961).