

SOME PHENYL-SUBSTITUTED SILICON-NITROGEN COMPOUNDS

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SUMMARY

Procedures for the synthesis of a series of phenyl-substituted silylamines, disilazanes, cyclotrisilazanes, and cyclodisilazanes are reported, and relevant new observations on the synthesis of silicon-nitrogen compounds are pointed out. NMR and IR spectral characteristics useful in the identification and characterization of these and related compounds are summarized.

INTRODUCTION

In earlier publications on silicon-nitrogen compounds, we have reported the properties of a number of new phenyl-substituted silicon-nitrogen compounds including tris(dimethylphenylsilyl)amine and other trisilylamine derivatives¹, *N,N'*-bis(dimethylphenylsilyl)tetramethylcyclodisilazane², *N*-(dimethylphenylsilyl)hexamethylcyclotrisilazane¹, phenyl-substituted *N*-methylcyclotrisilazanes³, and phenyl-substituted *N*-methylcyclotrisilazanes⁴. This paper provides information on the synthesis and chemical properties of some related substances, most of which have not been reported previously, and supplies data useful in the characterization and identification of phenyl-substituted silicon-nitrogen compounds.

RESULTS AND DISCUSSION

Many of the substances in Table 1 were prepared by established procedures, but some of the results merit comment. Although the sodium hydride-induced condensation of aniline or a silylamine with a silyl hydride produces disilazanes in good yield⁷, a product requiring functional group redistribution [compound (X)] was obtained under the necessary conditions; therefore, the method does not unequivocally determine the structure of the product. In the procedure, significantly higher initiation temperatures were required for diphenylmethylsilane than for dimethylphenylsilane.

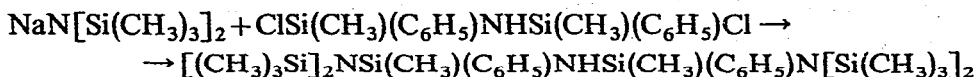
A first attempt to prepare *N,N'*-bis(chlorodimethylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane [compound (XVII)] by heating *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane with dichloromethylphenylsilane at atmospheric pressure in the manner described for the perphenylated derivative⁸ failed owing to the 205° limitation of the dichloromethylphenylsilane boiling point. A 2nd attempt to

TABLE I
SUMMARY OF PHENYL-SUBSTITUTED SILICON-NITROGEN COMPOUNDS

Compound Number	Structure	Procedure for Preparation	B.p. [°C(mm)]	M.p. (°C)	n_D^{20}	Analyses found (calcd.) (%)			
						C	H	N	Si
(I)	$(C_6H_5)_2Si(NHC_6H_5)_2$	A	123 (0.09) ^a		1.5532	70.99 (71.05)	8.28 (8.20)	10.43 (10.39)	10.43 (10.36)
(II)	$(C_6H_5)(CH_3)_2Si(NHCH_3)$	A	83 (10)		1.5040	65.19 (65.39)	9.15 (9.15)	8.46 (8.47)	16.91 (16.99)
(III)	$(C_6H_5)(CH_3)Si(NHC_6H_5)_2$	A		71-74		74.34 (74.95)	6.83 (6.62)	9.06 (9.20)	8.74 (9.23)
(IV)	$(C_6H_5)(CH_3)Si[N(CH_3)_2]_2$	A	108-109 (11)		1.4982				
(V)	$(C_6H_5)(CH_3)Si(NHCH_3)_2$	A	108-109		1.5113				
(VI)	$(C_6H_5)_2Si(NHCH_3)_2$	A	103 (0.01)		1.5718	69.20 (69.37)	7.55 (7.48)	11.62 (11.56)	11.64 (11.59)
(VII)	$(C_6H_5)_2(CH_3)Si(NHC_6H_5)$	B		96-97 ^b					
(VIII)	$(C_6H_5)(CH_3)_2Si(NHC_6H_5)$	B	98-99 (0.02)		1.5822	74.01 (73.95)	7.68 (7.54)	6.28 (6.16)	12.36 (12.35)
(IX)	$[(C_6H_5)(CH_3)_2Si]_2NH$	A	144-146 (4) ^c		1.5369				
(X)	$[(C_6H_5)_2(CH_3)Si]_2NH$	B		88-89					
(XI)	$[(C_6H_5)(CH_3)ClSi]_2NH$	C	158-160 (0.2)			75.60 (76.22)	6.59 (6.64)	3.51 (3.42)	13.66 (13.71)
(XII)	$\{(C_6H_5)(CH_3)[N(CH_3)_2Si]_2NH$	A	168-169 (0.4)	44-51		51.35 (51.52)	5.32 (5.25)	4.26 (4.29)	16.92 (17.21)
(XIII)	$[(C_6H_5)(CH_3)_2Si]_2NCH_3$	B	105-106 (0.02)		1.5420	62.84 (62.91)	8.49 (8.51)	12.14 (12.23)	16.24 (16.35)
(XIV)	$[(C_6H_5)(CH_3)_2Si][C_6H_5(CH_3)Si]NCH_3$	B	143-145 (0.02)		1.5764	68.16 (68.16)	8.41 (8.41)	4.68 (4.68)	18.72 (18.75)
(XV)	$\{[(CH_3)_3Si]_2N\}_2Si(CH_3)(C_6H_5)_2NH$	D	191-192 (0.2)		1.5370	72.97 (73.06)	7.63 (7.53)	3.83 (3.87)	15.39 (15.54)
(XVI)	$[(C_6H_5)(CH_3)NH]_3$ (mixed isomers)	A	195-197 (0.05)			55.06 (54.29)	9.29 (9.11)	7.16 (7.30)	28.56 (29.30)
(XVII)	$ClSi(CH_3)(C_6H_5)[NSi(CH_3)(C_6H_5)]_2Si(CH_3)(C_6H_5)Cl^d$	E	218-220 (0.02)	100-110		57.93 (58.00)	5.57 (5.56)	4.92 (4.85)	19.19 (19.38)
(XVIII)	$(CH_3)_2NSi(CH_3)(C_6H_5)[NSi(CH_3)(C_6H_5)]_2Si(CH_3)(C_6H_5)N(CH_3)_2$	A	206-210 (0.01)		1.5728	64.19 (64.37)	7.82 (7.43)	9.36 (9.38)	18.96 (18.82)

^a Lit. b.p. 126° (0.3 mm), n_D^{20} 1.5528. ^b Lit. m.p. 96°. ^c Lit. b.p. 168-170° (9-10 mm), n_D^{20} 1.5384. ^d Found: Cl, 12.23%.

prepare compound (XVII) by treating 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane with sodium bis(trimethylsilyl)amide in a manner analogous to the procedure that has been described for the preparation of the permethylated derivative from 1,3-dichlorotetramethyldisilazane⁹ led to an unexpected product. When the product, which was presumed to be the chlorine-substituted cyclodisilazane, was treated with dimethylamine and worked up in the usual way to isolate the dimethylamino derivative, it was found that the simple substitution product [29% based on the quantity of sodium bis(trimethylsilyl)amide used] was formed rather than the cyclodisilazane.



Compound (XVII) was ultimately obtained by heating a 2/3 mole ratio of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane and dichloromethylphenylsilane to 280°.

TABLE 2

SUMMARY OF PROTON CHEMICAL SHIFTS IN THE NMR SPECTRA OF PHENYL-SUBSTITUTED SILICON-NITROGEN COMPOUNDS IN CARBON TETRACHLORIDE

Compound number	$\tau[\text{Si}(\text{CH}_3)]$	$\tau(\text{NH})$	$\tau[\text{N}(\text{CH}_3)]$
(II)	9.75		7.55 (d, $J = 7$ Hz)
(III)	9.40	6.23	
(IV)	9.76		7.49
(VI)		9.08	7.38 (d, $J = 7$ Hz)
(VII)	9.22	6.41	
(VIII)	9.52	6.61	
(IX)	9.74, 9.68 (d ?)		
(X)	9.52		
(XI)	9.45, 9.34		
(XII)	9.68, 9.73 (d)	7.51	
(XIII)	9.68	7.53	
(XIV)	9.74, 9.47	7.52	
(XV)	9.84, 9.54		
(XVI)	9.54, 9.61, 9.65 (d)	9.22	
(XVII)	9.14–9.54 (m) 9.65–9.74 (m)		
(XVIII)	9.94–10.09 (m) 9.38–9.48 (m)		7.64–7.80 (m)

The NMR spectra of some of the compounds are summarized in Table 2. Silylmethyl proton shifts were observed about 0.25 ppm downfield for each phenyl or anilino group present on a methyl-substituted silicon. Of particular interest were the spectra of compounds (XI), (XII), and (XVI), which provided evidence for isomerism in these substances. The silylmethyl absorption in (XI) occurred as two nearly equal peaks at τ 9.34 and 9.45 indicating two distinct, but probably equal environments for the silylmethyl protons. An even more complex pattern was observed in (XII) and (XVI).

In connection with compound (XVI), we had reported earlier that after the ammonolysis product of dichloromethylphenylsilane was treated with ammonium

sulfate, two crystalline products, one melting at 114–116° and the other at 202–205° could be separated by fractional crystallization⁴. The two substances showed singlets in their NMR spectra at τ 9.53 and 9.66, respectively. We have subsequently found that when the ammonolysis product is distilled directly, a distillate with four NMR peaks is obtained: τ 9.54 (singlet), τ 9.61 (singlet), and τ 9.65 (doublet, $J=1$ Hz). The 9.54 peak can be identified with the 114–116° melting isomer, which crystallizes and can be separated in part from the mixture by filtration. It is improbable that the remaining peaks are attributable to more than one remaining isomer in the uncrystallized portion. When the NMR spectrum of compound (XII) was examined, a pattern almost identical to the remaining peaks in compound (XVI) was observed: A singlet and a doublet upfield about 5 Hz with peak height ratios of 2/1. It can be assumed that this pattern would be associated with the lower energy *trans*-configuration, which could be the predominant configuration in the linear disilazane structure of compound (XII). We have not been able to isolate the 202–205° melting component from mixtures not treated with ammonium sulfate. It is probable that the substance melting at 114–116° is the higher melting isomer and has the *cis* configuration.

The ranges in which IR bands, useful in characterizing the substances in Table 1, were found are summarized in Table 3. Bands included in Table 3 have been observed by us in numerous other derivatives containing the silicon–nitrogen structure. Many of the absorptions included in the table are relatively strong and occur in all the substances with little change in frequency.

In substances containing the disilazane structure, the asymmetric stretch

TABLE 3

SUMMARY OF CHARACTERISTIC GROUP FREQUENCIES (cm^{-1}) IN THE IR SPECTRA OF PHENYL-SUBSTITUTED SILICON–NITROGEN COMPOUNDS

SiC_6H_5 [(I)–(XVIII)]	$\text{SiNH}(\text{CH}_3)$ [(II), (V), (VI)]
691–703	1096–1110
991–1001	1460–1472
1018–1030	3400–3480
1107–1120	
1416–1428	$\text{SiN}(\text{CH}_3)_2$ [(IV), (XII), (XVIII)]
1580–1605	990
	1068
SiCH_3 [(II)–(V), (VII)–(XVIII)]	1175
1240–1260	1280
Si_2NH [(IX)–(XII), (XV), (XVI)]	SiNHC_6H_5 [(III), (VII), (VIII)]
931–937	895–898
1162–1200	1281–1290
3330–3410	3400
Si_2NCH_3 [(XIII), (XIV)]	$\text{SiNH}(\text{C}_2\text{H}_5)$ (I)
898–903	935
1055–1058	1060
1180	1120
	1260
	1388
	3460

frequency was observed at $931\text{--}937\text{ cm}^{-1}$, but was shifted to lower frequencies, $898\text{--}903\text{ cm}^{-1}$ in *N*-methyl-substituted disilazanes. In the cyclotrisilazane, 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane, melting point $114\text{--}116^\circ$, two bands were observed in the Si_2N stretch region, a strong one at 950 cm^{-1} and a weaker band at 924 cm^{-1} . An NH absorption occurred as two bands of nearly equal intensity at 1186 and 1205 cm^{-1} .

A second band, observed in these phenyl-substituted *N*-methyldisilazanes and also found in all other *N*-methyldisilazane derivatives, is a strong absorption at about 1060 cm^{-1} , which has been assigned to the CN structure^{10,11}. Characteristic of all methylamino derivatives is a strong band at about 1100 cm^{-1} and of dimethylamino derivatives is a strong band at 990 cm^{-1} . The dimethylamino derivatives also characteristically exhibit a somewhat weaker band at 1068 cm^{-1} . These bands have also been assigned to the CN structure in studies of similar molecules^{10,11}.

The absorption bands listed for the $\text{SiNH}(\text{CH}_3)$, $\text{SiNH}(\text{C}_6\text{H}_5)$, and $\text{SiNH}(\text{C}_2\text{H}_5)$ groups have all also been found in the spectra for tetrakis(methylamino)silane, tetraanilinosilane, and tetrakis(ethylamino)silane, respectively. Randall recently offered an unequivocal assignment of bands at 899 and 1294 cm^{-1} in anilino-trimethylsilane as the Si-N and C-N stretch, respectively¹⁰. Although these absorptions are consistently observed in the substances with the anilinosilane group in Table 1, an additional band is found in substances with multiple anilino substitution. In dianilino-methylphenylsilane, the band is found at 925 cm^{-1} , and is equal in intensity to the 895 cm^{-1} band. In tetraanilinosilane, the band occurs at 932 cm^{-1} and is much stronger than an 899 cm^{-1} band. For another dianilino derivative, dianilino-dimethylsilane, two strong absorptions of nearly equal intensities are found at 903 and 910 cm^{-1} . In view of these observations, the 899 cm^{-1} assignment of anilino-trimethylsilane should not be considered sole characteristic absorption attributable to the Si-N stretch in anilinosilanes.

EXPERIMENTAL

Reactions were carried out in glass equipment that had been flame-dried and flushed with dry nitrogen before use. Reactants were protected from atmospheric moisture with Drierite-packed tubes or a positive pressure of dry nitrogen as needed. Analyses were by Spang Microanalytical Laboratory. IR spectra (Nujol mulls or liquid films) were determined with a Perkin-Elmer Infracord spectrophotometer and NMR spectra were determined with a Varian Associates Model A60 or HA100 spectrometer with cyclohexane as an internal standard.

Procedure A

Compounds (I)–(VI), (IX), (XII), (XVI) and (XVIII) were prepared by adding the organochlorosilane to a solution of an excess of an amine or ammonia in an inert solvent. Petroleum ether was the solvent in all the preparations, except for compound (III) in which ether was used, and was present in the ratio of about 500 ml per equivalent of organochlorosilane. The amine/solvent mixtures were cooled in a Dry Ice/isopropyl alcohol bath when ammonia, methylamine, or dimethylamine was employed, in an ice bath with ethylamine and at room temperature with aniline. After the addition of the organochlorosilane, the mixtures were warmed to room

temperature, the amine salts were filtered off, and the silylamines or silazanes were distilled, except for compound (III), which was crystallized from petroleum ether. In the preparation of (XVIII), a stoichiometric quantity of lithium dimethylamide was prepared from butyllithium and dimethylamine and condensed with the chlorosilyl-cyclodisilazane. The following yields were obtained: (I) 90%; (II), 76%; (III), 59%; (V), 84%; (VI), 94%; (IX), 65%; (XVI), 91%; and (XVIII), 57%.

Procedure B

Equimolar quantities of an organosilane and an organosilylamine or aniline were heated with a catalytic quantity of sodium hydride until hydrogen evolution was initiated, then heating was continued until the calculated quantity of hydrogen had evolved. Compounds (VII) and (X) were recrystallized from petroleum ether; the others were distilled. In the preparations, the following were the wt-% sodium hydride (based on organosilane); initiation temperature; final temperature; and yield: (VII), 0.3%, 60°, 105°, 84%; (VIII), 0.5%, 130°, 170°, 70%; (X) [product from treating *N,N'*-bis(aminodimethylsilyl)tetramethylcyclodisilazane with methyldiphenylsilane], 0.4%, 110°, 170°, 34% (based on organosilane); (XIII), 2%, 150°, 185°, 68%; and (XIV), 0.5%, 160°, 190°, 67%.

Procedure C

A mixture of 20.3 g (0.050 mole) of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane and 38.2 g (0.20 mole) of dichloromethylphenylsilane was maintained at a temperature of 180° for 16 h. Vacuum distillation of this mixture afforded 15.9 g (33%) of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane (XI).

Procedure D

A solution of 15.0 g (0.046 mole) of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane in 70 ml of diethyl ether was added dropwise to a stirred solution of 8.5 g (0.046 mole) of sodium bis(trimethylsilyl)amide in 125 ml of diethyl ether. After the mixture was stirred for 2 h at room temperature and then filtered, 3.5 g (calcd., 2.8 g) of sodium chloride was obtained. When the solvent was removed from the filtrate in a rotary evaporator and the residue was vacuum distilled, 9.3 g of a distillate boiling above 192° (0.04 mm) was obtained. A solution of the distillate in 30 ml of petroleum ether was added dropwise to a solution of 3.5 g (0.080 mole) of condensed dimethylamine in 40 ml of petroleum ether which was cooled with a Dry Ice/isopropyl alcohol bath. After the addition of the solution was complete, the mixture was slowly warmed to room temperature and filtered to remove 0.7 g of dimethylamine hydrochloride. After the filtrate was concentrated on a rotary evaporator, fractional distillation gave 4.3 g [29% based on sodium bis(trimethylsilyl)amide] of 1,3-bis[bis(trimethylsilyl)amino]-1,3-dimethyl-1,3-diphenyldisilazane (XV).

Procedure E

After a mixture of 61.7 g (0.15 mole) of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane and 43.8 g (0.23 mole) of dichloromethylphenylsilane was heated at 175° for 48 h and then at 280° for 4 h and the viscous reaction product was decanted from 9.4 g (calcd. 6.2 g) of ammonium chloride, fractional distillation gave 44.6 g (45%) of *N,N'*-bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (XVII).

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