nature of the "dynamic" form. In view of this we would like to stress once more what we have clearly pointed out in previous publications[1,11], *viz.* that essentially only two different forms of the allyl group exist; a σ-bonded form, in which only one carbon atom is taking part in the bonding with the metal atom, and a π-bonded one, where all three carbon atoms are involved. The NMR spectrum of the "dynamic" form is a consequence of a rapid equilibrium between the two forms, as has also been suggested by other authors[6-10].

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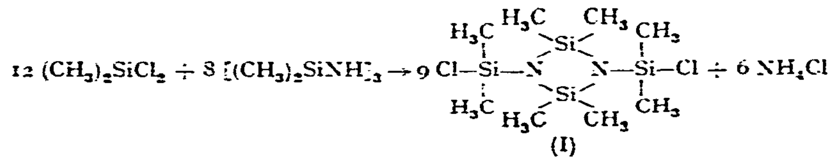
Functionally substituted cyclodisilazane derivatives

Wannagat recently observed that a four-membered ring compound, N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane, was obtained in a surprisingly high yield during attempts to produce dichlorotrisilazanes by equilibrating dichlorodimethylsilane and cyclotrisilazanes or cyclotetrasilazanes[1]. In studies of the same equilibration in this laboratory, N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (I) has been obtained in a mean yield of 54% when dichlorodimethylsilane and hexamethylcyclotrisilazane were equilibrated for 48 h at 175°.


(I)

Good yields are also obtained under other conditions of time and temperature and in the equilibration of dichlorodimethylsilane and octamethylcyclotetrasilazane. The compound can be obtained in a semipure state by distillation of the equilibrated product at reduced pressure and can be further purified by sublimation. In the preparation of derivatives, it is convenient to convert the crude equilibration mixtures or the semipure distillates to compounds that are more easily purified, since I is extremely unstable against hydrolytic decomposition. The ready access of the cyclodisilazane structure by this method has led to the synthesis and identification of a number of new functional cyclodisilazane derivatives.

1,5-Dichlorotrisilazane is a secondary product of the equilibration reaction. When an equilibrated mixture was treated with ammonia, hexamethylcyclotrisilazane was identified as one of the products. Similarly, an equilibration mixture and methylamine gave 1,5-bis(methylamino)trisilazane (II). No derivatives of 1,3-dichlorodisilazane could be isolated from these mixtures.

Treatment of distilled I with ammonia or methylamine gave N,N'-bis(aminodimethylsilyl)tetramethylcyclodisilazane (III) or N,N'-bis(methylaminodimethylsilyl)tetramethylcyclodisilazane (IV), respectively, in yields of about 60%. Unlike most silylamines, III resists self-condensation. It can readily be purified at 100°/7 mm, and on differential thermal analysis at a heating rate of 15°/min shows no decomposition below its normal boiling point, 236°. Heated at 200° for several hours, III showed little evidence of change, but upon the addition of catalytic quantities of ammonium sulfate, about 15% of III was converted to hexamethylcyclotrisilazane. At 175° with ammonium sulfate IV gave about 35% of 1,2,2,4,4,5,6,6,8,8-decamethylcyclotetrasilazane (V). III has been hydrolyzed in moist ether or in contact with atmospheric moisture to N,N'-bis(hydroxydimethylsilyl)tetramethylcyclodisilazane (VI) in 35–40% yields. With the appropriate alcohols, III was also converted to N,N'-bis(dimethylmethoxysilyl)tetramethylcyclodisilazane (VII) and N,N'-bis(dimethylethoxysilyl)tetramethylcyclodisilazane (VIII).

The lithium aluminum hydride reduction of I gave 35% of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane (IX). Selective reduction of functional groups in compounds containing the silicon–nitrogen linkage has not been previously reported. I and methyllithium or methylmagnesium bromide afforded N,N'-bis(trimethylsilyl)tetramethylcyclodisilazane X, which has been prepared by other methods[2,3].

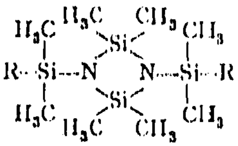
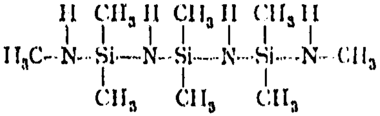
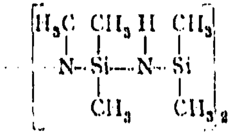
In the NMR spectra of the cyclodisilazane derivatives that have so far been prepared, the ring Si-methyl protons resonate at τ 9.76–9.79 and the pendant Si-methyl protons at τ 10.01–10.05 (10 per cent solutions in CCl_4). The only exceptions are I, which shows a singlet at τ 9.65 and IX, in which the pendant Si-methyl protons appear as a doublet at τ 9.95.

The infrared spectra of the series contain some interesting features. The Si_2N stretch, which universally has been observed in the 900 to 950 cm^{-1} region, shifts to an unusually low frequency. In most of the cyclodisilazane derivatives, this band appears at 880 to 890 cm^{-1} with either no absorption or very weak absorption in the 900 to 950 cm^{-1} region. A band, apparently characteristic of structures containing N-silylated silicon–nitrogen ring compounds[4,5], was observed at 1030 cm^{-1} in all the cyclodisilazanes.

Studies of the equilibration reaction are continuing as well as investigations of the chemical and physical properties of functional cyclodisilazane derivatives.

TABLE 1

PROPERTIES OF CYCLODISILAZANES AND RELATED COMPOUNDS

Compound nr.	Compound structure		B.p.(°/mm)	M.p.(°)	n_D^{20}	Analyses Calcd. (Found)				
						C	H	N	Si	Cl
I[a]		R = Cl	153–154/46 243/atm.	66–67		28.98 (28.82)	7.30 (7.26)	8.45 (8.51)	33.89 (33.97)	21.39 (21.42)
III		R = NH_2	99–100/7	33–35		32.83 (32.67)	9.64 (9.48)	19.15 (19.06)	38.39 (38.24)	
IV		R = $NH(CH_3)$	118/8	—	1.4518	37.45 (37.37)	10.06 (10.09)	17.47 (17.52)	35.03 (35.16)	
VI		R = OH	—	122–123	—	32.60 (32.94)	8.89 (8.76)	9.50 (9.48)	38.13 (38.20)	
VII		R = OCH_3	104–106/6	—	1.4368	37.21 (37.32)	9.37 (9.24)	8.68 (8.90)	34.82 (34.61)	
VIII		R = OC_2H_5	115–116/8	—	1.4332	41.09 (41.22)	9.77 (9.91)	7.99 (8.31)	32.03 (31.84)	
IX		R = H	65–66/8	—	1.4312	36.58 (36.50)	9.98 (9.96)	10.07 (10.77)	42.78 (42.51)	
X[b]		R = CH_3	85–86/7	42–43	—	41.31 (41.35)	10.40 (10.20)	9.64 (9.50)	38.65 (38.48)	
II	 $H_3C-NH-Si(CH_3)_2-NH-Si(CH_3)_2-NH-Si(CH_3)_2-NH-CH_3$		64/8	—	1.4409	36.31 (36.19)	10.66 (10.73)	21.17 (20.82)	31.85 (31.45)	
V	 $[-N(CH_3)-Si(CH_3)_2-NH-Si(CH_3)_2-]_2$		87–89/12	—	1.4479	37.44 (37.26)	10.06 (10.16)	17.47 (17.36)	35.03 (34.96)	

[a] Reported m.p.: 70° (Ref. 6); 59–60° (Ref. 7); 68–69° (Ref. 1). [b] Reported m.p.: 38–39°, b.p. 85°/7 mm (Ref. 3).

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