PHYSICAL AND CHEMICAL PROPERTIES OF *N*-HALOHEXAMETHYLDISILAZANES

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INTRODUCTION

This paper describes a comparative study of the physical properties of the three *N*-halohexamethyldisilazanes, $(Me_3Si)_2NX$ where X = Cl, Br and I; and a study of several chemical reactions, particularly of $(Me_3Si)_2NBr$. *N*-Halosilazanes were unknown until 1962, when Wiberg and Gieren[1] reported the synthesis of $(Me_3Si)_2NCl$, obtained from *N*-sodiohexamethyldisilazane and chlorine in ether at —50°. A recent communication reported the synthesis of $(Me_3Si)_2NBr$ from $(Me_3Si)_2NH$ and *N*-bromosuccinimide in CCl_4[2], and Wannagat has announced the preparation of $(Me_3Si)_2NI$ orally at a meeting[3], but the properties of the latter compound have not been published. The preparation of some other *N*-chlorosilazanes, $(Ph_3Si)_2NCl$ and Ph_3SiNCl_2, has also been reported[4].

In our work all of the *N*-halohexamethyldisilazanes were obtained by treating $(Me_3Si)_2NNa$ with the free halogen in isopentane solution at —70°. This method resembles that used by Wiberg and Gieren for the *N*-chloro compound, although it was developed independently before their synthesis was published. $(Me_3Si)_2NNa$ was prepared by metallation of hexamethyldisilazane with sodium in refluxing heptane using styrene as a hydrogen acceptor[5].

$$(Me_3Si)_2NH + Na \xrightarrow[\text{heptane } 100^\circ]{\text{styrene}} (Me_3Si)_2NNa$$

$$(Me_3Si)_2NNa + X_2 \xrightarrow[-70^\circ]{\text{iso-}C_5H_{12}} (Me_3Si)_2NX + NaX$$

The halogenation was carried out at low temperature to avoid reaction of the product with the sodium salt. Typical yields were 20 %, 54 % and 43 % for the chloride, bromide and iodide respectively.

PHYSICAL PROPERTIES

All of these *N*-halodisilazanes appear to be stable indefinitely at room temperature; however, the iodide appears to decompose slowly in light. The bromide has been kept for several months in room light without apparent decomposition. In physical appearance they are all liquids at room temperature which fume on exposure to moist air. Their colors parallel those of the corresponding free halogens (Table I).

TABLE 1

PHYSICAL PROPERTIES OF *N*-HALOHEXAMETHYLDISILAZANES

	$(Me_3Si)_2NI$	$(Me_3Si)_2NBr$	$(Me_3Si)_2NCl$
Color	Dark red	Orange-red	Pale yellow-green
λ_{max} Å (ε)	3440 (192) 4080 (135) 5130 (60)	2300 (300) 3440 (89)	2950 (62)
B. pt. (mm)	83° (16)[3]	67–68° (12) 165° (750)	63° (25) lit.[1] 42° (11)
M. pt.	10°	—22°	
Density (24°)	1.275	1.121 lit.[2] 1.13 (21°)	0.882
n_D^{25}	*ca.* 1.47	1.4564 lit.[2] 1.4580 (20°)	1.4284
^1H NMR	9.80_3	9.80_3	9.82_0
$J(^{13}C\text{–}H)$ (cps)	119.0	119.2	120.0
$J(^{29}Si\text{–}C\text{–}H)$ (cps)	6.50	6.58	6.50

The proton magnetic resonance chemical shifts and ^{13}C–H coupling constants of all three *N*-halohexamethyldisilazanes are virtually identical. The *C*-halogen compounds, chloromethyltrimethylsilane and iodomethyltrimethylsilane, also have nearly identical NMR chemical shifts and coupling constants for the methyl protons ($\tau = 9.89$, $J(^{13}C\text{–}H)$ 120.0 cps and $\tau = 9.85$, $J(^{13}C\text{–}H)$ 119.5 cps respectively). Thus both carbon and nitrogen insulate silyl methyl protons from inductive effects of substituents. If dative π-bonding takes place from N to Si, it does not seem to provide an especially effective route for the transmission of electronic effects from the halogen to the silicon in *N*-halohexamethyldisilazanes.

All of the *N*-halohexamethyldisilazanes show near ultraviolet absorption, the energy of the transitions decreasing in the order Cl > Br > I (Fig. 1). These electronic

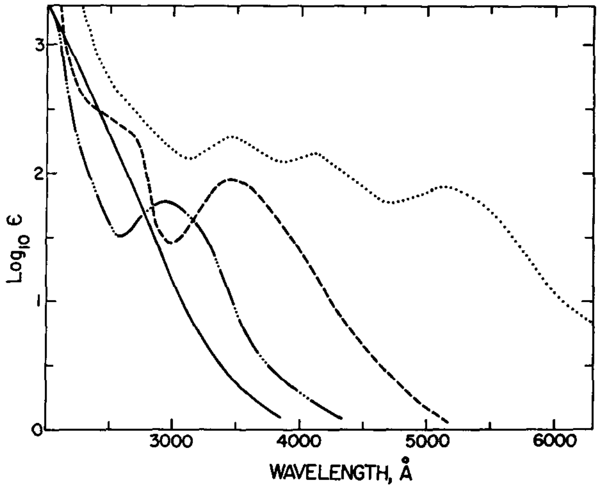

Fig. 1. Electronic spectra. ······, $(Me_3Si)_2NI$; – – – –, $(Me_3Si)_2NBr$; —··—··—, $(Me_3Si)_2NCl$; ——, $(Me_3Si)_2NBBr_2$.

absorption bands probably result from transitions of electrons in lone pairs on nitrogen or halogen into antibonding σ orbitals of the N–X bond (Fig. 2)[*]. The decreasing transition energies with the heavier halogens can be associated with decreased N–X bond strength and consequent lowering of the energies of the antibonding orbitals (σ^*). The higher energy of the non-bonding electrons in heavier halogens should also decrease the energy of the observed transitions.

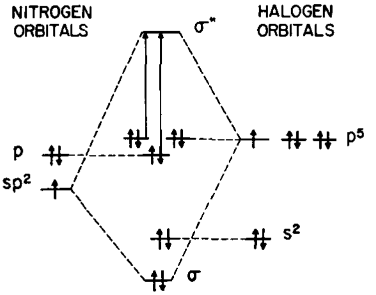

Fig. 2. Proposed correlation diagram for the nitrogen–halogen bond in *N*-halodisilazanes, showing transitions from nonbonding orbitals to σ^* antibonding orbital.

Information on electronic spectral properties of other *N*-haloamines is lacking in the literature, but it is probable that purely organic compounds of this class will show similar absorptions. For example we find an absorption maximum for *N*-bromopiperidine at 3150 Å (ε = 600). Other known *N*-bromoamines have also been reported to be yellow or orange[**]. *N*-Haloimides do not show this absorption above 3000 Å[***]; the N–X bond is stronger in these compounds and the antibonding orbitals are expected to lie at higher energies.

A weak broad electron spin resonance signal near the free electron position was observed on irradiation of pure $(Me_3Si)_2NI$ with ultraviolet light at —50°. Incipient fine structure was visible at —30° but rapid decomposition of the radicals at higher temperatures prevented resolution of the spectrum. The signal was probably due to the hexamethyldisilazyl radical since $I^\bullet$ does not give an ESR signal under these conditions.

CHEMICAL PROPERTIES

The only chemical reactions for *N*-halosilazanes previously reported are the reaction of $(Me_3Si)_2NCl$ with $(Me_3Si)_2NNa$[4], discussed below, and the coupling of lithium azide with $(Me_3Si)_2NCl$ to yield 1,1-bis(trimethylsilyl)tetrazadiene[1].

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[*] The absorption maximum of $(Me_3Si)_2NI$ at 5100 Å appears to be due to elemental iodine produced photochemically in solution. This peak grows and the others decrease with time, particularly if the sample is exposed to strong light.

[**] *N*-Bromodimethylamine has been reported to be a yellow oil[6]. *N*-Bromomethylamine has also been reported as a yellow oil[7]. *N,N*-Dibromopiperazine is formed as yellow crystals[8].

[***] The ultraviolet absorption of *N*-haloimides is nearly the same as that of the nonhalogenated compounds. For example, *N*-iodosuccinimide has absorption maxima at 2900 and 2240 Å (*Sadtler Standard Spectra*, Number 15719, Sadtler Research Laboratories, Philadelphia, Pa.) while succinimide has an absorption maximum at 2760 Å (*ibid.*, Number 482). *N*-Bromophthalimide absorbs at 2905, 2370, 2285 and 2150 Å (*ibid.*, Number 16557) and *N*-bromomethylphthalimide at 2930, 2385 and 2173 Å (*ibid.*, Number 6635).

We chose to study the chemical reactions of *N*-bromohexamethyldisilazane. This compound reacts vigorously with water to give a variety of products depending on the pH. Hydrolysis in a basic solution containing KI liberates about 1.5 equivalents of I_2, whereas in acidic solution the value is about 0.3 to 0.5 equivalents. Basic hydrolysis in a Zerewitinoff apparatus yields only a small amount of N_2 (*i.e.*, less than 5 % of the total nitrogen). Acidic hydrolysis, on the other hand, yields 40 % of the total nitrogen as N_2. Because of possible reactions between different hydrolysis products, the amount of N_2 given off is also somewhat dependent on the rates of stirring and addition.

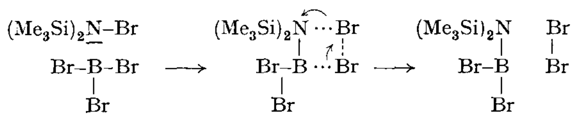
These observations can be explained by the two limiting reactions expressed in equations (1) and (2):

$$[(CH_3)_3Si]_2NBr + H_2O \xrightarrow{(OH^-)} [(CH_3)_3Si]_2NH + HOBr \qquad (1)$$
$$\llcorner\!\!\longrightarrow [(CH_3)_3Si_2]O + NH_3$$

$$[(CH_3)_3Si]_2NBr + H_2O \xrightarrow{(H^+)} [(CH_3)_3Si]_2O + NH_2Br \qquad (2)$$
$$\llcorner\!\!\longrightarrow N_2H_4 + N_2 + HBr$$

In basic solution initial cleavage of the N–Br bond to give HOBr as in equation (1) would result in two equivalents of oxidizing power per mole. This first reaction is analogous to the hydrolysis of *N*-bromosuccinimide (NBS) where HOBr is produced quantitatively. The data indicate that this is also the major reaction observed in basic solution for $(Me_3Si)_2NBr$. In acidic solution, however, the results suggest that reaction (2) also takes place, with initial cleavage of the Si–N bond. Mass-spectroscopic analysis shows that no gas other than N_2 is evolved in appreciable amount. It is of interest that both reactions (1) and (2) require positive character for the *N*-bonded bromine.

The positive nature of the bromine in $(Me_3Si)_2NBr$ is also illustrated by the smooth reaction with boron tribromide, with loss of elemental bromine to yield *N*-(dibromoboryl)hexamethyldisilazane, $(Me_3Si)_2NBBr_2$. This pale yellow liquid has no electronic spectrum other than end absorption near 2000 Å. In this new compound the ^1H NMR is at $\tau = 9.613$ and the Si–N–Si asymmetric stretch frequency is 880 cm^{-1}. The low-field chemical shift and low Si–N–Si frequency may reflect the contribution of nitrogen–boron π-bonding in withdrawing electron density from the Si–N–Si system. The reaction of $(Me_3Si)_2NBr$ with BBr_3 could take place by attack of the nitrogen lone pair on the boron followed by loss of bromine to yield the new product.



A similar mechanism has been suggested by Becke-Goehring and Krill for the reaction of metallic trihalides with hexamethyldisilazane[9]:

$$[(CH_3)_3Si]_2NH + MX_3 \longrightarrow (CH_3)_3SiNHMX_2 + (CH_3)_3SiX$$

However, in their studies the Si–N bond was always attacked with the formation of an

Si–X bond. A similar compound, $[(CH_3)_3Si]_2NBF_2$, has been prepared recently by Russ and MacDiarmid[10]. However, it was obtained by a completely different method which involved treatment of *N*-lithiohexamethyldisilazane or tris(trimethylsilyl)amine with boron trifluoride.

A familiar reaction of many *N*-halo compounds is free radical or allylic bromination. The mechanism and conditions of bromination with *N*-bromosuccinimide (NBS) have been studied extensively during the last few years[11–17]. It has now been established that in NBS bromination the succinimido radical does not act as a free radical chain carrier, but rather that Br_2 is the chain carrier. The Br_2 is derived from a two step reaction wherein hydrolysis of a small part of the NBS produces HBr which in turn reacts with remaining NBS to eliminate Br_2. This Br_2 then reacts with the free radical initiator to give $Br^{\bullet}$ which abstracts an allylic or benzyllic hydrogen to give HBr and $R^{\bullet}$; the allylic or benzylic radical then combines with another Br_2 to regenerate $Br^{\bullet}$.

We have found that $(Me_3Si)_2NBr$ also shows activity as a free radical brominating agent. It is somewhat less active than *N*-bromosuccinimide but might be useful under special circumstances. Toluene is brominated by $(Me_3Si)_2NBr$ using benzoyl peroxide catalyst in refluxing CCl_4 to give benzyl bromide in 85 % yield. With cyclohexene containing the equilibrium concentration of hydroperoxides[18], 0.42 *M*, a moderate yield of 3-bromocyclohexane is obtained after several hours reflux. Under similar conditions NBS requires only a few minutes for complete reaction. The difference in reactivity between NBS and $(Me_3Si)_2NBr$ is not surprising since the HBr formed can attack the Si–N bonds to give Si–Br and N–H rather than the N–Br bond to give more Br_2. Trimethylbromosilane, a compound containing bromine not available for further reaction, is formed as a by-product.

Alkyllithium compounds react with $(Me_3Si)_2NBr$ to give predominantly exchange at low temperatures followed by coupling to give *N*-alkylhexamethyldisilazanes or further reaction to yield $(Me_3Si)_2NH$. Methyllithium in ether gives nearly equal amounts of $(Me_3Si)_2NH$ and the coupling product, $(Me_3Si)_2NMe$. Phenyllithium and *n*-butyllithium in ether undergo exchange to yield organic bromide and the stable complex $(Me_3Si)_2NLi \cdot O(C_2H_5)_2$[19], which couples only slowly with 1-bromobutane or bromobenzene. Biphenyl is also found as a minor product of the reaction with C_6H_5Li. *sec*-Butyllithium reacts immediately at —70° with $(Me_3Si)_2NBr$ in ether solution to give 2-butene and $(Me_3Si)_2NH$. On reaction in ether solution ethylmagnesium bromide yields predominantly $(Me_3Si)_2NH$ together with a small amount of coupling product.

The formation of $(Me_3Si)_2NH$ in these reactions could result from either of two possible reactions. The alkyllithium compound may be oxidized to the olefin as is observed with *sec*-butyllithium, or the exchange product, $(Me_3Si)_2NLi$, may react with remaining $(Me_3Si)_2NBr$ to give LiBr and $(Me_3Si)_2N^{\bullet}$, which could be converted to $(Me_3Si)_2NH$ by hydrogen abstraction from the solvent.

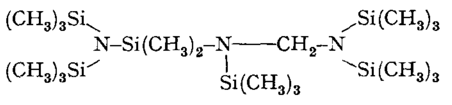
The reaction of $(Me_3Si)_2NBr$ with $(Me_3Si)_2NNa$ was studied, to investigate the point mentioned above and also in the hope of preparing tetrakis(trimethylsilyl)-hydrazine. Reaction takes place in an isopentane suspension at —20° to give a quantitative yield of $(Me_3Si)_2NH$. Evidently, if the hydrazine is formed, it is so crowded sterically that it undergoes homolytic cleavage to the radical which then abstracts a proton from the solvent. Wiberg and Raschig[4] obtained somewhat different results

TABLE 2

INFRARED ABSORPTION FREQUENCIES FOR *N*-HALOHEXAMETHYLDISILAZANES

$(Me_3Si)_2NCl$	$(Me_3Si)_2NBr$	$(Me_3Si)_2NI$	*Assignment*
2955 s	2955 s	2955 s	CH stretch[21]
2900 m	2895 m	2895 m	
1435 w	1440 w	1440 w	CH_3 deformation[21]
1405 m	1400 m	1410 m	
1305 w	1305 w	1305 w	
	1265 m		
1255 vs	1255 vs	1255 vs	$SiMe_3$[21]
930–965 vs	935–960 vs	920–950 vs	SiNSi asymmetric stretch[21]
	870 s		CH_3 rocking[21]
820–875 vs	835 vs	820–875 vs	
775 w	770 w	775 w	
755 m	755 m	760 m	CH_3 rocking[21]
685 m	680 m	685 m	asymmetric SiC_3 stretch[21]
620 m	620 m	620 m	Me_3Si (overtone of SiC_3 def.)[21]
420 w	395 w		
320 m	320 m	320 m	

in their reaction of $(Me_3Si)_2NCl$ and $(Me_3Si)_2NNa$. Hydrogen was apparently abstracted from a methyl group followed by CH_2 migration and subsequent addition of the starting materials to give the following complex product:



$$[(CH_3)_3Si]_2N{-}Si(CH_3)_2{-}N[Si(CH_3)_3]{-}CH_2{-}N[Si(CH_3)_3]_2$$

However, their experimental conditions (not reported) may have been somewhat different from ours.

EXPERIMENTAL

Materials and spectra

Reagents were all of reagent grade and were used as received. Organolithium reagents were obtained from Foote Mineral Co. Hexamethyldisilazane was prepared from trimethylchlorosilane and ammonia according to the standard method[20]. All reactions involving moisture-sensitive compounds were carried out under a nitrogen atmosphere.

Visible and ultraviolet spectra were determined in cyclohexane or 2,2,4-trimethylpentane (Matheson Colman and Bell Co., Spectroquality) using a Cary Model 14 automatic recording spectrophotometer. Infrared spectra in the sodium chloride region were taken of thin liquid films between NaCl plates using a Perkin–Elmer Model 237 grating spectrometer. Spectra in the far infrared (300–650 cm^{-1}) region were determined using polyethylene plates and a Beckman IR-10 spectrometer. Proton NMR spectra were determined using a Varian Model A-60 spectrometer.

N-Bromohexamethyldisilazane

Sodium (9.2 g, 0.4 mole) and 500 ml of *n*-heptane were placed in a 1-l three-necked flask fitted with condenser, wire stirrer and addition funnel. After heating to reflux, a mixture of 65 g (0.4 mole) of $(Me_3Si)_2NH$ and 36 g (0.35 mole) of styrene was added in 15 min with vigorous stirring. The mixture was then refluxed for 4 h with stirring after which time nearly all the sodium had been consumed. On cooling, $(Me_3Si)_2NNa$ crystallized out and was filtered and washed with isopentane in a dry-box.

The $(Me_3Si)_2NNa$ was transferred to a 500-ml flask which was fitted with a wire stirrer, condenser, and addition funnel, and 300 ml of isopentane was added. The mixture was chilled to —70° and 19.4 ml of bromine (0.36 mole) was added over a period of 30 min with vigorous stirring maintaining the temperature constant. After 2 h of stirring at —70°, the mixture was allowed to warm up to room temperature. About 5 g of powdered antimony was added and the mixture was stirred for 2 additional h to remove any excess bromine. The mixture was filtered in a dry-box, the solvent was stripped off and the remaining liquid was rapidly distilled under reduced pressure to remove nonvolatile materials. The distillate was then fractionally distilled through a Vigreaux column, b.p. 67–68° (12 mm), yield of product 52.2 g (54 % based on hexamethyldisilazane). (Found: C, 29.92; H, 7.78; Br, 33.29; N. 5.84. $C_6H_{16}BrNSi_2$: calcd.: C, 29.98; H, 7.56; Br, 33.25; N, 5.83 %.)

N-Iodohexamethyldisilazane

A 500-ml three-necked flask was fitted with a wire stirrer, a nitrogen inlet and specially constructed solids addition funnel, having a teflon screw to control addition of powdered solids. In the flask was placed 18.7 g (0.1 mole) of $(Me_3Si)_2NNa$ prepared as described above, and 125 ml of isopentane. The mixture was cooled to —70° and 25.4 g (0.1 mole) of powdered iodine was added slowly with vigorous stirring. The mixture was then stirred for about 6 h at —70°, allowed to warm up to room temperature, and filtered in a dry-box; the solvent was stripped off and the remaining liquid was decanted from the small amount of precipitate. When this liquid was placed in a refrigerator at 0°, the product solidified forming dark red prismatic crystals from which the mother liquor was removed; m.p. 10°; yield 12 g (43 %). (Found: C, 25.30; H, 6.01; I, 44.45; N, 5.02. $C_6H_{18}INSi_2$ calcd.: C, 25.08; H, 6.32; I, 44.17; N, 4.88 %.)

Caution. When exposed to the atmosphere, $(Me_3Si)_2NI$ forms a black, acetone-insoluble, violently explosive solid, similar in its appearance and shock sensitivity to "nitrogen triiodide".

N-Chlorohexamethyldisilazane

Elemental chlorine (15 g, 0.2 mole) was bubbled into a stirred suspension of 37 g (0.2 mole) of $(Me_3Si)_2NNa$, prepared as above, in 150 ml of isopentane at —70°. After stirring for 2 h, the mixture was boiled for 10 min to expel excess chlorine and filtered in a dry-box. The pentane was removed by distillation and the $(Me_3Si)_2NCl$ distilled; b.p. 63–65° (25 mm); yield 8 g (20 %).

Preparation of N-bromopiperidine

N-bromopiperidine was prepared by a modification of the method of Lellman and Schwaderer[22]. Piperidine (17.3 g, 0.2 mole) was treated with 22.5 ml (0.2 mole) of 48 % hydrobromic acid. A solution of sodium hypobromite (0.2 mole) was slowly added to the solution of piperidine hydrobromide with stirring and cooling. The *N*-bromopiperidine was insoluble in water and was separated from the aqueous solution for use. It decomposes slowly on standing at room temperature to give a dark brown tar and piperidine hydrobromide.

Hydrolysis of $(Me_3Si)_2NBr$

Determination of the volume of gas released on hydrolysis was accomplished by injection of 0.50 ml (0.0023 mole) of $(Me_3Si)_2NBr$ into 10 ml of 0.5 *N* HCl, 0.1 *N* NaOH or pure water at 0° in a Zerewitinoff apparatus. In HCl solution, reaction was instantaneous, releasing approximately 9.5 ml (0.00043 mole) of N_2 at STP corresponding to 37 % of the total nitrogen. With dilute NaOH solution, less than 1 ml of N_2 was evolved after 30 min stirring, which is less than 5 % of the total nitrogen. In pure water, there was an induction period of about 3 min after which evolution of N_2 proceeded rapidly; 13.7 ml (0.00061 mole) at STP or 53 % of total nitrogen was found.

For analysis of the gaseous products by mass spectroscopy, $(Me_3Si)_2NBr$ was hydrolyzed in an argon atmosphere. A flask equipped with an argon inlet, magnetic stirrer and rubber septum, and containing 30 ml of 1 *N* H_3PO_4, 1 *N* NaOH or water was thoroughly flushed with argon, heating the solution to drive out dissolved N_2 and O_2. A sample of the atmosphere of the solution prior to the hydrolysis was injected into an evacuated sample tube and its mass spectrum used as a blank. After injection of 1.00 ml (0.0047 mole) of $(Me_3Si)_2NBr$, the mixture was stirred for 5 min and a second sample of the solution atmosphere was analyzed. Under no conditions, acidic, basic or neutral, was any gaseous product (*e.g.* N_2O, NO, O_2) other than nitrogen observed in a yield greater than 2 % of the volume of nitrogen.

N-(Dibromoboryl)hexamethyldisilazane

To 14.5 g (0.0605 mole) of neat $(Me_3Si)_2NBr$ was added 15.2 g (0.0605 mole) of boron tribromide at 0°. The mixture was stirred for 20 min at this temperature, the bromine was removed by distillation at reduced pressure, and the product was fractionally distilled; b.p. 87–89° (3 mm), m.p. 20°, yield 15 g (75 %), n_D^{25} 1.4780, d_4^{22} 1.351. (Found: C, 21.99; H, 5.10; Br, 48.57; N, 4.45. $C_6H_{18}BBr_2NSi_2$ calcd.: C, 21.77; H, 5.48; Br, 48.28; N, 4.23 %.) The observed infrared absorption frequencies for $(Me_3Si)_2NBBr_2$ are: 2960 m, 2900 w, 1415 m, 1315 s, 1255–1300 vs, 830–900 vs, 770 m, 740 w, 720 s, 685 w, 670 w.

Bromination of cyclohexene

Cyclohexene was "aged" by bubbling oxygen through it, letting it stand overnight and then saturating it with nitrogen to build up the hydroperoxide concentration to about 0.42 *M*[18]; 4.0 g (0.048 mole) was then dissolved in 25 ml of CCl_4 and added to 9.0 g. (0.037 mole) of $(Me_3Si)_2NBr$. After 8 h reflux the orange color of the $(Me_3Si)_2NBr$ was still visible. Distillation of the mixture gave 2.5 g of $(Me_3Si)_2NH$ (40 %), a small amount of Me_3SiBr, unchanged cyclohexene, and 2.5 g of 3-bromocyclohexene, b.p. 73° (28 mm) (40 %), infrared and NMR spectra identical with authentic 3-bromocyclohexene. Polymeric material (1.49 g) was also produced.

Bromination of toluene

In 25 ml of CCl_4, 5.6 g (0.023 mole) of $(Me_3Si)_2NBr$ and 2.3 g (0.025 mole) of toluene were mixed; 10 mg of benzoyl peroxide catalyst was then added. After 2 h refluxing the reaction no longer gave a positive test with potassium iodide–starch paper. Analysis of the reaction mixture by NMR and infrared spectroscopy established that 82 % of the original $(Me_3Si)_2NBr$ had been converted into $(Me_3Si)_2NH$, 3 % into Me_3SiBr and 15 % was unchanged. 80 % of the theoretical yield of benzyl bromide was also present.

Reaction of $(Me_3Si)_2NBr$ *with methyllithium*

Methyllithium (0.047 mole) in ether was added to 11.2 g (0.047 mole) of $(Me_3Si)_2NBr$ in 40 ml ether at —70°. After warming to room temperature, most of the ether was removed by distillation and the mixture was filtered and distilled using a spinning band column. The yield of $(Me_3Si)_2NMe$ was 2.5 g (30 %), b.p. 142.5–144°, lit.[23] 148°, n_D^{25} 1.4187, lit.[23] n_D^{20} 1.4220. $(Me_3Si)_2NH$ (3.0 g, 40 %) was also recovered. (Found: C, 47.98, 48.00; H, 12.06, 11.96; N, 8.21. $C_7H_{21}NSi_2$ calcd.: C, 47.92; H, 12.07; N, 7.98 %.)

Reaction of $(Me_3Si)_2NBr$ *with ethylmagnesium bromide*

Ethylmagnesium bromide (0.023 mole) in ether solution was added to 5.6 g (0.023 mole) of $(Me_3Si)_2NBr$ in 50 ml of ether at —70°. After warming to room temperature, the ether was removed by distillation, the mixture was filtered and the filtrate distilled. The $(Me_3Si)_2NH$ fraction (2.0 g, 50 %) was found to contain about 5 % of $(Me_3Si)_2NCH_2CH_3$, identified by its infrared and NMR spectra.

Reaction of $(Me_3Si)_2NBr$ *with sec-butyllithium*

sec-Butyllithium (0.023 mole) in hexane was added to 5.6 g (0.023 mole) of $(Me_3Si)_2NBr$ in 25 ml of ether at —70°. Reaction was immediate to give a precipitate of LiBr. Distillation of the mixture yielded 2.8 g of $(Me_3Si)NH$ (75 %) and a low-boiling fraction containing about 0.023 mole of *cis*-2-butene, identified by comparison of its infrared spectrum with that of an authentic sample. The yield of *cis*-2-butene, as estimated from gas chromatography of the low-boiling fraction, was essentially quantitative.

Reaction of $(Me_3Si)_2NBr$ *with n-butyllithium*

To 3.36 g (0.014 mole) of $(Me_3Si)_2NBr$ in 30 ml ether at —70° was added 0.014 mole of *n*-butyllithium in hexane. An immediate reaction took place with the formation of a precipitate. The ether was removed by distillation after warming to room temperature. Volatile products were then removed under 0.1 mm pressure and the solid residue was extracted with isopentane. Redistillation of the volatile product gave 1 g (40 %) of $(Me_3Si)_2NH$ and a small amount of $(Me_3Si)_2NC_4H_9$. The isopentane extract on evaporation followed by recrystallization from heptane gave 1.5 g (40 %) of $(Me_3Si)_2NLi\cdot O(C_2H_5)_2$, m.p. 100–110 d., lit.[19] 95–110 d., identified by its infrared and NMR spectra.

Reaction of $(Me_3Si)_2NBr$ *with phenyllithium*

Phenyllithium (0.014 mole) in benzene–ether was added to 3.36 g (0.014 mole) of $(Me_3Si)_2NBr$ in 25 ml of ether at —70°. Reaction was slow but was apparently complete on warming to room temperature. The ether was removed by distillation, the residue diluted with heptane and filtered to remove LiBr. On vacuum distillation, 1.3 g (55 %) of bromobenzene and 0.6 g (35 %) of $(Me_3Si)_2NH$ were found along with a small amount of $(Me_3Si)_2NC_6H_5$, bis(trimethylsilyl)aniline. In the nonvolatile residue, 0.2 g (15 %) of biphenyl and 1.8 g (50 %) $(Me_3Si)_2NLi \cdot O(C_2H_5)_2$ were found.

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SUMMARY

The three *N*-halohexamethyldisilazanes, $(Me_3Si)_2NX$ where X = Cl, Br, I, have been prepared by the halogenation of *N*-sodiohexamethyldisilazane. Infrared, electronic and NMR spectra of the three compounds have been investigated and some chemical reactions of $(Me_3Si)_2NBr$ have been studied. $(Me_3Si)_2NBr$ acts as a positive halogen compound, reacting with BBr_3 to form a novel boron compound, $(Me_3Si)_2NBBr_2$; toward toluene and cyclohexene, it serves as a fairly good allylic brominating agent. Alkyllithium compounds undergo halogen-metal exchange with $(Me_3Si)_2NBr$ at low temperatures, followed by reduction to hexamethyldisilazane or coupling to give *N*-alkylhexamethyldisilazane, the proportions depending on the nature of the alkyl group. Hydrolysis of $(Me_3Si)_2NBr$ is also discussed.

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