Weeks and Matheson[4b,10] studied the photochemistry of formation of xenon difluoride from Xe and F_2. They irradiated the Xe–F_2 mixture (in an all-nickel system with sapphire windows at room temperature and 1000 mm. pressure) with ultraviolet light at 3130 Å. The intensity of light varied from 0.8×10^{15} to 50×10^{15} quanta/sec. The quantum yields were of the order of 0.3–0.7. In our experiments the gaseous Xe–F_2 or Xe–OF_2 mixtures were irradiated with normal daylight. Thus, the intensity of the radiation energy over the entire absorption bands of F_2 and OF_2, as well as the transmission coefficients of window and Pyrex glass, have to be taken into consideration. Fluorine absorbs light over practically the whole ultraviolet range with the maximum at about 2900 Å.[11] Its absorption in the visible range is very low. The absorbance of OF_2 is different[12]; its extinction coefficient is negligible down to about 2400 Å. and increases sharply at lower wave lengths. The transmission coefficient of glass, on the contrary, is negligible below 3100 Å. and increases rapidly at higher wave lengths.[13,14] The intensity of the sunlight at our latitude in winter (when the experiments were made) is considered to be about 1000 μwatts/cm.[2,13,15] An estimate of the amount of radiation energy passed through the window glass and through the Pyrex glass walls of the flasks and absorbed by fluorine at the conditions of our experiments with the Xe–F_2 mixtures (10-cm. thick layer of F_2 at 0.5 atm. pressure) gave a value of 0.37×10^{20} quanta/hr. The production of XeF_2 (relating to the four most luminous hours of a day) was about 9 mg./hr. or 0.32×10^{20} molecules/hr. Thus, in view of the approximate character of our calculations, the formation of XeF_2 should be completely accounted for by the photochemical reaction between Xe and F_2 with a quantum yield of about 1.

In the process of formation of XeF_2 from Xe–OF_2 mixtures, the oxygen difluoride probably does decompose first to oxygen and fluorine under the action of ultraviolet light.[16] The liberated fluorine then reacts with xenon as in the experiments with the Xe–F_2 mixtures.

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(10) J. L. Weeks and M. S. Matheson, ref. 3, p. 89.

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The Preparation of Chlorodisilazanes and Some of Their Derivatives

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The only chlorodisilazanes reported in the literature are trimethyltrichlorodisilazane[1] and 1,3-dichlorotetramethyldisilazane.[2] Trimethyltrichlorodisilazane was prepared from hexamethyldisilazane and silicon tetrachloride; 1,3-dichlorotetramethyldisilazane was prepared by brominating 1,3-diphenyltetramethyldisilazane to 1,3-dibromotetramethyldisilazane (yield ~15%) and converting it to the corresponding dichlorodisilazane with silver chloride (yield ~18%). It has also been reported that dimethyldichlorosilane does not react with hexamethyldisilazane.[3]

Attempts to prepare silazanes of the type $\mathrm{Cl{-}\overset{|}{\underset{|}{Si}}{-}NH{-}\overset{|}{\underset{|}{Si}}{-}Cl}$ by partial reaction of chlorosilanes with ammonia were unsuccessful.[2] We tried to find a suitable method for the preparation of these highly reactive materials. We find that hexamethyldisilazane, when refluxed with dimethyldichlorosilane using a Lewis acid as a catalyst, results in an exchange of silyl groups

$$\mathrm{(CH_3)_3SiNHSi(CH_3)_3 + (CH_3)_2SiCl_2 \longrightarrow \underset{I}{(CH_3)_3SiNHSi(CH_3)_2Cl} + (CH_3)_3SiCl}$$

$$\mathrm{(CH_3)_3SiNHSi(CH_3)_2Cl + (CH_3)_2SiCl_2 \longrightarrow \underset{II}{Cl(CH_3)_2SiNHSi(CH_3)_2Cl} + (CH_3)_3SiCl}$$

If a long-chain silazane polymer, or the cyclic trimeric or tetrameric polysilazane, is allowed to react with dimethyldichlorosilane, an analogous reaction takes place, yielding 1,3-dichlorotetramethyldisilazane (II). These latter reactions proceed even without a catalyst.

As monochlorosilanes react in the same way, we obtained pentamethylphenyldisilazane and 1,3-diphenyltetramethyldisilazane by the reactions

$$\mathrm{(CH_3)_3SiNHSi(CH_3)_3 + C_6H_5Si(CH_3)_2Cl \longrightarrow (CH_3)_3SiNHSi(CH_3)_2C_6H_5 + (CH_3)_3SiCl} \quad (1)$$

$$\mathrm{(CH_3)_3SiNHSi(CH_3)_2C_6H_5 + C_6H_5Si(CH_3)_2Cl \longrightarrow C_6H_5(CH_3)_2SiNHSi(C_6H_5)(CH_3)_2 + (CH_3)_3SiCl} \quad (2)$$

We find further that 1,3-dichlorotetramethyldisilazane (II) reacts with lithium phenylate to yield 1,3-diphenyltetramethyldisilazane (III). Compound III

$$\mathrm{Cl(CH_3)_2SiNHSi(CH_3)_2Cl + 2LiC_6H_5 \longrightarrow \underset{III}{C_6H_5(CH_3)_2SiNHSi(C_6H_5)(CH_3)_2} + 2LiCl}$$

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(1) H. Gross-Ruyken and K. Schaarschmidt, *Chem. Techn.* (Berlin), **11** (8), 451 (1959).

(2) H. Kriegsmann and G. Engelhardt, *Z. anorg. allgem. Chem.*, **310**, 100 (1961).

(3) R. Fessenden and J. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

was identical with the 1,3-diphenyltetramethyldisilazane obtained in reaction 2.

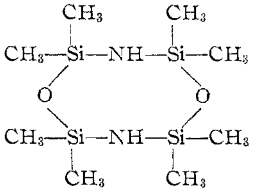
1,3-Dichlorotetramethyldisilazane (II) reacts with sodium methylate to yield 1,3-dimethoxytetramethyldisilazane, a compound which, to our knowledge, has not yet been described in the literature

$$Cl(CH_3)_2SiNHSi(CH_3)_2Cl + 2NaOCH_3 \longrightarrow (CH_3O)(CH_3)_2SiNHSi(CH_3)_2(OCH_3) + 2NaCl$$

On heating compound II with ammonium fluoride, we obtained dimethyldifluorosilane

$$Cl(CH_3)_2SiNHSi(CH_3)_2Cl + 4NH_4F \longrightarrow 2(CH_3)_2SiF_2 + 3NH_3 + 2NH_4Cl$$

On refluxing 1,3-dichlorotetramethyldisilazane with zinc oxide in toluene, we obtained the cyclic compound



IV

Compound IV has also been prepared by Rochow and Krüger in a different way.[4]

Experimental

Preparation of Pentamethylmonochlorodisilazane and 1,3-Dichlorotetramethyldisilazane.[5]—Hexamethyldisilazane (20 g., 0.12 mole) was mixed with 60 g. (0.46 mole) of dimethyldichlorosilane and a catalytic amount of approximately 100 mg. of aluminum chloride was added. The mixture was refluxed for 2 hr., and the trimethylmonochlorosilane formed was continuously distilled off. Upon distillation, 8 g. (0.044 mole) of pentamethylmonochlorosilane was obtained, b.p. 70.5–72° (32 mm.); yield 36.7% (calculation based on hexamethyldisilazane). *Anal.* Calcd. for $(CH_3)_3SiNHSi(CH_3)_2Cl$: C, 33.1; H, 8.8; N, 7.73; Si, 30.9; Cl, 19.6. Found: C, 33.16; H, 8.4; N, 7.62; Si, 30.3; Cl, 19.6. Also obtained was 7.5 g. (0.04 mole) of 1,3-dichlorotetramethyldisilazane, b.p. 78–79° (26 mm.), 170° (695 mm.); yield 33.3% (calculation based on hexamethyldisilazane). *Anal.* Calcd. for $Cl(CH_3)_2SiNHSi(CH_3)_2Cl$: C, 23.7; H, 6.4; N, 6.9; Si, 27.7; Cl, 35.0. Found: C, 23.9; H, 6.47; N, 6.98; Si, 27.3; Cl, 35.0. The two chlorodisilazanes are hydrolytically highly unstable. The analogous reaction was carried out with dimethyldichlorosilane and higher linear and cyclic dimethylpolysilazanes and 1,3-dichlorotetramethyldisilazane was obtained in yields of 75–80% (calculation based on the silazane polymer).

Preparation of Pentamethylphenyldisilazane and 1,3-Diphenyltetramethyldisilazane.—Hexamethyldisilazane (20 g., 0.12 mole) was refluxed for 15 hr. with an excess of dimethylphenylchlorosilane using aluminum chloride as a catalyst. The trimethylchlorosilane formed was continuously distilled off. Of the dimethylphenylchlorosilane used, 15 g. (0.09 mole) underwent reaction. Distillation yielded 10.2 g. (0.04 mole) of pentamethylphenyldisilazane, b.p. 204–205° (690 mm.); yield 38% (calculation based on hexamethyldisilazane); $n^{25}\text{D}$ 1.4799; d^{25} 0.914 (g./ml.). *Anal.* Calcd. for $(CH_3)_3SiNHSi(CH_3)_2C_6H_5$: C, 59.3; H, 9.4; N, 6.2; Si, 25.1. Found: C, 59.6; H, 9.26; N, 6.1; Si, 24.7. Also obtained was 7.1 g. (0.02 mole) of 1,3-diphenyltetramethyldisilazane, b.p. 128–129° (0.4 mm.); yield 16.6% (calculation based on hexamethyldisilazane); $n^{25}\text{D}$ 1.5395; d^{25} 0.987 (g./ml.). *Anal.* Calcd. for $C_6H_5(CH_3)_2SiNHSi(CH_3)_2C_6H_5$: C, 67.9; H, 7.72; N, 4.92; Si, 19.6. Found: C, 67.29; H, 7.92; N, 4.87; Si, 19.2.

Reaction of 1,3-Dichlorotetramethyldisilazane with Lithium Phenylate.—To a solution of 0.18 mole of lithium phenylate in 300 ml. of dry ether was added 20.2 g. (0.1 mole) of 1,3-dichlorotetramethyldisilazane in 100 ml. of dry ether and the mixture finally was refluxed for 30 min. Distillation yielded 18.6 g. (0.07 mole) of 1,3-diphenyltetramethyldisilazane; yield 77.8%. The compound was identical with the 1,3-diphenyltetramethylsilazane described in the previous example.

Reaction of 1,3-Dichlorotetramethyldisilazane with Sodium Methylate.—Solid sodium methylate (12.6 g., 0.22 mole) (prepared by titrating sodium in liquid ammonia with methanol in liquid ammonia[6]) was added in portions to 21 g. (0.1 mole) of 1,3-dichlorotetramethyldisilazane in 200 ml. of dry ether, and the reaction mixture finally was left for 2 hr. Distillation yielded 8.3 g. (0.04 mole) of 1,3-dimethoxytetramethyldisilazane, b.p. 157–158° (690 mm.); yield 43%; $n^{25}\text{D}$ 1.4093; d^{25} 0.920 (g./ml.). *Anal.* Calcd. for $(CH_3O)(CH_3)_2SiNHSi(CH_3)_2(OCH_3)$: C, 37.8; H, 9.86; N, 7.25; Si, 29.03. Found: C, 37.31; H, 10.05; N, 7.35; Si, 28.3.

Reaction of 1,3-Dichlorotetramethyldisilazane with Ammonium Fluoride.—A mixture of 28 g. (0.14 mole) of 1,3-dichlorotetramethyldisilazane, 100 g. of bis(2-methoxy)ethyl ether (distilled over sodium hydride), and 27 g. (0.73 mole) of ammonium fluoride was heated together to 140°. After 4 hr. 20 ml. of dimethyldifluorosilane was collected in the cooling trap, b.p. 2° (690 mm.). *Anal.* Calcd. for $(CH_3)_2SiF_2$: F, 39.9. Found: F, 39.6. The compound was identical with the dimethyldifluorosilane described by Newkirk.[7]

Reaction of 1,3-Dichlorotetramethyldisilazane with Zinc Oxide.—A solution of 20 g. (0.1 mole) of 1,3-dichlorotetramethyldisilazane in 20 ml. of dry toluene was refluxed with 20 g. (0.25 mole) of zinc oxide for 24 hr. Distillation of the reaction mixture yielded 5 g. (0.02 mole) of $O(Si(CH_3)_2NHSi(CH_3)_2)_2O$; yield 34%. This cyclic compound was identical with that prepared by Rochow.[4]

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(4) R. Krüger and E. G. Rochow, *Angew. Chem.*, **74**, 492 (1962).

(5) All analytical samples given were obtained by preparative gas chromatography using a glass column (15 ft. × 3/8 in.; packing: 30% silicone SE 30 on 60/80 Chromosorb P).

(6) J. Chablay, *Compt. rend.*, **140**, 1340 (1905).

(7) A. E. Newkirk, *J. Am. Chem. Soc.*, **68**, 2736 (1946).

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A New Variety of Organoborane

By Martel Zeldin and Thomas Wartik

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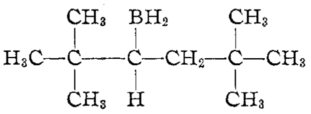
To our knowledge, only one authenticated case of a monomeric monoalkyl borane appears in the literature. Logan and Flautt,[1] through hydroboration of the sterically hindered olefin, di-*t*-butylethylene, prepared the compound



$$H_3C-C(CH_3)_2-CH(BH_2)-CH_2-C(CH_3)_2-CH_3$$

and implied that its stability (with respect either to association or further reaction with olefins) was at-

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(1) T. J. Logan and T. J. Flautt, *J. Am. Chem. Soc.*, **82**, 3446 (1960).