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

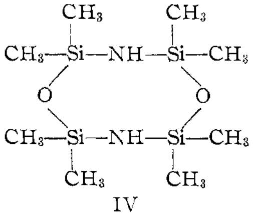
1,3-Dichlorotetramethyldisilazane (II) reacts with sodium methylate to yield 1,3-dimethoxytetramethyldisilazane, a compound which, to our knowledge, has not yet been described in the literature

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

On heating compound II with ammonium fluoride, we obtained dimethyldifluorosilane

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

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 $\mathrm{(CH_3)_3SiNHSi(CH_3)_2Cl}$: 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 $\mathrm{Cl(CH_3)_2SiNHSi(CH_3)_2Cl}$: 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); $n^{25}\mathrm{D}$ 1.4799; $d^{25}$ 0.914 (g./ml.). *Anal.* Calcd. for $\mathrm{(CH_3)_3SiNHSi(CH_3)_2C_6H_5}$: 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); $n^{25}\mathrm{D}$ 1.5395; $d^{25}$ 0.987 (g./ml.). *Anal.* Calcd. for $\mathrm{C_6H_5(CH_3)_2SiNHSi(CH_3)_2C_6H_5}$: 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%; $n^{25}\mathrm{D}$ 1.4093; $d^{25}$ 0.920 (g./ml.). *Anal.* Calcd. for $\mathrm{(CH_3O)(CH_3)_2SiNHSi(CH_3)_2(OCH_3)}$: 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 $\mathrm{(CH_3)_2SiF_2}$: 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 $\mathrm{O(Si(CH_3)_2NHSi(CH_3)_2)_2O}$; 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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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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## A New Variety of Organoborane

BY MARTEL ZELDIN AND THOMAS WARTIK

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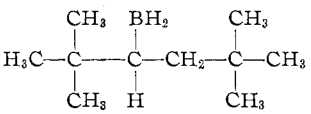
To our knowledge, only one authenticated case of a monomeric monoalkyl borane appears in the literature. Logan and Flautt,[1] through hydroboration of the sterically hindered olefin, di-*t*-butylethylene, prepared the compound



$$\mathrm{H_3C{-}C(CH_3)_2{-}CH(BH_2){-}CH_2{-}C(CH_3)_2{-}CH_3}$$

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

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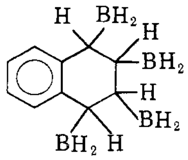
[1] T. J. Logan and T. J. Flautt, *J. Am. Chem. Soc.*, **82**, 3446 (1960).

tributable to the bulky *t*-butyl groups, which rendered such secondary processes sterically unfavorable.

We now wish to describe another organoborane which contains the $-BH_2$ group and which also apparently exhibits no tendency to associate. The substance in question, 1,2,3,4-tetrakisdihydroboryl-1,2,3,4-tetrahydronaphthalene, probably has the structural formula



and represents also the first substantiated case of the isolation of an organoborane containing more than one $-BH_2$ group per molecule. The compound is prepared by adding to an ether solution of lithium borohydride the substance $C_{10}H_8(BCl_2)_4$, which, in turn, is produced by the procedure of Fox and Wartik.[2]

That the new polydihydroboryl compound is stable enough to be isolated and characterized at room temperature we attribute to high rotational barriers of the bonds between the carbons to which the $-BH_2$ groups are attached. This characteristic, because it would tend to discourage achievement of a favorable transition state, might be expected to render decomposition or association more difficult. Such evidence as is presently available[3] indicates that $BH_2C_2H_4BH_2$, in which the barrier to rotation about the carbon–carbon bond is low, is thermally quite unstable at room temperature. Efforts to confirm our views by examining the stabilities of a variety of appropriate polydihydroboryl compounds are now in progress.

$C_{10}H_8(BCl_2)_4$ was prepared, as described earlier,[2] by the interaction of $B_2Cl_4$ with naphthalene at room temperature. (By using refined molecular distillation techniques in the purification process, we have now shown that pure $C_{10}H_8(BCl_2)_4$ is not a liquid at room temperature, as originally reported, but exists as fine pale yellow needles which melt at 46.5–47.5°.) This substance (0.54 mmole) was then added to an excess of lithium borohydride dissolved in ether, and the mixture was stirred at room temperature for several hours. (Other similar reactions were allowed to proceed for periods up to 1.5 days with no substantial change in nature or quantity of products.) When the volatile materials resulting from this procedure were subjected to fractional condensation through a U-trap held at $-23°$, 26.8 mg. of a colorless liquid was retained. Passing through the U-trap, in addition to the solvent ether, were trimethoxyborane, ethyl chloride, diborane, and a trace of hydrogen.

When a sample of the colorless liquid was subjected to analysis (fuming nitric acid at 350° in a sealed tube) it was found to contain 24.6% B, 67.4% C, and a C/B ratio of 2.47. The calculated values for $C_{10}H_8(BH_2)_4$ are 24.1%, 66.9%, and 2.50, respectively. Treatment with excess water resulted in the release of 7.64 moles of hydrogen per mole of $C_{10}H_8(BH_2)_4$ (calculated value = 8.0). Based on the equation

$$C_{10}H_8(BCl_2)_4 + 8LiBH_4 \longrightarrow C_{10}H_8(BH_2)_4 + 8LiCl + 4B_2H_6$$

the yield of the polydihydroboryl compound was 28%. This low yield can be attributed, at least in part, to the loss of some of the $C_{10}H_8(BCl_2)_4$ through its interaction with the solvent ether, as shown by the formation of ethyl chloride and trimethoxyborane. $C_{10}H_8(BH_2)_4$ has a vapor pressure somewhat below 1 mm. at room temperature. It is rapidly destroyed upon exposure to air, a behavior which is characteristic of aliphatic substances containing boron–carbon bonds. On standing in the vacuum system it slowly liberates diborane and leaves behind a nonvolatile residue.

The infrared spectrum of $C_{10}H_8(BH_2)_4$ resembles that of the polydichloroboryl compound from which it was prepared except for the absence of the characteristic $BCl_2$ stretch band from 870 to 1000 cm.$^{-1}$,[4] and the presence of a new peak at 2490 cm.$^{-1}$ (assigned to $BH_2$ stetch) and a doublet at 1162, 1190 cm.$^{-1}$ (assigned to $BH_2$ deformation).[5] The absence of absorption in the 1700 cm.$^{-1}$ region would appear to rule out inter- or intramolecular hydrogen bridge bonding.

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[2] W. B. Fox and T. Wartik, *J. Am. Chem Soc.*, **83**, 498 (1961).

[3] Efforts to prepare $BH_2C_2H_4BH_2$ by the reaction of $BCl_2C_2H_4BCl_2$ with lithium borohydride yielded an as yet uncharacterized liquid which, above $-45°$, decomposed with the liberation of diborane. In an earlier study G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger [*J. Am. Chem. Soc.*, **76**, 5299 (1954)] reported that their efforts to hydrogenate $BCl_2C_2H_4BCl_2$ resulted in products "unstable and difficult to purify."

[4] L. P. Lindemann and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956).

[5] L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

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# Correspondence

## The Probable Structure of $Fe_3(CO)_{12}$ as Obtained from the Structure of $HFe_3(CO)_{11}^-$

*Sir:*

The structure of triiron dodecacarbonyl has been the subject of much speculation and frustration, and no less than six widely differing molecular models have been proposed since its discovery.[1–6] An X-ray study of $Fe_3(CO)_{12}$ by Dahl and Rundle[7] *strongly* indicated that the iron atoms are located at the corners of a tri-

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(1) W. Hieber and E. Becker, *Ber.*, **63**, 1405 (1930).

(2) R. Brill, *Z. Krist.*, **72**, 36 (1931).

(3) W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

(4) N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc.* (London), **A144**, 521 (1934).

(5) R. K. Sheline, *J. Am. Chem. Soc.*, **73**, 1615 (1951).

(6) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **27**, 323 (1957).

(7) L. F. Dahl and R. E. Rundle, *ibid.*, **26**, 1751 (1957).