Photochemistry of Tetrakis(dimethylamino)diborane(4)

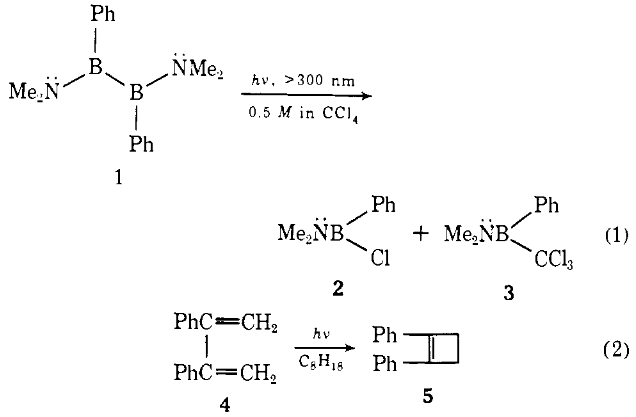
Kenneth G. Hancock,* Anthony K. Uriarte,[1a] and David A. Dickinson[1b]

Contribution from the Department of Chemistry, University of California at Davis, Davis, California 95616. *Received April 30, 1973*

Abstract: Tetrakis(dimethylamino)diborane(4) reacts photochemically at 300 nm in carbon tetrachloride to give chlorotris(dimethylamino)diborane(4) in 74% yield at 95% conversion, as well as smaller amounts of bis(dimethylamino)methane, tris(dimethylamino)borane, and chloroform. Irradiation of tetrakis(dimethylamino)diborane(4) in chloroform gave chlorotris(dimethylamino)diborane(4) in 58% yield at 93% conversion, plus smaller amounts of tris(dimethylamino)borane, bis(dimethylamino)borane, and methylene chloride. In methylene chloride, tris(dimethylamino)borane was the major product, and chlorotris(dimethylamino)diborane(4), bis(dimethylamino)borane, and methyl chloride were formed in lesser yields. Reaction was most efficient in carbon tetrachloride, least efficient in dichloromethane. The products were shown to arise by competing boron–boron and boron–nitrogen homolyses, of which only the latter was visible in carbon tetrachloride at ambient temperatures. Low-temperature irradiations in carbon tetrachloride revealed transient formation of bis(dimethylamino)chloroborane as an important photoproduct. Rapid dark reaction between bis(dimethylamino)chloroborane and tetrakis(dimethylamino)diborane(4) at room temperature gave tris(dimethylamino)borane and chlorotris(dimethylamino)diborane(4), the normally observed products. The hydrogen source for formation of bis(dimethylamino)borane in chloroform was shown not to be the solvent by deuterium labeling. Absence of bis(dimethylamino)borane in carbon tetrachloride was explained by the demonstration that photochlorination of bis(dimethylamino)borane to bis(dimethylamino)chloroborane is very efficient ($\Phi = 0.17$) in carbon tetrachloride but not in chloroform. The relationship of the mechanisms of these reactions to the photochemistry of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) and to the reported thermal behavior of tetrakis(dimethylamino)diborane(4) is discussed.

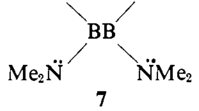
Aminoboranes and homologous compounds are isoelectronic polar-π-bond analogs of olefins, dienes, and related chromophores. As such they are potentially valuable probes for the effects of electronegativity on the ordering of molecular energy levels and, consequently, on photochemical reactivity. Simple aminoboranes have, for example, been shown to undergo photochemical reactions superficially reminiscent of isoelectronic olefins—*e.g.*, cis–trans isomerizations.[2] Superficial similarities, however, are belied by mechanistic disparities (*i.e.*, different excited states)[2] and by occurrences of other photoreactions (*e.g.*, cleavage of alkyl groups adjacent to electron-deficient boron) which have their parallel in the photochemistry of similarly polarized ketones.[3]

The situation is equally complex in B–N analogs of 1,3-dienes. Ultraviolet irradiation of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) (**1**) resulted in boron–boron homolysis leading, in carbon tetrachloride, to (dimethylamino)phenylchloroborane (**2**) and (dimethylamino)phenyltrichloromethylborane (**3**) (eq 1).[4] In contrast, the all-carbon analog, 2,3-diphenyl-1,3-butadiene (**4**), photocyclizes to 1,2-diphenylcyclobutene (**5**) (eq 2).[5] Cleavage of the central σ bond in a four-atom π system, observed for $\ddot{N}BB\ddot{N}$ system **1** but not for diene **4**, did have analogy, however, in the carbon–carbon cleavage of biacetyl photochemistry[6] and in nitrogen–nitrogen cleavage of azines.[7,8]



The thermodynamically reasonable but nonetheless striking reactivity differences between compounds **1** and **4** was rationalized in terms of INDO and EHT–SCC calculations on the parent compound, bis(amino)diborane(4) (**6**),[9] which considered the possible involvement of low-lying σ–π* states in the photochemistry of bis(amino)diborane(4) systems. In addition, the computations on **6** pointed up significant differences between quantum-chemical molecular parameters (*e.g.*, bond orders) of **6** and those reported previously[10] for the closely related but more electron-rich tetrakis(dimethylamino)diborane(4) (**7**). Accordingly, we undertook a study of the photochemistry of tetrakis(dimethylamino)diborane(4) (**7**), the results of which are reported here.

$H_2\ddot{N}BHBH\ddot{N}H_2$
6



7

It was not only as an analog of **1**, however, that the photochemistry of **7** seemed pertinent. Mechanistically

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[1] (a) National Science Foundation Trainee, 1969–1972; (b) Petroleum Research Fund Predoctoral Fellow, 1971–1973.

[2] K. G. Hancock and D. A. Dickinson, *J. Amer. Chem. Soc.*, **94**, 4396 (1972).

[3] K. G. Hancock and D. A. Dickinson, *ibid.*, **95**, 280 (1973).

[4] K. G. Hancock and A. K. Uriarte, *ibid.*, **92**, 6374 (1970).

[5] E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).

[6] See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 421, for leading references.

[7] R. W. Binkley, *J. Org. Chem.*, **33**, 2311 (1968); **34**, 931, 3218 (1969).

[8] R. K. Brinton, *J. Amer. Chem. Soc.*, **77**, 842 (1955).

[9] A. K. Uriarte and K. G. Hancock, *Inorg. Chem.*, **12**, 1428 (1973).

[10] (a) P. G. Perkins and D. H. Wall, *J. Chem. Soc. A*, 1207 (1966); (b) N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, **45**, 2059 (1967).

intriguing and synthetically useful dichotomies often exist between thermal (ground-state) and photochemical (excited-state) reactions, and the pyrolysis of **7** at 300° has been reported to give bis(dimethylamino)borane (**8**, 39%), tris(dimethylamino)borane (**9**, 20%), and methane as volatile products (eq 3).[11]

$$\underset{7}{(Me_2N)_2BB(NMe_2)_2} \xrightarrow{300^\circ} \underset{8}{(Me_2N)_2BH} + \underset{9}{(Me_2N)_3B} + CH_4 \quad (3)$$

Furthermore, analogs of **7** such as tetrakis(dimethylamino)ethylene (**10**) have been noted as strong electron donors and effective reducing agents for polyhalocarbons.[12] Photoelectron spectroscopic analysis of the molecular orbitals of **7** and **10**,[13] however, may be interpreted as predicting a significantly less negative reduction potential for **7** than for **10** because of the additional vacant π orbital in **7**.

Results

Tetrakis(dimethylamino)diborane(4) (**7**) was synthesized from bis(dimethylamino)chloroborane (**11**) and sodium in refluxing xylene, according to the method of Brotherton, McCloskey, Petterson, and Steinberg.[14,15]

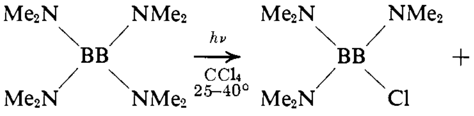
Photolyses of **7** were typically carried out on degassed 5% solutions in purified halocarbon solvents at 300 nm, and at 25–40°, on scales from 50 mg to 20 g with comparable results.[16] On a microscale, photolysates were analyzed by pmr spectroscopy (and ir where useful) and glpc. On a macroscale, products were isolated by vacuum distillation. Table I compares microscale runs carried out in carbon tetrachloride, chloroform, and methylene chloride.

Table I. Photolyses of Tetrakis(dimethylamino)diborane(4) in Polychloromethanes

Solvent	Irradiation time, hr	% conversion[a]	% yields[b]			
			12	9	8	13
CCl_4	1	>95	78	8	c	18
$CHCl_3$	14	93	64	15	10	c
CH_2Cl_2	72	80	35	50	25	c

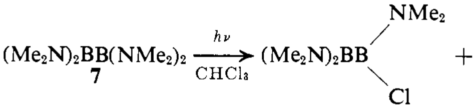
[a] Based on conversion of 99 mg (0.5 mmol) in 750 μl of degassed solvent at 300 nm and 35°. [b] Based only upon reacted starting material **7**. [c] Below limits of detection (0.1% est) if any.

Photolysis in Carbon Tetrachloride. In carbon tetrachloride (*cf.* Table I), disappearance of *ca.* 100 mg of **7** was 95% complete after 1 hr of irradiation. The effective (*vide infra*) quantum yield for disappearance of **7** was 0.20 mol/einstein. The major product of irradiation was chlorotris(dimethylamino)diborane(4) (**12**), 74% yield, identified by comparison with authentic material independently synthesized according to Nöth and Meister.[17] Other volatile products included tris(dimethylamino)borane (**9**, 8%, mol:mol basis), bis(dimethylamino)methane (**13**, 18% mol:mol), chloroform, and traces of hexachloroethane and bis(dimethylamino)chloroborane (**11**), in addition to *ca.* 5% of unreacted **7** (eq 4). In addition to the volatile products, there was *ca.* 30% by weight of solid, consisting of amine hydrochlorides and boron–nitrogen polymeric residue. Attempts to reduce the extent of polymerization by photolysis at higher dilution were unsuccessful. However, 85–90% of the boron is accounted for in eq 4, whereas products **9** and **13** together account for only 45% of the dimethylamino moieties lost in the **7** → **12** transformation, the remainder being largely converted to amine hydrochlorides. The potential products tetramethylhydrazine (**14**)[18] and chlorodimethylamine (**15**)[19] were shown to be absent (<0.1%) by independent synthesis.



$$\underset{7}{(Me_2N)_2BB(NMe_2)_2} \xrightarrow[CCl_4,\ 25\text{–}40^\circ]{h\nu} \underset{12}{(Me_2N)_2BB(NMe_2)Cl} + \underset{9}{(Me_2N)_3B} + \underset{13}{(Me_2N)_2CH_2} \quad (4)$$

Photolysis in Chloroform. As indicated in Table I, irradiation of **7** in chloroform at 300 nm and *ca.* 35° caused several changes in the results (eq 5). At low conversions, the quantum efficiency for disappearance of **7** dropped to *ca.* 0.1 mol/einstein. The time required for "complete" (93%) conversion of **7** increased more than tenfold. The ratio of **12**:**9** dropped from 9:1 in CCl_4 to 4:1 in $CHCl_3$. Bis(dimethylamino)methane (**13**) was no longer detectable as a product. Most significantly, approximately 10% of bis(dimethylamino)borane (**8**) was formed. The relatively high reactivity of **8** made isolation from mixtures containing **9** and **12** somewhat difficult. However, *in situ* analysis for **8** could be simplified by addition of excess dimethylamine to the photolysate, causing reversion of **12** to **7** with no effect on **8**. By use of this same technique and then continuing photolysis, the percentage of **8** in the photolysate could be increased.



$$\underset{7}{(Me_2N)_2BB(NMe_2)_2} \xrightarrow[CHCl_3]{h\nu} \underset{12}{(Me_2N)_2BB(NMe_2)Cl} + \underset{9}{(Me_2N)_3B} + \underset{8}{(Me_2N)_2BH} + CH_2Cl_2 \quad (5)$$

Irradiations in deuteriochloroform gave exactly the same product distribution as photolyses in protiochloroform; no deuterium incorporation was noted except in by-product methylene chloride.

Photolysis in Methylene Chloride. Irradiations were also carried out in methylene chloride as solvent, using conditions otherwise identical with those in the other solvents. As can be gleaned from Table I, the results

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(11) L. L. Petterson and R. J. Brotherton, *Inorg. Chem.*, **2**, 423 (1963).

(12) (a) N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3223 (1963); (b) W. Carpenter, *J. Org. Chem.*, 30, 3082 (1965); (c) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 7, 754 (1968); (d) N. Wiberg, *ibid.*, 7, 766 (1968).

(13) B. Cetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Chem. Commun.*, 1370 (1971).

(14) R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Amer. Chem. Soc.*, **82**, 6242 (1960).

(15) The gift of a generous sample of **7** from Dr. W. G. Woods at U. S. Borax Research Corp. is gratefully acknowledged.

(16) Details are reported for selected, typical irradiations in the Experimental Section. Hanovia 450-W lamps with Pyrex filtering and Rayonet RUL-3000 Å lamps were used essentially interchangeably. Representative irradiation times are recorded, although they were strongly dependent on the optics employed. Reactions could also be effected with RUL-3500 Å lamps but were appreciably slower.

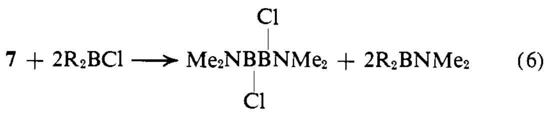
(17) H. Nöth and W. Meister, *Z. Naturforsch. B*, 17, 714 (1962).

(18) R. T. Beltrami and E. R. Bissell, *J. Amer. Chem. Soc.*, **78**, 2467 (1956).

(19) V. L. Heasley, P. Kovacic, and R. M. Lange, *J. Org. Chem.*, **31**, 3050 (1966).

are qualitatively similar to those from irradiations in chloroform (eq 5). The major quantitative differences were substantially longer irradiation times, a lower ratio of **12**:**9** (*ca.* 1:1),[20] and formation of methyl chloride as a by-product.

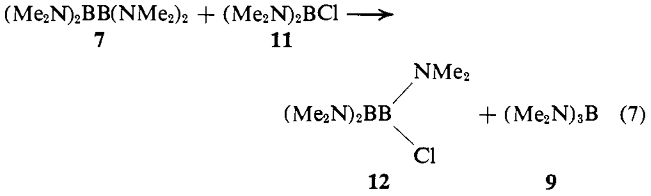
Photolysis at Reduced Temperature. Nöth, *et al.*, had demonstrated that chloro- and aminoboranes and chloro- and aminodiboranes(4) are prone to disproportionation reactions[21] and had reported reaction of **7** with chlorodialkylboranes (2 equiv) gave 1,2-bis(dimethylamino)-1,2-dichlorodiborane(4) (**16**) and an (amino)dialkylborane (eq 6).[21]



$$\mathbf{7} + 2R_2BCl \longrightarrow Me_2N\underset{Cl}{B}\overset{Cl}{B}NMe_2 + 2R_2BNMe_2 \qquad (6)$$

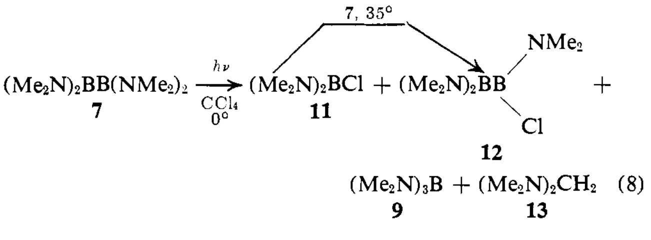
16

We observed that **7** and independently prepared bis(dimethylamino)chloroborane (**11**) underwent a similar, spontaneous disproportionation (in the dark) to give chlorodiborane(4) **12** and tris(dimethylamino)borane (**9**) (eq 7). The stoichiometry of reactants and products



was 1:1, and the rate was sufficiently slow that monitoring by nmr spectroscopy at 35–40° was convenient. The equilibrium, reached only after 18 hr on a one-millimole scale, favored **9** and **12** over **7** and **11** by better than 10:1. Thus, any **11** formed by photolysis of **7** at 35° would have been lost to this dark reaction with starting material **7**.

To test this possibility, a sample of **7** in carbon tetrachloride was irradiated at 0° in a specially constructed dewar, arranged to maximize light capture from the 450-W Hanovia lamp. The pmr spectrum recorded immediately after a 45-min photolysis displayed, in addition to all peaks corresponding to isolable products, an additional resonance at δ 2.73, the correct chemical shift for chloroborane **11** (eq 8). The amount of **11**



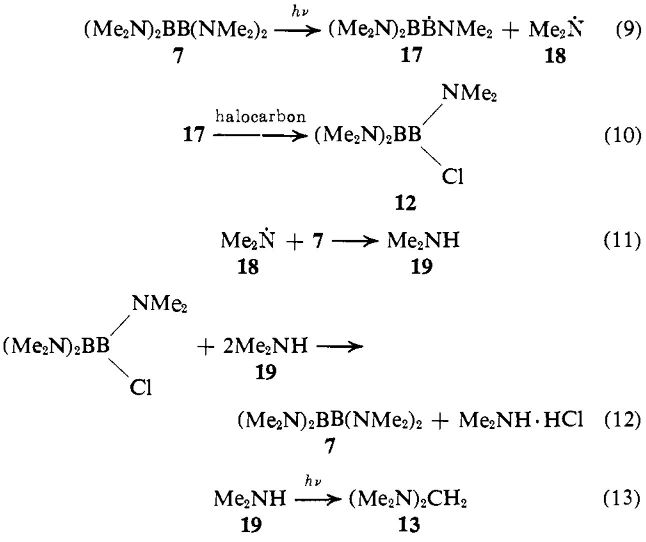
present appeared to be about 25% of the amount of **12**. Within 6 min in the nmr probe, the intensity of the δ 2.73 peak had decreased 60%, accompanied by proportional changes in the peaks corresponding to **7**, **12**, and **9**. Within 12 hr, only a trace of **11** (<5%) was still visible in the pmr spectrum. Disappearance of **11** by disproportionation was rapid at nmr-probe temperatures, but thermal reaction appeared quite slow at 0°. Additionally, the low-temperature photolysate contained only *ca.* 11% (peak-height analysis) as much tris(dimethylamino)borane **9** as chloroborane **11**.

Discussion

By piecing together the systematically varying results from the three solvents and the low-temperature experiments, one can obtain a reasonably clear picture of the photochemical reactivity of tetrakis(dimethylamino)diborane(4) as competing B–N and B–B cleavage routes.

The Boron–Nitrogen Homolysis Mechanism. Boron–nitrogen cleavage (Scheme I) is dominant in carbon tetrachloride. The major product (**12**) in carbon tetrachloride is the direct result of B–N homolysis (eq 9) followed by chlorine abstraction from solvent by tris(dimethylamino)dibor(4)yl radical **17** (eq 10). No evidence for H abstraction by **17** was found. Dimethylamino radicals (**18**), generated along with **17** in the homolysis step, abstract hydrogen (most likely from **7** since that is the major hydrogen source), giving dimethylamine (**19**) (eq 11). Dimethylamino radicals **18** generated photochemically and pyrolytically, both in vapor phase[22] and in solution,[23] have been previously shown to undergo both dimerization to tetramethylhydrazine (**14**) and disproportionation to dimethylamine (**19**) and *N*-methylenemethylamine (**20**), which polymerizes.[23,24] Neither of these processes were detected in our photolyses.

Scheme I



Another possibility that existed was an SH2 displacement reaction between dimethylamino and **7** (eq 14),

$$\underset{\mathbf{18}}{Me_2N\cdot} + \mathbf{7} \xrightarrow{S_H2} \underset{\mathbf{9}}{(Me_2N)_3B} + \underset{\mathbf{21}}{(Me_2N)_2B\cdot} \qquad (14)$$

giving **9** and a bis(dimethylamino)boryl radical (**21**). A similar SH2 displacement of alkyl from trialkylboranes by dimethylamino radicals generated by photolysis of tetramethyltetrazene (**22**) has been reported,[25]

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[20] Although the **12**:**9** ratio in the one run cited in Table I was actually 0.7:1.0, several runs had ratios ranging from 0.7 to 1.2, and averaging about 1:1.

[21] H. Nöth, H. Schick, and W. Meister, *J. Organometal. Chem.*, **1**, 401 (1964).

[22] P. W. Jones and H. D. Gesser, *J. Chem. Soc. B*, 1873 (1971).

[23] J. S. Watson, *J. Chem. Soc.*, 3677 (1956).

[24] J. R. Majer, S-A. Naman, and J. C. Robb, *J. Chem. Soc. B*, 93 (1970).

[25] A. G. Davies, S. C. W. Hook, and B. P. Roberts, *J. Organometal. Chem.*, **22**, C37 (1970).

as have other variations on the SH2 reaction at boron.[26] In the present case, however, the rather small yields of **9** argued against the importance of eq 14 in carbon tetrachloride. Moreover, generation of dimethylamino radicals by photolysis of solutions of **7** containing added tetrazene **22**[27] gave largely polymeric material and no increase in the amount of **9**. The failure of added tetramethyltetrazene to enhance yields of **9** also argues against production of **9** by direct combination of dimethylamino (**18**) and boryl radical **21**.

Dimethylamine is known to react with **12** to give starting material **7** and dimethylamine hydrochloride.[28] To the extent this dark reaction (eq 12) is important, it reduces the measured quantum yield for disappearance of **7**. However, the 2:1 reaction stoichiometry of **19**:**12** would prevent complete **12** → **7** reversion and partially accounts for the absence of **19** in photolysates.

That transient formation of **19** is indeed the major fate of dimethylamino radicals in carbon tetrachloride is confirmed by the presence of bis(dimethylamino)methane (**13**) as a major product, accounting for 34% of the dimethylamino units. Compound **13**, mentioned as a product of dimethylamine photolysis only once in the literature as a minor by-product,[23] is actually a major photoproduct produced when dimethylamine is irradiated in carbon tetrachloride.[29,30] Thus, transient formation of dimethylamine (**19**) by H abstraction and/or disproportionation is the major reaction mode for the dimethylamino species generated by photochemical B–N scission. Precise assessment of the relative importance of the dark (eq 12) *vs.* photochemical (eq 13) reactions destroying **19**, however, is difficult.

The Boron–Boron Homolysis Mechanism. Although the boron–nitrogen cleavage scheme adequately accounts for the occurrence of chlorodiborane(4) **12** from photolysis of **7** in carbon tetrachloride, it does not adequately explain the presence of tris(amino)borane **9** or detection of chloroborane **11** in low-temperature irradiations; neither does it explain the different photochemical behavior of **7** in chloroform and methylene chloride. A second mechanism involving boron–boron homolysis (Scheme II) is required.

Boron–boron cleavage (Scheme II) is apparently the exclusive fragmentation mechanism in methylene chloride. Homolysis (eq 15) gives two bis(dimethylamino)boryl radicals **21** which abstract chlorine from solvent (eq 16) and hydrogen from **7** (eq 17). The latter process has no analogy in the reactivity of dibor(4)yl radical **17**. Chloroborane **11**, however, was observable only transiently after low-temperature irradiation because of rapid disproportionation at 35–40° to give chlorodiborane(4) **12** and tris(dimethylamino)borane (**9**) (eq 7). This dark reaction is the major source of **9**. The 1:1 stoichiometry of the disproportionation predicts a 1:1 ratio of **12**:**9** when B–B cleavage is the only fragmentation, because H abstraction (eq 17) has no effect on the **12**:**9** ratio. This is the situation in methylene chloride.

Scheme II. Summary of Photochemistry *via* Boron–Boron Homolysis

$$\underset{\mathbf{7}}{(Me_2N)_2BB(NMe_2)_2} \xrightarrow{h\nu} \underset{\mathbf{21}}{2(Me_2N)_2B\cdot} \qquad (15)$$

$$\underset{\mathbf{21}}{(Me_2N)_2B\cdot} \xrightarrow{\text{halocarbon}} \underset{\mathbf{11}}{(Me_2N)_2BCl} \qquad (16)$$

$$\underset{\mathbf{21}}{(Me_2N)_2B\cdot} \xrightarrow{\mathbf{7}} \underset{\mathbf{8}}{(Me_2N)_2BH} \qquad (17)$$

$$\mathbf{11} + \mathbf{7} \longrightarrow \mathbf{12} + \mathbf{9} \qquad (7)$$

$$\underset{\mathbf{8}}{(Me_2N)_2BH} \xrightarrow[CCl_4]{h\nu} \underset{\mathbf{11}}{(Me_2N)_2BCl} \qquad (18)$$

Existence of borane **8** as a photoproduct is *prima facie* evidence for formation of boryl radicals **21**. The alternative mechanistic possibility of formation of radicals **21** by SH2 displacement rather than by homolysis was eliminated by the irradiations containing added tetramethyltetrazene **22** (*vide supra*). Similarly, the possibility of SH2 reactions initiated by the boryl radicals **21** was considered. However, no evidence for formation of pentakis(dimethylamino)triborane (**23**)[31] was found, indicating both boryl (**21**) and dimethylamino (**18**) radicals were formed by homolysis and do not participate significantly in SH2 reactions.

That borane **8** was seen only in methylene chloride and chloroform, not in carbon tetrachloride, might have been puzzling since **7** and not solvent was shown by deuterium labeling to be the hydrogen source. However, it was demonstrated independently that **8** was efficiently ($\Phi = 0.17$) photochlorinated to **11** in carbon tetrachloride (eq 18), but not in the other halocarbons. Thus, the absence of **8** in carbon tetrachloride is simply the result of a very effective secondary photochemical reaction. Interestingly, thermal chlorination of **8** in carbon tetrachloride was not observed, even after 60 hr at 100°. Because borane **8** was shown to be stable under photolysis conditions except to photochlorination in carbon tetrachloride, its presence or absence has no effect on the **12**:**9** product ratio: borane **8** may be viewed as merely a cul-de-sac for boryl radicals **21**. Thus, the **12**:**9** product ratio becomes diagnostic, gauging the competition between B–B and B–N scission.

Measuring the B–B:B–N Cleavage Competition. In methylene chloride the 1:1 ratio of **12**:**9**[20] is compatible with exclusive B–B cleavage (eq 15), followed by thermal disproportionation (eq 7) of transiently formed chloroborane **11**. The **9**:**8** ratio of 2:1 suggests that for energetic and statistical reasons, boryl radicals **21** preferentially abstract halogen (eq 16) rather than hydrogen (eq 17). The slight excess of **9** (relative to **12**) observed at long irradiation reflects further photode-

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[26] (a) A. G. Davies, S. C. W. Hook, and B. P. Roberts, *ibid.*, 23, C11 (1970); (b) A. G. Davies, D. Griller, B. P. Roberts, and J. C. Scaiano, *Chem. Commun.*, 196 (1971); (c) J. Grotewald, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc. B*, 1187 (1971), and references therein.

[27] A sample of tetramethyltetrazene was graciously provided by Professor A. L. Balch and Mr. J. Boehm.

[28] M. P. Brown and H. B. Silver, *Chem. Ind.* (*London*), 85 (1963).

[29] (a) K. G. Hancock and D. A. Dickinson, submitted for publication. (b) Bis(dimethylamino)methane was also a minor (2%) product from autoxidation of tetrakis(dimethylamino)ethylene (**10**) in methylene chloride and other solvents: W. H. Urry and J. Sheeto, *Photochem. Photobiol.*, 4, 1067 (1965).

[30] Although photochemical destruction of dimethylamine in chloroform has been shown to be slow,[29] dark reaction of **19** with both chlorodiborane(4) **12** and any chloroborane **11** would be rapid, regenerating **7** in one case (eq 12) and yielding tris(dimethylamino)borane **9** in the other. Isolable products did not allow firm distinction between these two possibilities. In methylene chloride, dark reaction of **19** and solvent has been shown to give diamine **13** in virtually quantitative yields.[19a] Thus, failure to detect **13** in methylene chloride is strong evidence against any formation of **19** and, by extrapolation, against B–N cleavage.

[31] K. H. Hermannsdörfer, E. Matejcikova, and H. Nöth, *Chem. Ber.*, 103, 516 (1970).

composition of chlorodiborane(4) **12**, as tris(amino)-borane **9** is stable to further photolysis.[32]

In chloroform, the **12**:(**9** + **8**) ratio of *ca.* 3:1 indicates roughly equal competition between B–B and B–N cleavage modes, since the dark reaction of **11** and **7** (eq 7) is the major source of **9**. Thus, the amount of **9** detected places a limit on the extent of the disproportionation reaction and, by extrapolation, on the amount of B–B cleavage.

Interestingly, even in carbon tetrachloride, where isolable products gave no firm evidence in themselves for B–B scission, homolysis of the B–B bond is important. Again using the **12**:**9** ratio as diagnostic we estimate a B–B/B–N homolysis ratio of *ca.* 1:6 in CCl_4. The low-temperature irradiation results support this estimate.

Another interesting point concerned the apparently quite different reactivity of boryl (**21**) and dibor(4)yl (**17**) radicals. Only chlorinated products of the diborane(4) skeleton were found, whereas only B–H and no B–Cl derivatives of the borane system occurred in photolysates. Although the precise reasons for differing H-abstraction reactivity of **21** and **17** are not clear, the results are not surprising. No B–H derivatives of the aminodiborane(4) system have been reported in the literature; however, **8** was a known reduction product of chlorobis(dimethylamino)borane (**11**).[33]

Rationale for the Solvent Effect. The contrast between the photochemistry of tetrakis(dimethylamino)-diborane(4) (**7**) and that of the closely related 1,2-bis-(dimethylamino)-1,2-diphenyldiborane(4) (**1**) is dramatic. Photochemical production of chloroborane **2** and trichloromethylborane **3** from **1** (eq 1) was compatible only with a mechanism of exclusive boron–boron scission. In fact, it had been anticipated that added electron density in **7** compared with **1** might begin to make B–N cleavage competitive with B–B cleavage. Baird and Whitehead[10b] had noted that SHMO calculations predicted lower B–N and higher B–B π-bond orders in tetrakis(amino)diborane(4) systems ($P_{BN} = 0.50, P_{BB} = 0.13$) than in bis(amino)diborane(4) systems ($P_{BN} = 0.59$, $P_{BB} = 0.10$). Nevertheless, the B–B bond in **7** remained the thermodynamically most labile, and the extent of B–N cleavage in carbon tetrachloride requires explanation.

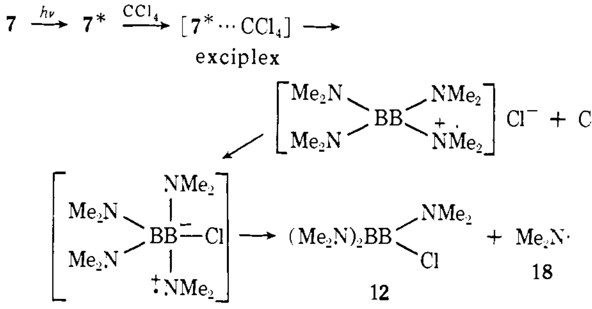
The most plausible explanation for the strong solvent effect on the photoreactivity of **7**, where none had been noted for the related bis(amino)diborane(4) **1**,[4] derives from the added electron density in **7** relative to **1**. As noted earlier, tetrakis(dimethylamino)ethylene (**10**)—the olefinic analog of **7**—is an effective reducing agent for carbon tetrachloride.[12] The special photoreactivity of amine–polyhalocarbon charge-transfer complexes is also well documented.[34] A useful generalization in these reactions seems to be that the degree of charge-transfer complexation and reactivity increases with the extent of halogenation of the solvent—*i.e.*, $CCl_4 > CHCl_3 > CH_2Cl_2$. In the case of **7**, which surely has a lower electron density than **10** and a less negative reduction potential, the drop-off in charge-transfer complexation and amine–halocarbon reactivity could be sharp from highly halogenated solvents to those less chlorinated.

Thus, the behavior of **7** in methylene chloride may be viewed as "normal," *i.e.*, predominant boron–boron cleavage, in agreement with thermodynamics, the molecular orbital models,[9,10] and the known photochemistry of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) (**1**).[4] In fact, no evidence for charge-transfer complexation between **7** and methylene chloride was found.

Although the "abnormal" reactivity of **7** in carbon tetrachloride seems suggestive of some form of charge-transfer complexation, the effect of that solvent on the ultraviolet absorption of **7** was minimal. The method of continuous variations[35] gave no extrema in a plot of mole fraction *vs.* the difference between measured and calculated absorbances, and no new absorptions were noted. The only effect was slight enhancement of absorptivity. Although charge-transfer complexes do not always manifest themselves dramatically in electronic absorption spectra,[36,37] reactions of **7** could *not* be initiated in the dark by cuprous chloride, an effective catalyst for many amine–halocarbon charge-transfer-complex reactions.[34]

In the absence of evidence for ground-state charge-transfer complexation of **7** with carbon tetrachloride, it is attractive to postulate the involvement of an exciplex of **7** and solvent. MO calculations indicate that twisting about a B–N bond, reducing the bond order, is a favorable process in the lowest excited state of **7**.[10a] An excited **7** with twisted dimethylamino group and reduced π delocalization might be more prone than the ground state to a typical amine–halocarbon type of complexation. A mechanism invoking this hypothesis can be written (Scheme III).

Scheme III. Exciplex Mechanism for B–N Homolysis



Such a scheme has ample precedent in reported interactions of chlorocarbons and excited-state species, for which a variety of mechanisms have been postulated.[38] In particular, exciplexes have been implicated in quenching of the fluorescence of electron-rich aromatics by chlorocarbons.[39] In the case of electron-rich **7**, the dramatic solvent effect is the strongest argument in favor of the exciplex mechanism.[40]

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[32] Although the photochemistry of **12** has not been studied in detail, inefficient boron–boron homolysis appears to predominate.

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[40] Fluorescence quenching studies were attempted to further test this mechanism.[41] However, only at high carbon tetrachloride concentrations was even inefficient quenching noted, and this was ambiguous because of direct competition between **11** and concentrated chlorocarbon for incident light.

In short, the photochemical reactivity of 7 largely parallels the behavior of the less electron-rich analog 1, except in carbon tetrachloride and chloroform, where charge-transfer complexation, apparently in the excited state, causes B–N cleavage to compete with boron–boron homolysis.

Experimental Section

Materials and Techniques. All solvents (reagent grade or spectrograde) were dried over sodium ribbon or (for halocarbons) Linde 3-A molecular sieves. All syntheses and operations were carried out in oven-dried glassware under nitrogen or argon atmospheres, using glove boxes and syringes for transfers. Standard high-vacuum techniques[42–45] were used for product separations, along with a Nester-Faust NFT-51 spinning-band column. Gas-liquid-partition chromatographic analyses were done on Hewlett-Packard 776 and Varian-Aerograph A90-P3 instruments. Proton nmr spectra were recorded at 60 and/or 100 MHz on Varian A60A and/or Jeolco MH-100 spectrometers; chemical shifts are reported in ppm downfield from internal tetramethylsilane, $\Delta\delta \pm 0.01$ ppm. Ir spectra were obtained on a Beckman IR-8 spectrophotometer, $\Delta\nu \pm 2$ cm^{-1}. Mass spectra were obtained at 70 eV on Varian M-66 and CEC 21-104 instruments.

Tris(dimethylamino)borane. Tris(dimethylamino)borane was prepared according to Skinner and Smith,[46] from 135 g (3.00 mol) of dimethylamine and 58.5 g (0.500 mol) of boron trichloride, in 41% yield: bp 60–62° (45 mm) (lit.[46] 43° (12 mm)); pmr (CCl$_4$) resonance at δ 2.51; ir (CCl$_4$) absorption at 1379 cm^{-1} ($\nu_{\mathrm{B-N}}$) [lit.[47] 1379 cm^{-1}].

Bis(dimethylamino)chloroborane.[14] From 23 g (0.16 mol) of tris(dimethylamino)borane and 9.35 g (80.0 mmol) of boron trichloride at −78° was obtained 21 g (66%) of bis(dimethylamino)chloroborane: bp 65–67° (42 mm) [lit.[14] 50–52° (25 mm)]; pmr (CCl$_4$) resonance at δ 2.73; ir (CCl$_4$) absorptions at 1530 ($\nu_{\mathrm{B-N}}$) and 899 cm^{-1} ($\nu_{\mathrm{B-Cl}}$) [lit.[48] 1530 and 898 cm^{-1}].

Tetrakis(dimethylamino)diborane(4).[14] From 3.6 g (0.16 g-atom) of sodium and 19 g (0.14 mol) of bis(dimethylamino)chloroborane in xylene at 145° was obtained, after purification, 10.5 g (75%) of tetrakis(dimethylamino)diborane(4): bp 89–91° (10 mm) [lit.[14] 55–57° (2.5 mm)]; pmr (CCl$_4$) resonance at δ 2.65; ir absorptions (CCl$_4$) at 2900, 1495, 1440, 1406, 1350 cm^{-1} [lit.[49] 1409 cm^{-1} ($\nu_{\mathrm{B-N}}$)]. Spectral parameters were identical with those of an authentic sample.[16]

Bis(dimethylamino)borane. Under nitrogen, a solution of 2.3 g (17 mmol) of bis(dimethylamino)chloroborane in 5 ml of dry ether was added dropwise to a suspension of 0.36 g (10 mmol) of lithium aluminum hydride (Alfa Inorganics) in 10 ml of dry ether that was cooled to −5°. The reaction mixture was allowed to warm to room temperature and refluxed for 48 hr. The ether was removed by distillation under nitrogen. The residue was distilled through a 10-cm Vigreux column to give 0.70 g (41%) of bis(dimethylamino)borane: bp 96–98° [lit.[33] 106–108°]; pmr (CCl$_4$) resonance at δ 2.69 (sharp singlet, *N*-methyls); ir (CCl$_4$) absorptions at 2445 and 2360 ($\nu_{\mathrm{B-H}}$) and 1525 cm^{-1} ($\nu_{\mathrm{B-N}}$) [lit.[48] 2450 ($\nu_{\mathrm{B-H}}$), 1530 cm^{-1} ($\nu_{\mathrm{B-N}}$)].

Chlorotris(dimethylamino)diborane(4). According to the procedure of Nöth and Meister[17] 3.66 g (18.5 mmol) of tetrakis(dimethylamino)diborane(4) in 10 ml of anhydrous ether and 30.3 ml (37.0 mmol) of 1.2 *M* hydrogen chloride in ether solution at −23° gave, after distillation, 0.95 g (28%) of chlorotris(dimethylamino)diborane(4): bp 50–51° (2 mm) [lit.[17] 28–30° (0.005 mm)]; pmr (CCl$_4$) resonances at δ 2.91 and 2.87 (6 H) and 2.67 (12 H); ir 1505 and 975 cm^{-1}; mass spectral parent peak at *m/e* 189.

Dimethylchloramine. Dimethylchloramine was synthesized by the method of Heasley, Kovacic, and Lange[19] in 60% yield from dimethylamine hydrochloride and sodium hypochlorite at 0°: pmr (CCl$_4$) resonance at δ 2.83.

Tetramethylhydrazine.[18] Tetramethylhydrazine was synthesized by the method of Beltrami and Bissell[18] by successive methylation of *unsym-N,N*-dimethylhydrazine with methyl formate and was isolated by preparative glpc on a 5-ft × 0.25-in Carbowax 20 M (alkali treated, 20% on firebrick) column: pmr (CCl$_4$) resonance at δ 2.21.

Dark Reaction of Bis(dimethylamino)chloroborane with Tetrakis(dimethylamino)diborane(4). Tetrakis(dimethylamino)diborane(4) (0.198 g, 1.00 mmol) in 0.70 ml of carbon tetrachloride was added to 0.301 g (2.24 mmol) of bis(dimethylamino)chloroborane in 0.70 ml of carbon tetrachloride. At 40°, disproportionation ensued at a rate that was easily monitored by pmr spectroscopy. Within 5 min of mixing, *ca.* 0.6 mmol each of chlorotris(dimethylamino)diborane(4) and tris(dimethylamino)borane had formed. After 18 hr, reaction had neared completion, giving 0.93 mmol (93%) each of chlorotris(dimethylamino)diborane(4) and tris(dimethylamino)borane. Similar results were obtained when tetrakis(dimethylamino)diborane(4) was in excess rather than bis(dimethylamino)chloroborane. Control experiments consisting of mixing other actual and potential (chloramine, hydrazine) photoproducts in varying proportions revealed no other spontaneous dark reactions.

Photolysis of Tetrakis(dimethylamino)diborane(4) in Carbon Tetrachloride. In a typical microscale experiment, 62.0 mg (0.313 mmol) of tetrakis(dimethylamino)diborane(4) in 0.50 ml of carbon tetrachloride in a Pyrex nmr tube was irradiated with a Pyrex-filtered 450-W medium-pressure mercury lamp (Hanovia). After 45 min, *ca.* 95% of the starting material had reacted; the photolysate was analyzed by pmr spectroscopy and gas–liquid chromatography on a 5-ft × 0.25-in Carbowax 20 M (alkali treated, 20% on firebrick) column at 98° (55 ml/min), giving 0.054 mmol of bis(dimethylamino)methane (δ 2.15, 12 H; 2.60, 2 H; 1.50-min glpc retention time), 0.024 mmol of tris(dimethylamino)borane (δ 2.51), 0.23 mmol (74%) of chlorotris(dimethylamino)diborane(4) (δ 2.92, 2.88, 6 H; δ 2.67, 12 H), 0.41 mmol of chloroform (5.3 min), and traces of hexachloroethane (22.0 min) and of bis(dimethylamino)chloroborane, in addition to unreacted starting material. Another typical microscale run is summarized in Table I.

On a larger scale, a solution of 4.76 g (23.4 mmol) of tetrakis(dimethylamino)diborane(4) in 40 ml of carbon tetrachloride in a 50-ml cylindrical Pyrex flask was degassed by three freeze–pump–thaw cycles and sealed under vacuum. Irradiation in a Rayonet reactor (Southern New England Ultraviolet Co.) with eight RUL-3000Å lamps for 16.5 hr effected conversion comparable to the microscale experiment (*vide supra*). Separation and isolation of the volatile components by distillation under vacuum gave chloroform, bis(dimethylamino)methane, tris(dimethylamino)borane, and chlorotris(dimethylamino)diborane(4) in yields comparable to those obtained on the microscale. In all cases isolated products had pmr, ir, and mass spectra identical with those of independently synthesized materials. In addition, chlorotris(dimethylamino)diborane(4) could be identified *in situ* by quantitative conversion to tetrakis(dimethylamino)diborane(4) upon addition of dimethylamine. In addition to the volatile products, there was *ca.* 30% by weight of solid material consisting of amine hydrochlorides and boron–nitrogen polymeric residue. Attempts to reduce the extent of polymerization by high-dilution photolysis were unsuccessful.

Photolysis of Tetrakis(dimethylamino)diborane(4) at Reduced Temperature. A silvered Pyrex dewar with a transparent window, equipped with an iron–constantan thermocouple, was cooled to 0° by regulating the flow of a precooled stream of dry nitrogen. Through the window, a 0.63 *M* degassed carbon tetrachloride solution of tetrakis(dimethylamino)diborane(4) in a Pyrex nmr tube was irradiated 45 min at 0° with a 450-W mercury lamp (Hanovia). The pmr spectrum recorded immediately after photolysis displayed, in addition to all peaks corresponding to isolable products, an additional resonance at δ 2.73, with peak intensity (corrected for number of protons included) integrating to *ca.* 25% of the chlorotris(dimethylamino)diborane(4) resonances at δ 2.91, 2.87, and 2.67. Peak-height analysis (integration of small, closely spaced peaks appeared less reliable) indicated a 9:1 ratio of bis(dimethylamino)chloroborane to tris(dimethylamino)borane. Within 6 min in the dark at 40°, the intensity of the δ 2.73 peak relative to cyclohexane as internal standard had decreased by *ca.* 60%, with concomitant and proportional decrease in the resonance for tetrakis(dimethylamino)diborane(4) and corresponding increases in the peaks for tris(dimethylamino)borane and chlorotris(dimethylamino)diborane(4). Over 12 hr, the δ 2.73 resonance, ascribed

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because of the above dark reaction to bis(dimethylamino)chloroborane, decreased to only trace intensity (<5% in pmr spectrum).

Photolysis of Tetrakis(dimethylamino)diborane(4) in Chloroform. In a typical microscale experiment, a solution containing 0.087 g (0.44 mmol) of tetrakis(dimethylamino)diborane(4) in 0.70 ml of purified chloroform was placed in a Pyrex nmr tube, and irradiated in a Rayonet reactor equipped with eight Rayonet RUL-3000 lamps at 40°. After 13 hr of irradiation, 93% of the starting material had reacted to give 0.06 mmol of tris(dimethylamino)borane, 0.26 mmol (58%) of chlorotris(dimethylamino)diborane(4), 0.04 mmol of bis(dimethylamino)borane, and 0.18 mmol of methylene chloride, by nmr spectral analysis (*vide infra*). Another microscale run was summarized in Table I.

The photoreaction could also be effected when the samples were irradiated at 350 nm, although longer irradiation times were required. For example, 22 hr of irradiation were necessary for a 50% reaction of 0.50 mmol of tetrakis(dimethylamino)diborane(4) in 0.5 ml of purified chloroform. However, product identities and yields were otherwise unaffected.

In a preparative photolysis, a solution of 20 g (0.10 mol) of tetrakis(dimethylamino)diborane(4) in 100 ml of chloroform (Mallinckrodt, chromatographed on alumina, distilled, and dried over 3-A molecular sieves) in a 100-ml cylindrical flask was degassed by three freeze–pump–thaw cycles and then irradiated in a Rayonet reactor with eight RUL-3000 lamps. After 80 hr, *ca.* 70% of the starting material had reacted. Characteristic pmr absorptions in the photolysate at 100 MHz were δ 2.50, tris(dimethylamino)borane; 2.65, unreacted tetrakis(dimethylamino)diborane(4); 2.69, bis(dimethylamino)borane; 2.67, 2.87, and 2.91, chlorotris(dimethylamino)diborane(4); 5.3, methylene chloride; a small absorption at δ 2.59 was not identifiable. By-product methylene chloride, bp 40°, and solvent chloroform, bp 60–61°, were removed by distillation through a Nester-Faust NFT-51 spinning-band column. Distillation at reduced pressure gave successive fractions containing bis(dimethylamino)borane (1.0 g), tris(dimethylamino)borane (2.0 g), chlorotris(dimethylamino)diborane(4) (9.0 g, 45%), and tetrakis(dimethylamino)diborane(4) (3.0 g), all of which were identified by pmr, ir, and mass spectra.

Isolation of bis(dimethylamino)borane could be facilitated by adding to the photolysate sufficient dimethylamine to convert chlorotris(dimethylamino)diborane(4) back to starting material. By continued photolysis after dimethylamination, yields of bis(dimethylamino)borane could be increased.

Photolysis of Tetrakis(dimethylamino)diborane(4) in Methylene Chloride. In a typical microscale experiment, 0.082 g (0.416 mmol) of tetrakis(dimethylamino)diborane(4) in 0.50 ml of dichloromethane was irradiated with a Pyrex-filtered 450-W mercury lamp. After 24 hr, only 45% of the starting material had reacted, giving 0.091 mmol of tris(dimethylamino)borane, 0.047 mmol of bis(dimethylamino)borane, 0.107 mmol of chlorotris(dimethylamino)diborane(4), and 0.075 mmol of methyl chloride. Analytical procedures were as described for irradiations in chloroform and carbon tetrachloride. Longer irradiation led to higher conversion (*ca.* 80%), with comparable percentages of photoproducts. The results of a similar run are summarized in Table I.

Photolysis of Bis(dimethylamino)borane in Carbon Tetrachloride. A solution of 0.052 g (0.52 mmol) of bis(dimethylamino)borane in 0.50 ml of carbon tetrachloride in a Pyrex nmr tube was irradiated in a Rayonet chamber reactor equipped with eight Rayonet RUL-3000 mercury lamps. After irradiation for 10 hr, an nmr spectrum of the dark photolysate indicated 80% reaction of starting material to give 0.10 mmol of bis(dimethylamino)chloroborane, isolated by removal of solvent and distillation under high vacuum, identified by comparison of spectra with authentic material.

No thermal reaction was observed when an identical solution of bis(dimethylamino)borane in carbon tetrachloride was heated at 50° for 96 hr or at 100° (sealed tube) for 60 hr.

Photolysis of Bis(dimethylamino)borane in Chloroform. Bis(dimethylamino)borane (0.043 g, 0.43 mmol) in 0.50 ml of purified chloroform in a Pyrex nmr tube was irradiated in a Rayonet chamber reactor equipped with eight RUL-3000 mercury lamps. After irradiation for 72 hr, a pmr spectrum indicated no formation of bis(dimethylamino)chloroborane, although some photodecomposition to a complex mixture had occurred.

Quantum Yield Determinations. In adaptation of the method of Hatchard and Parker,[50] 0.70-ml aliquots of 0.15 *M* potassium ferrioxalate solution in Pyrex vessels were irradiated 30.0 sec at 300 nm in a merry-go-round apparatus, then withdrawn and assayed for ferrous content spectrophotometrically.[50] Samples of tetrakis(dimethylamino)diborane(4) in chloroform or carbon tetrachloride and of bis(dimethylamino)borane in carbon tetrachloride were prepared with concentrations adjusted so that both actinometer and substrate had comparable total absorbances, and would transmit less than 0.1% of incident light. Following irradiation, samples were assayed for substrate disappearance and photoproduct appearance by glpc and nmr techniques against precisely weighed undecane or cyclohexane as internal standard. When necessary, quantum yields were extrapolated to zero conversion from multiple runs. Measured quantum yields for disappearance of tetrakis(dimethylamino)diborane(4) were 0.2 mol/einstein in carbon tetrachloride and 0.1 in chloroform, but must be treated as approximations even at low conversions because of concomitant dark reaction between tetrakis(dimethylamino)diborane(4) and bis(dimethylamino)chloroborane. The quantum yield for disappearance of bis(dimethylamino)borane in carbon tetrachloride was 0.17 mol/einstein.

Investigation of Possible Charge-Transfer Complexation between Tetrakis(dimethylamino)diborane(4) and Halocarbon Solvents. In modification of the method of continuous variations,[35] a series of eight solutions of tetrakis(dimethylamino)diborane(4) and carbon tetrachloride were prepared in cyclohexane, with mole fraction of the diborane(4) varied from 3×10^{-5} to 1.00. Electronic absorption spectra were recorded on a Cary 15 spectrometer *vs.* a reference sample with an identical concentration of carbon tetrachloride in cyclohexane but without the diborane(4). A plot of mole fraction *vs.* difference between measured and calculated absorbance at several arbitrarily chosen wavelengths showed no extrema. No new bands were observed in any of the spectra. The only visible effect was slight enhancement of the molar absorptivity at high diborane(4) dilution (*e.g.*, for a 10^4 mole ratio of carbon tetrachloride to diborane(4), $\epsilon_{260} = 2.9 \times 10^3$ *vs.* $\epsilon_{260} = 1.9 \times 10^3$ at a 10^2 mole ratio).

Irradiation of Tetrakis(dimethylamino)diborane(4)–Tetramethyltetrazene Mixtures in Carbon Tetrachloride. A mixture of 30.9 mg (0.156 mmol) of tetrakis(dimethylamino)diborane(4) and 155.4 mg (1.34 mmol) of tetramethyltetrazene in 1.0 ml of carbon tetrachloride containing 1.70 mmol of cyclohexane as internal standard was irradiated in a merry-go-round apparatus in a Rayonet reactor equipped with RUL-3000 lamps. In parallel, control solutions of 26.7 mg (0.135 mmol) of the diborane(4) in 1.0 ml of carbon tetrachloride and 145.0 mg (1.25 mmol) of tetrazene in 1.0 ml of carbon tetrachloride, each containing 1.70 mmol of cyclohexane, were also irradiated. After 15 min, reaction in the diborane(4) control sample was 66% complete, with formation of 0.045 mmol of chlorotris(dimethylamino)diborane(4), 0.010 mmol of tris(dimethylamino)borane, and 0.015 mmol of bis(dimethylamino)methane. No reaction was detectable by nmr in the tetrazene control sample. In the mixture, 21% reaction of the diborane(4) was indicated by nmr, with little (<5%) decomposition of tetrazene. However, the amounts of chlorodiborane(4) and tris(dimethylamino)borane formed were too small for accurate measurement.

After 1.5 hr of illumination, the diborane(4) sample was totally reacted; in addition, extensive secondary photoreactions had taken place. In the tetrazene control sample, 20% reaction had occurred, by nmr analysis. In the mixture, 100% reaction of the diborane(4) and 15% reaction of the tetrazene had occurred. However, only negligible amounts of chlorodiborane(4) and tris(dimethylamino)borane were formed and the major product (49%) was bis(dimethylamino)methane, in contrast to the diborane(4) control.

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