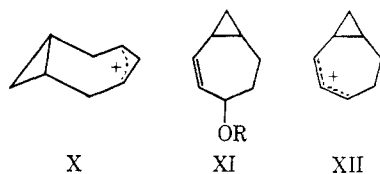


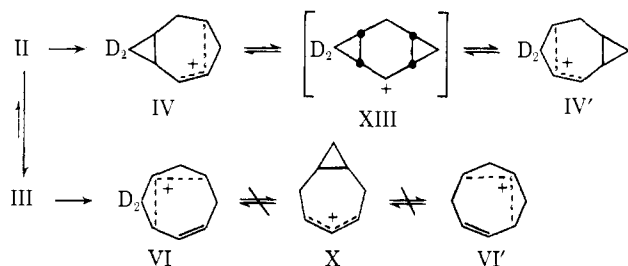
since it is not produced from the ion IV. At this point in the analysis, it appears that 16–22% (*cis*-VII) of the reaction products can be attributed to cyclopropane participation, and the remainder are adequately accounted for by double bond participation.

We prepared *cis*-VII-OH from bicyclo[5.1.0]octan-4-one² by the method of Gore,⁹ and solvolyzed the corresponding tosylate. It should be noted that the allylic ion X produced from *cis*-VII-OTs is quite different from ion VI, so the system is a poor model for cyclopropane participation. In fact, *cis*-VII-OTs on acetolysis pro-



duces only XI-OAc, which is not present in the mixture from either *cis*-I-OTs or *cis,cis*-V-OPNB. Apparently X prefers the hydride-shift path leading to the more stable allylic ion XII. These results prove that ion X is not in equilibrium with the ion(s) produced from *cis*-I-OTs or *cis,cis*-V-OPNB (IV, VI). It follows that ion VI can therefore never equilibrate with its mirror image VI', since the intermediacy of X would be required for such a process (Scheme II). Also, *cis*-VII-

Scheme II



OAc must come directly from VI, rather than from X. On the other hand, ion IV is expected to equilibrate rapidly with its mirror image, since ion XIII is unstable with respect to IV. A simple deuterium labeling experiment can therefore substantiate that the product *cis*-I comes only from double bond participation. If *cis*-I-OTs labeled with deuterium in the cyclopropane ring as in Scheme II were solvolyzed, product *cis*-I from double bond participation should have deuterium scrambled between positions across the ring ($IV \rightleftharpoons IV'$), whereas *cis*-I from cyclopropane participation must have the deuterium only in the initially labeled position ($VI \rightleftharpoons VI'$). Since formolysis did yield scrambling of the label, the product *cis*-I must come only from IV. Considerable internal reorganization of the molecule has thus occurred before it is regenerated with high stereoselectivity.

In conclusion, the solvolytic reactivity of *cis*-I-OTs is partitioned into contributions from double bond and cyclopropane participation. About 80% of the products are derived from the former mode and 20% from the latter. The transition state from II must therefore be about 0.8 kcal/mol lower than that from III. Since the ground-state structure II is 2–4 kcal/mol higher in

(9) J. Gore, J. P. Drouet, and J. J. Barieux, *Tetrahedron Lett.*, 9 (1969).

energy than III because of "prow–prow" buttressing, the energy of activation for double bond participation in II must be 3–5 kcal/mol smaller than that for cyclopropane participation in III.

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The Photochemistry of 1,2-Bis(dimethylamino)-1,2-diphenyldiborane(4). An Isoelectronic Heteroatom Analog of Dienes

Sir:

We wish to record the discovery of a new primary photoprocess operative in organoboron chemistry which may have mechanistic implications in the photochemistry of dienes, azines, and related compounds. Olefins, dienes, and many of their heteroatom analogs have been the objects of extensive photochemical investigation.¹ Yet, one of the most intriguing groups of analogs—the B–N "double bonds" of aminoboranes and related compounds—has remained virtually unexplored,² although their isoelectronic and nearly isosteric³ relationship to olefins makes the aminoboranes and homologous chromophores uniquely adapted to studies of electronegativity effects in the photochemistry of π systems. It is apparent that the differing electronegativities of boron and nitrogen cause important differences in the ground-state chemistry of olefins and B–N analogs, and even simple quantum-mechanical considerations suggest that the excited states of aminoboranes and homologs may also behave quite differently from olefins and dienes.⁴

We report here the preliminary results of our investigation of the photochemistry of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) (**1**), a boron–nitrogen analog of conjugated dienes chosen partly for its structural and electronic similarity to the previously studied 2,3-diphenyl-1,3-butadiene⁵ and benzalazine.⁶

(1) R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966; E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, 23, 482 (1969); D. Bryce-Smith, A. Gilbert, W. M. Horspool, and D. Phillips, "Photochemistry," Vol. 1, The Chemical Society, London, 1970.

(2) Exceptions known to us are the recent reports by (a) P. J. Grisdale and J. L. R. Williams, *J. Org. Chem.*, 34, 1765 (1969), and (b) M. Oertel and R. F. Porter, *Inorg. Chem.*, 9, 904 (1970), and earlier papers cited therein.

(3) G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970).

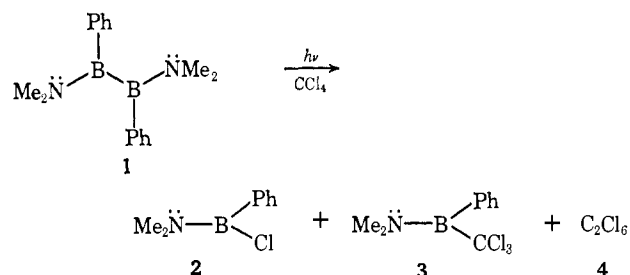
(4) (a) R. Hoffmann, *J. Chem. Phys.*, 40, 2474 (1964); (b) D. R. Armstrong, B. J. Duke, and P. G. Perkins, *J. Chem. Soc. A*, 2566 (1969).

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

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

(7) Nitrogen–nitrogen cleavage products were also found in the photochemistry of acetaldazine: R. K. Brinton, *J. Amer. Chem. Soc.*, 77, 842 (1955).

The synthesis of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) has been previously described.⁸ Irradiation of *ca.* 0.5 *M* solutions of **1** in carbon tetrachloride at wavelengths above 300 nm resulted in formation of three products (**2**, **3**, and **4**) in approximately a 4:2:1 ratio. In a typical microscale experiment, irradiation of 0.23 mmol of **1** for 20 hr gave 0.22 mmol of **2**, 0.13



mmol of **3**, and 0.06 mmol of **4**.^{9,10} Extended irradiations apparently caused no secondary decomposition of the accumulating photoproducts.

The first photoproduct was identified as (dimethylamino)phenylchloroborane (**2**) by comparison of spectra with an independently prepared sample.⁸ The proton nmr spectrum of the second photoproduct (**3**) exhibited two *N*-methyl singlets (3 H each) at δ 2.32 and 2.40 (carbon tetrachloride solution) and a complex, phenyl multiplet (5 H) at δ 7.1–7.6. Hydrolysis of the second photoproduct (**3**) gave phenylboronic acid, chloroform, and dimethylamine. Thus, the spectroscopic and chemical evidence require that **3** must be (dimethylamino)phenyltrichloromethylborane. The third product was identified, also by comparison with an authentic sample, as hexachloroethane (**4**).

The identities and relative amounts of the two photoproducts and hexachloroethane suggest that the single dominant primary photoprocess is dissociation of an excited state of **1** into two (dimethylamino)phenylboryl radicals, which subsequently abstract chlorine atoms from the solvent (Scheme I). The remaining aminoboryl and trichloromethyl radicals may either combine with each other to give **3**, or dimerize to give hexachloroethane and **1**. However, the extent of aminoboryl radical recombination within a solvent cage—representing one possible decay mechanism—is not directly measurable in these reactions.

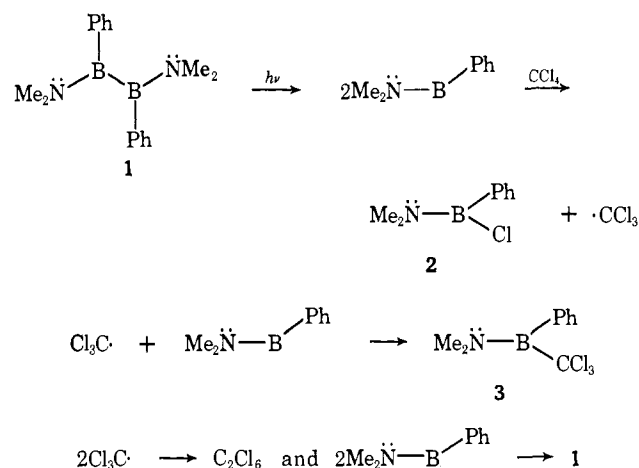
The possible involvement of free chlorine and/or trichloromethyl radicals generated in a primary process arising from direct photolysis of carbon tetrachloride can be excluded on the following bases. First, 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) absorbs a minimum of 99.9% of the incident light above 280 nm. Secondly, under irradiation conditions in which solutions

(8) R. J. Brotherton, H. M. Manasevit, and A. L. McCloskey, *Inorg. Chem.*, **1**, 749 (1962).

(9) Photolyses were effected with Hanovia 450-W medium-pressure and Rayonet RUL-3500 and RUL-3000 mercury lamps through multiple Pyrex filters, under both air and nitrogen atmospheres, on scales ranging from 50 mg to several grams, with comparable results. Irradiation times were highly dependent on the optics employed; reaction of 1 g of **1** in 350 ml of CCl_4 was complete after 13 hr of irradiation at 300 nm. Temperatures were 25–40°.

(10) Product yields were determined by glpc separation of **2** from **4** on both 5 ft \times 0.25 in. SE-30, 3% on Varaport 30 and 7 ft \times 0.25 in. 1,4-butanediol succinate, 15% on Chromosorb W columns at 150°, *vs.* hexachloroethane as external standard; and by nmr integration of peak areas for **2** and **3**, with added *tert*-butylbenzene as internal standard. Compound **3** decomposes during attempted vapor-phase chromatography under the above conditions.

Scheme I



of **1** in carbon tetrachloride react normally, the photoaddition of carbon tetrachloride to 1-octene¹¹ does not proceed.¹² Thirdly, when a mixture of 0.24 mmol of **1** and 0.36 mmol of 1-octene in carbon tetrachloride was irradiated 7 hr at 350 nm, total disappearance of 1-octene was accompanied by production of 0.32 mmol of 1,1,1,3-tetrachlorononane, 0.03 mmol of **2**, and only trace amounts of **3**, thus suggesting that trichloromethyl radicals may be formed by attack of aminoboryl radicals on the solvent and that, furthermore, addition of trichloromethyl radicals to 1-octene is more than competitive with chain termination by combination of trichloromethyl and aminoboryl radicals to form **3**. The 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) may thus be playing the role of initiator for the free-radical chain addition of carbon tetrachloride to 1-octene.

However, a mechanism in which bisaminodiboron-photosensitized homolysis of carbon tetrachloride is followed by radical displacements on boron by chlorine and/or trichloromethyl radicals cannot be discounted. When trichloromethyl radicals are generated independently in the presence of **1** by either (a) heating mixtures of the bisaminodiboron and benzoyl peroxide in carbon tetrachloride at 90°,¹¹ or (b) photolyzing bromotrichloromethane¹³ or hexachloroacetone¹⁴ solutions of **1**, (dimethylamino)phenyltrichloromethylborane (**3**) is always a prominent product. A similar, borazine-photosensitized homolysis of alkyl halides (including carbon tetrachloride) has been advanced by Oertel and Porter^{2b} as a mechanism for the B-photohalogenation reaction of borazine.

While our experiments provide chemical evidence for transient (dialkylamino)phenylboron radicals, the concept is not new.^{15,16} Bis(dimethylamino)boron radicals have been postulated¹⁵ as intermediates in the synthesis

(11) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, **69**, 1100 (1947). The production of 1,1,1,3-tetrachlorononane does proceed efficiently at shorter wavelengths.

(12) Comparative studies were made on the basis of multiple irradiations in a merry-go-round type apparatus.

(13) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Amer. Chem. Soc.*, **69**, 1105 (1947); M. S. Kharasch and M. Gage, *J. Org. Chem.*, **14**, 537 (1949); B. P. McGrath and J. M. Tedder, *Bull. Soc. Chim. Belg.*, **71**, 772 (1962).

(14) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 3015 (1961); J. R. Majer and J. P. Simons, *Advan. Photochem.*, **2**, 137 (1964).

(15) J. N. Friswell and B. G. Gowenlock, *Advan. Free-Radical Chem.*, **1**, 51 (1965).

(16) M. F. Lappert in "The Chemistry of Boron and its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 448.

of tetrakis(dimethylamino)diboron (**5**) from sodium and chlorobis(dimethylamino)borane,¹⁷ and their ready recombination has been advanced as a possible explanation for the relatively high thermal stability of **5**.¹⁸ Butyl(dimethylamino)boron radicals have been suggested as possible intermediates in the decomposition of 1,2-bis(dimethylamino)-1,2-di-*n*-butyldiborane(**4**).¹⁹

Although the observed cleavage of the boron-boron bond in 1,2-bis(dimethylamino)-1,2-diphenyldiborane(**4**) is a unique process in organoboron photochemistry, the similarity to the azine cases^{6,7} and difference from the all-carbon diene case³ are noteworthy. Despite the elucidation of the gross reaction mechanism, the precise nature of the reactive excited state of **1** and the scope of the boron-boron cleavage reaction remain undetermined. These detailed aspects of the reactions of bis(amino)diborons and related compounds are currently under investigation.

Acknowledgment. Financial support from the Research Corporation and from the Petroleum Research Fund administered by the American Chemical Society (Grant No. 1409-G1), and helpful discussions with Professors D. H. Volman and G. S. Zweifel are gratefully acknowledged.

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

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

(19) H. Nöth and P. Fritz, *Z. Anorg. Allg. Chem.*, **324**, 129 (1963); H. Nöth, P. Fritz, K. H. Hermannsdorfer, W. Meister, H. Schick, and G. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **3**, 148 (1964).

(20) National Science Foundation Trainee, 1969-1970.

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A 1,3-Bromine Migration. The Deamination of 3-Bromo-2,2-bis(bromomethyl)propylamine

Sir:

The intermediacy of 1,2-halonium ions in the addition of halogen to double bonds has been known for many years.^{1,2} Recently examples of 1,4-halonium ions³⁻⁵ and 1,5-halonium ions³ also have been reported. The intermediacy of 1,3-halonium ions has been postulated in the addition of bromine to bicyclo[2.1.0]pentane^{6a} and to a substituted bicyclo[2.2.1]heptane.^{6b} An unsuccessful attempt to observe 1,3-halogen shifts under identical conditions where 1,2- and 1,4-halonium ions could be generated was recently reported.³

(1) Credit for the idea of 1,2-halonium ions is generally given to I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).

(2) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); **90**, 947, 2587 (1968), and references therein.

(3) P. E. Peterson and F. J. Slama, *ibid.*, **90**, 6516 (1968).

(4) (a) P. E. Peterson and E. V. P. Tao, *ibid.*, **86**, 4503 (1964); (b) P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966); **85**, 2865 (1963); (c) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. M. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967); (d) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968); (e) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968); (f) P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1283 (1967); (g) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *ibid.*, **92**, 2834 (1970).

(5) P. E. Peterson and J. E. Coffey, *Tetrahedron Lett.*, 3131 (1968).

(6) (a) R. T. LaLonde, *J. Amer. Chem. Soc.*, **87**, 4217 (1965); (b) M. M. Avram, I. Pogany, F. Badea, I. G. Dinulescu, and C. D. Nenitzescu, *Tetrahedron Lett.*, 3851 (1969).

We now wish to report the first example of a 1,3-bromine migration⁷ which occurred during the deamination of 3-bromo-2,2-bis(bromomethyl)-1-*d*₂-propylamine perchlorate (**4**). The deuterated amine (**4**) was synthesized in three steps from 3-bromo-2,2-bis(bromomethyl)propionamide (**1**).⁸ Dehydration of **1** with thionyl chloride in the presence of dimethylformamide as catalyst produced 3-bromo-2,2-bis(bromomethyl)propionitrile (**2**)⁹ in 75% yield, mp 43.5-46.5°. Reduction of **2** with B₂D₆¹⁰ by a modified procedure of Brown,¹¹ followed by the addition of excess ethanol and hydrogen bromide, gave 3-bromo-2,2-bis(bromomethyl)-1-*d*₂-propylamine hydrobromide (**3**) in 49% yield, mp 233-236° dec. The nmr spectrum of **3** (DMSO-*d*₆, TMS internal standard) showed the absence of the CH₂-NH₃Br⁻ signal which appears at -3.05 ppm in the undeuterated amine hydrobromide. The perchlorate salt **4** was prepared by reaction of **3** with silver perchlorate. The nmr spectrum of **4** (DMSO-*d*₆-D₂O, TMS) exhibited a singlet at -3.67 ppm. Deamination of the perchlorate salt **4** in glacial acetic acid gave a total of 11 components by glpc analysis. The two major components were isolated by preparative glpc and identified¹² as 3-bromo-2,2-bis(bromomethyl)-1-propyl acetate (**5**, R = H, 45% yield)¹² and 3-bromo-2-(bromomethyl)-1-propene (**6**, 5.5% yield).¹²

A 1,3-bromine shift was demonstrated by the presence of a significant CH₂OAc signal at -4.21 ppm (CDCl₃) in the nmr spectrum of the deuterated acetate product **5** (R = H) (see Scheme I). The integrated ratio of the CH₂OAc signal (-4.21 ppm, CDCl₃) to the CH₂Br signal (-3.57 ppm, CDCl₃) in the nmr spectrum was 1:6.5. The expected ratios for possible mechanisms of bromine involvement are summarized in Table I.

Table I. Nuclear Magnetic Resonance Signal Ratios of the Deamination Products for Possible Mechanisms of Bromine Involvement

	Acetate 5 CH ₂ OR: CH ₂ Br	Olefin 6 =CH ₂ : CH ₂ Br
No 1,3-bromine shift	0	0
Single bromonium ion (B)	1:5	1:4 or 3
Equilibrating Br ion (B and C)	1:3	1:2
Actual ratio (HOAc) ^a	1:6.5	1:2
Actual ratio (CF ₃ CO ₂ H) ^a	1:3.9	<i>b</i>

^a Accuracy of integration = 5%. ^b Not determined.

These ratios assume that any secondary deuterium isotope effects are small and would not be detected by nmr integration of the signals.¹³ The low 1:6.5 ratio

(7) The phenomenon of internal return, where allylic halides undergo a 1,3-halogen shift simultaneously with double bond migration, is known, but quite different from a 1,3-halogen shift in a saturated system. See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, N. Y., 1959, pp 286-289.

(8) F. Nerdel, A. Heymons, and H. Croon, *Chem. Ber.*, **91**, 938 (1958).

(9) Satisfactory analyses were obtained on all new compounds.

(10) The precursor for B₂D₆ was NaBD₄ (>96% D) obtained from Alfa Inorganics.

(11) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **82**, 681 (1960).

(12) Yields were calculated from the integrated glpc peak areas relative to an internal standard that was precalibrated with the identified components. Identifications were first carried out on the products from deamination of the undeuterated amine perchlorate. The minor components have not yet been fully characterized, but are possible bromomethyl migration products.