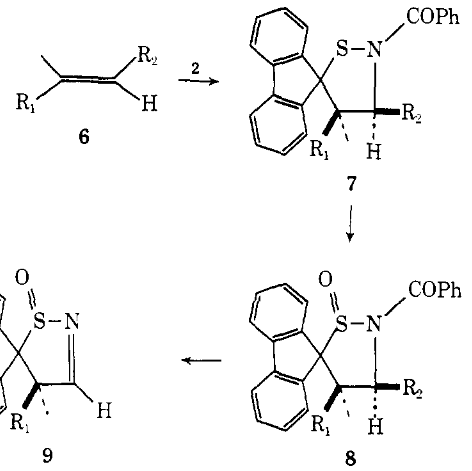
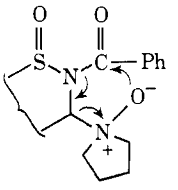
H), 1.76 (m, 4 H), 1.66 (s, 3 H), 0.58 (s, 3 H)] and from *N*-propenylpiperidine (**6b**) an analogous adduct [mp 159–161° (dec); ir ($CHCl_3$) 1637 (C=O), 1600 (C=C) cm^{-1}; nmr δ 7.46 (m, 13 H), 5.60 (d, J = 8 Hz, 1 H), 3.17 (m, 5 H), 1.59 (bd s, 6 H), 0.56 (d, J = 6.5 Hz, 3 H)].[8] The isothiazoline structures **7a** and **7b** have been assigned these adducts based on the above spectral evidence as well as the results of the following degradative sequence.[9] Oxidation of **6** with 1 equiv of *m*-chloroperbenzoic acid in CH_2Cl_2 solution at 30° provided (>50%) the *S*-oxides **8a** [mp 210–213° dec; ir ($CHCl_3$) 1665 (C=O), 1290 (S=O) cm^{-1}; nmr δ 7.61 (m, 13 H), 5.94 (s, 1 H), 3.31 (m, 4 H), 1.85 (s, 3 H), 1.80 (m, 4 H), 0.66 (s, 3 H)] and **8b** [mp 218–219° dec; ir ($CHCl_3$) 1665 (C=O), 1295 (S=O) cm^{-1}; nmr δ 7.60 (m, 13 H), 5.78 (d, J = 8.5 Hz, 1 H), 3.32 (m, 5 H), 1.55 (s, 6 H), 0.77 (d, J = 7.0 Hz, 3 H)]. The assignment of a cis relationship of R_1 and R_2 to the oxide function in **8b** rests upon the observed nmr downfield shift of the C-4 hydrogen relative to the **7b** system and the C-4, C-3 hydrogen coupling constant. The mass spectrum of **8a** displayed prominent fragment ions at *m*/*e* 240 and 206 corresponding to 1,5 and 3,4 bond cleavage. The action of an additional equivalent of *m*-chloroperbenzoic acid in CH_2Cl_2 solution at 30° resulted in the formation of the dihydroisothiazole **9a**; mp 168–169°; ir ($CHCl_3$) 1595 (C=N) cm^{-1}; nmr δ 7.46 (m, 9 H), 1.67 (s, 3 H), 0.96 (s, 3 H) with mass spectral ions at *m*/*e* 281 (M^+), 233 (M^+ − SO), and 206 (M^+ − HCNSO, base peak). This last oxidative elimination step may be the result of decomposition of an intermediate *N*-oxide (**10**).

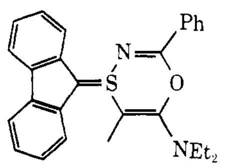


a, R_1 = CH_3; R_2 = $N(CH_2)_4$
b, R_1 = H; R_2 = $N(CH_2)_5$

Although **2** underwent 1,3-cycloadditions with enamines involving the CSN unit, a different system appeared to be important in reaction with ynamines. Addition of 1-(diethylamino)-1-propyne to THF solutions of **2** at −78° rapidly provided an unstable 1:1 adduct, mp 125–126° dec, which decomposed in solution at room temperatures or at the melting point to give benzonitrile. Structure **11** is tentatively assigned to this adduct based on the observed ir [(KBr) 1590, 1525, and 1500 (C=C and C=N) cm^{-1}] which was transparent between 1600 and 2900 cm^{-1}. The ultraviolet spectrum in $CHCl_3$ was similar to fluorenethione *S*-oxide[2] but with a hypsochromic shift λ_{max} (ϵ) 310 (3980), 300 (4980), 277 (12,700), 263 (16,600), and 242 (28,800) nm. Nonequivalent *N*-ethyl groups were apparent in the nmr ($CDCl_3$, −30°): δ 7.58 (m, 13 H), 3.75 and 3.60 (q, J = 7.3 Hz, 4 H), 2.72 (s, 3 H), 1.54 and 1.06 (t, J = 7.3 Hz, 6 H).



10



11

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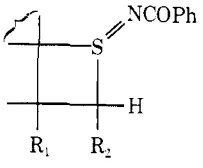
[8] All nmr spectra were recorded at 60 MHz in $CDCl_3$ solution.

[9] The possibility exists that **7** is the ultimate rearrangement product of a penultimate adduct, **i**, resulting from the action of **2** as a 1,2-dipolariphile. Assignment of a structure such as **i** to **7** is excluded on the observed C=O absorption at 1665 cm^{-1} in the infrared. The frequency range observed for acyclic acyl iminosulfurans has been 1600–1540 cm^{-1}: H, Kise, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, **37**, 1121 (1972).



i

Photochemistry of Aminoboranes. Boron–Carbon Cleavage as a General Primary Photoprocess in Boron–Nitrogen Analogs of Stilbenes

Sir:

We wish to report that (*N*-methylanilino)phenylalkylboranes—isoelectronic boron–nitrogen analogs of stilbenes—undergo a general photochemical reaction that has little parallel in the solution-phase photochemistry of stilbenes or other alkenes. This new primary photoprocess is excited-state cleavage of a boron–alkyl bond.

For example, Pyrex-filtered ultraviolet irradiation of a deoxygenated 0.5 *M* solution of (methylphenylamino)benzylphenylborane[1] (**1a**, R = $PhCH_2$) in carbon tetrachloride at 35° led to nearly complete destruction of starting material and a mixture of products.[2] Analysis of a typical photolysis mixture, taken to *ca.* 80% conversion of **1a**, by a combination of vacuum-line and glpc techniques, revealed a complex mixture of photo-

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[1] Aminoboranes were synthesized by modifications of the general method of K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, **82**, 4223 (1960). Satisfactory spectral data and analyses were recorded for new compounds, the details to be reported in full later.

[2] Typical conversion times were *ca.* 30 hr for *ca.* 90% reaction of *ca.* 1 g of starting aminoborane, depending on the optics employed. The relatively long times required for high conversion were necessitated by the gradual accumulation of opaque polymeric material which greatly reduced the usable light absorbed by the aminoborane solution and made complete destruction of starting material difficult.

products, including (methylphenylamino)phenylchloroborane (**2**), (methylphenylamino)phenyltrichloromethylborane (**3**), benzyl chloride (**4a**), 1,1,1-trichloro-2-phenylethane[3] (**5a**), and other organic products in the percentage yields indicated in Table I.[4]

Table I. Product Distributions[a] in Photolysis of Alkyl(*N*-methylanilino)phenylboranes in Carbon Tetrachloride

1

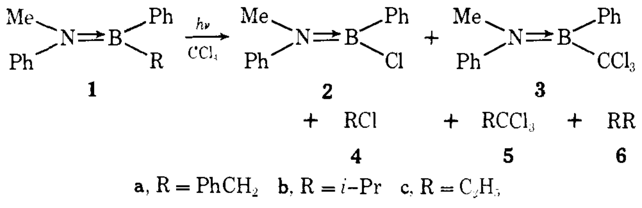
Reactant, R =	% conversion[b,c]	2	3	RCl 4	RCCl$_3$ 5	RR 6	CHCl$_3$	C$_2$Cl$_6$
1a, benzyl[e]	80	22	21	6	35	5	30	12
1b, isopropyl	60	22	20	55	*d*	*d*	33	28
1c, ethyl	60	16	12	41	*d*	*d*	47	30

[a] Percentage yields. [b] Product photolability reduces yields at long irradiation time. [c] Yields do not total 100% because of polymerization. [d] Not detected. [e] 8% toluene isolated.

Identities of **2**, **4a**, **5a**, and **6a** were established by comparison of ir and nmr spectra and glpc retention times with those of authentic samples. The identity of the trichloromethylborane **3** (pmr *N*-methyl, δ 3.05, CCl$_4$) was determined by independent synthesis from photolysis of chloroborane **2** in either carbon tetrachloride or hexachloroacetone and from reaction of chloroborane **2** and trichloromethyllithium.[5] The photosynthesis of **3** from **2** suggests that much, but not all, of the trichloromethylborane arises in a secondary photoreaction.

Analogous photochemical reactions were observed for (methylphenylamino)isopropylphenylborane (**1b**) and (methylphenylamino)ethylphenylborane (**1c**) (Scheme I).[1] Chloroborane **2**, trichloromethylborane **3**, and alkyl chloride **4** were the predominant products (*cf.* Table I), isolated and identified as described above.

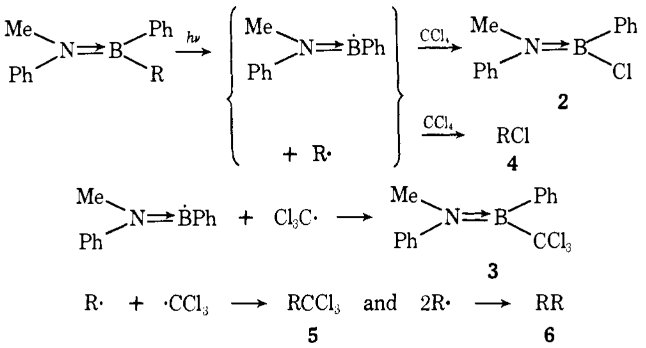
Scheme I



Clearly, a simple mechanism compatible with these results is excited-state cleavage of the boron–alkyl bond, generating alkyl and (methylphenylamino)phenylboryl radicals (Scheme II). Both the alkyl and boryl radicals may then undergo abstraction reactions with solvent and recombination reactions with various radical moieties, accounting for the observed products.

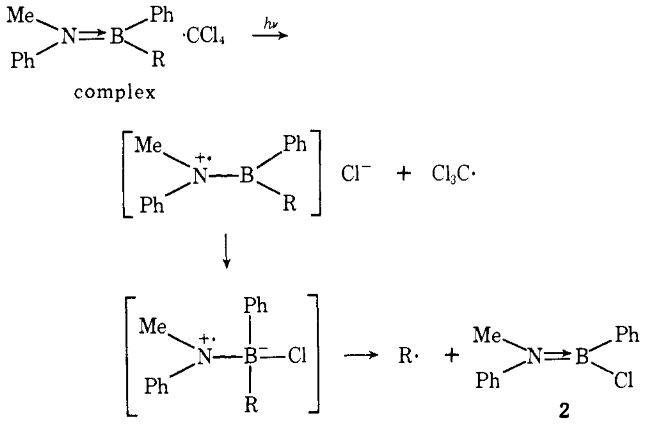
However, several not-so-simple mechanistic alternatives could not be easily discounted. Thus, direct or photosensitized homolysis of solvent, followed by radical-chain displacements at boron by trichloromethyl, seemed an *a priori* possibility. Quantum yields for disappearance of the three alkyl(*N*-methylanilino)phenylboranes were therefore measured.[6] Values of 0.15, 0.10, and 0.04 mol/einstein for cleavage of the B–benzyl, B–isopropyl, and B–ethyl bonds, respectively, do not support a chain mechanism. Furthermore, the quantum yields were unaffected by addition of 1-octene as trichloromethyl radical scavenger.

Scheme II



A second, more subtle possibility was photolysis of a charge-transfer complex of the aminoborane and carbon tetrachloride (Scheme III). Such a mechanism would have ample precedent in the known photoreactivity of amine–halocarbon donor–acceptor complexes.[8] In fact, the enhanced ultraviolet absorption of aminoboranes in carbon tetrachloride (λ_{max} 295 nm, ϵ 1650, C$_6$H$_{12}$; ϵ 2000, 3 *M* CCl$_4$ in C$_6$H$_{12}$) suggests some complexation. However, the photochemical reactions of amine–carbon tetrachloride complexes have quantum yields in the 1–100 range, characteristic of chain mechanisms. Additionally, dark reaction of these complexes can be initiated by cuprous ion and quenched by trichloromethyl radical scavengers.[8] In the present case, the aminoborane cleavage reaction could not be initiated in the dark by cuprous chloride, and the low quantum efficiency of the photocleavage could not be quenched.

Scheme III



The evidence thus seems most compatible with the straightforward mechanism involving excited-state homolysis of the boron–alkyl bond of the CCl$_4$-sol-

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(3) A. V. Dombrouskii and N. I. Ganuschak, *Zh. Obshch. Khim.*, **31**, 1896 (1961); **32**, 1282 (1962).

(4) Yields vary by a few per cent from run to run because several of the products (*e.g.*, **2**) are themselves photolabile.

(5) K. G. Hancock and A. K. Uriarte, manuscript in preparation.

(6) Quantum yields were determined at 3000 Å with aminoborane absorbing ≥99% of incident light, by nmr and glpc analysis at ≤15% conversion, employing potassium ferrioxalate actinometry.[7]

(7) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **253**, 518 (1956).

(8) (a) D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, **84**, 149 (1962); (b) K. M. C. Davis and M. F. Farmer, *J. Chem. Soc. B*, 28 (1967); (c) W. J. Lautenberger, E. N. Jones, and J. G. Miller, *J. Amer. Chem. Soc.*, **90**, 1110 (1968), and references therein.

vated aminoborane. Boron–alkyl photocleavage has no parallel in the solution-phase photochemistry of stilbenes[9] and olefins. Superficially, the boron–alkyl scission resembles the α-cleavage reaction of ketone photochemistry and fragmentation β to an amino function observed in the mass spectrometer. Both the quantum efficiency for boron–alkyl cleavage and the chemical yield of alkyl–trichloromethyl radical coupling products decrease in the order benzyl, isopropyl, and ethyl, roughly reflecting the stability of the alkyl radical being generated. The generally low quantum yields of boron–alkyl cleavage were to be expected in light of our recent demonstration that photochemical cis–trans isomerization of aminoboranes is an efficient ($\Phi \sim 0.4$) deactivation mechanism.[10]

One further conclusion can be drawn from our work. Similar bicoordinate aminoboryl radicals have been previously implicated[5,11] as reaction intermediates in the photochemistry of bis(amino)diborane(4) diene analogs. Recombination of such radicals was proposed as one possible, but undemonstrated, decay mechanism. The absence of bis(methylphenylamino)-diphenyldiborane(4) in detectable amounts as a photoproduct of (*N*-methylanilino)alkylphenylboranes suggests that coupling of boryl radicals is not an efficient process.

Acknowledgment. Financial support from the Petroleum Research Fund, administered by the American Chemical Society (Grants No. 1409-G1 and 5860-AC3), and from the Research Corporation is gratefully acknowledged.

(9) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

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

(11) K. G. Hancock and A. K. Uriarte, *ibid.*, **92**, 6374 (1970).

(12) Petroleum Research Fund Predoctoral Fellow, 1971–1973.

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Bond Energy Ordering by Isotope Effects and the Structure of Substituted 2-Bromoethyl Radicals[1]

Sir:

The relationship between bond strengths and isotope effects in hydrogen atom transfer, long understood qualitatively,[2] has been recently put on a more quantitative basis.[3,4] The earlier work on addition of mercaptans to olefins[4] is here extended to the free radical chain addition of hydrogen bromide.

The isotope effect is determined in the hydrogen transfer step

$$R\dot{C}HCH_2Br + \overset{*}{H}Br \longrightarrow RCH\overset{*}{H}CH_2Br + Br\cdot \qquad (1)$$

The tritium isotope effects, measured as the ratio of specific molar activity of hydrogen bromide divided by that of the addition product, RCH_2CH_2Br, when the addition is done in the presence of a large excess of trace tritium labeled HBr,[5] are presented in Table I for various substituents R.

Table I. Isotope Effects in the Radical Addition of HBr to $RCH{=}CH_2$

R	k_H/k_T[a]
p-Tolyl	1.04, 1.03[b]
Phenyl	1.46, 1.47[c]
p-Chlorophenyl	1.55, 1.62[d]
tert-Butyl	1.99, 1.99[e]
n-Hexyl	2.07, 2.07[e]
Br	2.83[e]
H	4.14, 4.25[f]

[a] Duplicate results shown when done. All experiments in diethyl ether solution at 0°, initiated by photolysis of azobisisobutyronitrile. [b] Product counted as crystalline pyridine derivative, *N*-2-*p*-tolylethylpyridinium bromide, mp 179–181°. [c] Counted as pyridinium salt, mp 178°. [d] Counted as pyridinium salt, mp 151–153°. [e] Counted as such after gc purification. [f] Converted *via* the Grignard reagent and phenyl isocyanate to propionanilide, mp 103–104°, for counting.

In one respect the results confirm the results with the mercaptan addition, for the order of increasing isotope effects in the table is also the expected order for increasing strength of the forming CH bond, or decreasing stability of the analogous radical $R\dot{C}HCH_3$. However, the quantitative interpretation of the isotope effects, both with respect to the lack of a maximum and the very small magnitude,[6] requires special consideration, which we attribute to two factors: (1) the fact that HBr is diatomic, and (2) the special influence of the β-bromine. We have experimentally shown that the small isotope effects are not a consequence of isotopic equilibration of the product and the labeled hydrogen bromide.

The special effect of a diatomic reagent appears in any complete treatment of isotope effects[7-9] but is not a feature of simplified treatments which are successful with most molecules. Two factors left out of the simplified treatments are, first, HBr and TBr differ in moments of inertia by a factor of 3, and, second, there are two perpendicular bending modes in any transition state for attack on HBr uncompensated by any bending vibration in the reagent. The latter factor is in the opposite direction from normal isotope effects and is responsible for the low values of the isotope effect. The isotope effects arising from these two special sources are conveniently illustrated for the reaction $BrH + \cdot Br \rightarrow Br\cdot + HBr$ for which the isotope effects neglecting tunneling can be exactly calculated by Melander's equations 2–5[8] for various values of the frequency of the doubly degenerate transition state bending vibration, $\nu_H^{\ddagger}$, the only unknown for this symmetric system. Thus at 0°, $k_H/k_T = 49.5$, 11.5, 7.1, 3.2, and 1.7 for $\nu_H^{\ddagger} = 0$, 500, 800, 1200, and 1500 cm^{-1}, respectively. The last value of $\nu_H^{\ddagger}$ is unreasonably high, being even greater than the corresponding frequency of the bihalide ions, which have an electro-

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(1) This work was supported by a grant from the Robert A. Welch Foundation.

(2) K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, **80**, 3033 (1958).

(3) W. A. Pryor and K. G. Kneipp, *ibid.*, **93**, 5584 (1971).

(4) E. S. Lewis and M. M. Butler, *Chem. Commun.*, 941 (1971).

(5) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1962, p 58.

(6) The value for addition to vinyl bromide in the table is entirely compatible with the value $k_H/k_D = 2.5$ at a lower temperature for the addition of HBr to 2-bromo-2-butene: H. L. Goering and D. W. Larsen, *J. Amer. Chem. Soc.*, **81**, 5937 (1959).

(7) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(8) L. Melander, ref 5, pp 9–15.

(9) The special features of HBr as a reagent appear in the model calculations of R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967).