Nucleophilic Substitution at Tetrahedral Boron. Trimethyl- and Triethylamine–Borane Substrates

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Abstract: Both trimethylamine–borane and triethylamine–borane react with tri-*n*-butylphosphine in *o*-dichlorobenzene solution to produce tri-*n*-butylphosphine–borane and the corresponding amine. Both reactions are second order overall and an SN2-B mechanism is proposed to account for this fact. A secondary kinetic α-deuterium isotope effect was not observed with Me_3N^+–BD_3^- substrate, and this observation is in agreement with the proposed SN2 mechanism. Thermodynamic activation parameters obtained with the Me_3N^+–BH_3^- reaction give $\Delta H^{\ddagger} = 23.4$ kcal/mol and $\Delta S^{\ddagger} = -5 \pm 3$ eu, values which again support an SN2 mechanism.

Boron and carbon are members of neighboring groups in the periodic table and, as such, share certain chemical properties, such as the ability to form trigonal and tetrahedral configurations. It is the purpose of this and the following papers of this series to examine the relative reactivities and, where possible, to explore the similarities in mechanism of nucleophilic displacement reactions which occur at tetrahedral boron and carbon.

Since ground-state boron contains one less electron than ground-state carbon and since both elements have 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals available for bonding, it follows that the trigonal boron counterparts of carbonium ions are neutral species (boranes) and the tetrahedral boron counterpart of tetrahedral carbon displays a formal negative charge (borohydride ion). Thus, direct necleophilic attack at tetrahedral boron would necessitate attack at a formally negative center and would most likely be impeded. In order to compensate for this seemingly adverse Coulombic effect we have chosen amine–boranes (R_3B^-–NR_3^+) as reaction substrates. In these cases the reactant molecule is a zwitterionic species having compensated charges.[2] Furthermore, representative examples of displacement reactions may be found in the literature which involve substrates of this charge type and uncharged nucleophiles.

Graham and Stone[3] observed the reactions shown in eq 1 and 2 and Baldwin and Washburn[4] have described reaction 3. A related example was described by Burg and Schlesinger[5] (4). We have therefore undertaken a study of the nucleophilic displacement reactions which occur with amine–borane substrates having hydrogen, alkyl, aryl, and diaryl substituents on boron. Amines or tri-*n*-butylphosphine were chosen as representative uncharged nucleophiles. Mechanistic criteria chosen for study were (i) kinetic order of reactions, (ii) steric and electronic effects, (iii) α and β secondary kinetic deuterium isotope effects, and (iv) the effect of solvent

$$e_3M\overset{+}{P}\text{—}\overset{-}{B}F_3 + Me_3N \longrightarrow Me_3P + Me_3\overset{+}{N}\text{—}\overset{-}{B}F_3 \qquad (1)$$

$$Me_3\overset{+}{N}\text{—}\overset{-}{B}H_3 + Me_3P \longrightarrow Me_3N + Me_3\overset{+}{P}\text{—}\overset{-}{B}H_3 \qquad (2)$$

$$Et_3\overset{+}{N}\text{—}\overset{-}{B}H_3 + (n\text{-}Bu)_3P \longrightarrow Et_3N + (n\text{-}Bu)_3\overset{+}{P}\text{—}\overset{-}{B}H_3 \qquad (3)$$

$$\overset{+}{O}{\equiv}C\text{—}\overset{-}{B}H_3 + Me_3N \longrightarrow CO + Me_3\overset{+}{N}\text{—}\overset{-}{B}H_3 \qquad (4)$$

polarity upon reaction rates in systems where solvent could be varied. Ultimately, a search was made for representative examples of SN1 and SN2 displacement mechanisms which, in the case of boron reaction centers, we have chosen to label as SN1-B and SN2-B processes.

Results and Discussion

Thermochemistry of the B–N Dative Bond in Amine–Boranes. The experimental thermochemistry of the B–N dative bond in R_3N^+–BH_3^- species has not been extensively examined. However, Brown and coworkers[6] have reported the ΔH of the reaction of pyridine with $^1/_2B_2H_6$ in nitrobenzene solution as -17.9 kcal/mol. Estimates of the dissociation energy of $B_2H_6 \leftrightarrows 2BH_3$ have ranged from approximately 28 to 38 kcal/mol.[7,8] Taking a rough value of 17 kcal/mol for ΔH_{diss} of $^1/_2$-B_2H_6, one concludes that the ΔH for the reaction BH_3 + py $\rightarrow$ py^+–BH_3^- is approximately -35 kcal/mol when all solvation effects are neglected. In the case of B-substituted amine–boranes, the data available are representative of the results obtained by Brown and coworkers[9] from ΔH_{diss} of Me_3B adducts with NH_3, $MeNH_2$, Me_2NH, and Me_3N. The ΔH_{diss} values obtained vary from 13.75 to 19.26 kcal/mol, with NH_3 representing the lower value and Me_2NH the maximum. In certain of the substrates examined in this work, one and two substituents, but not three, were placed upon the boron reaction site. We would therefore estimate ΔH for dissociative (SN1-B) processes with our systems to fall in the range of approximately 20–35 kcal/mol,[10]

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(2) Hoffmann has carried out extended-Hückel calculations for H_3B^-–NH_3^+ [R. Hoffmann, *J. Chem. Phys.*, 40, 2474 (1964)] and concluded that the B–N bond is polarized *with nitrogen more negative than boron.* This effect is modified by B^+–H^- and N^-–H^+ contributions. However, the *microscopic* B–N bond moment is probably not in the formally written direction, although we retain this formalism throughout these papers for simplicity and the fact that Me_3N^+–BH_3^- exhibits a dipole moment of 4.45 D in benzene at 25°: H Nöth and H. Beyer, *Chem. Ber.*, **93**, 928 (1960).

(3) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(4) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **26**, 3549 (1961).

(5) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **59**, 780 (1937).

(6) H. C. Brown, D. Gintis, and L. Domash, *ibid.*, **78**, 5387 (1956).

(7) S. H. Bauer, *ibid.*, **78**, 5775 (1956).

(8) M. E. Garabedian and S. W. Benson, *ibid.*, **86**, 176 (1964).

(9) H. C. Brown, H. Bartholomay, and M. D. Taylor, *ibid.*, **66**, 435 (1944).

(10) This estimate is based upon the assumption that the difference between Me_3B and H_3B adducts is largely due to steric and inductive

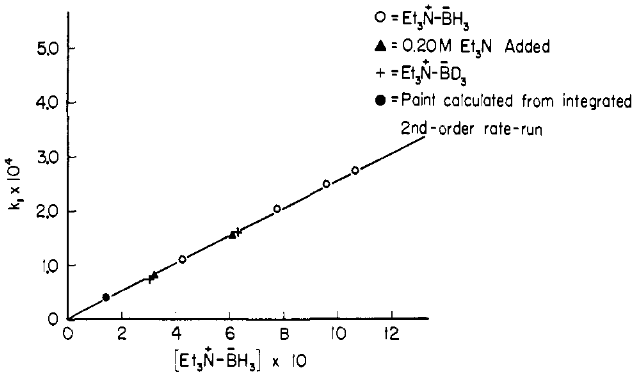

Figure 1. Plot of pseudo-first-order rate constant *vs.* triethylamine-borane concentration. Point denoted by ● obtained using using equivalent tri-*n*-butylphosphine- and triethylamine-borane concentrations.

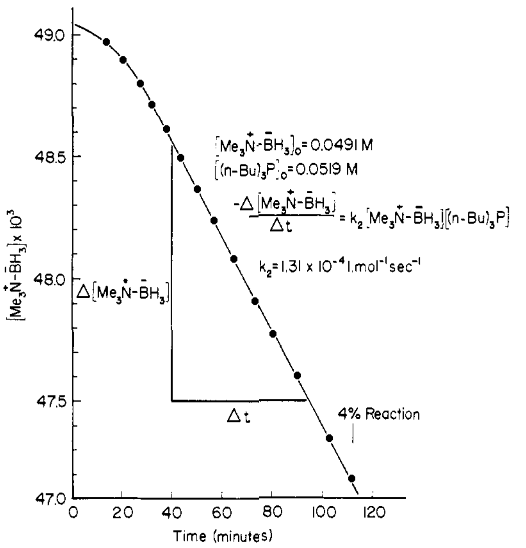

Figure 2. Plot of initial rate data obtained using trimethylamine-borane with tri-*n*-butylphosphine nucleophile.

with unsubstituted (BH_3) cases lying near 35 kcal/mol.

Kinetic Method. At the outset of this study a kinetic method was devised in which the nucleophile was limited to (n-Bu)$_3$P and displacement reactions were followed by monitoring the consumed phosphine as a function of time.[11] This method took advantage of the fact the (n-Bu)$_3$P formed a colored adduct with CS_2 (λ_{max} 483 mμ, ϵ 67.6). Thus, reaction mixture aliquots were quenched with CS_2 and the 483 mμ absorption used as a measure of the instantaneous phosphine concentration. This method was quite restrictive, and rate runs were limited to those in which sizable changes in phosphine concentration occurred during the reaction.

A second, and more general method,[11] was devised which made use of the volatility of Me_3N and similar amines when these amines were employed as the leaving group in the displacement reaction. As amine was liberated by the displacement reaction it was continually swept by an inert gas stream into aqueous acid containing bromthymol blue indicator. The time of indicator color change was noted and the time required for the neutralization of a known amount of acid was thus determined. Figure 3 (see Experimental Section) illustrates the apparatus employed with the latter method. This method was sufficiently sensitive to allow initial (first 2–10% of the overall reaction) rates to be accurately determined,[12] and specific reaction rate constants could then be evaluated from the differential form of the rate expression. The colorimetric and amine vaporization methods were used interchangeably in several cases and reproduced one another within a few per cent.

Reaction of Triethylamine–Borane with (n-Bu)$_3$P. Figure 1 presents a plot of pseudo-first-order rate constants determined using the colorimetric method and containing initial $Et_3N^+\text{–}BH_3^-$ concentrations in large excess over that of the (n-Bu)$_3$P reactant. *o*-Dichlorobenzene was employed as the reaction solvent at 49.6°. Initial amine–borane concentrations were randomly varied over a tenfold range and reactions were followed to at least 70% completion. The apparent second-order nature of the reaction is apparent with $k_2 = 2.55 \times 10^{-4}$ l. mol^{-1} sec^{-1}. In addition, initially added Et_3N had no effect upon the observed rate constant. In one rate run both reactants were initially present at low and nearly equivalent concentrations, and the rate constant was calculated by the integrated second-order equation with good agreement up to 70% reaction.

The method of Davis and coworkers[13] was employed to prepare $Et_3N^+\text{–}BD_3^-$. The specific rate constant for the reaction of this substrate with (n-Bu)$_3$P was identical, within experimental error, with that observed in the hydrogen-containing substrate. Thus, $k_2^H/k_2^D = 1.0$, which is in general agreement with previously observed α-deuterium kinetic isotope results obtained with carbon reaction centers in normal SN2 reactions.[14] We therefore conclude that $Et_3N^+\text{–}BH_3^-$ reacts with (n-Bu)$_3$P by a dominant second-order displacement process (SN2-B). The product obtained from a facsimile kinetic run was identified as essentially pure (n-Bu)$_3$P$^+$–BH$_3^-$ by its characteristic infrared spectrum.

Reaction of Trimethylamine–Borane with (n-Bu)$_3$P. When $Me_3N^+\text{–}BH_3^-$ was employed as the reaction substrate in *o*-dichlorobenzene solution with (n-Bu)$_3$P as the nucleophile, it was possible to utilize the flow method of kinetic analysis. Figure 2 presents a representative instantaneous rate plot of a reaction carried out at 49.6° from which a second-order rate constant of 1.31×10^{-4} l. mol^{-1} sec^{-1} was obtained. Table I lists the results of several rate runs carried out under these conditions, and one rate run which was followed by the colorimetric method to 70% completion. In one run reported in Table I, approximately 2×10^{-3} M Me_3N was added initially and an inverse induction period was observed. This result is in sharp contrast with the typical induction period[12] observed in Figure 2. The near constancy of the second-order rate constants reported in Table I coupled with the tenfold variation of both initial reactant concentrations strongly supports an SN2-B

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effects. It should be emphasized that these values are only meant to serve as guidelines.

[11] (a) M. F. Hawthorne and W. L. Budde, *J. Amer. Chem. Soc.*, **86**, 5337 (1964); (b) M. F. Hawthorne, W. L. Budde, and D. E. Walmsley, *ibid.*, **86**, 5337 (1964).

[12] An induction period was invariably observed which was due to the establishment of a steady-state amine concentration of approximately 10^{-4} M (see Figure 2).

[13] R. E. Davis, A. E. Brown, K. Hopmann, and C. L. Kibby, *J. Amer. Chem. Soc.*, **85**, 487 (1963).

[14] See A. Streiwieser, Jr., "Solvolytic Displacement Reactions," Supplement, McGraw-Hill, New York, N. Y., 1962, for collected examples.

Table I. Collected Instantaneous Rate Data for the Reaction of $(n\text{-}Bu)_3P$ with $Me_3N^+\text{-}BH_3^-$ in *o*-Dichlorobenzene at 49.6°

$[Me_3N^+\text{-}BH_3^-]_0 \times 10^2$	$[(n\text{-}Bu)_3P]_0 \times 10^2$	k_2, l. mol^{-1} sec^{-1}, $\times 10^4$
9.95	1.05	1.29^a
1.04	10.4	1.25
4.91	5.20	1.31
4.87	1.11	1.23
1.05	5.50	1.47
3.34	3.50	1.47^b
1.11	10.8	1.44^b
		Av 1.33

[a] Reaction followed to 70% completion by colorimetric method. [b] 2×10^{-3} *M* Me_3N added initially and inverse induction period observed.

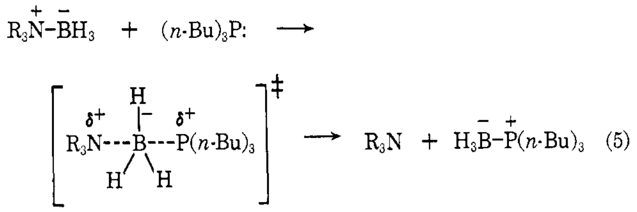
mechanism for this simple displacement reaction. As in the case of $Et_3N^+\text{-}BH_3^-$ reactant, the product of a control rate run proved to be essentially pure $(n\text{-}Bu)_3P^+\text{-}BH_3^-$.[4]

A series of reactions were studied over a 33° temperature range and the observed second-order rate constants are presented in Table II along with the calculated thermodynamic activation parameters. The $\Delta H^{\ddagger}$ value of 23.4 ± 2 kcal/mol is considerably less than that expected for a purely dissociative process (*vide supra*), and the small and negative $\Delta S^{\ddagger}$ is in the proper direction to support the existence of an SN2-B reaction.

Table II. Thermodynamic Data for the Reaction of $Me_3N^+\text{-}BH_3^-$ with $(n\text{-}Bu)_3P$ in *o*-Dichlorobenzene

Temp, °C	k_2, l. mol^{-1} sec^{-1}, $\times 10^5$
30.0	1.30
40.0	4.41
49.6	13.3
63.3	47.2
$\Delta H^{\ddagger}$ = 23.4 kcal/mol	$\Delta S^{\ddagger}$ = −5 ± 3 eu

From the foregoing results it may be concluded that the reaction of $Et_3N^+\text{-}BH_3^-$ and $Me_3N^+\text{-}BH_3^-$ with $(n\text{-}Bu)_3P$ in *o*-dichlorobenzene proceeds through a dominant SN2-B process which should result in inversion of configuration at the reaction site.



$$R_3\overset{+}{N}\text{-}\overset{-}{B}H_3 + (n\text{-}Bu)_3P: \longrightarrow \left[\overset{\delta+}{R_3N}\text{---}\underset{H\quad H}{\overset{H}{B}}\text{---}\overset{\delta+}{P}(n\text{-}Bu)_3\right]^{\ddagger} \longrightarrow R_3N + H_3\overset{-}{B}\text{-}\overset{+}{P}(n\text{-}Bu)_3 \quad (5)$$

Experimental Section

Materials. *o*-Dichlorobenzene was obtained from Matheson Coleman and Bell and purified by distillation from calcium hydride, bp 79° (25 mm). Trimethylamine-borane was obtained from the Callery Chemical Co. and sublimed before use, mp 94–95° (sealed capillary). Trimethylamine-borane was obtained from the same source and purified by repeated trap-to-trap distillation under high vacuum. Triethylamine-borane-d_3 of 85% isotopic purity (estimated from mass spectral parent ion intensities) was prepared by the method of Davis.[13] Tri-*n*-butylphosphine was purified by distillation under nitrogen with a spinning-band column, bp 130° (23 mm), and stored under nitrogen.

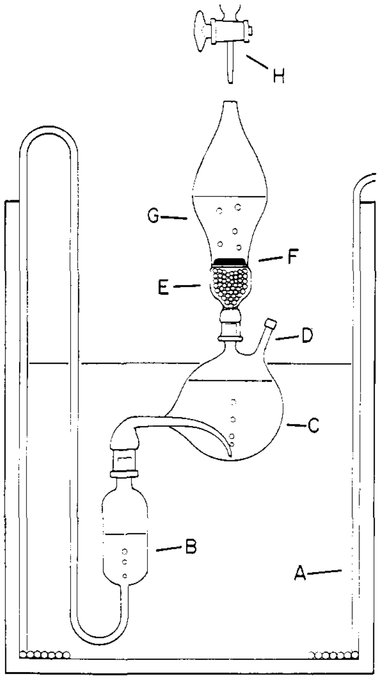


Figure 3. Drawing of "flow method" apparatus. See text for component descriptions.

Kinetic Procedures. Colorimetric Determination of $(n\text{-}Bu)_3P$. The quantitative reaction of $(n\text{-}Bu)_3P$ with excess CS_2 generates a red product (λ_{max} 483 mμ, ϵ 67.6) which obeyed Beer's law at all concentrations. A Beckman DU spectrophotometer was employed to obtain optical density measurements. Control experiments confirmed the fact that amine–boranes did not interfere with the formation and stability of the red product which was measured. In a typical rate determination, stock solutions (1–4 *M*) of $(n\text{-}Bu)_3P$ and the amine–borane in *o*-dichlorobenzene were prepared under nitrogen and used the same day. The kinetic reaction vessel consisted of a 50-ml round-bottomed flask carrying a dry nitrogen inlet connected to a mercury bubbler. An attached side arm carried a rubber stopple through which aliquots of reaction solution were periodically removed with a calibrated hypodermic syringe. In order to commence a rate run, the proper volume of solvent *o*-dichlorobenzene was added to the reaction vessel and nitrogen swept through the system by opening the side arm. The calculated volume of amine–borane stock solution was then introduced and the assembly placed in a thermistor-controlled thermostat. After thermal equilibrium had been reached (25 min) the calculated volume of $(n\text{-}Bu)_3P$ stock solution was introduced through the side-arm stopple to begin the reaction. Aliquots (1.00 ml) were periodically removed and quenched with 2 ml of a solution containing 15 ml of CS_2 in 100 ml of *o*-dichlorobenzene which had been placed in a 5- or 10-ml volumetric flask. The colorimetric solution was then made up to the mark with *o*-dichlorobenzene and its optical density recorded at 483 mμ. The optical density data were converted to instantaneous $(n\text{-}Bu)_3P$ concentrations and the data plotted using the appropriate integrated rate equation. Normally, rate runs were carried out under pseudo-first-order conditions with a large excess of amine–borane. Reactions were followed to at least 70% completion.

Kinetic Procedures. Flow Method. Figure 3 presents a diagram of the apparatus employed and consisted of a copper coil (A) through which dry nitrogen was delivered to the solvent saturator bulb (B) which contained the same solvent as that employed in the reaction under study. The bulb (C) is the reaction vessel (100 ml) through which the nitrogen gas stream continually flowed at a moderate rate. The side arm (D) carried a rubber stopple and was employed to introduce reactants. The glass beads (E) were employed to decrease the free volume of the reaction vessel and to prevent entrainment of the reaction mixture. A pool of mercury metal placed on a sintered glass plate (F) served as a one-way gas outlet under the aqueous indicator (bromthymol blue) solution (G). The buret (H) was of 10-ml capacity and contained standardized 0.10 *N* aqueous hydrochloric acid.

In a typical rate run, the calculated volume of solvent was placed in (C), followed by the proper volume of amine–borane stock solution (through the stopple). The system was placed in the thermostat and nitrogen bubbled through the apparatus at a rate of 50–200 ml/min. Control experiments established that the observed reaction rate is independent of flow rate. After 30 min of thermal equilibration the vessel (G) was filled with indicator solution, the buret attached and the second reactant introduced at (D). After a short induction period, trimethylamine was steadily evolved and its rate of evolution followed with the acid titrant and a timer. It was found to be most convenient to "lead" the reaction by introducing small increments of acid to (G) and noting the time of indicator change due to reaction with amine. Data obtained resembled those shown in Figure 2, and the initial reaction rate was used to evaluate the second-order rate constant by means of the equation $d[R_3N^+\text{–}BH_3^-]/dt = k_2[R_3N^+\text{–}BH_3^-]_0[(n\text{-Bu})_3P]_0$.

Product Isolation. Essentially the same procedure was employed with $Me_3N^+\text{–}BH_3^-$ and $Et_3N^+\text{–}BH_3^-$ substrates, using the flow method for the former material and the static method (colorimetric) for the latter. Reaction mixtures (50 ml) were prepared which contained equal molar quantities of amine–borane and $(n\text{-Bu})_3P$ (0.20 *M*) in *o*-dichlorobenzene, thermostated at 49.6°. The reaction was then carried out as described above and allowed to proceed to essential completion. Removal of solvent (and liberated Et_3N) was accomplished by pumping on a vacuum line, and the residue was examined by infrared spectroscopy. In all cases the observed infrared spectrum was essentially that of pure $(n\text{-Bu})_3P^+\text{–}BH_3^-$ as prepared by the method of Baldwin and Washburn.[4]

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Nucleophilic Substitution at Tetrahedral Boron. Trimethylamine–Alkyl- and -Arylborane Substrates

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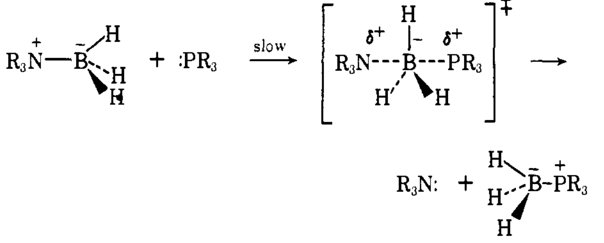
Abstract: The four isomeric trimethylamine–butylboranes and six para- and ortho-substituted trimethylamine–arylboranes were examined as substrates in displacement reactions with tri-*n*-butylphosphine as the nucleophile. Kinetic data gave good evidence for second-order SN2-B displacement reactions in all cases except that of trimethylamine-*tert*-butylborane, which gave a predominant first-order SN1-B displacement reaction. The aryl systems gave second-order, SN2-B terms, which in the *p*-anisyl- and mesitylborane cases had small first-order terms superimposed upon them. Secondary deuterium kinetic isotope effects were observed with the *sec*-butyl system. Activation parameters, solvent effects, and other associated data point to the simultaneous operation of SN1-B and SN2-B displacement processes when moderately bulky groups are attached to the boron atom of the amine–borane substrate.

In the previous paper of this series,[2] the reactions of $Et_3N^+\text{–}BH_3^-$ and $Me_3N^+\text{–}BH_3^-$ with tri-*n*-butylphosphine to form $(n\text{-Bu})_3P^+\text{–}BH_3^-$ were examined from the viewpoint of reaction mechanism using reaction kinetics as the principal mechanistic criterion. The conclusion was drawn that both of these reactions proceeded through SN2-like transition states (SN2-B, eq 1).

(SN2-B, eq 1)

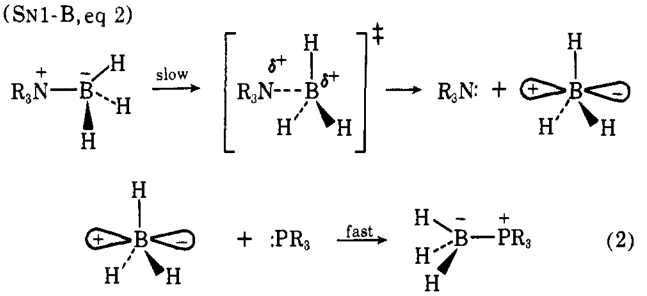


(1)

No evidence was obtained to support the existence of an analogous SN1-B reaction (eq 2) having a trigonal borane intermediate analogous to a weakly solvated carbonium ion.

In this paper we describe similar mechanism studies with *B*-alkyl- and *B*-aryl-substituted trimethylamine–boranes which have provided evidence pointing to the existence of the SN1-B reaction mechanism. As in the work previously reported,[2] extensive use was made of deuterium kinetic isotope effects as mechanistic probes. A brief account of these results was presented some time ago.[3]

(SN1-B, eq 2)



Results and Discussion

Trimethylamine–*B*-Alkyl- and -Arylboranes. The four isomeric trimethylamine–butylboranes were selected as substrates for study since all four were known materials and readily available[4] through lithium aluminum hydride reduction of the corresponding trialkylboroxines in the presence of trimethylamine. In order to accomplish α- and β-deuterium[5] kinetic isotope studies,

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(2) W. L. Budde and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 3147 (1971).

(3) M. F. Hawthorne, W. L. Budde, and D. E. Walmsley, *ibid.*, **86**, 5337 (1964).

(4) M. F. Hawthorne, *ibid.*, **83**, 831 (1961).