stat 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 $d[R_3N^+-BH_3^-]/dt = k_2[R_3N^+-BH_3^-]_0[(n-Bu)_3P]_0$.

Product Isolation. Essentially the same procedure was employed with $Me_3N^+-BH_3^-$ and $Et_3N^+-BH_3^-$ substrates, using the flow method for the former material and the static method (colori-

metric) for the latter. Reaction mixtures (50 ml) were prepared which contained equal molar quantities of amine–borane and (n-Bu)$_3$P (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$_3$N) 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-Bu)$_3$P$^+$-BH$_3^-$ as prepared by the method of Baldwin and Washburn.[4]

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

Donald E. Walmsley, William L. Budde, and M. Frederick Hawthorne*[1]

Contribution from the Department of Chemistry, The University of California, Riverside, California 92502. Received September 28, 1970

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 S_N2-B displacement reactions in all cases except that of trimethylamine-$tert$-butylborane, which gave a predominant first-order S_N1-B displacement reaction. The aryl systems gave second-order, S_N2-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 S_N1-B and S_N2-B displacement processes when moderately bulky groups are attached to the boron atom of the amine–borane substrate.

I n the previous paper of this series,[2] the reactions of Et$_3$N$^+$-BH$_3^-$ and Me$_3$N$^+$-BH$_3^-$ with tri-n-butylphosphine to form (n-Bu)$_3$P$^+$-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 S_N2-like transition states (S_N2-B, eq 1).

(S_N2-B, eq 1)
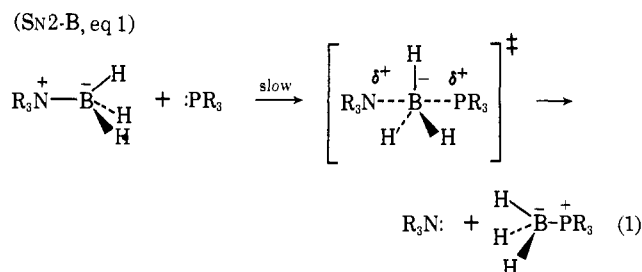
No evidence was obtained to support the existence of an analogous S_N1-B reaction (eq 2) having a trigonal borane intermediate analogous to a weakly solvated carbonium ion.

In this paper we describe similar mechanism studies with B-alkyl- and B-aryl-substituted trimethylamine–boranes which have provided evidence pointing to the

(S_N1-B, eq 2)
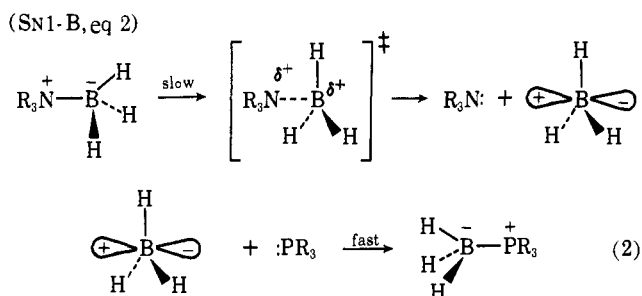
existence of the S_N1-B reaction mechanism. As in the work previously reported,[2] extensive use was made of deuterium kinetic isotope effects as mechanistic probes. A brief account of these results was presented some time ago.[3]

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,

(1) To whom correspondence should be addressed at the Department of Chemistry, the University of California, Los Angeles, Calif. 90024.

(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).

Table I. Characterization Data for Trimethylamine–Arylboranes

Aryl group	Yield, %	Mp,[a] °C	Analysis, % Calcd C	Calcd H	Calcd B	Found C	Found H	Found B
Phenyl[b]	30	68–69	72.52	10.82	7.26	72.30	11.00	7.15
p-Bromophenyl	33	80–82	47.41	6.63	4.74	47.63	6.54	4.88
p-Anisyl	60	71–73	67.07	10.13	6.04	67.25	10.02	5.92
p-Tolyl	41	48–49	73.64	11.12	6.63	73.45	11.16	6.76
o-Tolyl	33	c	73.64	11.12	6.63	73.54	10.83	6.80
Mesityl	37	89–90	75.40	11.60	5.66	75.69	11.65	6.01

[a] Uncorrected. [b] Reference 7. [c] Liquid at room temperature, distilled at 33° (3 × 10⁻⁵ mm).

two specifically labeled trimethylamine–2-butylboranes were prepared: $Me_3N^+-BD_2CH(CH_3)(C_2H_5)^-$ and $Me_3N^+-BH_2CD(CH_3)(C_2H_5)^-$. The former material was obtained by $LiAlD_4$ reduction of the boroxine and the latter by $LiAlH_4$ reduction of labeled 2-butylboroxine prepared from 2-bromobutane-2-d.[6]

A series of trimethylamine–arylboranes was prepared by the method previously devised for the synthesis of trimethylamine–phenylborane.[7] The yield and characterization data associated with these compounds are presented in Table I.

Kinetic Method. The volatilization of liberated trimethylamine product in the previously described flow system[2] served as the means for determining initial reaction rates over a 10–20-fold range of reactant concentrations. The most commonly employed reaction medium was o-dichlorobenzene, although a study of specific reaction rate vs. solvent bulk dielectric constant was carried out with a selected substrate, $Me_3N^+-BH_2-(2-Bu)^-$. The choice of o-dichlorobenzene as the principal reaction medium allowed a comparison to be made between the data obtained here and those obtained in the cases of the unsubstituted amine–boranes.[2] As before,[2] tri-n-butylphosphine was employed as the standard nucleophile. In several rate runs 2,2-diphenylethylamine was utilized as the nucleophile with trimethylamine–2-butylborane substrate. In the following paper of this series, this amine was adopted as the standard nucleophile in reactions with methylamine–diarylborane substrates. No evidence of trimethylamine liberation was detected in the absence of nucleophile except in those systems where first-order kinetic terms exist.

Displacement Reactions of Trimethylamine–Butylboranes. The kinetics of the reaction of trimethylamine–n-butylborane (I) with tri-n-butylphosphine was studied at 40.1 and 49.8° in o-dichlorobenzene. Examination of the rate data proved that the overall rate law was composed of two kinetic terms (eq 3). Table II contains collected reaction rate data and Figure 1 presents a plot of specific initial reaction rate, $k' = \{d[NMe_3]/dt\}/[amine–borane]_0$ (sec⁻¹) evaluated from initial rates at 40.1°, vs. initial n-Bu₃P concentration.

$$k' = (d[NMe_3]/dt)/[amine–borane]_0 =$$
$$k_1 + k_2[n-Bu_3P]_0 \quad (3)$$

tains collected reaction rate data and Figure 1 presents a plot of specific initial reaction rate, $k' = \{d[NMe_3]/dt\}/[amine–borane]_0$ (sec⁻¹) evaluated from initial rates at 40.1°, vs. initial n-Bu₃P concentration.

The reaction of trimethylamine–isobutylborane (II) with (n-Bu)₃P was examined in an identical manner at

(5) The α position is designated as the BH_2 group which bears the leaving group and the β position is the C atom of the alkyl group bonded to the BH_2 group.
(6) G. K. Helmkamp and N. Schnautz, J. Org. Chem., 24, 529 (1959).
(7) M. F. Hawthorne, J. Amer. Chem. Soc., 80, 4291 (1958).

Table II. Collected Rate Constants for Reactions of (n-Bu)₃P with $Me_3N^+-BH_2R^-$ Substrates in o-Dichlorobenzene Solution

R in $Me_3N^+-BH_2R^-$	Temp, °C	$k_1 \times 10^6$, sec⁻¹ [a]	$k_2 \times 10^5$, l. mol⁻¹ sec⁻¹ [a]
H[b]	40.0	c	4.41 ± 0.4
n-Butyl	40.1	2.41 ± 0.33	5.91 ± 0.23
n-Butyl	49.8	16.4 ± 1.1	17.1 ± 2.1
Isobutyl	40.1	4.32 ± 0.10	3.19 ± 0.07
Isobutyl	49.8	20.7 ± 1.1	11.5 ± 0.4
tert-Butyl	29.5	17.7 ± 1.1	c
tert-Butyl	40.1	115.3 ± 0.3	4.08 ± 2.0[d]
sec-Butyl	29.5	1.90 ± 0.09	3.65 ± 0.05
sec-Butyl	40.1	13.3 ± 0.5[e]	11.4 ± 0.5[e]
sec-Butyl	49.8	68.3 ± 6.1	26.9 ± 1.7
sec-Butyl-d₂ (α-III-d₂)	29.5	1.44 ± 0.12	3.55 ± 0.07
sec-Butyl-d (β-III-d)	29.5	1.66 ± 0.12	3.32 ± 0.06
Phenyl	30.0	c	11.6± ±0.6
p-Anisyl	30.0	1.22 ± 0.08	13.9 ± 0.8
p-Bromophenyl	30.0	c	12.6 ± 0.08
p-Tolyl	30.0	c	11.1 ± 0.08
o-Tolyl	30.0	c	51.5 ± 3.0
Mesityl[f]	30.0	63.9 ± 1.5	546 ± 20

[a] Modified in some cases from the values previously reported in ref 3. [b] From ref 2. [c] Too small to detect if present. [d] Judged to be unreliable (see text). [e] With 2,2-diphenylethylamine as nucleophile $k_1 = 13.1 \pm 0.9$ sec⁻¹ and $k_2 = 20.6 \pm 0.4$ l. mol⁻¹ sec⁻¹. [f] Rate constants determined from integrated first-order rate expression to 80% reaction; see text.

40.1 and 49.8° in o-dichlorobenzene. The rate data obtained obeyed the general rate equation (3) and are presented in Table II. Figure 1 presents a plot of initial specific reaction rate, k', at 40.1° vs. initial (n-Bu)₃P concentration.

The reaction of trimethylamine–sec-butylborane (III) with (n-Bu)₃P was similarly studied at 29.5 and 40.1°. Table II contains the collected rate data and Figure 2 presents the 40.1° rate data plotted in accord with the rate equation (3). In order to test the validity of eq 3, several rate runs were made using 2,2-diphenylethylamine as the nucleophile with trimethylamine–sec-butylborane. These data are collected in Table II and plotted in Figure 2. Examination of the latter figure proves that the first-order kinetic term is independent of nucleophile identity, but the second-order term was appreciably altered by the change in nucleophile.

Trimethylamine–t-butylborane (IV) was similarly studied in its reaction with (n-Bu)₃P in o-dichlorobenzene at 29.5 and 40.1°. As before, the initial rate data are recorded in Table II and Figure 3 presents a plot of the 40.1° rate data fitted to eq 2. While no second-order kinetic term was observed at 29.5°, a small second-order term appeared in the 40.1° rate data
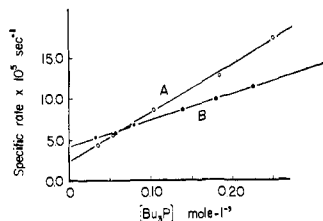
Figure 1. Plot of specific rate, $\{d[NMe_3]/dt\}/[amine–borane]_0$, sec^{-1}, vs. initial tri-n-butylphosphine concentration for A = Me_3-N^+-$BH_2(n$-Bu)$^-$ and B = Me_3N^+-$BH_2(i$-Bu)$^-$.
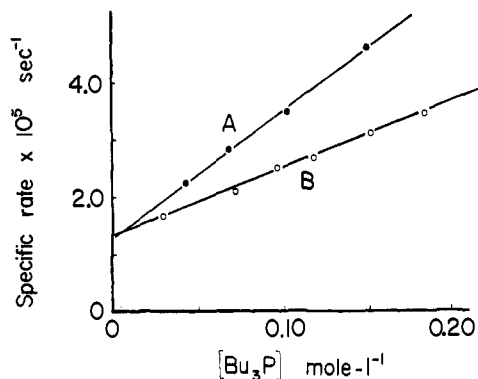
Figure 2. Plot of specific rate, $\{d[Me_3N]/dt\}/[Me_3N^+$-$BH_2(sec$-Bu$^-)]_0$, vs. initial nucleophile concentration for A = 2,2-diphenyl-ethylamine and B = tri-n-butylphosphine.

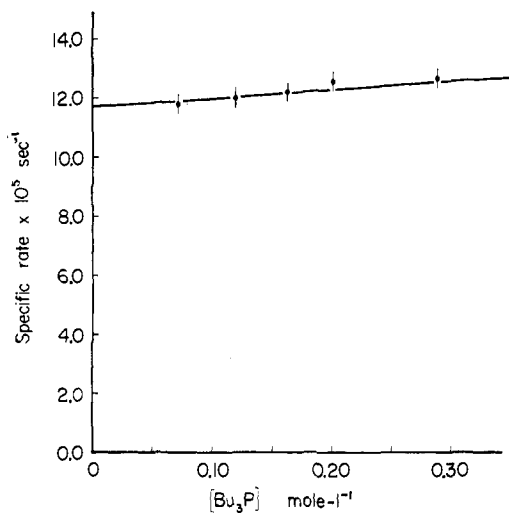Figure 3. Plot of specific rate, $\{d[Me_3N]/dt\}/[Me_3N^+$-$BH_2(tert$-Bu)$^-]_0$, vs. initial tri-n-butylphosphine concentration.

(Figure 3). While this may be a true second-order kinetic term, this conclusion appears to be unreliable owing to the inherent scatter in the rate data and the existence of the rather large first-order term on which it is superimposed.

Deuterium Kinetic Isotope Effects. As seen above, trimethylamine-sec-butylborane exhibits reaction kinetics which contain appreciable and easily evaluated first- and second-order terms. In order to aid in the mechanistic assignment of these two kinetic terms a series of rate studies was undertaken with specifically deuterated trimethylamine-sec-butylboranes,[5] α-III-d_2 and β-III-d. Table II contains the rate data obtained in the reaction of α-III-d_2 and β-III-d with $(n$-Bu)$_3$P at
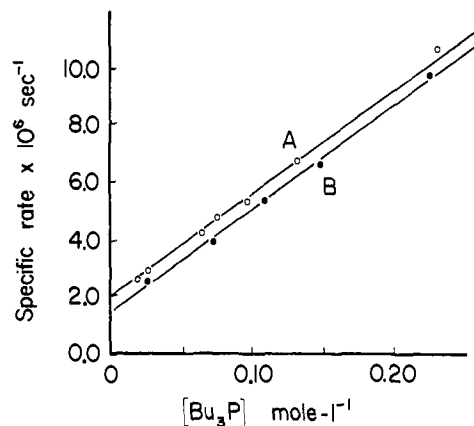

Figure 4. Plot of specific rate, $\{d[Me_3N]/dt\}/[amine–borane]_0$, vs. initial tri-$n$-butylphosphine concentration for A = Me_3N^+-BH_2-$(sec$-Bu)$^-$ and B = Me_3N^+-$BD_2(sec$-Bu)$^-$.
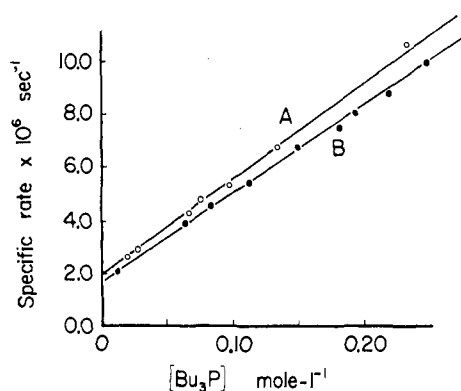
Figure 5. Plot of specific rate, $\{d[Me_3N]/dt\}/[amine–borane]_0$, for A = Me_3N^+-$BH_2(sec$-Bu)$^-$ and B = Me_3N^+-$BH_2(sec$-Bu-$d)^-$.

29.5° in o-dichlorobenzene. Figure 4 presents, in graphical form, the data obtained with α-III-d_2 plotted according to eq 3, while Figure 5 is a similar plot obtained for β-III-d. In both cases, kinetic isotope effects are apparent. The k_H/k_D values obtained from these data for both the k_1 and k_2 terms are summarized in Table III. In agreement with previously reviewed

Table III. Summary of Secondary Deuterium Kinetic Isotope Effects at 29.5° in o-Dichlorobenzene

Substrate	k_1^H/k_1^D	k_2^H/k_2^D
(2-Bu)BD$_2^-$-N(CH$_3$)$_3^+$ (α-III-d_2)	1.32 ± 0.18	1.02 ± 0.03
(2-Bu-2-d)BH$_2^-$-N(CH$_3$)$_3^+$ (β-III-d_1)	1.14 ± 0.15	1.09 ± 0.03

observations,[8] the substrate α-III-d_2 gave a rather large kinetic isotope effect in the first-order term and, within experimental error, gave no kinetic isotope effect in the second-order term. In the case of β-III-d, kinetic isotope effects were observed in both the first- and second-order kinetic terms. While we do not wish to speculate as to the true physical origin of these isotope effects, the data obtained with α-III-d_2 are in agreement with the operation of S_N1-B and S_N2-B mechanisms[8] seen in reac-

(8) See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," Supplement, McGraw-Hill, New York, N. Y., 1962, for collected examples.

Table IV. Taft Equation Correlation of First-Order Kinetic Terms at 40.1°

R	$\sigma^{*\,a}$	$E_s{}^b$	Log $(k/k_0)^c$	δE_s	$\rho^*\sigma^*$	Log $(k/k_0)^d$
Methyl	0.000	0.00	0.00	0.00	0.00	0.00
1-Butyl	−0.130	−0.39	1.21	0.47	+0.47	0.94
2-Methyl-1-propyl	−0.125	−0.93	1.46	1.02	+0.45	1.47
2-Butyl	−0.210	−1.13	1.95	1.36	+0.76	2.12
2-Methyl-2-propyl	−0.300	−1.54	2.89	1.85	+1.08	2.93

^{a} From ref 9. ^{b} C. K. Hancock, E. A. Meyers, and B. J. Vager, *J. Amer. Chem. Soc.*, **83**, 4211 (1961). ^{c} Experimental. ^{d} $\delta E_s + \rho^*\sigma^* =$ log (k/k_0). Calculated: $\rho^* = -3.6, \delta = 1.2, k_0 = 1.48 \times 10^{-7}$ sec^{-1}.

tions at carbon centers and is also in agreement with data obtained[2] for α-deuterated Me$_3$N$^+$-BH$_3^-$. In the case of β-III-d, the first-order term effect is again in agreement with the presence of an S$_N$1-B mechanism[8] while the second-order term effect is less easily interpreted, although the presence of this effect does not rule out the existence of a loosely bound leaving group in an S$_N$2-B mechanism.

Application of the Taft Equation to Stereoelectronic Effects. The Taft equation,[9] log $k/k_0 = \rho^*\sigma^* + \delta E_s$, has provided a widely used tool for the separate evaluation of steric and electronic effects in aliphatic systems. In the present study, we have applied this method to the first-order kinetics terms of the isomeric compounds I, I1, III, and IV. Table IV presents the results of a least-squares calculation of k_0 (Me$_3$N$^+$-BH$_2$CH$_3^-$ reactant, $k_0 = 1.48 \times 10^{-7}$ sec^{-1}), ρ^*, and δ. Inspection of Table IV shows that the best fit of the data was obtained with $\rho^* = -3.6$ and $\delta = -1.2$. These values are in agreement with the expected acceleration of the first-order dissociation process by electron-releasing substituents and by increasing effective size of the substituent. It must be remembered that four measured values were employed to determine three variables: k_0, ρ^*, and δ. A similar correlation of the second-order kinetic terms was not possible since no reasonable value for k_2 was available for the reaction of IV with (n-Bu)$_3$P at 40.1 or 29.5°.

Effect of Solvent Polarity on Rate. Inspection of the transition-state charge distributions for S$_N$1-B and S$_N$2-B processes (eq 2 and 1, respectively) indicates that the dipolar reactant with a dipole moment of approximately 4 D[10] disperses the formal charge separation on going toward the S$_N$1-B or S$_N$2-B transition states. As earlier predicted by Hughes and Ingold[11] and subsequently demonstrated in many displacement reaction studies at carbon centers, such a charge dispersal should result in decreasing reaction rate with increasing solvent polarity. In the present study, three solvents with markedly different bulk dielectric constants were employed in the reaction of III with (n-Bu)$_3$P at 29.5°. Table V presents the rate data obtained in these solvent

systems: undecane, o-chlorotoluene, and o-dichlorobenzene. In all cases observed, both the first- and second-order rate constants decreased markedly as solvent polarity was increased, in agreement with expectations.

Thermodynamic Activation Parameters. Table VI presents $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained for each of the isomeric trimethylamine–butylborane substrates examined in o-dichlorobenzene. The first-order kinetic

Table VI. Activation Parameters for the Reactions of RBH$_2^-$-NMe$_3^+$ with (n-Bu)$_3$P in o-Dichlorobenzene

R	First-order term^a		Second-order term^a	
	$\Delta H_1{}^{\ddagger}$	$\Delta S_1{}^{\ddagger}$	$\Delta H_2{}^{\ddagger}$	$\Delta S_2{}^{\ddagger}$
n-Butyl	38 ± 9^b	40 ± 30^b	22 ± 3^b	−9 ± 10^b
Isobutyl	32 ± 3	18 ± 10	26 ± 2	5 ± 6
sec-Butyl	31 ± 3	19 ± 7	19 ± 2	−17 ± 6
$tert$-Butyl	32 ± 2	25 ± 6		

^{a} Enthalpies of activation reported in kcal mol^{-1}, entropies of activation in eu. ^{b} Estimated maximum probable errors.

terms are characterized by $\Delta H^{\ddagger}$ values in the range generally assumed to represent ΔH_{diss} for the B–N bonds in amine–boranes[2] and large positive $\Delta S^{\ddagger}$ values associated with dissociation accompanied by desolvation of reactant species. On the other hand, the second-order rate terms exhibited a much less positive range of $\Delta S^{\ddagger}$ values and lower $\Delta H^{\ddagger}$. These observations are in agreement with an S$_N$2-B mechanism which requires assistance from nucleophile for B–N bond rupture[10] and increased ordering in the transition state.

Trimethylamine–Arylboranes as Substrates. A study of the reactions of the trimethylamine–arylboranes listed in Table I with (n-Bu)$_3$P was undertaken in order to delineate the limits of the S$_N$1-B and S$_N$2-B mechanisms and detect resonance effects. Table II presents kinetic data collected in o-dichlorobenzene solvent at 30.0°. Since the reaction of the 2,4,6-trimethylphenylborane system was too rapid to measure at 30.0° using the initial rate method, a series of pseudo-first-order rate runs were made with varying excesses of (n-Bu)$_3$P. These reactions were followed to approximately 80% completion and the pseudo-first-order rate constant was evaluated. The component first- and second-order rate constants listed in Table II were then obtained from a least-squares plot of the pseudo-first-order rate constants vs. [(n-Bu)$_3$P]$_0$. In each case a second-order term was observed (eq 3) which was not greatly sensitive to substituent unless the substituent occupied at least one position ortho to the position occupied by the Me$_3$-N$^+$-BH$_2^-$ reaction center. In the latter cases, o-CH$_3$- and 2,4,6-trimethyl-substituted trimethylamine–phenylboranes, an enhancement of the second-order rate con-

Table V. Solvent Effects in S$_N$-B Reactions of Trimethylamine–sec-Butylborane with (n-Bu)$_3$P at 29.5°

Solvent	Dielectric constant, 25°	$k_1 \times 10^5$, sec^{-1}	$k_2 \times 10^4$, 1. mol^{-1} sec^{-1}
Undecane	2.01	3.00 ± 0.15	4.58 ± 0.02
o-Chlorotoluene	4.73	0.39 ± 0.02	0.567 ± 0.01
o-Dichlorobenzene	9.93	0.19 ± 0.01	0.365 ± 0.005

(9) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.
(10) See footnote 2 of ref 2 for pertinent discussion.
(11) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

Table VII. Characterization Data for Tri-*n*-butylphosphine-Arylboranes

Aryl group	Yield, %	Mp,[a] °C	Analysis, %					
			Calcd			Found		
			C	H	B	C	H	B
Phenyl	72 (75)[b]	47–48	73.97	11.72	3.70	74.08	11.97	3.79
p-Bromophenyl	71	39–40	58.25	8.96	2.92	58.51	9.22	3.00
p-Anisyl	62	37–38	70.81	11.26	3.36	71.11	11.26	3.46
p-Tolyl	85	43–45	74.50	11.85	3.53	74.20	11.55	3.40
o-Tolyl	60	c	74.50	11.85	3.53	74.25	11.85	3.45
Mesityl	62	51–52	75.44	12.06	3.24	75.32	12.09	3.14

[a] Uncorrected. [b] Obtained by reduction of boroxine (see text). [c] Liquid, bp 55° (10⁻⁴ mm).

stant was observed. In the typical case of S_N2 attack at benzylic carbon, a similar small, and often erratic, scatter in second-order rate constants was observed with meta and para substituents.[12] In the cases of the *o*-CH₃- and 2,4,6-trimethyl-substituted trimethylamine–phenylboranes, a 4.4-fold acceleration in second-order rate is seen in the former case while a 47-fold acceleration of second-order rate is observed in the latter. While these numerical values are not astounding, they do represent a trend which suggests that steric crowding in the substrate contributes to the instability of the B–N bond and produces an acceleration of rate in an S_N2-B process.

In two systems *p*-CH₃O- and 2,4,6-trimethyl-substituted trimethylamine–phenylboranes, a first-order kinetic term was observed which was superimposed upon the second-order term (eq 3). While small first-order rate contributions may be present in the other systems investigated, they were not detected within our limits of experimental error. In the *p*-CH₃O-substituted case the first-order kinetic term most likely becomes significant owing to electronic stabilization of the electron-deficient borane formed through dissociation of trimethylamine. The first-order kinetic term seen in the 2,4,6-trimethyl-substituted system probably arises from the similar electronic stabilization afforded the borane by the three methyl substituents. In addition, the relatively large first-order contribution to rate seen in this case may be attributed to greatly increased steric crowding at the reaction site owing to the presence of two ortho substituents, as commonly observed in the reactions of mesityl systems having carbon reaction centers.[13–15]

Product Analyses. Each of the isomeric trimethylamine–butylboranes was heated with an equimolar quantity of (*n*-Bu)₃P in benzene solution and the liberated amine titrated with standard acid using the flow system apparatus.[2] Amine recoveries varied from 97 to 104%. Benzene was employed as the reaction solvent in order to simplify the recovery of the (*n*-Bu)₃P⁺–BH₂(Bu)⁻ products by distillation of solvent at low pressures. In all cases the reaction products were air-sensitive high-boiling viscous liquids which could not be purified without some decomposition. The infrared spectrum obtained for each crude product contained B–H stretching absorptions near 2300 cm⁻¹ and differed markedly from the infrared and ¹¹B nmr spectra of the

corresponding Me₃N⁺–BH₂(Bu)⁻ starting materials. Attempts to interpret the 60-MHz ¹H nmr spectra of the crude reaction products were not rewarding, although each product gave a unique spectrum. However, in one case the crude product was shown to be essentially identical with authentic (*n*-Bu)₃P⁺–BH₂(*tert*-Bu)⁻. The authentic material was prepared by the lithium aluminum hydride reduction of the corresponding trialkylboroxine in the presence of (*n*-Bu)₃P.

The products formed from the reaction of tri-*n*-butylphosphine with Me₃N⁺–BH₂(aryl)⁻ substrates were prepared under kinetic conditions using benzene as the reaction solvent. In every case, crystalline products were isolated in high yield and identified as the proper (*n*-Bu)₃P⁺–BH₂(aryl)⁻ product by elemental analyses and the presence of B–H stretching bands in their infrared spectra. Table VII records the properties and characterization data obtained for these compounds. In the single case of tri-*n*-butylphosphine–phenylborane, the phosphine adduct was also obtained by reduction of diethyl phenylboronate with lithium aluminum hydride in the presence of 1 equiv of tri-*n*-butylphosphine. The product obtained was identical with that formed in the amine displacement reaction.

Conclusions. The results presented above strongly support the existence of S_N1-B and S_N2-B reaction mechanisms which appear in many cases to be simultaneous processes. This conclusion is supported by (i) observed reaction orders, (ii) deuterium secondary kinetic isotope effects which appear, unsurprisingly, to resemble those observed in analogous carbon-center reactions, (iii) a Taft equation correlation of the first-order terms observed with the isomeric trimethylamine–butylborane substrates, (iv) the effect of nucleophile identity upon observed first- and second-order kinetic terms, (v) thermodynamic activation parameters, and (vi) substituent effects in the trimethylamine–arylborane series.

The relative reactivities of the trimethylamine–butylboranes deserves special comment. Comparison of the relative k_1 and k_2 values obtained for this series of reactions shows no outstanding change in k_2 in progressing from Me₃N⁺–BH₃⁻ through the series I–III inclusive. In the case of IV, no definitely detectable k_2 is observed, while the greatest second-order reactivity was exhibited by III. These results coupled with the data obtained with the ortho-substituted phenylborane systems suggest that the relief of steric compression energies provides some driving force for formation of the S_N2-B transition state. The very hindered substrate IV is, of course, analogous to the neopentyl carbon system which is known[15] to be normally slow in normal S_N2 reactions. In the case of the k_1 values observed in both

(12) *E.g.*, J. W. Baker, *J. Chem. Soc.*, 1128 (1933), reports a typical insensitivity to meta and para substitution in the reactions of substituted benzyl bromides with pyridine in acetone solution at 30.5°.

(13) G. Baddely and J. Chadwick, *J. Chem. Soc.*, 368 (1951).

(14) W. T. Nauta and J. W. Dienske, *Recl. Trav. Chim. Pays-Bas*, 55, 1000 (1936).

(15) E. L. Eliel in ref 9, Chapter 2.

the I–IV series and the trimethylamine–arylborane series, the substrates which have obviously high steric requirements exhibit the largest k_1 values. The p-methoxyphenylborane system remains as the only clear case in which electronic stabilization of the borane intermediate appears to present a detectable first-order kinetic expression owing to electron release from the para substituent.

In the following paper of this series the consequences of SN1-B transition-state stabilization by electron-releasing para substituents is demonstrated with methylamine–diarylborane substrates and primary amine nucleophiles.

Experimental Section

Materials. o-Dichlorobenzene, o-chlorotoluene, and n-undecane were obtained from Matheson Coleman and Bell and purified by distillation from calcium hydride. Tri-n-butylphosphine was purified by distillation with a spinning-band column under nitrogen, bp 130° (23 mm), and stored under nitrogen. The 2,2-diphenylethylamine was purified by distillation under high vacuum, mp 48–49°, and stored under nitrogen.

Trimethylamine–Butylboranes I, II, III, and IV. The isomeric substrates I, II, III, and IV were prepared as previously described[4] and distilled at 10^{-3} mm using a Hickman molecular still immediately before use. Precautions were taken to prevent the exposure of these materials to air.

Trimethylamine–sec-Butylborane-d_2 (α-III-d_2). This substrate was prepared using the normal procedure[4] except that 98% LiAlD$_4$ was substituted for LiAlH$_4$ in the reduction step. The infrared spectrum of the product contained no band associated with a B–H stretching mode.

Trimethylamine–sec-Butylborane-d_1 (β-III-d). The normal procedure was employed in the preparation of this compound except that 2-bromobutane-2-d^6 was employed in the preparation of the boroxine starting material.

Trimethylamine–Arylboranes. The trimethylamine–arylboranes were prepared by the LiAlH$_4$ reduction of the corresponding diethyl arylboronate esters using a procedure previously described[7] for the preparation of trimethylamine–phenylborane. The 2,4,6-trimethylphenyl derivative was obtained from the corresponding diethyl arylboronate which was prepared from mesityleneboronic acid[16] by the usual procedure.[4] Table I presents the yield and characterization data pertinent to the trimethylamine–arylboranes.

Kinetic Procedure. All kinetic runs were carried out in thermistor-controlled thermostats using the "flow method" described in the previous paper of this series.[2] Reactions were followed to approximately 10% completion and instantaneous rates evaluated from the slope of reaction $vs.$ time.[2] In the case of trimethylamine–2,4,6-trimethylphenylborane, the initial reaction rates were too rapid to follow using the instantaneous rate method. Consequently, these reactions were followed to 80% completion under pseudo-first-order conditions (excess (n-Bu)$_3$P) and the observed pseudo-first-order rate constants plotted against [(n-Bu)$_3$P]$_0$. Least-squares analysis produced the reported k_1 and k_2 (Table II) values using 14 data points. All other data collected in Table II were fit to eq 3 by a least-squares computer program.

Product Analysis. Tri-n-butylphosphine–Butylboranes. Each of the isomeric trimethylamine–butylboranes was examined for total available trimethylamine as follows. Approximately 3 mmol (0.4 g) of the amine–borane was accurately weighed and dissolved in 50 ml of dry benzene. Approximately 3 mmol of pure tri-n-butylphosphine (0.6 g) was added to the amine–borane solution after the latter had been placed in the flow apparatus.[2] The reaction mixtures were thermostated at 49.8° and a slow stream of dry nitrogen was passed through the apparatus. Trimethylamine evolution was followed by titration with 0.10 N aqueous acid until

(16) M. F. Hawthorne, *J. Org. Chem.*, **23**, 1579 (1958).

acid ceased to be consumed. Amine recoveries varied from 97 to 104% of theory.

Following the liberation of amine, each of the reaction product solutions was pumped to remove benzene on a conventional vacuum line with care being taken to exclude air and moisture. The resulting oils were weighed and yields of 92–104% of theory were obtained. Attempted molecular distillation of the isolated oils at 45° in a Hickman still at 10^{-4} mm led to slow decomposition and the resulting distillates were judged to be impure. Infrared spectra were obtained for each of the crude products and they differed from one another, but each contained strong B–H stretching bands at 2200–2350 cm^{-1}. Proton nmr spectra (60 MHz) revealed differences between the isomeric products, but were complicated by the phosphine moiety. Examination of the ^{11}B (19.3 MHz) nmr spectra of the crude products revealed broad singlets, while the ^{11}B nmr spectra of the amine–borane starting materials were clear triplets. Table VIII records the ^{11}B nmr data obtained. In each

Table VIII. Position of ^{11}B Nmr Absorption for the Butylamine– and Phosphine–Boranes

R	RBH$_2^-$–NMe$_3^+$ ^{a}	RBH$_2^-$–PBu$_3^+$ ^{a}
Isobutyl	10.6	23.9
$tert$-Butyl	15.2	43.8
sec-Butyl	16.4	45.2
n-Butyl	20.5	48.4

^{a} δ of envelope center in ppm relative to trimethyl borate.

case a marked upfield shift of the ^{11}B nmr envelope is observed following tri-n-butylphosphine substitution.

In the single case of trimethylamine–$tert$-butylborane, it was possible to prepare and purify and authentic sample of the corresponding (n-Bu)$_3$P complex. This was accomplished by carrying out the reduction of $tert$-butylboroxine[4] in the presence of 3 mol equiv of tri-n-butylphosphine. The normal work-up procedure was employed and the oily product (37% crude yield on a 0.10-mol scale) was distilled using a Hickman still at 10^{-4} mm and 45°. A middle fraction was isolated for elemental analyses and for comparison with the corresponding crude product obtained from the direct displacement reaction. *Anal.* Calcd for C$_{16}$H$_{38}$PB: C, 70.70; H, 13.96; P, 11.40; B, 3.97. Found: C, 70.58; H, 14.30; P, 11.75; B, 4.16. The ^{1}H, ^{11}B, and infrared spectra of this product were identical with the corresponding spectra of the displacement reaction product.

Product Analyses. Tri-n-butylphosphine–Arylboranes. Tri-n-butylphosphine–arylboranes were prepared by direct displacement of trimethylamine by tri-n-butylphosphine. Yield and characterization data appear in Table VII. The procedure employed in all cases is described for the preparation of tri-n-butylphosphine–phenylborane. Trimethylamine–phenylborane (3.0 g, 20 mmol) was dissolved in 25 ml of dry o-dichlorobenzene and placed in the "flow apparatus." Tri-n-butylphosphine (4.0 g, 20 mmol) was added through the side arm of the reaction vessel after the apparatus had been purged with nitrogen. The reaction was maintained at 75° for 24 hr, during which time a slow stream of nitrogen was continuously passed through the system to remove amine. The reaction mixture was then attached to a vacuum system and the o-dichlorobenzene removed by a short-path distillation at 50°. The crystalline residue was recrystallized from diethyl ether–pentane at −78° to give 4.2 g (72%) of product, mp 45–46°. An identical product was obtained through the reduction of 0.05 mol of diethyl phenylboronate in the presence of 0.05 mol of tri-n-butylphosphine. The previously described procedure[7] was followed, except no amine was present in the reaction mixture. The product was obtained in 75% yield, mp 44–47°, after recrystallization from diethyl ether–pentane at −78°.