wax at 160° was used for the naphthalene analyses and a 2-ft × 0.25-in. column of 10% Carbowax was used for the anthracene–dihydroanthracene analyses.

Kinetic Procedures. A typical kinetic experiment was carried out as follows. THF (89.9 g, 102 ml) was distilled from the sodium benzophenone ketyl under argon into the radical anion generating flask. The solvent was distilled directly onto a piece of freshly cut sodium (~0.5 g, 21.7 mg-atoms) and a glass-covered magnetic stirring bar. At the end of the distillation, the flask was removed from the still and naphthalene (81.3 mg, 0.635 mmol) was added. The flask was resealed and stirred for several hours. The concentration of this stock solution was determined to be 0.0176 *M* from the absorbance at 365 nm.

The water and anthracene stock solution was prepared from 0.1697 g (0.954 mmol) of anthracene, 30.0 μl of water, and 78 ml (68.6 g) of THF. The water concentration determined by Karl–Fischer titration was 0.0357 *M*.

The stopped-flow apparatus, which was thermostated at 20°, was prepared for kinetic runs by flushing the entire apparatus successively twice with pure THF and a relatively concentrated (~0.3–0.5 *M*) solution of sodium naphthalene in THF. Stock solutions were transferred to the stopped-flow apparatus by gas tight syringes. After several flushes with the stock solutions in the respective chambers, the oscilloscope traces of four kinetic runs at 365 nm were recorded. The reaction products were collected at the exit port in aqueous ammonium chloride. Gas chromatographic analysis revealed that the products were anthracene and 9,10-dihydroanthracene.

In addition to the kinetic trace on the oscilloscope, reference lines for ground and the maximum output of the phototube were recorded. The oscilloscope screen was photographed and the intensities at various times were determined. The remainder of the calculations was done by a computer program which converted the intensities to absorbance and plotted ln A_t *vs.* time to obtain the slope by the method of least squares.

Acknowledgment. We acknowledge with gratitude support of this work by the National Science Foundation. We are grateful for the able assistance of Miss Bette Puls in obtaining the infrared spectra of the water–ether solutions.

Measurement of the Kinetics and Activation Parameters for the Hydroboration of Tetramethylethylene and Measurement of Isotope Effects in the Hydroboration of Alkenes[1,2]

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Abstract: The kinetics of the hydroboration of tetramethylethylene (TME) with borane in tetrahydrofuran (THF) have been studied. The rate of formation of 2,3-dimethyl-2-butylborane is found to be first order in both borane and TME. The activation energy and entropy for the reaction are 9.2 ± 0.4 kcal/mol and −27 ± 1 eu. The hydrogen–deuterium kinetic isotope effect is found to be 1.18. The reaction is considered to involve the direct reaction between a molecule of the borane–THF complex and alkene in a very early transition state. The $^1H/^3H$ isotope effects in the hydroboration of various alkenes with borane and selected mono- and dialkylboranes have been measured. The $k_{^1H}/k_{^3H}$ decreases markedly as the degree of substitution on the double bond increases: monosubstituted alkenes, 10.0–11.3 (calculated on the basis of no hydrogen exchange between borane species); disubstituted alkenes, 8.7–9.0; trisubstituted alkenes, 4.2–4.3; and TME, ~3.3. Similarly, $k_{^1H}/k_{^3H}$ decreases as the degree of substitution on boron increases. The $k_{^{10}B}/k_{^{11}B}$ isotope effect in the hydroboration of various substituted alkenes with borane increases only slightly with increasing substitution on the double bond (1.03 to 1.05).

Despite the great synthetic utility and wide applicability of the hydroboration reaction, many of the intimate details of the mechanism of the reaction have not been investigated. The relatively slow reaction of diborane with simple alkenes in the gas phase to produce trialkylboranes was discovered by Hurd in 1948.[3] In a kinetic study of the gas phase reaction of diborane with ethylene, Whatley and Pease[4] observed that the rate of reaction followed the kinetic expression $-dp/dt = k[B_2H_6]^{3/2}/(1 - 2.0[B_2H_6]/[C_2H_4])$, and proposed the following sequence of steps to account for the observed kinetics.

$$B_2H_6 \rightleftharpoons 2BH_3$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9$$

$$B_3H_9 + C_2H_4 \longrightarrow B_2H_5C_2H_5 + BH_3$$

More recently, Fehlner[5] has studied the gas phase reaction of borane, derived by the pyrolysis of borane–trifluorophosphine, with ethylene. The rate of reaction to form ethylborane (~2 × 10^9 l. mol^{-1} sec^{-1}) is approximately 10^3 faster than the reaction of diborane with ethylene, and is first order in both borane and ethylene,[6] the absolute rate constant being given by the expression

$$\text{rate} = 10^{10.2} \exp\{-2000/RT\} \text{ l. mol}^{-1} \text{ sec}^{-1}$$

The hydroboration of alkenes in diglyme solution was

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(1) Part XXIV of a series on Transfer Reactions Involving Boron; for part XXIII, see D. J. Pasto and P. W. Wojtkowski, *J. Organometal. Chem.*, **34**, 251 (1972).

(2) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (Grant No. 1225, A1,3), and to the National Institutes of Health for partial support (Grant No. CA-07194).

(3) D. T. Hurd, *J. Amer. Chem. Soc.*, **70**, 2053 (1948).

(4) A. T. Whatley and R. N. Pease, *ibid.*, **76**, 835 (1954).

(5) T. P. Fehlner, *ibid.*, **93**, 6366 (1971).

(6) This observation is not consistent with the observation and mechanistic scheme proposed by Whatley and Pease[4] in that borane, if present, would be expected to react faster with ethylene than the other borane species.

first discovered in 1956 by Brown and Rao.[7] The reaction in the presence of the donor solvent was observed to be greatly enhanced over the rate of reaction of diborane with alkenes in the gas phase. From a study of the stereochemistry of the hydroboration of substituted cycloalkenes and styrenes, Brown and Zweifel proposed that the reaction occurs *via* a four-centered transition state,[8] and that the direction of approach to the double bond[9] and the regiospecificity are strongly controlled by steric and electronic factors.[8,9] Brown and Sharp[10] have reported that the log (terminal/internal product ratios) derived in the hydroboration of substituted styrenes in diglyme correlates with σ^+ with $\rho = -0.7$. The relative reactivities of a number of alkenes toward hydroboration with borane in diglyme have been determined relative to 1-hexene and cyclopentene.[11] Although many of the relative reactivities are nearly the same, several alkenes exhibit considerably different reactivities relative to the two standard alkenes.

Klein and coworkers[12] have studied the kinetics of the hydroboration of substituted styrenes in THF carried out under pseudo-first-order conditions in the presence of a great excess of borane.[13] They report that no single Hammett correlation satisfactorily correlated all of the data, but that plots of log k/k_0 *vs.* σ for attack by boron at the α position of the meta- and para-substituted styrenes and at the β position of the meta-substituted styrenes produced linear correlations with ρ of 0.5, 1.2, and -0.5, respectively, but that no reasonable correlation was evident with log k/k_0 for attack at the β position in the para-substituted styrenes.[14] The kinetic dependence on borane, or diborane, concentration could not be evaluated from the results obtained from this study due to the pseudo-first-order conditions of the experiments.

The kinetics of the hydroboration of alkenes with bis-3-methyl-2-butylborane (disiamylborane) and monochloroborane have been studied. Brown and Moerikofer[15] have studied the reaction of disiamylborane with alkenes and have shown that the rate of reaction is first order in disiamylborane dimer. Pasto and Kang[16] have shown that the reaction of monochloroborane with alkenes is first order in monochloroborane. In the reaction of monochloroborane with substituted styrenes the log (terminal/internal product ratio) correlates with σ with a ρ of -0.65. The kinetic hydrogen–deuterium isotope effect (k_H/k_D) for the addition to styrene was observed to be 1.90.[16]

More detailed studies on the reaction of borane with alkenes have not been carried out, apparently because of the rapid rate of reaction and the complications arising from monomer–dimer equilibria and redistribution reactions. The overall reaction of borane with an alkene is very complex, involving three consecutive addition reactions (eq 1–3), three redistribution equilibria (eq 4–6), and five monomer–dimer equilibria (eq 7–11).[17] In a previous investigation in our laboratories the redistribution and monomer–dimer equilibrium constants for the *n*-propyl and isopropyl systems (R = *n*-C_3H_7 and *i*-C_3H_7, respectively, in eq 4–11) were determined at 25 and 40°.[17]

Addition reactions are

$$\text{alkene} + BH_3 \xrightarrow{k_1} RBH_2 \tag{1}$$

$$\text{alkene} + RBH_2 \xrightarrow{k_2} R_2BH \tag{2}$$

$$\text{alkene} + R_2BH \xrightarrow{k_3} R_3B \tag{3}$$

Redistribution reactions are

$$BH_3 + R_3B \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R_2BH + RBH_2 \tag{4}$$

$$2RBH_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} R_2BH + BH_3 \tag{5}$$

$$2R_2BH \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} RBH_2 + R_3B \tag{6}$$

Monomer–dimer equilibria are

$$BH_3 + RBH_2 \rightleftharpoons H_2BH_2BHR \tag{7}$$

$$BH_3 + R_2BH \rightleftharpoons H_2BH_2BR_2 \tag{8}$$

$$2RBH_2 \rightleftharpoons RHBH_2BHR \tag{9}$$

$$RBH_2 + R_2BH \rightleftharpoons R_2BH_2BHR \tag{10}$$

$$2R_2BH \rightleftharpoons R_2BH_2BR_2 \tag{11}$$

The present article describes the results of kinetic studies on the hydroboration of tetramethylethylene (TME), and the measurement of the kinetic hydrogen–deuterium isotope effect in the hydroboration of TME, and the measurement of the hydrogen–tritium and ^{10}boron–^{11}boron isotope effects in the hydroboration of a number of alkenes with borane and selected mono- and dialkylboranes. The accompanying article[18] describes the determination of the $k_2{:}k_1$ ratios and the determination of the rate constants of the redistribution reactions.

Results

Measurement of the Kinetics of the Hydroboration of Tetramethylethylene (TME). The previous kinetic investigation of the solution phase hydroboration of substituted styrenes[12] was carried out under pseudo-first-order conditions and did not yield sufficiently accurate data to allow assignment of the kinetic dependence of borane, or diborane, on the rate of the reaction. The rate of reaction of the styrenes was followed by

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(7) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **78**, 2582, 5694 (1956).

(8) H. C. Brown and G. Zweifel, *ibid.*, 81, 247 (1959).

(9) H. C. Brown and G. Zweifel, *ibid.*, 82, 4708 (1960).

(10) H. C. Brown and R. L. Sharp, *ibid.*, **88**, 5851 (1966).

(11) H. C. Brown and A. W. Moerikofer, *ibid.*, **85**, 2063 (1963).

(12) J. Klein, E. Dunkelblum, and M. A. Wolff, *J. Organometal. Chem.*, 7, 377 (1967).

(13) The authors rule out the possibility of di- and trialkylborane formation because of the great excess of borane present during the reaction. However, no experimental confirmation of this assumption was made.

(14) It is somewhat surprising that the linear free-energy correlations reported by Brown and Sharp[10] and by Klein and coworkers[12] should be so distinctly different, although different reaction conditions were employed and only relatively few substituted styrenes were used in each of the studies. Brown and Sharp[10] employed the *in situ* generation of borane in diglyme under conditions where di- and trialkylborane formaition would be expected to be favored. In contrast, Klein and coworkers[12] used prepared solutions of borane in THF. The correlations of Klein and coworkers[12] are based on only the *m*- and *p*-chloro- and methoxystyrenes (in addition to styrene), whereas the correlation of Brown and Sharp[10] is based on data derived with the *m*- and *p*-chloro-, methoxy-, trifluoromethyl-, and *m*-nitrostyrenes. Significant differences in the reported product distribution ratios are also evident.

(15) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **83**, 3417 (1961).

(16) D. J. Pasto and S.-Z. Kang, *ibid.*, 90, 3797 (1969).

(17) D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, **8**, 594 (1969).

(18) D. J. Pasto, B. Lepeska, and V. Balasubramaniyan, *J. Amer. Chem. Soc.*, **94**, 6090 (1972).

spectrophotometric techniques which essentially precluded the running of reactions in which borane and the styrenes were present in comparable concentrations.

In order to circumvent these problems we have constructed a fast-flow quenching kinetic apparatus (see Experimental Section for the details of the apparatus) which allows us to carry out kinetic studies using comparable concentrations (0.2–0.6 *M* initial concentrations) of borane and alkene. In order for this technique to be applicable, a suitable quenching reagent had to be found which would quench the reaction of borane with the alkene as well as quench any further reaction of mono- and dialkylborane with alkene such that a suitable analytical procedure could be carried out on the quenched reaction mixture to determine the amount of unreacted alkene, as well as the extent of formation of mono- and dialkylborane. Solutions of an alkene and an inert internal standard (for glpc analysis) in tetrahydrofuran (THF) were rapidly mixed with a solution of borane in THF and allowed to stir for a very short period of time. A solution of a quenching reagent in THF was then added and the "quenched" reaction mixture was periodically analyzed by glpc and ^{11}B nmr spectroscopy. Reaction mixtures derived with alkenes capable of reacting to form dialkylboranes could not be successfully quenched with triethylamine (TEA) or diazabicyclooctane (Dabco). These quenching reagents successfully quenched the reaction of borane with the alkene, but did not quench the subsequent reaction of the monoalkylboranes with alkene. These latter reactions were considerably slowed down but not to the extent necessary to affect suitable quantitative analyses as indicated above. Attempts to monitor the reactions of mono-, di-, and trisubstituted alkenes with borane, which lead to the formation of di- and trialkylboranes, were temporarily suspended, and our attention was turned to studies of alkenes capable of reacting with borane to form only monoalkylboranes.

The reaction of tetramethylethylene (TME) with borane proved to be eminently suitable for these studies. The reaction of TME with borane proceeds effectively only to the monoalkylborane stage,[19] and is completely quenched by TEA or Dabco. In THF solution the 2,3-dimethyl-2-butylborane (thexylborane) exists only in the self-hydrogen-bridged dimeric form (eq 9).[20] No evidence was obtained (^{11}B nmr) indicating that the product enters into dimer formation with borane (eq 7).[21] Standardized solutions of TME and an internal standard (either methylcyclohexane or toluene) and borane in THF were rapidly mixed and quenched using the fast-flow quenching kinetic apparatus. The quenched reaction mixtures were analyzed directly by glpc; the olefin:internal standard area ratios were corrected to weight ratios by the use of predetermined response ratios. The concentration *vs.* time data were analyzed by computer techniques. Excellent linear plots were obtained using a second-order kinetic expression, with first order in both borane and TME (see Figure 1). Analysis of the data using other kinetic expressions, such as second order in borane (or first order in diborane, B_2H_6) and three-halves order in diborane (as suggested by Klein and Dunkelblum for the reduction of ketones with borane[22]) produced substantially nonlinear plots. The initial borane:TME ratio was varied over a fourfold range, producing the same second-order rate constants within experimental error (see Table I). The second-order rate constants were determined at 10, 25, 35, and 40° and the activation parameters E_a and $\Delta S^{\ddagger}$ were calculated to be 9.2 ± 0.4 kcal/mol and -27 ± 1 eu, respectively. The rate of reaction with perdeuterioborane was similarly measured, giving a value for k_1 = 1.26 l. mol^{-1} sec^{-1} (at 25°).

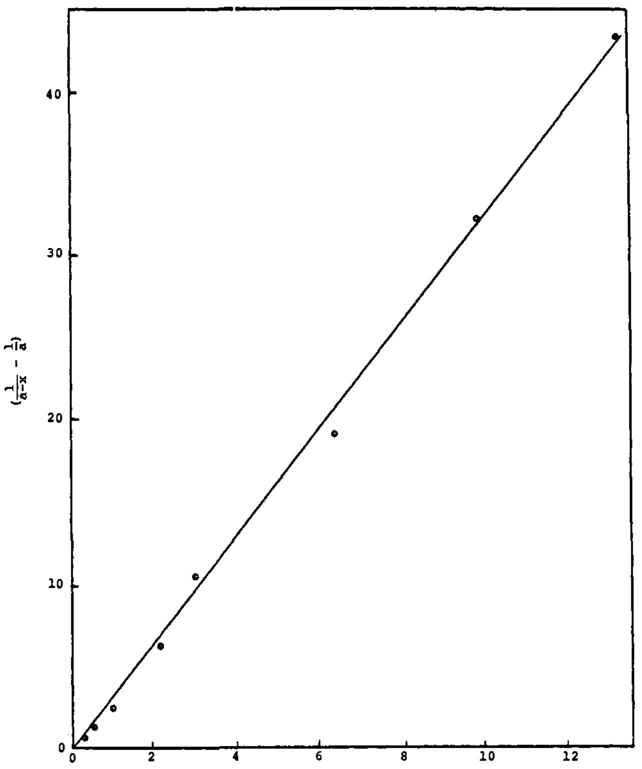

Figure 1. Second-order plot of the reaction of TME (0.350 *M*) with BH_3 (0.350 *M*) in THF at 40°.

Table I. Rate Constants for the Hydroboration of TME in THF

[TME], *M*	$[BH_3]$, *M*	Temp, °C	*k*, l. mol^{-1} sec^{-1}
0.355	0.355	10	0.667
0.354	0.362	25	1.48
0.353	0.364	35	2.08
0.350	0.351	40	3.23
0.353	0.173	25	1.63
0.354	0.357	25	1.45
0.353	0.580	25	1.75

Measurement of the Kinetic Isotope Effects. Hydrogen–Tritium Isotope Effects. Tritium-labeled borane in THF was prepared from tritium-labeled lithium alu-

(19) H. C. Brown and A. W. Moerikofer (*J. Amer. Chem. Soc.*, **84**, 1478 (1962)) have reported that reaction of borane with TME leads rapidly to the formation of the monoalkylborane (determined by monitoring the unreacted TME by glpc), and that over considerably longer periods of time dialkylborane is formed. Under the very short reaction times involved in the present kinetic experiments only monoalkylborane is formed (*vide infra*).

(20) In contrast, H. C. Brown and G. J. Klender (*Inorg. Chem.*, **1**, 204 (1962)) report that 2,3-dimethyl-2-butylborane reacts reversibly with borane in diglyme to form a monoalkyldiborane (by equilibrium absorption and ir measurements).

(21) The sensitivity of ^{11}B analysis is estimated to be ±5%, thus placing an upper limit of ~5% for the concentration of monoalkyldiborane in solution.

(22) J. Klein and E. Dunkelblum, *Tetrahedron*, **23**, 205 (1967).

minum hydride and boron trifluoride in diglyme, the labeled diborane being bubbled into THF in a stream of nitrogen. The [^{3}H]borane concentration was determined by hydrolysis of aliquots of the solution and measurement of the volume of hydrogen evolved. The tritium content was determined by treating an aliquot of the [^{3}H]borane solution with a large excess of 1-hexene, the resulting reaction mixture being subjected to oxidation, the hexanol fraction isolated and purified, and the tritium content determined by standard counting procedures.

The hydrogen–tritium isotope effects for the hydroboration of a number of mono-, di-, tri-, and tetrasubstituted alkenes were determined in the following manner. Aliquots of the standardized [^{3}H]borane solution were rapidly mixed with weighed portions of the alkenes dissolved in THF (molar ratio of [^{3}H]borane to alkene of 1.0:0.3). The reaction mixtures were allowed to stir at room temperature for a sufficient period of time to ensure completion of the addition reaction (determined in control experiments by glpc analysis of the reacting mixtures). The reaction mixtures were subjected to oxidation and hydrolysis, and the alcohols were isolated and purified by distillation or preparative glpc. The tritium content of the alcohols was measured by standard counting techniques. The $k_{^1\mathrm{H}}/k_{^3\mathrm{H}}$ values were calculated using the equation

$$k_{^1\mathrm{H}}/k_{^3\mathrm{H}} = 1/[\log (1 - fr)/\log (1 - r)]^{23}$$

where r is the alkene–borane ratio and f is the fraction of the tritium incorporated in the product alcohol.

The calculation of the isotope effects is complicated by the possible presence of hydrogen exchange reactions between alkylborane and unreacted [^{3}H]borane. If the exchange rate is considerably slower than the rate of hydroboration, the [^{3}H]borane contained in the alkylborane does not exchange with the unreacted borane and the calculation of the isotope by the above equation is valid. However, if the rate of hydrogen exchange is faster than the rate of hydroboration, due to the greater reactivity of [^{1}H]borane relative to [^{3}H]borane, the tritium content of the unreacted borane will increase faster than expected from the operation of an isotope effect under nonexchanging conditions, and the isotope effect will represent an integrated isotope effect over the course of the reaction. Isotope effects were calculated on the basis of no exchange and complete exchange, assuming the equivalency of all B–H's in the initial system. The kinetic isotope effects thus calculated represent extreme values, the real isotope effect under exchanging conditions being intermediate in value. Fortunately, the extremes of the ranges of the isotope effects in the hydroboration of mono-, di-, tri-, and tetrasubstituted alkenes are relatively narrow and do not overlap, and thus present a distinct trend in the isotope effects with the degree of substitution on the double bond (see Table II).

Table II. Hydrogen–Tritium Isotope Effects in the Hydroboration of Alkenes in an Approximate 1.0:0.3 Borane–Alkene Ratio

Alkene	Hydroborating agent	$k_{^1\mathrm{H}}/k_{^3\mathrm{H}}$ No exchange	$k_{^1\mathrm{H}}/k_{^3\mathrm{H}}$ With exchange
Monosubstituted alkenes			
1-Hexene	BH_2	10.85	9.59
		11.29[a]	10.00[a]
Styrene (terminal	BH_3	10.44	9.09
(internal)		10.35	9.00
Disubstituted alkenes			
3-Hexene	BH_3	8.73	6.92
2-Octene[b]	BH_3	8.89	7.38
2-Ethyl-1-hexene	BH_3	8.99	7.47
Propenylbenzene[b]	BH_3	9.01	7.24
Trisubstituted alkenes			
2-Methyl-2-butene	BH_3	4.22	3.55
		4.36[a]	3.72[a]
Tetrasubstituted alkenes			
TME	BH_3	3.43	2.91
		3.27[c]	

[a] Duplicate run. [b] Isomeric product alcohols were not separated before counting. [c] Alkene–borane ratio of 1.0:1.0.

A second complicating factor in the calculation of the isotope effects is the formation of dialkylboranes in addition to the formation of monoalkylborane.[24] Even using a borane–alkene ratio of 1.0:0.3, 50–70% of dialkylborane was formed in the reactions with 2-ethyl-1-hexene, 2-octene, 3-hexene, and 2-methyl-2-butene (see the accompanying article for the quantitative determination of the ratios of $k_2:k_1$[15]). Thus in these cases the calculated isotope effects represent the averaging of 30–40% of the isotope effect for the second addition step (eq 2) in with the isotope effect for the first step (eq 1). In the case of 1-hexene, styrene, and propenylbenzene, only 20–30% of dialkylborane was formed, leading to a contribution of approximately 17–22% of the isotope effect for the second step to the isotope effect for the first step. The contribution of the isotope effect for the second step in the above calculations of the isotope effect for the first step leads to a slight reduction in the value of the isotope effect for the first step. An example of this effect is illustrated with 2-methyl-2-butene which, on hydroboration in a 1.0:0.3 mole ratio, gives an isotope effect for the first step of 4.22–4.36, whereas the isotope effect derived when using a 1.0:2.0 mole ratio is calculated to be 3.01–3.25. In contrast, the hydroboration of TME, which proceeds only to the monoalkylborane stage, employing 1.0:0.3 and 1.0:1.0 mole ratios of borane to alkene, gave isotope effects of 3.43 and 3.27, respectively.

^{10}B/^{11}B Isotope Effects. The ^{10}B–^{11}B isotope effects were determined using borane of normal isotopic distribution by measuring the change in the ^{10}B–^{11}B isotope abundance ratio on partial reaction of borane with an alkene. An aliquot of a standardized THF solution of borane was hydrolyzed and the boric acid was isolated by evaporation of the solvent. A second aliquot was treated with the appropriate alkene (borane–alkene ratio of approximately 1.0:0.25) and then quenched with methanol after completion of the hydroboration reaction. The quenched reaction mixture was subjected to distillation until ~80% of the volume had been distilled. The resulting distillate, containing THF, methanol, and trimethyl borate, was treated with water and then evaporated to dryness, leaving a residue of boric acid. The samples of boric acid were recrystallized twice from water and were air-dried. The ^{10}B–^{11}B isotope ratios in the samples of boric acid were

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(23) L. C. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

(24) See ref 18 and H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Amer. Chem. Soc.*, 82, 4703 (1960).

determined by mass spectral techniques using an AEI MS-9 mass spectrometer. The samples of boric acid were placed in a quartz crucible and placed directly into the ionization chamber *via* the direct injection probe. The slits were adjusted and the instrument was focused to give broad, flat-topped peaks for the parent ions of $^{10}B(OH)_3$ and $^{11}B(OH)_3$ at *m/e* 61 and 62, respectively. (The high resolution mass spectrum of boric acid indicated a negligible contribution of the P − 1 peak of $^{11}B(OH)_3$ at *m/e* 61.) The *m/e* 61 and 62 peaks were superposed by peak-matching techniques and the intensities of the two peaks were alternately measured with a digital voltmeter by manually switching back and forth between the high and low mass channels. An average of 40–50 sets of intensity ratios was measured for each sample. The intensity ratios were averaged and refined by rejection of ratios whose deviation from the average exceeded twice the root-mean-square deviation. Boric acid samples from the unreacted and reacted borane were run consecutively (within 15 min) under identical instrumental conditions. The $k_{^{10}B}/k_{^{11}B}$ values were calculated using the equation

$$k_{^{10}B}/k_{^{11}B} = (\log {}^{10}a/{}^{10}a_0)/(\log {}^{11}a/{}^{11}a_0)$$

where ^{10}a and ^{11}a are the final concentrations of $^{10}BH_3$ and $^{11}BH_3$, respectively, and $^{10}a_0$ and $^{11}a_0$ are the initial concentrations of $^{10}BH_3$ and $^{11}BH_3$, respectively.[20] Values of the $^{10}B-^{11}B$ isotope effects are given in Table III. Values of the isotope effects calculated from repetitive analyses of the same samples of boric acid agreed within the uncertainty error of the calculations. Values calculated for separate hydroboration experiments generally agreed within the uncertainty error of the calculations.

Table III. $^{10}B-^{11}B$ Isotope Effects for the Hydroboration of Selected Alkenes with Borane in Tetrahydrofuran

Alkene	$k_{^{10}B}/k_{^{11}B}$	
1-Decene	1.031 ± 0.006	1.034 ± 0.004[a,b]
	1.028 ± 0.006[a,b]	1.032 ± 0.003[a,b]
Styrene	1.026 ± 0.006	1.036 ± 0.005[a]
2-Ethyl-1-hexene	1.033 ± 0.005	1.038 ± 0.006[a]
Propenylbenzene	1.032 ± 0.005	1.035 ± 0.005[a]
2-Methyl-2-butene	1.044 ± 0.006	1.057 ± 0.006[a]
TME	1.045 ± 0.006	1.035 ± 0.005[a]

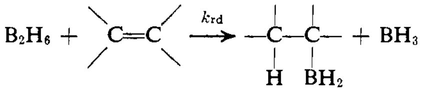
[a] Duplicate hydroboration run. [b] Duplicate analysis.

Discussion

Hydroboration of Tetramethylethylene. A discussion of the mechanism of the addition of borane to TME must take into consideration the nature of the reactants and products in solution. Solutions of diborane in THF are routinely referred to as containing either diborane or borane. All of the available physical evidence, however, indicates that the species in THF solution is a 1:1 complex of borane with THF. The solubility of diborane in THF increases as the square root of the diborane pressure suggestive of the formation of a borane–THF complex in solution.[25] In contrast, in the more weakly basic solvent diethyl ether, the solubility of diborane increases only slightly faster than the diborane pressure and approaches only one-eighth of that in THF.[25] Low temperature phase studies of THF solutions of diborane indicate compound formation occurs with a stoichiometry of $BH_3\cdot THF$.[26] ^{11}B nmr spectra of THF solutions of diborane display only a quartet, as would be expected for BH_3 in solution.[27] ^1H nmr measurements of the chemical shift of the α hydrogens of THF reveal that the chemical shift of the α hydrogens of THF is linearly dependent on the concentration of BH_3, with a $\Delta\delta$ of 9 Hz for the α hydrogens in a 1:1 $BH_3\cdot THF$ complex relative to pure THF.[27] The rate of exchange of BH_3 between THF molecules is considerably greater than 20 sec^{-1}, as indicated by the lack of exchange line broadening at 25°.[27] Thus all of the evidence indicates that dissolution of diborane in THF produces a solution of $BH_3\cdot THF$ in THF.

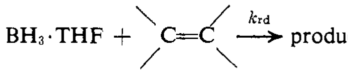
The reaction of borane with TME in THF is first order in both borane and TME. This observation precludes the possibility that diborane, which might be formed in very low concentrations by the dimerization of borane (eq 12), reacts with alkene (eq 13) in the rate-determining step. A more difficult question to answer is: does the $BH_3\cdot THF$ complex react directly with the alkene (eq 14), or does the $BH_3\cdot THF$ complex undergo a prior dissociation to produce free borane which then reacts with the alkene (eq 15 and 16)?

$$2BH_3 \rightleftharpoons B_2H_6 \tag{12}$$



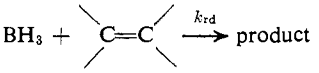
$$B_2H_6 + \rangle C{=}C\langle \xrightarrow{k_{rd}} -\underset{H}{C}-\underset{BH_2}{C}- + BH_3$$

(13)



(14)

$$BH_3\cdot THF \rightleftharpoons BH_3 + THF \tag{15}$$



(16)

An analysis and comparison of the activation parameters of various hydroboration reactions which have thus far been studied suggest that these reactions involve the direct reaction of a borane–solvent complex with the alkene. In the direct reaction of a complexed borane with an alkene involving partial nucleophilic displacement of the solvent ligand by the alkene, the dissociation energy of the borane–solvent complex will be reflected in the activation enthalpy of the reaction (*i.e.*, the greater the dissociation energy, the higher the activation enthalpy). For the two-step process (eq 15 and 16) two extreme situations may obtain. If the dissociation of the borane–solvent complex is the slow step (rate limiting), the rate of hydroboration will be zero order in alkene and the activation enthalpy for the reaction will be that for the dissociation step. On the other hand, if the dissociation of the complex is fast, the rate of reaction and activation enthalpy will be those for the addition step.

A comparison of the activation enthalpy of the reaction of TME with borane in THF (9.2 kcal/mol) with that for the gas phase reaction of ethylene with borane (2 ± 3 kcal/mol)[5] suggests that the solvent plays an important role in the reaction. The earlier works by

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(25) J. R. Elliott, W. L. Roth, G. F. Roedel, and E. M. Boldebuck, *J. Amer. Chem. Soc.*, **74**, 5211 (1952).

(26) B. Rice, J. A. Livasy, and G. W. Schaeffer, *ibid.*, **77**, 2750 (1955).

(27) D. J. Pasto and P. Balasubramaniyan, *ibid.*, **89**, 295 (1967).

Brown and Moerikofer[11] and Klein and coworkers[12] both indicate that the rate of hydroboration of alkenes is a sensitive function of the structure of the alkene. These combined data for the reaction of borane with alkenes thus are most consistent with a mechanism involving the direct reaction of borane–THF with the alkene to form a monoalkylborane.

A similar analysis of the kinetic data for the reactions of monochloroborane with alkenes leads to a similar conclusion. Monochloroborane forms a stronger complex with THF than does borane,[27] and reacts considerably slower with alkenes; however, the rate of reaction is dependent on the structure of the alkene.[16] If prior dissociation of the BH_2Cl–THF complex were occurring, one would anticipate that the overall rate of reaction would be dependent only on the rate of dissociation of BH_2Cl–THF, the reaction of monochloroborane with an alkene being expected to occur more rapidly than with borane. This expectation is based on the greater electrophilicity of monochloroborane relative to borane as indicated by acidity measurements and extended Hückel calculations[27] which should result in enhanced reactivity toward electrophilic attack on an alkene. The data are obviously not consistent with the predictions and suggest that the reaction of monochloroborane with alkenes in THF occurs by the direct reaction of BH_2Cl–THF with the alkene.[28]

A comparison of the activation entropies for the reactions similarly suggests that the solution reactions of borane in THF involve the direct reaction between the $BH_3 \cdot$THF complex with the alkene. The entropies of activation of bimolecular reactions proceeding *via* nonlinear transition states leading to the formation of a *single product* average in general between -12 and -21 eu[29]. The entropy of activation of -12.9 eu for the gas phase reaction of ethylene with borane[5] falls within this range. The predicted entropy of activation for the gas phase reaction of borane with TME is $\sim$29 eu, with the replacement of the hydrogens of ethylene with methyl groups causing a change in the entropy of activation of ~ -4 eu per methyl group.[29] Assuming that the transition state for the hypothetical reaction of uncomplexed borane with TME in the condensed phase in a relatively nonpolar solvent such as THF is the same as in the gas phase, the entropy of activation in the condensed phase should be ~ -29 eu. The release of a molecule of solvent prior to, or in going to the transition state, would be expected to lead to a considerably less negative entropy of activation. Unfortunately, however, there appears to be no reliable method which allows one to predict the expected magnitude in the change of $\Delta S^{\ddagger}$ due to the release of a molecule of solvent either prior to or in the rate-determining transition state. The observed entropy of activation of -27 eu for the reaction of borane with TME in THF is consistent only with the direct reaction of $BH_3 \cdot$THF with TME, leading to a very early transition state in which the molecule of THF is still rather tightly coordinated with the boron atom.

The conclusion that the reactions of borane and monochloroborane with alkenes in THF occur *via* direct reaction of the borane–THF complex with the alkene may not prove to be universal for the reactions of other substituted boranes with alkenes. It is not beyond the realm of possibility that the reactions of other substituted boranes with alkenes might occur *via* one of the other mechanisms outlined and discussed in the foregoing paragraphs.

Isotope Effects. The hydrogen–deuterium kinetic isotope effect for the hydroboration of TME is found to be 1.18. This value represents a superimposition of a primary and a secondary isotope effect; the former is expected to be greater than unity (a maximum value of $\sim$2.8 based on the stretching frequencies of the bonds involved in the reaction), while the latter is expected to be less than unity.[30] The value of 1.18 for k_H/k_D seems reasonable when compared to the vaue of $\sim$3.3 for $k_{^1H}/k_{^3H}$ (see later discussion) in which the complication of superposed secondary isotope effects is not present, and are consistent with the values of k_H/k_D of 2.4 and 1.9 for the hydroboration of 1-hexene and styrene, respectively, with monochloroborane in THF.[16,31]

The hydrogen–tritium isotope effects measured in the present study are not true kinetic isotope effects, but are product formation isotope effects which conceivably might not be arising in the rate-determining transition state. However, the $k_{^1H}/k_{^3H}$ derived with TME seems very reasonable for a true kinetic isotope effect when compared with the value of the k_H/k_D derived with TME, and thus we believe that the $k_{^1H}/k_{^3H}$ values reported in this article are true kinetic isotope effects.

The hydrogen–tritium isotope effects determined in the present study decrease markedly with increasing substitution on the double bond, as well as with increasing substitution on the boron of the borane.[18] This trend is consistent with a decrease in C–H bond formation and B–H bond breaking in the transition state due to increasing steric factors. The observed isotope effects are not consistent with a secondary isotope effect which might be expected to arise from the formation of a π complex between borane and alkene in a rate-determining step. Such an isotope effect would be much smaller and would be inverse.

The ^{10}B–^{11}B isotope effect appears to increase very slightly with increasing substitution on the double bond. This trend is consistent with an increase in the bonding interaction between boron and carbon due to the increase in the π-electron density of the double bond arising from the inductive effects of the substituents attached to the double bond. This electronic effect offsets the steric effects which would tend to decrease the isotope effect as the degree of substitution on the double bond increases as observed with the hydrogen–tritium isotope effects.

The combination of the hydrogen–tritium and ^{10}B–^{11}B isotope effects is consistent with the formation of an unsymmetrical, four-centered transition state in which C–H and C–B bond formation and B–H and C=C bond-breaking processes occur in concert.

Nature of the Transition State. The foregoing discussion has presented arguments that the reaction of borane

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[28] Similar implications were suggested previously (ref 16 and 27 and G. Zweifel, *J. Organometal. Chem.*, 9, 215 (1967)).

[29] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 71, 2903 (1967).

[30] The effect of such an inverse secondary isotope effect has been suggested in the reduction of ketones with sodium borohydride (D. C. Wigfield and D. J. Phelps, *Chem. Commun.*, 1152 (1970)).

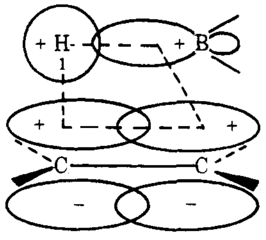
[31] The values of 2.4 and 1.9 do not represent the full primary isotope effects, again because of the simultaneous operation of a secondary isotope effect. However, in these reactions the secondary isotope effect is due to only a single C–D bond, whereas in the BD_3 reactions the secondary isotope effect of two C–D bonds is involved.

with TME in THF occurs by attack of $BH_3 \cdot THF$ on TME, and that the transition state involves the concerted formation of the C–H and C–B bonds and cleavage of the B–H and C=C bonds. The assumed concertedness of the reaction based on the isotope effects is supported by the consideration of the reverse of the addition reaction. The facile elimination of >B–H from alkylboranes occurs in rearrangement[32] and alkene displacement[33] reactions at 100–160°, and as low as 25° in the case of reactions involving diisopinocampheylborane with alkenes.[34] A two-step process involving homolytic dissociation of the carbon–boron bond would require a minimum activation energy equal to the carbon–boron bond energy (~84 kcal/mol[35]), a process which is not possible under the reaction conditions. The facile elimination of >B–H from an alkylborane must therefore occur *via* a concerted process in which the bond formation processes offset the activation energy required for the bond breaking processes. According to the principle of microscopic reversibility, the addition of >B–H to a carbon–carbon double bond must therefore also be concerted.

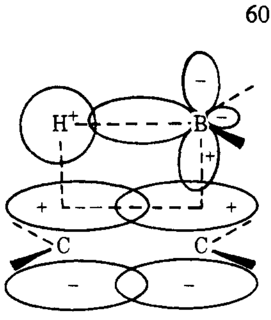
The intimate details of the bond formation processes and the orbitals involved provide an intriguing theoretical problem. The direct, concerted cycloaddition of >B–H to a carbon–carbon double bond involving only the orbitals of the B–H σ bond and the π bond of the double bond (transition state **1**) is not allowed by orbital symmetry considerations[36] although the orbital symmetry is partially destroyed in the unsymmetrical B–H σ bond.[37] However, arguments can be presented that highly exothermic reactions with very low activation energies proceed *via* very early transition states (the Hammond postulate[38]) in which orbital symmetry control is either not developed sufficiently to control the course of the reaction or does not apply. ΔH for the hydroboration of ethylene is estimated to be ~ -33

$$BH_3 + 3CH_2{=}CH_2 \longrightarrow B(C_2H_5)_3,\ \Delta H = \sim -99 \text{ kcal/mol}$$

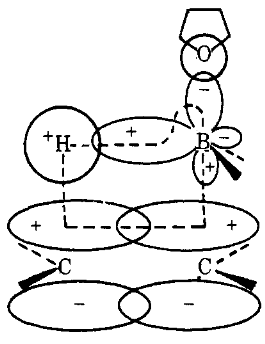
kcal/mol per B–H bond consumed as calulated from the data for the reactions $2BH_3 \rightleftharpoons B_2H_6$, $\Delta H = -28$ kcal/mol,[39] and $B_2H_6 + 6CH_2{=}CH_2 \rightarrow 2B(C_2H_5)_3$, $\Delta H = -170.5$ kcal/mol.[40] A study of the steric effects in the hydroboration reaction has revealed that the transition state must be very early, involving very little rehybridization about the carbon atoms of the double bond.[41] Thus the gas phase reaction of ethylene with borane, which is characterized with a very low activation energy (2 kcal/mol),[5] might not be controlled by orbital symmetry considerations and thus may proceed *via* a transition state such as **1**.



1



2



3

An alternate bonding process for the transition state of the gas phase reaction of ethylene with borane can be visualized in which the vacant p orbital on boron becomes involved in bond formation, as is illustrated in transition state **2**. In this process the original p orbital becomes involved in forming the B–C σ bond, and the sp^2 hybrid orbital on boron originally involved in the B–H bond becomes the new vacant orbital on boron. This process is allowed by orbital symmetry considerations.

In the reaction of $BH_3 \cdot THF$ with TME in THF, the second description of the bonding in the transition state becomes more complex because of the bonding interaction of THF with the vacant orbital on the boron atom of borane (making the geometry about boron in $BH_3 \cdot THF$ tetrahedral). The transition state can, however, be visualized as involving partial nucleophilic displacement of the THF by development of bonding between one of the p orbitals of the π-electron system and the backside lobe of the sp^3 orbital on boron involved in the boron–oxygen bond and development of bonding between the hydrogen 1s orbital with the other p orbital of the π-electron system (transition state **3**). In this process the THF must ultimately either become dissociated as the transition state proceeds past the point of maximum energy, which in the case of a very early transition state would not have a significant effect on the entropy of activation of the reaction, or undergo migration from its bonding orbital on boron to the orbital being vacated by the hydrogen. Either process is consistent with the experimental observations reported in the literature and in this article.

The present studies do not provide any information regarding the possible formation of an intermediate π complex prior to reaching the rate-determining transition state.[42]

Experimental Section

Measurement of the Rate of Hydroboration of Tetramethylethylene. The reaction of TME with borane in THF was monitored

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(32) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **88**, 1433 (1966), and references cited therein.

(33) H. C. Brown and M. V. Bhatt, *ibid.*, **88**, 1440 (1966); H. C. Brown, M. V. Bhatt, T. Munekata, and G. Zweifel, *ibid.*, **89**, 567 (1967).

(34) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 1071 (1964).

(35) W. H. Johnson, M. V. Kilday, and E. J. Prosen, *J. Res. Nat. Bur. Stand., Sect. A*, **65**, 215 (1961).

(36) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(37) R. G. Pearson, *Accounts Chem. Res.*, **4**, 152 (1971).

(38) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(39) S. H. Bauer, A. Shapp, and R. E. McCoy, *ibid.*, **75**, 1003 (1953).

(40) A. E. Pope and H. A. Skinner, *J. Chem. Soc. London*, 3704 (1963).

(41) D. J. Pasto and F. M. Klein, *J. Org. Chem.*, **33**, 1468 (1968).

(42) A. Streitwieser, Jr., L. Verbit, and R. Bittman, *ibid.*, **32**, 1530 (1967).

using a fast-flow, quenching kinetic apparatus. The borane–THF solution and TME–THF solution (containing an inert internal standard for glpc analysis) are rapidly mixed in a reaction cell consisting of a four-jet tangential mixing chamber (operating under turbulent flow conditions) and tubular reaction chamber which then feeds into a second four-jet, tangential mixing chamber in which the quenching reagent (triethylamine or Dabco) is rapidly mixed with the reacting solution.[43] The entire cell and tubular reaction chamber are constructed of Teflon and are immersed in a constant temperature bath. The reagent solutions are transferred to jacketed 50-ml syringes (maintained at the same temperature as the constant temperature bath) which are driven by a Servo-Tek precision-speed (0.1% rpm reproducibility) variable-rpm motor. The time constants for the reaction cell and the tubular reactors were measured by accurately determining the volume of the cell and the tubular reactor and the volume flow per unit time at a given drive speed (motor rpm).

The quenched reaction mixtures were analyzed for the amount of unreacted TME by glpc.

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[43] The reaction cell is modeled after that designed by W. R. Ruby (*Rev. Sci. Instrum.*, **26**, 460 (1955)). The authors gratefully acknowledge Eastman Kodak Co. and Drs. W. R. Ruby and C. A. Bishop for providing design blueprints and technical advice.

Measurement of the Relative Rate Ratios of the First and Second Steps of the Hydroboration Reaction and the Rates of Alkylborane Redistribution Reactions. Discussion of the Overall Mechanism of the Hydroboration Reaction[1,2]

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Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received November 22, 1971*

Abstract: The relative rates of the first and second steps of the hydroboration reaction of alkenes capable of proceeding to the di- and trialkylborane stage have been measured. In all cases studied the rate constant for formation of the dialkylborane from monoalkylborane and alkene is larger than the rate constant for the formation of alkylborane from borane and alkene. The rate constants for the redistribution reactions $BH_3 + R_3B \rightleftarrows R_2BH + RBH_2$, $2RBH_2 \rightleftarrows R_2BH + BH_3$, and $2R_2BH \rightleftarrows R_3B + RBH_2$ have been determined at 40° for the *n*-propylborane system ($R = n\text{-}C_3H_7$). All of the bimolecular rate constants for the forward and reverse redistribution reactions are considerably smaller than the hydroboration reaction rate constants. The formation of dialkylborane from monoalkylborane and alkene in systems in which alkylborane monomer–dimer equilibrium constants are not prohibitively large is proposed to occur *via* reaction between an alkylborane monomer–tetrahydrofuran complex and alkene. The greater reactivity of the monoalkylborane relative to borane is attributed to a weaker complexing interaction in the monoalkylborane–tetrahydrofuran complex than in the borane–tetrahydrofuran complex, thus resulting in a lowering of the activation energy for nucleophilic attack by an alkene on borane–tetrahydrofuran with partial displacement of the tetrahydrofuran. The differing stereochemical results obtained in the hydroboration of alkenes with monoisopinocampheylborane under various conditions are discussed in terms of the relative rates of addition *vs.* redistribution reactions. It is concluded that hydroboration with monoisopinocampheylborane produces alcohol of one configuration, whereas hydroboration with diisopinocampheylborane produces alcohol of opposite configuration. The results and conclusions reported in this article reinforce the conclusion that the hydroboration of an alkene with borane in tetrahydrofuran involves the direct reaction between a molecule of the borane–tetrahydrofuran complex and a molecule of the alkene.

In the previous article we discussed the possible mechanisms for the hydroboration of alkenes with borane and substituted boranes, and presented kinetic and thermodynamic data for the hydroboration of tetramethylethylene (TME) with borane in tetrahydrofuran (THF), as well as $^{1}H/^{3}H$ and $^{10}B/^{11}B$ kinetic isotope data for the hydroboration of other alkenes with borane and alkylboranes.[3] It was reported that the hydroboration of TME with borane in THF is first order in both TME and borane. From an analysis and comparison of rates and activation parameters for various possible mechanisms it was concluded that the hydroboration of alkenes with both borane and monochloroborane[4] occurs by nucleophilic attack by alkene on a borane–THF complex in a rather early transition state involving a concerted, syn addition of B–H to the double bond, as proposed earlier.[5]

In the present paper we wish to present kinetic data pertaining to the formation of di- and trialkylboranes under hydroboration conditions in THF (eq 1–3), alkylborane–borane redistribution reactions (eq 4–6), and equilibrium constant data on alkylborane monomer–dimer equilibria (eq 7–11). (In eq 2 and 3 reaction may occur either *via* the alkylborane monomer ($n = 1$) or the alkylborane dimer ($n = 2$). Competi-

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[1] Part XXV of a series of Transfer Reactions Involving Boron; for part XXIV, see D. J. Pasto, B. Lepeska, and T.-C. Cheng, *J. Amer. Chem. Soc.*, **94**, 6083 (1972).

[2] Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (Grant No. 1225, A1,3), and to the National Institutes of Health for partial support (Grant No. CA 07194).

[3] See ref 1.

[4] D. J. Pasto and S.-Z. Kang, *J. Amer. Chem. Soc.*, **90**, 3797 (1969).

[5] H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).