ether. Part of the solvent was removed, and the residue was dried over anhydrous magnesium sulfate. Analyses by gas chromatography on an Empol 1022 dimer acid column using heptanoic acid as an internal standard revealed a 79% yield of hexanoic acid.

A slightly different procedure was utilized for analysis of the neutral oxidation products. In this case a saturated solution of potassium carbonate was added to the basic reaction mixture. The organic phase which formed was separated, and the aqueous phase was extracted twice with tetrahydrofuran. The combined tetrahydrofuran extracts were dried and then examined by gas chromatography for 1-hexanol, hexaldehyde, and 1,2-hexanediol as described above.

Hydrolysis of the Dihydroboration Product Derived from 1-Hexyne-1-*d* and Deuteriodiborane. Deuterioborane (13.1 ml of a 1.40 *M* solution) in tetrahydrofuran was added to 2.078 g of 1-hexyne-1-*d* (25 mmoles) in 20 ml of tetrahydrofuran at −15°. The reaction mixture was kept for 1 hr at 0–5°, then diluted with 7.5 ml of 3 *N* sodium hydroxide, and immediately oxidized with 5.5 ml of 30% hydrogen peroxide. The resulting mixture was saturated with potassium carbonate ($K_2CO_3 \cdot 1.5H_2O$) and the upper layer formed was decanted. The aqueous phase was extracted twice with ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. Gas chromatographic analysis revealed 43% of 1-hexanol. The solvent was removed, and the 1-hexanol was isolated by preparative gas chromatography on a Ucon Polar column. Examination of the 1-hexanol ($n^{21}\mathrm{D}$ 1.4181) by nmr revealed the presence of one proton at the 1 position.

Dihydroboration of 1-Hexyne with Dicyclohexylborane. a. Hydrolysis. In a 250-ml flask was placed 9.035 g of cyclohexene (0.11 mole) in 30 ml of tetrahydrofuran. The flask was cooled to −15°, then 24.1 ml of a 2.3 *M* solution of borane in tetrahydrofuran was added slowly. During the borane addition, the dialkylborane precipitated from solution. This reagent was maintained for an additional hour at 0° prior to its use.

To the dicyclohexylborane formed (55 mmoles) was added at 0° a solution of 2.053 g of 1-hexyne (25 mmoles) in 15 ml of tetrahydrofuran. After standing for 6 hr at 25° the reaction mixture became homogeneous. The organoborane solution thus formed was cooled to 0°, diluted with 25 ml of 3 *N* sodium hydroxide, and immediately oxidized by adding 20 ml of 30% hydrogen peroxide.

The reaction mixture was worked up in the usual manner. Gas chromatographic analysis of the dried extract revealed 89% of 1-hexanol, 2% of 1,2-hexanediol, and 1% of hexaldehyde.

b. Oxidation with *m*-Chloroperbenzoic Acid. To the dihydroboration product formed from 25 mmoles of 1-hexyne and 55 mmoles of dicyclohexylborane was added 2 ml of methanol to decompose residual hydride. The flask was then immersed in an acetone–Dry Ice bath, and the organoborane was oxidized by adding dropwise 30 ml of a solution of *m*-chloroperbenzoic acid (41.46 g, 0.204 mole) in tetrahydrofuran while maintaining the temperature between −20 and 0°. The oxidation products were isolated as described earlier. Gas chromatographic examination revealed 96% of hexanoic acid and 2% of 1,2-hexanediol.

Dihydroboration of 1-Hexyne with 2,3-Dimethyl-2-butylborane. a. Hydrolysis. In a 250-ml flask was placed a solution which contained 2.310 g of 2,3-dimethyl-2-butene (27.5 mmoles) in 20 ml of tetrahydrofuran. The flask was immersed in an ice bath, and 12 ml of a 2.3 *M* solution of borane in tetrahydrofuran was added while stirring. After completion of the borane addition, the flask was permitted to remain for 2 hr at 0°.

To the monoalkylborane formed (27.5 mmoles) was added at 0° a solution of 2.053 g of 1-hexyne (25 mmoles) in 15 ml of tetrahydrofuran. The resulting clear solution was maintained for 2 hr at 0–5°, then 25 ml of 2 *N* sodium hydroxide was added, followed by dropwise addition of 10 ml of 30% hydrogen peroxide. The reaction mixture was worked up as described above, then analyzed by gas chromatography. The chromatogram revealed 79% of 1-hexanol, 10% of hexaldehyde, and 2% of 1,2-hexanediol.

b. Oxidation with *m*-Chloroperbenzoic Acid. The dihydroboration product derived from 25 mmoles of 1-hexyne and 27.5 mmoles of 2,3-dimethyl-2-butylborane was treated at −20–0° with 25 ml of a solution of *m*-chloroperbenzoic acid (0.113 mole) in tetrahydrofuran. The reaction products were isolated as described above. Gas chromatographic analysis indicated a 90% yield of hexanoic acid contaminated with 4% of 1-hexanol and 2% of 1,2-hexanediol.

Transfer Reactions Involving Boron. XI. The Reaction of Monochloro- and Dichloroborane with Olefins[1,2]

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Abstract: The reactivity of monochloro- and dichloroborane with 2-methylpropene, 1-hexene, and styrene in tetrahydrofuran has been investigated. The structures of the intermediate alkylchloroboranes formed in these reactions were determined by ^{11}B magnetic resonance spectroscopy and by oxidation to the corresponding alkanols and analysis by gas–liquid partition chromatography. The direction of addition of the chloroboranes to the olefins is the same as with borane in tetrahydrofuran with the exception that slightly higher percentages of the least substituted alkyl derivatives are formed relative to borane in tetrahydrofuran. The relative acidities of a variety of Lewis acids have been determined in tetrahydrofuran solutions by nuclear magnetic resonance and correlated with the charge on the central metal atom as determined by extended Hückel calculations. The direction of addition and the slow rate of reaction of the chloroboranes with the olefins are discussed in relation to the relative acidities of the haloboranes.

Recent investigations in our laboratories on the mechanism of product formation in the hydroboration of vinyl halides[3] have required a careful investigation of the use of haloboranes as hydroborating agents. The hydroboration of vinyl halides has been shown to produce both the α- and β-haloorganoboranes[3] **1** and **2**. The β-haloorganoborane undergoes a rapid elimination in tetrahydrofuran to produce the dehalogenated olefin and the haloborane. As the olefin generated in this elimination may undergo subsequent hydroboration with either borane or the haloborane, it was necessary to determine the directive properties and reactivity of the possible haloboranes

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(2) The authors gratefully acknowledge the financial support provided by the National Institutes of Health *via* Grant No. CA-07194.

(3) D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966).

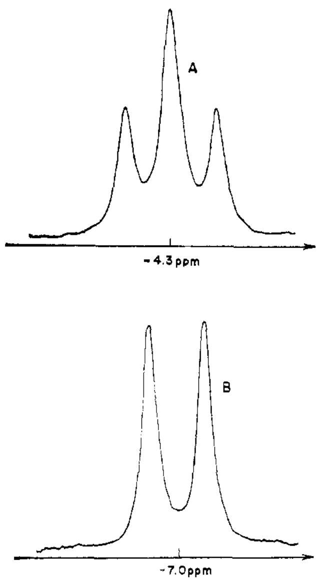
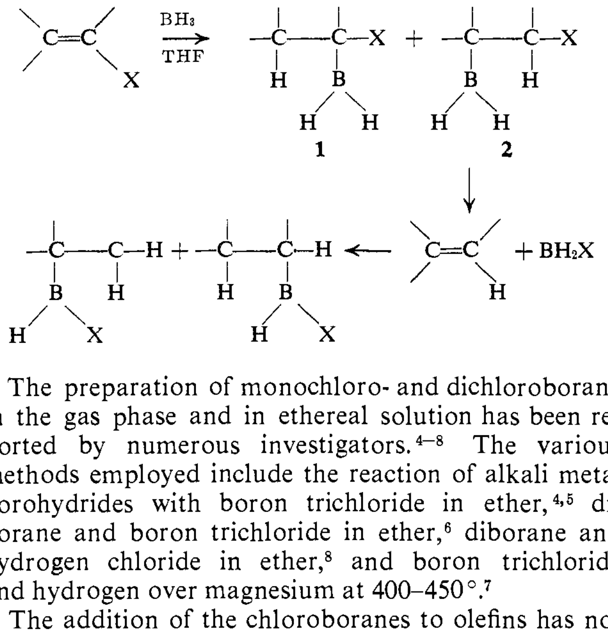


Figure 1. (A) ^{11}B magnetic resonance spectrum of monochloroborane; (B) ^{11}B magnetic resonance spectrum of dichloroborane.

relative to borane in the hydroboration of olefins in order to describe accurately the mechanism of product formation in the hydroboration of vinyl halides.



The preparation of monochloro- and dichloroborane in the gas phase and in ethereal solution has been reported by numerous investigators.[4-8] The various methods employed include the reaction of alkali metal borohydrides with boron trichloride in ether,[4,5] diborane and boron trichloride in ether,[6] diborane and hydrogen chloride in ether,[8] and boron trichloride and hydrogen over magnesium at 400–450°.[7]

The addition of the chloroboranes to olefins has not been extensively studied. Lynds and Stern have proposed that alkylboron dichlorides are formed in which the boron atom is attached to the most substituted carbon atom.[7,9] In contrast, the work of Shchegoleva and co-workers indicates that the direction of addition of monochloroborane to olefins parallels that of diborane.[8]

Results and Discussion

The monochloro- and dichloroboranes used in the present study were prepared by the slow addition of a calculated amount of boron trichloride in tetrahydropyran to a cooled solution of borane–tetrahydrofuran, or by the slow absorption of a calculated quantity of boron trichloride vapor into a cold solution of borane in tetrahydrofuran. The chemical and physical properties of the two different preparations were identical. The ^{11}B magnetic resonance spectra of solutions of monochloroborane displayed a symmetrical triplet at -4.3 ± 0.3 ppm (relative to boron trifluoride–diethyl ether internal capillary at 19.3 Mc) with $J_{BH} = 131$ cps (see Figure 1A). Heteronuclear spin decoupling produced a singlet, indicating that monochloroborane was the only species present in solution (estimated to be at least 95% pure). The ^{11}B magnetic resonance spectra of solutions of dichloroborane displayed a doublet at -7.0 ± 0.4 ppm with $J_{BH} = 162$ cps[10] (see Figure 1B). Again, heteronuclear spin decoupling resulted in a single peak, indicating the presence of a single species (estimated to be at least 97% pure). The solutions of monochloro- and dichloroborane in pure tetrahydrofuran did not undergo any detectable decomposition over a 24-hr period at room temperature or 2 months in a freezer.[11]

The results of the hydroboration of a few representative olefins with monochloroborane are presented in Table I. Initial experiments indicated that the hydroboration of olefins with monochloroborane was a relatively slow reaction compared with the reactions with borane in tetrahydrofuran. The reaction of excess 2-methylpropene with monochloroborane for 6 hr at room temperature gives, after hydrolysis and oxidation, a 56.2% yield of 2-methyl-1-propanol based on the two available "hydrides." Only a minute

Table I. Results of the Hydroboration of Olefins with Monochloroborane[a]

Olefin	Olefin: mono-chloro-borane	Reaction time, hr	Products	Yield, %
2-Methylpropene	Excess olefin	6	2-Methyl-1-propanol	56
			2-Methyl-2-propanol	Nil
1-Hexene	1:1	24	1-Hexanol	70.5
			2-Hexanol	2.9
Styrene	1:1	2.5	2-Phenylethanol	31.8
			1-Phenylethanol	3.5
Styrene	1:1	24	2-Phenylethanol	78.3
			1-Phenylethanol	9.0
Styrene	2:1	72	2-Phenylethanol	57
			1-Phenylethanol	8.7

[a] Reactions carried out at room temperature.

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(6) T. Onak, H. Landesman, and I. Shapiro, *J. Phys. Chem.*, **62**, 1605 (1958).

(7) L. Lynds and D. R. Stern, *J. Am. Chem. Soc.*, **81**, 5006 (1959); D. R. Stern and L. Lynds, British Patent, 853,379 (1960).

(8) T. A. Shchegoleva, E. M. Shashkova, V. G. Kiselov, and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 365 (1964); *Chem. Abstr.*, **60**, 12037*h* (1964).

(9) The structures were assigned on the basis that "Markovnikov's rule would indicate the products" would have the structures proposed. No chemical evidence was presented in support of the proposed structures.

(10) Reported −7.9 ppm ($J_{BH} = 152$ cps) for dichloroborane–diethyl ether (T. P. Onak, H. Landesman, R. W. Williams, and I. J. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959)).

(11) Attempts were made without success to prepare the monofluoro- and difluoroboranes and the monobromo- and dibromoboranes utilizing the methods outlined for the chloroboranes. Solutions of borane and boron trifluoride in tetrahydrofuran do not undergo equilibration with the formation of fluoroboranes, and the attempts to prepare solutions of the bromoboranes resulted in immediate solvent cleavage.

trace of 2-methyl-2-propanol was formed. Hydroboration of 1-hexene with monochloroborane in up to a 1:1 olefin:monochloroborane ratio produces reasonable yields of a mixture of 1- and 2-hexanol in a 96:4 ratio. Hydroboration of 1-hexene with borane in tetrahydrofuran produces 1- and 2-hexanol in a 94:6 ratio. The hydroboration with monochloroborane leads to slightly more terminal product relative to borane. Attempts to utilize both of the available "hydrides" of monochloroborane resulted in only a 42% yield of hexanols after 72 hr at room temperature (considerable olefin remained at the end of this time), indicating that only monoalkylmonochloroboranes were being formed. Confirmation of this was obtained by analysis of the methanolized hydroboration reaction mixtures by ^{11}B magnetic resonance spectroscopy which indicated the presence of only dimethyl alkylboronate from the monoalkylmonochloroborane. These results also indicate that there is no equilibration of the various alkylchloroboranes in the reaction mixture.

Similar results were obtained in the hydroboration of styrene with monochloroborane. The reaction of styrene with monochloroborane in a 1:1 mole ratio at 25° produced, after hydrolysis and oxidation, a 35% yield of alcohol in 2.5 hr, and an 87% yield after 24 hr. Analysis of the alcohol mixture by gas–liquid partition chromatography showed the mixtures to contain 89.8% 2-phenylethanol and 10.2% 1-phenylethanol. Analysis of the ^{11}B magnetic resonance spectrum of a methanolized sample of the hydroboration mixture indicated the presence of only a monoalkylborane.

The foregoing results are in distinct contrast with the results obtained in the hydroboration of 1-hexene and styrene with borane and phenylthioborane[12] in which the dialkylborane derivative is the predominant reaction product when the olefin and borane are present in a 1:1 mole ratio. Furthermore, the use of monochloroborane as a hydroborating agent followed by hydrolysis appears to be the preferred method of synthesis of alkylboronic acid derivatives compared to the equilibration of trialkylboranes with borane[13] or the hydroboration of an olefin with an excess of borane in tetrahydrofuran.

The results of utilizing dichloroborane as a hydroborating agent are given in Table II. The reactions of olefins with dichloroborane were much slower than with monochloroborane. Hydroboration of 2-methylpropene with dichloroborane in a 1:1 mole ratio at room temperature produced only a 56% yield of 2-methyl-1-propanol after 24 hr. No 2-methyl-2-propanol was formed. Similar treatment of 1-hexene with dichloroborane for 48 hr produced a 16% yield of 1-hexanol and 2-hexanol in which the 1-hexanol was the predominant product. Styrene underwent a very slow hydroboration with dichloroborane (41% after 72 hr at room temperature). The ratio of 2-phenylethanol to 1-phenylethanol was 96.3:3.7. No apparent polymerization of styrene had occurred. The ^{11}B magnetic resonance spectra of methanolized samples of the hydroboration mixtures showed the formation of only alkyldichloroboranes.

Table II. Hydroboration of Olefins with Dichloroborane[a]

Olefin	Reaction time, hr	Products	Yield, %
2-Methylpropene	24	2-Methyl-1-propanol	50
		2-Methyl-2-propanol	...
1-Hexene	48	1-Hexanol	15
		2-Hexanol	Small amount
Styrene	72	2-Phenylethanol	25
		1-Phenylethanol	1.6

[a] Reactions carried out at 25–30° employing a 1:1 mole ratio of olefin:dichloroborane.

The above results are not what one might expect based on the expected chemical properties of the chloroboranes. The chloroboranes should be more electrophilic and should, if the hydroboration reaction is visualized as an electrophilic attack by the borane on the olefin, thus react at a faster rate to give a higher percentage of terminal product relative to borane. In reality only the latter expectation is realized. The charge densities on the central boron atom for various boranes, as calculated by extended Hückel calculations, are given in Table III. The calculations were made employing Hoffmann's extended Hückel routine[14] as modified by Moore[15] to include atoms with principal quantum number 3. The resonance integrals were calculated as

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$$

Table III. Charge Densities in Substituted Boranes and Related Compounds

Compound	Charge densities M[a]	H[b]	X[c]
BH_3[d]	+0.4949	−0.1649	...
BH_2Cl	+0.7242	−0.2088	−0.3067
$BHCl_2$	+0.9687	−0.2492	−0.3597
BCl_3	+1.208	...	−0.4032
R_2BCl[e]	+1.0239	...	−0.3473 (Cl) −0.4424 (C)
$RBCl_2$[f]	+1.1207	...	−0.3770 (Cl) −0.4862 (C)
$(CH_3)_3B$[g]	+0.9577	...	−0.735
$C_6H_5SBH_2$[h]	+0.5057	−0.183 ± 0.01[i]	−0.1422
$C_6H_5SBH_2$[j]	+0.6183	−0.2004	−0.2381
$(CH_3)_2BSC_6H_5$[k]	+1.131	...	−0.8162 (S) −0.735 ± 0.003 (C)

[a] M represents the central boron atom. [b] H bonded directly to boron only. [c] X represents the heteroatoms (indicated in parenthesis after the numbers) bonded directly to boron. [d] The planar (bond angles 120°) conformation was calculated to be 1.1 ev more stable than with bond angles of 109° 28′ and 3.7 ev more stable than with bond angles of 90°. [e] R = 2-methylpropyl. [f] R = any primary alkyl group except methyl. Methyl boron dichloride is calculated to possess the following charge distribution: B, +1.0656; Cl, −0.3872; and C, −1.1363. [g] Higher primary alkylboranes would be expected to have a 5–6% higher charge density on the boron as indicated by calculations in related systems. [h] BH_2 group in the plane of the C_6H_5S moiety. [i] Average of the charge densities on the two hydrogens (difference is due to the unsymmetrical environment of the two hydrogens). [j] BH_2 group is perpendicular to the plane of the C_6H_5S moiety. The all-planar conformation is calculated to be more stable than the perpendicular conformation by 0.10 ev. [k] $(CH_3)_2B$ group is in the plane of the C_6H_5S moiety.

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(13) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *ibid.*, **82**, 4703 (1960).

(14) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(15) E. B. Moore, Jr., *ibid.*, **43**, 503 (1965).

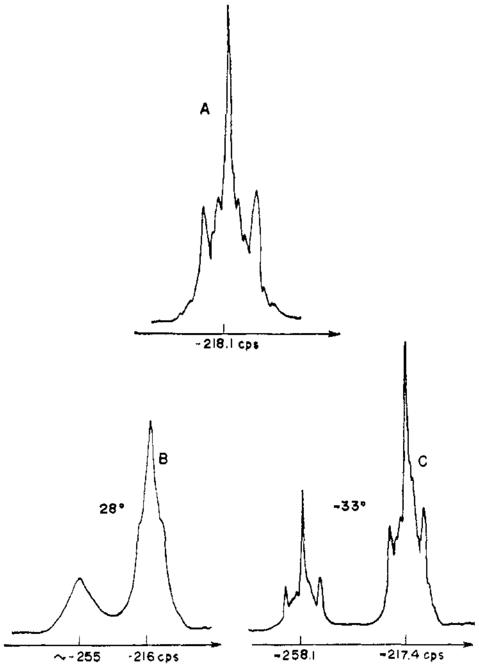

Figure 2. Proton magnetic resonance spectra of the α-hydrogens of tetrahydrofuran of a 1.15 *M* solution of borane in tetrahydrofuran at 28° (A) and a solution of monochloroborane in tetrahydrofuran at 28° (B) and at −33° (C).

where *K* was assigned the value 1.7500. The valence-state ionization potentials used are those given by Hinze and Jaffé.[16] The following molecular parameters were used in the calculations: bond lengths (A): B–H, 1.21; B–Cl, 1.72; B–C, 1.56; B–S, 1.81; C–C (aliphatic), 1.536; C–C (aromatic), 1.396; C–H, 1.091; and C–S, 1.81. The stereochemistry about the boron atom was taken as planar with bond angles of 120°; all other bond angles were taken as 109° 28′ (except in the phenyl group of phenylthioborane). Calculations on molecules containing alkyl groups were carried out on the most stable conformation of the molecule as judged by inspection of models.

The positive charge density associated with the central atom should reflect the Lewis acidity (neglecting steric effects) and the degree of electrophilic character. We have determined the relative acidities of several boranes in tetrahydrofuran solution employing the procedure of McCusker and Deters[17] in which the difference in chemical shift ($\Delta\delta_{\mathrm{THF}}$) between the α-hydrogens in pure tetrahydrofuran and the tetrahydrofuran in a 1:1 mole ratio with the Lewis acid is used as a measure of the relative acidity. As it was not always possible to prepare 1:1 mole ratios of the Lewis acid to tetrahydrofuran directly, the $\Delta\delta_{\mathrm{THF}}$'s for a series of dilute solutions of varying known concentrations of the Lewis acid in tetrahydrofuran were determined giving a linear $\Delta\delta_{\mathrm{THF}}$–concentration plot which was extrapolated to a 1:1 mole ratio to determine the 1:1 $\Delta\delta_{\mathrm{THF}}$

The proton magnetic resonance spectra of solutions of borane and phenylthioborane (up to 2 *M* concentration of borane) displayed a single set of multiplets identical in outline with the peaks in the spectrum in pure tetrahydrofuran but displaced to lower field (see Figure 2A). In contrast, the tetrahydrofuran solutions of monochloroborane at 27–30° displayed two sets of very poorly resolved multiplets (see Figure 2B). The position of the more intense higher field multiplets corresponded exactly to those for pure tetrahydrofuran. The position of the lower field multiplets did not change on changing the concentration of the monochloroborane; however, the relative intensities changed in a direct relationship to the change in concentration. . Lowering the temperature of the sample resulted in an increased resolution (see Figure 2C). The ratio of the areas of the multiplets for complexed and uncomplexed tetrahydrofuran corresponded exactly to the monochloroborane–tetrahydrofuran complex: tetrahydrofuran ratio. The chemical shift difference, $\Delta\delta_{\mathrm{THF}}$, was taken as the difference between the complexed and uncomplexed tetrahydrofuran multiplets. These results are consistent with a strong interaction between the monochloroborane and the tetrahydrofuran such that the rate of interchange of complexed and uncomplexed molecules of tetrahydrofuran with the monochloroborane was slower than the rate of observing the sample by the spectrometer. In contrast, the single tetrahydrofuran absorption peaks of solutions of borane and phenylthioborane indicate a more rapid exchange of tetrahydrofuran molecules and is consistent with their lower calculated Lewis acidity. The tetrahydrofuran solutions of monochloroborane displayed an apparent coalescence temperature of 57°; however, complete coalescence could not be obtained up to 82°. It would appear that this is due to extensive decomposition of the sample at the higher temperatures.

The proton magnetic resonance spectra of solutions of dichloroborane in tetrahydrofuran displayed two well-resolved sets of multiplets at 28° (see Figure 3). Coalescence of these multiplets could not be accomplished due to extensive decomposition of the sample above 65°. The proton magnetic resonance spectrum of a freshly prepared solution of boron trichloride in tetrahydrofuran also displayed two sets of well-resolved multiplets. This solution underwent rapid decomposition at 28°.

A plot of the relative acidity[18] *vs.* the calculated positive charge density on the central metal atom (Figure 4) gives a reasonably straight line incorporating borane, monochloro- and dichloroborane, boron trichloride, 2-methylpropylboron dichloride, and phenylthioborane. Bis(2-methylpropyl)boron chloride and di-*n*-butylboron chloride deviate substantially from the line, the former deviating the most. The deviation is such that the measured acidity is less than the calculated acidity and is readily explained on the basis of greater steric interactions in the Lewis acid–base complex, effectively reducing the strength of the complex formed. Consistent with this observation is the fact that trialkylboranes do not exhibit a measur-

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[16] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, 84, 540 (1962).

[17] J. F. Deters, Ph.D. Dissertation, University of Notre Dame, 1964.

[18] The proton magnetic resonance data for tetrahydrofuran solutions of bis(2-methylpropyl)boron chloride, 2-methylpropylboron dichloride, and aluminum chloride were taken from the Ph.D. Thesis of J. D. (ref 17). The data were obtained by measurements on 1:1 mole ratio mixtures of the Lewis acid and tetrahydrofuran, and it is not known whether there is a rapid or slow (compared to the magnetic resonance scale) exchange of solvent molecules with the Lewis acid molecules. Data on di-*n*-butylboron chloride, a relatively strong Lewis acid, indicate that exchange does occur.

Figure 3. Proton magnetic resonance spectrum of the α-hydrogens of tetrahydrofuran in a solution of dichloroborane in tetrahydrofuran at 28°.

able acidity under these conditions despite the relatively high positive charge calculated for the boron. Di-*n*-butylphenylthioborane similarly does not provide a measureable acidity.[19]

The relatively slow rate of hydroboration of olefins with monochloro- and dichloroborane is presently attributed to the decrease in the electrophilic character of the borane due to the relatively strong complexing of the boranes with the tetrahydrofuran.

The ratio of terminal to internal addition with styrene increases as the electrophilic character of the borane increases. Figure 5 shows a plot of the log (terminal addition)/(internal addition) *vs.* the calculated charge density on the boron atom which indicates a linear relationship and is consistent with the above view. We are currently extending our studies in this area and are studying the kinetics and electronic effects involved in the hydroboration of styrene and substituted styrenes with monochloro- and dichloroborane.

Experimental Section

General. Nuclear magnetic resonance spectra were obtained using a Varian Associates HR-60 spectrometer equipped with variable temperature hydrogen and ^{11}B probes and a NMR Specialties SD-60 heteronuclear spin decoupler. Gas–liquid partition chromatographic analysis were determined using added internal standards and correcting for differences in responses using predetermined response ratios. The extended Hückel calculations were carried out in a Univac 1107 computer.

Preparation of Solutions of Monochloroborane. A. Boron trichloride was absorbed in freshly dried, distilled tetrahydropyran under nitrogen at 0°. The amount of boron trichloride added to the tetrahydropyran was determined by weighing the tetrahydropyran before and after the addition of the boron trichloride. To a calculated amount of borane in tetrahydrofuran maintained in a Dry Ice–acetone bath was slowly added the boron trichloride–tetrahydropyran solution. The ^{11}B magnetic resonance spectrum of the resulting solution displayed a triplet at -4.59 ppm (relative to boron trifluoride etherate internal capillary) with $J_{BH} = 131$ cps.

B. A weighed quantity of boron trichloride was slowly absorbed, with stirring at $-10°$, into a measured volume of known concentration of borane in tetrahydrofuran. The ^{11}B resonance spectrum displayed a triplet at -4.29 ppm with $J_{BH} = 131.5$ cps.

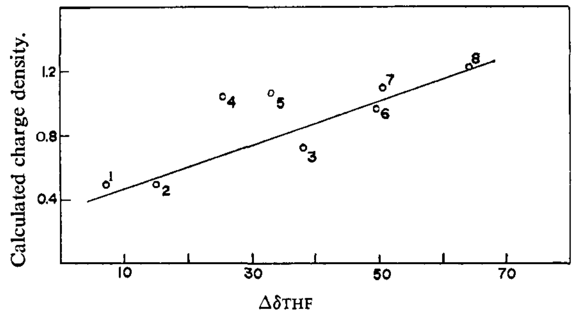

Figure 4. Plot of the calculated charge density on the central boron atom *vs.* the observed acidity ($\Delta\delta_{THF}$): (1) phenylthioborane, (2) borane, (3) monochloroborane, (4) bis(2-methylpropyl)butylboron chloride, (5) di-*n*-butylboron chloride, (6) dichloroborane, (7) *n*-butylboron dichloride, and (8) boron trichloride.

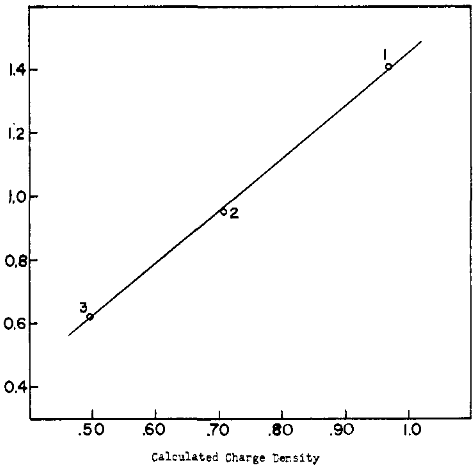

Figure 5. Plot of the log of the ratio of terminal:internal styrene addition product *vs.* the calculated charge density: (1) dichloroborane, (2) monochloroborane, and (3) borane.

Hydroboration of Olefins with Monochloroborane. To a solution of the olefin in tetrahydrofuran maintained at 0° was added the monochloroborane solution in an olefin:monochloroborane ratio indicated in Table I. The reaction mixture was allowed to come to room temperature and stand for the indicated lengths of time in Table I. (Preliminary experiments were run to determine suitable reactions times.)

A portion of the hydroboration mixture was removed and an excess of methanol was added to this portion, after which a majority of the solvent and trimethyl borate was removed under reduced pressure. The ^{11}B magnetic resonance spectrum of the resulting solution displayed a single symmetrical peak at -33 ± 1 ppm corresponding to a dimethyl alkylboronate. It would appear that the sample contained at least 95% of the dimethyl alkylboronate in all cases.

The remaining portion of the hydroboration mixture was hydrolyzed with an excess of 20% sodium hydroxide and oxidized by the addition of an excess of hydrogen peroxide. The oxidized reaction mixture was poured into water and extracted three times with ether. The ether extract was dried over magnesium sulfate. The residue, after removing the solvent, was analyzed by gas–liquid partition chromatography on a Carbowax 20M on firebrick column. The results of the analysis are presented in Table I.

Preparation of Dichloroborane. To a solution of boron trichloride in tetrahydropyran maintained at Dry Ice bath temperature was added a calculated volume of borane in tetrahydrofuran. The ^{11}B resonance spectrum displayed a doublet at -7.00 ± 0.5 ppm with $J_{BH} = 161$ cps.

Hydroboration of Olefins with Dichloroborane. To a solution of the olefin in tetrahydrofuran maintained at 0° under nitrogen was added an equimolar quantity of dichloroborane solution. The reaction mixture was allowed to stand at room temperature for the lengths of time indicated in Table II.

Methanolysis of a portion of the hydroboration mixture as above

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(19) Di-*n*-butylphenylthioborane does not react with ethers in cleavage reactions as does phenylthioborane. This also indicates a lack of interaction of the di-*n*-butylphenylthioborane with the tetrahydrofuran.

followed by analysis of the ^{11}B resonance spectrum showed the presence of only dimethyl alkylboronate.

The remaining portion of the hydroboration mixture was hydrolyzed and oxidized as described above and the residue was analyzed by gas–liquid partition chromatography. The results of the analysis are presented in Table II.

Determination of the Relative Acidities of the Substituted Boranes. Borane and Phenylthioborane. A relatively concentrated solution of borane in tetrahydrofuran (approximately 2 *M*) was diluted to several lower concentrations and the solutions were standardized by gas evolution measurements on hydrolysis or by titration of the boric acid formed on hydrolysis. The proton magnetic resonance spectra of these solutions were recorded, making approximately ten passes through the α- and β-hydrogen region of tetrahydrofuran with side bands being placed on each side of the multiplets. The average value for the center, most intense peak in the multiplets was determined and used to calculated the $\Delta\delta_{\mathrm{THF}}$. The $\Delta\delta_{\mathrm{THF}}$'s were plotted *vs.* the mole ratio of borane complex : tetrahydrofuran and the straight line was extrapolated to a 1:1 complex.

To the dilute standardized solutions of borane in tetrahydrofuran was added a slight excess of freshly distilled thiophenol. After the hydrogen evolution had ceased (approximately 10 min) the samples were sealed and the nuclear magnetic resonance spectra run immediately before extensive ether cleavage had occurred. The data were handled as described above.

Monochloro- and Dichloroborane. As preliminary experiments indicated that a relatively slow exchange of tetrahydrofuran molecules was occurring, freshly prepared monochloro- and dichloroborane solutions in pure tetrahydrofuran were prepared and used in the nuclear magnetic resonance experiments. The proton magnetic resonance spectra of the monochloroborane solution was taken at various temperature intervals from −35 to +82°. A coalescence temperature of 57° was evident (see text for discussion). The proton magnetic resonance spectra of dichloroborane displayed two sets of multiplets (see text for discussion).

Other Substituted Boranes. Tri-*n*-propylborane, di-*n*-butylboron chloride, and di-*n*-butylphenylthioborane were added to tetrahydrofuran to produce 1:1 mole ratios. The positions of the α-hydrogens of tetrahydrofuran in these mixtures were used to calculate $\Delta\delta_{\mathrm{THF}}$. A mixture of di-*n*-butylboron chloride and tetrahydrofuran in a 0.5:1 mole ratio displayed only a single set of multiplets in the nuclear magnetic resonance spectrum.

Electron Transfer Processes. VI. Disproportionation of *o*- and *p*-Nitrotoluenes in Basic Solution[1,2]

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Abstract: A wide variety of *o*- and *p*-nitrotoluene derivatives having an acidic α-hydrogen atom spontaneously disproportionate in basic solution, forming as the reduced species the radical anion derived from the parent nitroaromatic. This process has been considered in detail for *p*-nitrotoluene and it is concluded that the rate of formation of the radical anion is limited by the rate of ionization of *p*-nitrotoluene in *t*-butyl alcohol containing potassium *t*-butoxide.

The prolonged treatment of *o*- and *p*-nitrotoluene by strong base is recognized to give rise to a complicated mixture of products in which the methyl group has been oxidized and the nitro group reduced. Perkin first noted the formation of insoluble material by the action of hot alcoholic potassium hydroxide on *p*-nitrotoluene.[3] Klinger[4] obtained red amorphous and insoluble materials from a reduction of *p*-nitrotoluene with sodium in methanol. Bender and Schultz,[5] in a reinvestigation of this work, were able to show that 4,4′-diaminostilbene could be obtained from the reduction of the amorphous product described by Klinger. Also 4,4′-diaminostilbene-2,2′-disulfonic acid was prepared *via* similar reactions starting from 4-nitrotoluene-2-sulfonic acid. Fischer and Hepp[6] were able to isolate *p,p*′-dinitrobibenzyl and *p,p*′-dinitrostilbene from the reaction of *p*-nitrotoluene with sodium methoxide in methanol. However, the major product was a compound of empirical formula C_7H_5NO. Green[7] suggested the following structure for this compound ($C_{28}H_{20}N_4O_4$).

$$p\text{-}O_2NC_6H_4CH{=}CHC_6H_4N{=}NC_6H_4CH{=}CHC_6H_4NO_2\text{-}p$$

A number of ionic and molecular processes, some with unusual novelty, have been suggested for these oxidation–reduction reactions.[7,8]

Numerous *ortho,ortho*′-disubstituted *p,p*′-dinitrobibenzyls or stilbenes have been prepared by treating the appropriate *ortho*-substituted *p*-nitrotoluene with methanolic potassium hydroxide in the presence of an oxidizing agent.[7] A procedure for preparation of *p,p*′-dinitrobibenzyl from *p*-nitrotoluene in methanolic potassium hydroxide and air has been described.[9]

o,o′-Dinitrobibenzyl has been isolated from the treatment of *o*-nitrotoluene with diphenylamide anion in liquid ammonia solution.[10] Similarly *p,p*′-dinitrobibenzyl was formed from *p*-nitrotoluene with this base or with sodamide in piperidine.[11] Another product from the action of alkali and heat upon *o*-nitrotoluene is anthranilic acid.[12]

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(1) Reactions of Resonance Stabilized Anions. XXV.

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