ing agent, might exhibit markedly different selectivity than the saline borohydrides, as basic-type reducing agents, led us to explore the reducing potentialities of diborane. Ample data on the reducing properties of the borohydrides are now available for comparison.[3]

Diborane was prepared by adding a solution of sodium borohydride in diglyme to a solution of boron trifluoride etherate in the same solvent, and the gas was passed into a solution in diglyme or tetrahydrofuran of the compound under examination. After an appropriate interval of time, the residual hydride was determined by analysis. In cases where the group under study was one which is not reduced by sodium borohydride itself, the diborane could be conveniently generated within the reaction mixture by adding boron trifluoride etherate in diglyme to a solution of sodium borohydride and the compound in the same solvent.

Similar results were obtained in both procedures. The following data summarize typical observations using these procedures (the first figure in parenthesis gives the reaction time in hours, the second the moles of hydride utilized per mole of compound). All reactions were studied at room temperature.

Rapid Reduction	Slow or Negligible Reduction
Benzaldehyde (1.0, 1.0)	Benzoyl chloride (2.0, 0.4)
Benzophenone (1.0, 1.0)	Isobutyryl chloride (2.0, 0.4)
γ-Butyrolactone (1.0, 2.0)	Ethyl benzoate (2.0, 0.4)
Styrene oxide (1.0, 1.2)	Nitrobenzene (2.0, 0.1)
Azobenzene (1.0, 1.9)	1-Nitropropane (2.0, 0.1)
Benzoic acid (0.5, 2.8)	Naphthalene (2.0, 0.0)
p-Nitrobenzoic acid (0.5, 2.5)	
Benzonitrile (0.5, 2.0)	
n-Butyronitrile (1.0, 2.0)	

These results reveal remarkable differences in the reducing properties of diborane and the alkali metal borohydrides. Thus, in diglyme solution borohydride reduces acid chloride groups more readily than aldehyde or ketone groups,[4] whereas the reverse is true with diborane. Similarly, lithium borohydride reacts more readily with ester than with nitrile groups,[5] whereas diborane reacts far more rapidly with the nitrile than with the ester grouping. Finally, the rapid reduction of the carsboxylic acid group is in marked contrast to itusual stability and inertness. These results suggest that a judicious application of diborane and the alkali metal borohydride would make possible a truly remarkable selectivity in organic reductions.

The following preparations are typical of the two procedures utilized.

The diborane generator consisted of a 250-ml. flask containing a dropping funnel, an inlet for nitrogen, and an outlet for the diborane. In the flask was placed 28.5 g. (0.20 mole) of boron trifluoride etherate in 50 ml. of diglyme; in the dropping funnel, a solution of 5.1 g. (0.135 mole) of sodium borohydride in 125 ml. of diglyme. The flask was connected to the reaction flask containing 29.6 g. (0.20 mole) of *m*-nitrobenzonitrile in 150 ml. of tetrahydrofuran. The system was flushed out with nitrogen. The diborane (0.08 mole) was generated at an even rate over a period of an hour by dropping the sodium borohydride solution into the boron trifluoride etherate and passed into the flask containing the nitrile. (The exit gases were passed through a wash bottle containing acetone to catch and destroy unreacted diborane.) The reaction mixture was permitted to stand at room temperature for a second hour, ethanol was added to destroy excess diborane, followed by dry hydrogen chloride to convert the amine to the hydrochloride. After removal of solvent under reduced pressure, the reaction mixture was allowed to cool, the solid hydrochloride was collected on a filter, washed with ethanol, and dried. There was obtained 33.2 g., 88%, of the crude amine hydrochloride, m.p. 223–225°. Recrystallization from ethanol yielded pure *m*-nitrobenzylamine hydrochloride, m.p. 225–227°, in 79% yield.

p-Nitrobenzoic acid, 0.20 mole, was slowly added and dissolved in 0.18 mole of sodium borohydride in 150 ml. of diglyme (nitrogen atmosphere). Hydrogen was evolved. The flask was cooled in a water bath, stirred, and 0.22 mole of freshly distilled boron trifluoride etherate was added over a period of 1 hr. After a second hour, the contents were hydrolyzed, and the solid product was collected. There was obtained 24.1 g., 79% yield, of *p*-nitrobenzyl alcohol, m.p. 91–93°.

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(3) N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, 1956.

(4) Unpublished observations of Dr. K. Ichikawa.

(5) R. F. Nystrom, S. W. Chaikin, and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 3245 (1949).

Hydroboration of Olefins. A Remarkably Fast Room-Temperature Addition of Diborane to Olefins

Sir:

Diborane has been reported to react very slowly with simple aliphatic olefins at elevated temperatures[1,2] and with styrene at room temperature[3] to form the corresponding organoboron compounds.

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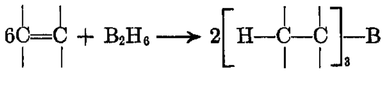
(1) D. T. Hurd, *J. Am. Chem. Soc.*, **70**, 2053 (1948).

(2) A. T. Whatley and R. N. Pease, *J. Am. Chem. Soc.*, **76**, 835 (1954).

(3) F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 2755 (1950).

In the course of investigating the facile conversion of olefins into trialkylboranes under the influence of the sodium borohydride–aluminum chloride reagent,[4] we have discovered that in the presence of organic ethers diborane adds to olefins with remarkable ease and speed at room temperature to form the corresponding organoboranes in yields of 90–95%.



$$6\overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} + B_2H_6 \longrightarrow 2\left[H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\right]_3{-}B$$

The reaction is reminiscent of the addition of aluminum-hydrogen bonds to olefins.[5] However, the latter reaction requires somewhat elevated temperatures (~ 100°) and occurs readily only with terminal olefins, $>C{=}CH_2$. On the other hand, the hydroboration reaction proceeds rapidly at room temperature with olefins of widely varying structural types, including ethylene, propylene, 1-hexene, 2-hexene, *t*-butylethylene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, cyclopentene, cyclohexene, styrene and 1,1-diphenylethylene.

The reaction can be carried out by passing diborane into the olefin contained in diglyme, tetrahydrofuran, or ethyl ether. The reaction occurs less readily with the pure olefin or with the olefin dissolved in hydrocarbon solvents. However, the traces of ether carried over by diborane generated in ether solvents are sufficient to catalyze the reaction markedly.

We have attempted to measure the velocity of the addition. However, at 25° we have observed half-lives of the order of 1 minute and we are presently engaged in developing methods for following reactions of such high velocities.[6]

The following synthesis of tri-*n*-hexylborane is typical. The apparatus consisted of a diborane generator and a reaction flask as described in the previous Communication.[7] Diborane, 0.067 mole, generated from the addition of 3.8 g. (0.1 mole) of sodium borohydride to 22.8 g. (0.16 mole) of boron trifluoride–etherate, was passed into the reaction flask containing 25.2 g. (0.3 mole) of 1-hexene in 100 ml. of diglyme. The reaction temperature was controlled through a water bath and by regulating the rate of generation of the diborane (30–60 min.). (Excess diborane was destroyed by passing the exit gases through a wash bottle containing acetone.) The reaction flask was disconnected, the solvent removed at room temperature, and the organoborane recovered by distillation at reduced pressure, all under protection of a nitrogen atmosphere. Tri-*n*-hexylborane, b.p. 185–188° at 30 mm., was obtained in 91% yield, 24.2 g. Oxidation with alkaline hydrogen peroxide yielded 3.94% boron (as boric acid) and 1-hexanol, b.p. 156–157° at 745 mm., n^{20}_{D} 1.4152.

Similar results were obtained with the other terminal olefins. Consequently, the addition of diborane to a terminal olefin occurs to place the boron atom on the terminal carbon atom.

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[4] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956).

[5] K. Ziegler, *Angew. Chem.*, **68**, 721 (1956).

[7] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957).

[6] Research in progress with Dr. Laura Case.

Selective Conversion of Olefins into Organoboranes Through Competitive Hydroboration, Isomerization, and Displacement Reactions

Sir:

The reactions of diborane with 1- and 2-pentene and 1- and 2-hexene in ether solvents are exceedingly fast reactions, being complete in a matter of minutes at room temperature.[1] In spite of its high velocity, the hydroboration reaction exhibits considerable selectivity. Treatment of an equimolar mixture of 1- and 2-pentene or 1- and 2-hexene with a deficiency of diborane results in the selective conversion of the terminal olefin into tri-*n*-pentylborane and tri-*n*-hexylborane.

One- and 2-pentene were converted into the organoboranes and the products were oxidized with alkaline hydrogen peroxide without isolation.[2] The organoborane from 1-pentene yielded 1-pentanol of at least 95% purity, as indicated by infrared examination. The organoborane from 2-pentene yielded a mixture of 63% 2-pentanol and 37% 3-pentanol (infrared analysis). However, after heating the crude organoborane from 2-pentene, 2-hexene, or 2-octene under reflux in diglyme solution for 4 hr., the products obtained in the oxidation were essentially pure primary alcohols. Apparently, under the influence of heat the 2- and 3-alyklboranes undergo a rapid isomerization into the corresponding 1-alkylboranes.[3] Indeed, it was possible to take a mixture of 2-, 3-, 4-, and 5-decenes and transform them by this procedure into 1-decanol in a yield of 80%. Similarly, mixed tetra-

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[1] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[2] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956).

[3] The isomerization of tri-*sec*-butylborane and tri-*tert*-butylborane to tri-*n*-butylborane and triisobutylborane, respectively, upon distillation at atmospheric pressure has recently been reported. G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, Abstracts of Papers, 130th Meeting of the American Chemical Society, September 16–21 (1956), p. 53-O.