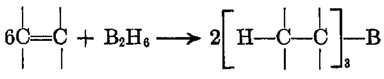
In the course of investigating the facile conversion of olefins into trialkylboranes under the influence of the sodium borohydride–aluminum chloride reagent,[4] we have discovered that in the presence of organic ethers diborane adds to olefins with remarkable ease and speed at room temperature to form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



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

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).

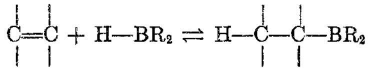
(2) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956).

(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.

decenes were converted into 1-tetradecanol in a yield of 70%.

Finally, we have observed that it is readily possible to displace a lower alkyl group in the trialkylborane with a higher alkyl group by heating the borane with the appropriate olefin and distilling the more volatile olefin from the reaction mixture.[4] In this way tri-*n*-hexyl-, tri-*n*-octyl- and tri-*n*-decylboranes have been synthesized by treating tri-*n*-pentylborane with 1-hexene, 1-octene, and 1-decene, respectively.

The facile isomerization and displacement reactions suggest the existence of a rapid and mobile equilibrium between the organoborane, olefin and boron-hydrogen bonds.



$$\overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} + H{-}BR_2 \rightleftharpoons H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}BR_2$$

Addition of a less volatile olefin displaces the more volatile olefin from the system. Similarly, internal olefins are rapidly isomerized by a series of addition and elimination reactions, and are converted finally into the more stable 1-alkylborane derivatives.

The following experiments are typical.

A mixture of 0.3 mole each of 1-hexene and 2-hexene in 100 ml. of diglyme was treated with 0.05 mole of diborane. Oxidation of the mixture yielded 1-hexanol in 90% yield, b.p. 156–157° at 750 mm., n_D^{20} 1.4150.

2-Hexene, 0.3 mole, in 100 ml. of diglyme, was treated with 0.06 mole of diborane. On oxidation there was obtained 24.7 g. of 2- and 3-hexanol, b.p. 136–137.5° at 750 mm. In a duplicate experiment, following the addition of the diborane, the reaction mixture (in diglyme) was heated under reflux (nitrogen atmosphere) for 4 hr. It was then cooled and oxidized as before. There was obtained 25.2 g., 82%, of 1-hexanol, b.p. 154–156° at 743 mm., n_D^{20} 1.4152.

Tri-*n*-pentylboron, 19.9 g., b.p. 150–152° at 30 mm., and 1-decene, 37.0 g., b.p. 170° at 750 mm., were placed in a dry 100-ml. flask and attached to a Todd column (nitrogen atmosphere). Over a period of 3 hr. there was obtained 17.7 g. (93%) of 1-pentene, b.p. 30–31° at 750 mm. The product, tri-*n*-decylborane, was recovered by distillation under reduced pressure: 32.3 g. (85% yield), b.p. 205–208° at 5 mm.

The remarkable ease with which these reactions proceed suggests that the hydroboration reaction should provide a useful and convenient synthetic route for the transformation of olefins into organoboranes, alcohols, and other functional derivatives.

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[4] Similar transformations have been observed in the organoaluminum compounds. K. Ziegler, *Angew. Chem.*, **68**, 721 (1956).