The results are summarized in Table VI.

Acknowledgment.—We wish to express our deep appreciation to Dr. K. W. Greenlee for providing one sample of *t*-butylethylene used in this study and to Dr. Akira Tsukamoto and Dr. George Zweifel for testing and extending the hydroboration procedures.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Hydroboration. II. A Remarkably Fast Addition of Diborane to Olefins—Scope and Stoichiometry of the Reaction

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RECEIVED MAY 11, 1959

Rigorously purified diborane and olefins react only slowly at room temperature. However, the presence of traces of ethers results in a rapid reaction which usually is complete in a matter of minutes at room temperature. Consequently, the rapid addition of diborane to olefins in ether solvents provides a new, convenient route to trialkylboranes: $6RCH{=}CH_2 + B_2H_6 \rightarrow 2(RCH_2CH_2)_3B$. This addition reaction of diborane to olefins appears to be applicable to olefins of widely different structural types. Among the olefins which have been demonstrated to react readily are: terminal olefins, such as 1-hexene, 1-octene, 1-decene, 1-tetradecene and 2,4,4-trimethyl-1-pentene; internal olefins, such as cyclopentene and cyclohexene; trisubstituted olefins, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene; tetrasubstituted olefins, such as 2,3-dimethyl-2-butene and 1,2-dimethylcyclohexene; and aryl substituted olefins such as styrene, α-methylstyrene, 1,1-diphenylethylene, stilbene and triphenylethylene. In general, the addition reaction proceeds to the trialkylborane stage, R_3B. However, in the case of trisubstituted olefins, the reaction at room temperature appears to halt at the dialkylborane stage, R_2BH, whereas the tetrasubstituted olefins yield the monoalkylboranes, RBH_2. Hydroboration of olefins can also be carried out conveniently by treating a solution of the alkali metal borohydride and olefin in a suitable ether solvent with a boron halide.

In preceding publications, we reported our observation that olefins react readily at room temperature with a solution of sodium borohydride–aluminum chloride in diglyme to form the corresponding organoboranes.[2] In the course of investigating possible reaction mechanisms, we were led to consider the possibility that diborane, present in small concentrations in the reaction mixtures, might be responsible for the hydroboration reaction. However, in view of earlier reports which emphasized the sluggishness of the reaction between diborane and olefins,[3-6] it appeared highly improbable that diborane could be an intermediate in the relatively rapid hydroboration reaction which we had observed.

However, we undertook a test experiment in which diborane was passed into a solution of 1-hexene in diglyme at room temperature. Unexpectedly, within a few minutes after the addition we observed that one mole of active hydride had disappeared per mole of olefin present. Tri-*n*-hexylborane was isolated readily from the reaction mixture by distillation. Consequently, the reaction must involve a rapid addition of diborane to the olefin

$$6n\text{-}C_4H_9CH{=}CH_2 + B_2H_6 \xrightarrow{\text{diglyme}} 2(n\text{-}C_6H_{13})_3B$$

This rapid addition of diborane to olefins appeared to offer a new, useful synthetic route to the organoboranes and their derivatives.[7] Accordingly, a detailed study of the scope, stoichiometry and applicability of the reaction was undertaken.

Results

In order to test the structural variations in the olefin component which might be accommodated in this reaction with diborane, we carried out a number of small scale experiments utilizing a variety of olefins. In these experiments, 6.0 mmoles of diborane (generated from sodium borohydride and boron trifluoride etherate) was passed over a period of 30 minutes into a solution of 18.0 mmoles of olefin dissolved in 15.0 ml. of diglyme at room temperature. The exit to the reaction vessel was connected to a wash bottle containing acetone, which converts diborane into diisopropoxyborane. The reaction mixture was permitted to remain at room temperature for a further 30 minutes. Then ethylene glycol was added to convert residual hydride in the reaction mixture to hydrogen. Diborane not absorbed in the reaction vessel was determined by titrating the acetone wash solution for boric acid (after hydrolysis). These two analysis yielded the hydride not utilized for addition. By difference, the hydride[8] utilized for reaction with the olefin is estimated.

The results of these experiments utilizing diglyme as a solvent are summarized in Table I.

In order to test whether ether solvents other than diglyme were applicable to this reaction, we carried out a number of hydroborations under identical conditions utilizing tetrahydrofuran as the solvent. The results are summarized in Table II.

Preliminary experiments indicate that the procedures should prove applicable to the hydroboration of olefins containing substituents which are

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[1] Post-doctorate research assistant, 1955–1957, on grants provided by The Upjohn Co., Parke, Davis and Co., and Merck and Co.

[2] H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 2582 (1956); **81**, 6423 (1959).

[3] D. T. Hurd, *ibid.*, **70**, 2053 (1948).

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

[5] A. T. Whatley and R. N. Pease, THIS JOURNAL, **76**, 835 (1954).

[6] F. G. A. Stone and W. A. G. Graham, *Chemistry & Industry*, 1181 (1955).

[7] A preliminary Communication describing this observation was published earlier; H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[8] It is convenient to discuss these reactions in terms of the total available hydride. Thus 1.0 mmole of diborane contains 6.0 mmoles of "hydride."

TABLE I

REACTION OF REPRESENTATIVE OLEFINS WITH EXCESS DIBORANE IN DIGLYME SOLUTION AT 25°

Olefin	Residual hydride mmoles	Boron in acetone, mmoles	Hydride used, mmoles	Hydride used/ olefin
Blank	10.5	8.24	0.8	
Blank	5.9	9.72	0.9	
1-Hexene	12.8	1.10	19.1	1.06
1-Octene	17.0	0.80	15.8	0.88
2,4,4-Trimethyl-1-pentene	7.7	3.10	18.2	1.00
2-Hexene	13.2	1.07	18.8	1.04
2-Octene	17.8	0.14	17.0	0.94
Cyclopentene	8.9	2.66	18.3	1.00
Cyclohexene	12.6	0.9	19.9	1.10
2-Methyl-2-butene[a]	15.3	.22	19.1	1.06
2,4,4-Trimethyl-2-pentene	19.2	.55	13.4	0.74
2,3-Dimethyl-2-butene	22.0	.08	12.7	.71
Styrene	13.6	1.59	16.8	.93
1,1-Diphenylethylene	15.3	0.49	18.3	1.01
trans-Stilbene[b]	12.9	.52	20.6	1.14
Triphenylethylene[c]	18.7	.92	13.4	0.74

[a] Reaction mixture cooled in ice because of volatility of compound. [b] Because of low solubility of stilbene in diglyme, reaction was carried out at 40–50°. [c] Precipitate observed during addition of diborane.

TABLE II

REACTION OF REPRESENTATIVE OLEFINS WITH EXCESS DIBORANE IN TETRAHYDROFURAN SOLUTION AT 25°

Olefin	Residual hydride, mmoles	Boron in acetone, mmole	Hydride used, mmoles	Hydride used/ olefin
Blank	35.0	0	1.0	
1-Hexene	16.5	0.04	18.4	1.02
1-Decene	17.7	.03	17.2	0.96
1-Tetradecene	17.7	.04	17.2	0.96
2-Hexene	16.7	.03	18.2	1.01
2,4,4-Trimethyl-2-pentene	21.9	.03	13.0	0.72
α-Methylstyrene	16.2	.02	18.7	1.04
Allyl ethyl ether	14.5	.0	20.5	1.14
Ethyl oleate	14.3	.0	20.7	1.15
Ethyl cinnamate	6.5	.0	28.5	1.60

TABLE III

REACTION OF DIBORANE AT 25° WITH REPRESENTATIVE OLEFINS PRESENT IN EXCESS

Olefin	Solvent[a]	Residual hydride, mmoles	Boron in acetone, mmoles	Hydride used, mmoles	Hydride used, %
1-Hexene	DG	0.0	0.92	33.2	92
	EE	.0	.78	33.7	93
	THF	.0	.14	35.5	98
	H	8.7	2.9	18.6	52
2-Hexene	DG	0.0	0.48	34.6	96
	EE	.0	.47	34.6	96
	THF	.0	.15	35.5	98
Cyclohexene	DG	.27	.31	34.8	97
2-Methyl-2-butene	DG	10.0	.30	25.1	70
2,4,4-Trimethyl-2-pentene	DG	11.6	.13	24.0	66
	DG[b]	12.9	.0	23.1	64
	THF	15.8	.0	20.2	56
2,3-Dimethyl-2-butene	DG	22.4	.03	13.5	37

[a] DG, diglyme; EE, ethyl ether; THF, tetrahydrofuran; H, heptane. [b] Four hours reaction time.

relatively inert to the reducing action of diborane. Thus allyl ethyl ether and ethyl oleate appear to undergo hydroboration smoothly, whereas in the case of ethyl cinnamate significant reduction of the ester grouping apparently accompanies the hydroboration reaction.

In the experiments reported in Tables I and II, hydride was present in excess: 36.0 mmoles of hydride (from 6.0 mmoles of diborane) to 18.0 mmoles of olefin. It appeared desirable to examine the extent of utilization of hydride by olefin present in excess. Accordingly, a number of experiments were carried out in which 6.0 mmoles of diborane was passed into 40 mmoles of olefin in 15.0 ml. of solvent over a period of 30 minutes, the reaction mixture allowed to stand for another 30 minutes, and the hydride utilization estimated as in the earlier experiments. The results are summarized in Table III.

In order to test the utility of this procedure for the conversion of olefins into organoboranes, several representative olefins (0.3 mmoles) were treated with diborane (20% excess). Both diglyme and tetrahydrofuran were utilized as solvents. When diglyme was used, the diborane was passed in at a slower rate, over two hours, to minimize losses of this reactant. Because of the high solubility of diborane in tetrahydrofuran, the gas could be passed into the reaction mixture more rapidly, one hour, without significant loss. The reaction mixtures were allowed to stand for two additional hours, the solvent removed under reduced pressure, and the residual organoborane recovered by a rapid distillation at reduced pressure.

The results are summarized in Table IV.

TABLE IV

SYNTHESIS OF TRIALKYLBORANES

Olefin[a]	Solvent[b]	Reaction product, borane	B.p. °C.	B.p. Mm.	Yield, %
1-Hexene	DG	Tri-*n*-hexyl-	185–188	30	91
2-Hexene	DG	Tri-*sec*-hexyl-	168–170	30	92
1-Octene	DG	Tri-*n*-octyl-	144–145	2	90
1-Decene	THF	Tri-*n*-decyl-	205–208	5	84
Cyclohexene	THF	Tricyclohexyl-	130–131	2	86
Cyclopentene	THF	Tricyclopentyl-	118–119	2	79

[a] 0.3 mole. [b] For notation, see Table III.

The observed boiling points agree closely with those previously noted for the organoboranes synthesized with the aluminum chloride–sodium borohydride reagent.[2] In the latter preparations the purities were confirmed by analysis of the reaction products for boron. In view of the narrow boiling ranges and the excellent agreement in the boiling points, a similar analysis of the products was considered unnecessary.

That the addition of diborane to terminal olefins occurs to place the boron predominantly at the terminal carbon was established by oxidation of the hydroboration reaction product. Thus 1-hexene yields 1-hexanol and 1-decene yields 1-decanol. On the other hand, internal olefins yield mixtures: 2-hexene yielding both 2- and 3-hexanol in equal amounts and 2,4,4-trimethyl-2-pentene yielding a mixture of isopropyl-*t*-butylcarbinol and 2,4,4-trimethyl-2-pentanol. In all respects the results appear identical with those previously noted in the conversion of olefins to alcohols through the hydroboration reaction utilizing the aluminum chloride–sodium borohydride reagent

As in that case, it proved possible to oxidize the organoborane reaction product in the reaction mixture without prior isolation. Consequently, hydroboration of olefins with diborane in tetrahydrofuran or diglyme solution, followed by oxidation with alkaline hydrogen peroxide, provides an alternative convenient procedure for the anti-Markownikoff hydration of double bonds.

The results of several such experiments are summarized in Table V.

TABLE V

DIRECT CONVERSION OF OLEFINS INTO ALCOHOLS

Olefin	Amt., mole	Alcohol	Yield, %	B.p. °C.	B.p. Mm.
1-Hexene	0.3	1-Hexanol	87	155–157	763
2-Hexene	.3	2- and 3-hexanol[a]	80	136–138	750
1-Decene	.3	1-Decanol	85	227–229	738
2,4,4-Trimethyl-2-pentene	.3	Isopropyl-*t*-butylcarbinol and 2,4,4-trimethyl-2-pentanol	85	145–155	743

Analysis by gas chromatography by Dr. George Zweifel has since shown that the two isomeric alcohols are formed in equal amounts.

In these experiments diborane was conveniently generated by adding a solution of sodium borohydride in diglyme, contained in a dropping funnel, to a solution of boron trifluoride etherate in diglyme contained in the generation flask.[9] In this procedure, diborane is evolved quantitatively in accordance with the amount of sodium borohydride added to the generation flask. In the alternative procedure, addition of boron trifluoride etherate to the borohydride contained in the generation flask, diborane is not evolved until most of the boron halide has been added. In the initial stages the diborane is retained in the generation flask in the form of an addition compound with sodium borohydride, $NaBH_4 \cdot BH_3$.[9]

It appeared that this feature might be of advantage for the hydroboration reaction. If the addition compound, $NaBH_4 \cdot BH_3$, reacted readily with olefins, the external generation of diborane could be avoided. Accordingly, we undertook to carry out the hydroboration of olefins by adding boron trifluoride etherate in diglyme solution to a mixture of the olefin and sodium borohydride in diglyme solution.

Under these conditions representative olefins proved to undergo hydroboration readily to form the trialkylboranes. Moreover, the procedure proved to have a number of advantages, especially in the fact that diborane can be retained readily in the reaction mixture by use of an excess of sodium borohydride until the hydroboration reaction is complete. The reaction product was analyzed for organically bound boron. The results confirm the yields estimated from the hydride utilization. The data are summarized in Table VI.

TABLE VI

REACTION OF REPRESENTATIVE OLEFINS WITH SODIUM BOROHYDRIDE–BORON TRIFLUORIDE ETHERATE IN DIGLYME SOLUTION AT 25°

Olefin	Olefin, mmoles	Hydride used, mmoles	Hydride/olefin	Organoborane Boric acid, mmoles	Organoborane Yield of R_3B, %
1-Hexene	11.8	12.0	1.02		
	12.1	12.1	1.00		
1-Octene	12.0	10.5	0.87	3.27	82
	12.0	10.6	.88	3.40	85
2,4,4-Trimethyl-1-pentene	10.3	9.4	.91	2.94	85
	9.7	8.4	.88	2.70	85
2-Hexene	10.7	10.9	1.02		
	11.9	12.1	1.02		
Cyclopentene	12.0	11.3	0.94	3.45	86
	10.6	10.3	.97	3.31	93
2,4,4-Trimethyl-2-pentene	10.4	9.1	.88	2.88	83
	9.7	8.6	.89	2.82	87
Styrene	7.3	7.4	1.01		
	6.0	6.8	1.13		
α-Methylstyrene	13.7	11.8	0.85		
	10.9	10.5	.96		
1,1-Diphenylethylene	10.6	10.4	.98		
	11.2	10.8	.97		

The results clearly indicate that treatment of a solution of sodium borohydride and olefin in diglyme with boron trifluoride etherate results in the ready hydroboration of the olefin. The procedure possesses the obvious advantage of avoiding the generation of diborane in a separate generator. It was demonstrated that the procedure could be utilized for the synthesis of organoboranes and for the direct conversion of the olefins into the corresponding alcohols. In these preparative experiments the sodium borohydride was utilized in 20% excess, although this does not appear to be a critical feature.

Either diglyme or triglyme may be utilized for the reaction. As in the corresponding syntheses with sodium borohydride–aluminum chloride, separation of the alcohol is facilitated by the preferential solubility of diglyme and triglyme in water. Consequently, these solvents are readily washed out of the ether solutions of the alcohol products. Alternatively, the reaction mixtures may be treated with solid sodium hydroxide, forming an upper layer of the alcohol product in diglyme or triglyme. Distillation of this layer readily yields the alcohol. Purification of the product can be facilitated by proper selection of the solvent (diglyme, b.p. 160°; triglyme, b.p. 216°).

In the case of lithium borohydride, with its general solubility in many ether solvents, the hydroboration reaction can be carried out in ethyl ether, tetrahydrofuran and numerous other solvents.

Typical syntheses on a preparative scale are summarized in Table VII.

Discussion

The fast reaction of diborane with olefins observed in this study is quite unexpected in view of the implications of earlier studies. Thus, Hurd, who in 1948 first noted a reaction between olefins and diborane,[3] reported that he had heated ethylene and diborane in a sealed tube at 100° for four days to obtain a liquid product identified through mass spectrometric analysis as triethylboron. In the case of isobutylene a reaction time

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(9) H. C. Brown and P. A. Tierney, THIS JOURNAL, **80**, 1552 (1958).

TABLE VII

DIRECT CONVERSION OF OLEFINS INTO ALCOHOLS[a]

Olefin	Amt., mole	Alcohol	Yield, %	B.p. °C.	B.p. Mm.
1-Hexene	0.3	1-Hexanol	95	154–156	738
1-Decene	.3	1-Decanol	92	227–229	743
t-Butylethylene[b]	.3	3,3-Dimethyl-1-butanol	62	140–145	745
2-Hexene	.3	2- and 3-hexanol	90	136–138	744
2,4,4-Trimethyl-2-pentene	.3	Isopropyl-*t*-butylcarbinol and 2,4,4-trimethyl-2-pentanol	85	145–155	743
Cyclopentene[b]	.5	Cyclopentanol	90	139–141	742
α-Methylstyrene	.5	2-Phenyl-1-propanol	92	110–112	15

[a] The solvent is diglyme, except where otherwise indicated. [b] Triglyme.

of 24 hours at 100° sufficed, and it was stated that the addition reaction was even slower at room temperature.[5]

Similarly, in attempting to polymerize acrylonitrile, methyl methacrylate and styrene, Stone and Emeleus reported that only a slow reaction yielding a complex product occurs between diborane and these unsaturated molecules at room temperature.[4] More recently, Stone and Graham observed that serious explosions resulted upon heating tetrafluoroethylene with diborane at 80–100° for extended periods of time. A simple addition reaction was not observed.[6,10] Finally, Whatley and Pease utilized temperatures of 130–177° in their study of the kinetics of the reaction of diborane with ethylene and related olefins.[5]

In view of this general agreement that the reaction of diborane with olefins is a sluggish one, requiring elevated temperatures for completion, the rapid reaction which we observed at room temperature was highly unexpected. It forced us to revise our tentative interpretation of the mechanism of the sodium borohydride–aluminum chloride hydroboration reaction and to seek an explanation of the vast difference between our observations and those of earlier workers.

One factor which might be responsible for the difference in the observations appeared to be our use of ethers as solvents for the reaction. Accordingly, we utilized *n*-heptane as a solvent for the hydroboration of 1-hexene (Table III). A 52% utilization of hydride was observed in contrast to the 92–98% reaction achieved in ether solvents. Although the result was in the direction anticipated for a solvent effect, it appeared to be a relatively small factor from the results of these experiments.

However, when we repeated the experiment in a high vacuum apparatus with carefully purified reactants, the situation was altered. The absorption of diborane by 1-octene in *n*-heptane solution was indeed slow, requiring many hours for completion.[11] The addition of minor amounts of ethers (or other weak Lewis bases) to the reaction system resulted in a fast reaction, too fast for convenient measurement. It appeared that in the experiment previously described to compare the relative effects of *n*-heptane and ether solvents upon the rate of the hydroboration reaction, the experiment was largely vitiated by the traces of diglyme carried over by the diborane from the generator flask.

It is probable that the ether functions to dissociate the diborane to some extent, producing in the reaction mixture a moderate concentration of a more active intermediate, the borane etherates. However a detailed discussion is best deferred until we have presented our observations on the stereochemistry of the addition,[12] as well as our data on the kinetics of the addition and the catalysis of the reaction.[11]

The present results indicate that in ether solvents diborane adds with remarkable ease at room temperature to olefins of all types. The structural variations examined are summarized in Table VIII.

TABLE VIII

SUMMARY OF OLEFINS WHICH ADD DIBORANE

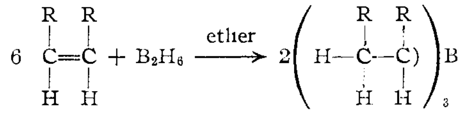
Olefin type	Examples
Terminal olefins	1-Hexene, 1-octene, 1-decene, 1-tetradecene, 3,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene
Internal olefins	
A. Dialkyl	2-Hexene and 2-octene
B. Cyclic	Cyclopentene and cyclohexene
C. Trialkyl	2-Methyl-2-butene and 2,4,4-trimethyl-2-pentene
D. Tetraalkyl	2,3-Dimethyl-2-butene and 1,2-dimethylcyclohexene[a]
Aryl substd. olefins	Styrene, α-methylstyrene, 1,1-diphenylethylene, *trans*-stilbene, triphenylethylene
Substd.-olefins	Allyl chloride, allyl ethyl ether, ethyl oleate, ethyl cinnamate

[a] Ref. 12. In this reference, the reaction has been extended to bicyclic olefins, such as norbornene and α-pinene.

Consequently, it appears that the hydroboration reaction is one of wide applicability, possibly as general a reaction as is the addition of hydrogen or halogen to a double bond.

Addition appears to occur smoothly, without rearrangement of the carbon skeleton. Thus, *t*-butylethylene undergoes hydroboration and oxidation to form the unrearranged alcohol, 3,3-dimethyl-1-butanol.[13]

In the case of the great majority of olefins the reaction appears to proceed to the complete utilization of the active hydrogen of the diborane molecule.



$$6\ \begin{matrix}R & & R\\ | & & |\\ C & = & C\\ | & & |\\ H & & H\end{matrix} + B_2H_6 \xrightarrow{\text{ether}} 2\left(\begin{matrix} & R & & R\\ & | & & |\\ H- & C & - & C\\ & | & & |\\ & H & & H\end{matrix}\right)_3 B$$

However, trisubstituted olefins, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, appear to react at room temperature to utilize only two-thirds of the active hydrogen, yielding a dialkylborane, R_2BH (or its dimer) as the reaction product.[14]

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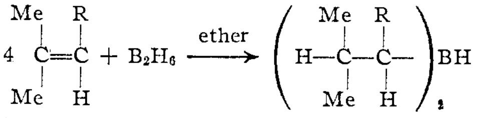
[10] Professor Stone has informed the authors that he has achieved the simple addition of diborane to tetrafluoroethylene by utilizing the ether-catalyzed reaction described in this publication.

[11] Unpublished observations of Dr. P. A. Tierney and Dr. Laura Case.

[12] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247 (1959).

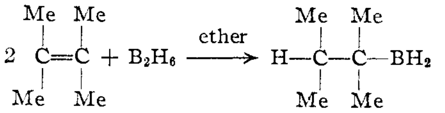
[13] Professor M. S. Newman of Ohio State University has accomplished the hydroboration of 1,1-di-*t*-butylethylene without rearrangement (private communication).

[14] For an interesting application of this observation, see H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 1512 (1959).



$$4\ \mathrm{Me_2C{=}C(R)H} + \mathrm{B_2H_6} \xrightarrow{\text{ether}} \left(\mathrm{H{-}CMe_2{-}CH(R){-}}\right)_2\mathrm{BH}$$

Finally, the reaction with tetrasubstituted olefins appears to halt at the monoalkylborane, RBH_2, stage.



$$2\ \mathrm{Me_2C{=}CMe_2} + \mathrm{B_2H_6} \xrightarrow{\text{ether}} \mathrm{H{-}CMe_2{-}CMe_2{-}BH_2}$$

With the present study there are now available three convenient procedures for the hydroboration of olefins under mild conditions: hydroboration with sodium borohydride–aluminum chloride, hydroboration with diborane at 0 or 25°, and hydroboration with sodium borohydride–boron trifluoride etherate.

$$9RCH{=}CH_2 + 3NaBH_4 + AlCl_3 \longrightarrow 3(RCH_2CH_2)_3B + AlH_3 + 3NaCl$$

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3 \longrightarrow 4(RCH_2CH_2)_3B + 3NaBF_4$$

$$6RCH{=}CH_2 + B_2H_6 \longrightarrow 2(RCH_2CH_2)_3B$$

Each of these procedures possesses certain advantages. Thus the use of diborane produces the trialkylborane in essentially quantitative yield in ether solution, with no inorganic salts or other by-products to be separated. For this procedure tetrahydrofuran has many advantages as a reaction medium. It is volatile and readily separated from the product by distillation, and diborane is highly soluble, favoring the absorption and complete utilization of the gas.

The sodium borohydride–aluminum chloride procedure does not liberate diborane and is therefore advantageous for large scale preparations. It suffers the disadvantage of being somewhat slower than the other procedures and of utilizing only 75% of the active hydrogen of the borohydride.

The sodium borohydride–boron trifluoride procedure possesses many advantages for large scale preparations where the presence of the reaction product, sodium borofluoride, offers no difficulty. For the last two procedures diglyme and triglyme are the preferred solvents. By taking advantage of the large difference in the boiling points of these two solvents, purification of the products can be facilitated.

At elevated temperatures olefins can be hydroborated by pyridine–borane or trialkylamine–borane.[15] These reactions require temperatures in the range of 100 to 200°, presumably proceeding through a partial dissociation of the addition compounds into their components. Under these conditions the trialkylboranes undergo isomerization.[16] Consequently, in instances where isomerization of the organoborane is not a factor, hydroboration utilizing the amine-boranes provides a fourth synthetic route from olefins to organoboranes. Since diborane is readily prepared from amine–boranes by treatment with Lewis acids,[17,18] it is apparent that the amine–boranes may be utilized with boron halides to accomplish the hydroboration of olefins at lower temperatures. Such reactions have been demonstrated, but are less convenient than those based on the alkali metal borohydrides.[19]

These hydroboration reactions render the organoboranes readily available. In addition to the advantages of possessing a simple synthesis of organoboranes, it appears that this reaction should possess wide utility in organic synthesis with the organoboranes being utilized primarily as reactive intermediates. The anti-Markownikoff hydration of olefins constitutes one example of such an application. We are currently examining other such applications and hope to report them shortly.

Experimental Part

Materials.—Diglyme (dimethyl ether of diethylene glycol) and triglyme (dimethyl ether of triethylene glycol) were obtained from the Ansul Chemical Co. and purified as described earlier.[9,20] Tetrahydrofuran (du Pont) was purified by standard procedures previously described.[9] Sodium borohydride (98⁺%) from Metal Hydrides, Inc., was used without purification. Boron trifluoride ethyl etherate (Matheson, Distillation Products) was distilled in an all-glass apparatus under reduced pressure and utilized shortly after the distillation.

With the exceptions noted below the olefins were Phillips Pure Grade (99%) where available and Technical Grade (95%) otherwise. 1-Decene and 1-tetradecene were from the Humphrey–Wilkinson Co. *t*-Butylethylene and 1,1-diphenylethylene were available from an earlier study.[2] *trans*-Stilbene was a commercial product (Distillation Products) and both triphenylethylene and tetraphenylethylene were synthesized by standard methods and recrystallized to constant m.p. 2,3-Dimethyl-2-butene was kindly supplied by Dr. K. W. Greenlee of Ohio State University.

Generation of Diborane.—Diborane was generated by adding a solution of sodium borohydride in diglyme to a solution of a slight excess of boron trifluoride etherate in diglyme,[9] in accordance with the equation: $3NaBH_4 + 4BF_3{:}OEt_2 \rightarrow 2B_2H_6 + 3NaBF_4$. In a vacuum line, the reaction is quantitative. Using ordinary apparatus, the yields were in the range of 90 ± 5%. The decrease in yield presumably arises from traces of water and other impurities containing active hydrogen in the solvents and apparatus. In general the hydroborations with external generation were carried out on the basis of a 90% yield of diborane.

The generator consisted of a 250-ml. 3-necked flask equipped with a pressure-equalized dropping funnel, an inlet for nitrogen (alternatively the nitrogen can be introduced through the dropping funnel), an outlet for the diborane and a magnetic stirrer. The diborane outlet was connected by a short length of Tygon tubing to a T-tube dipping in mercury to serve as a safety release valve, with provision for diborane escaping through the mercury to be led into running water to destroy the gas. The diborane then passed through a sintered glass dispersion tube into the solution contained in the reaction flask. The exit from the reaction vessel was connected through a mercury bubbler to a wash bottle containing acetone. (Diborane reacts with acetone rapidly to form diisopropoxyborane, $[(CH_3)_2CHO]_2BH$.) Consequently, hydrolysis of an aliquot of the solution, followed by titration for boric acid, provides an estimate of the diborane which had not been utilized in the reaction.

Hydroboration with Isolation of the Organoborane.—In the reaction flask was placed 25.2 g. of 1-hexene (0.300 mole) dissolved in 100 ml. of diglyme. In the dropping funnel of the diborane generator was placed 0.100 mole of sodium borohydride (100 ml. of a 1.00 *M* solution in diglyme) and in

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[15] M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958); E. C. Ashby, Abstracts, 1959, A. C. S. Meeting, Boston, Mass., p. 31M.

[16] G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, THIS JOURNAL, **79**, 5190 (1957); H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957).

[17] G. W. Schaeffer and G. D. Barbaras, U. S. Patent 2,533,696 (Dec. 12, 1950).

[18] R. Köster and K. Ziegler, *Angew. Chem.*, **69**, 94 (1957).

[19] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 4106 (1959).

[20] H. C. Brown, E. J. Mead and D. C. Subba Rao, *ibid.*, **77**, 6209 (1955).

the flask of the generator was placed 0.220 mole of boron trifluoride etherate (excess) in 50 ml. of diglyme. The apparatus was flushed with nitrogen. The nitrogen flow was reduced almost to zero, and the sodium borohydride solution was added slowly, over a period of 2 hours, to the generator flask. When the addition was complete, the generator flask was warmed to 60–70° and, after a few minutes, the nitrogen flow increased for several minutes to drive residual diborane into the reaction flask. The reaction mixture was then allowed to stand for another 2 hours at room temperature. The reaction flask was removed, quickly connected to a short Vigreux distilling head, and the solvent removed under reduced pressure. The residue, crude trialkylborane, was distilled rapidly to obtain 24.2 g. of tri-*n*-hexylborane, b.p. 185–188° at 30 mm., a yield of 91%. Analysis of a sample showed that it contained 97% of the boron expected on the basis of the formula $(C_6H_{13})_3B$.

This procedure, utilizing a short Vigreux distilling head and rapid distillation, was adopted in order to minimize the loss of olefin. Rosenblum[21] had reported a slow decomposition of tri-*n*-butylborane into *n*-butyldiboranes and butene upon refluxing for 10 days at 125–130°. R. Köster has reported that he observed a breakdown of tri-*n*-decylborane into 1-decene and di-*n*-decylborane upon attempted distillation.[22] While we cannot eliminate the possibility of the existence of a minor amount of such breakdown materials in our products, both the narrow range of the boiling point and the excellent boron analyses indicate that this decomposition was not a significant factor in our preparations. We are unable to account for the difference between Dr. Koster's and our observations on this point.

Identical procedures were utilized for the hydroboration of 1-octene, 1-decene, 2-hexene, cyclohexene and cyclopentene. In all cases the yields were 80–90%. Data for the individual preparations are summarized in Table IV.

Hydroboration with Direct Synthesis of Alcohol.—Utilizing the identical hydroboration procedure, 42.0 g. of 1-decene, b.p. 62° at 15 mm., was converted in the tri-*n*-decylborane. At the end of the reaction, the dropping funnel was replaced with a condenser and the reaction mixture was treated with 20 ml. of water to hydrolyze residual hydride. After the hydrogen evolution had ceased, 40 ml. of 3 *N* aqueous sodium hydroxide was added, followed by 40 ml. of 30% aqueous hydrogen peroxide, added in small batches at a rate to maintain a gentle reflux. The hot reaction mixture was stirred for another hour, then ice-water was added, and the alcohol present was taken up in ethyl ether. The ether extracts were washed with small portions of ice-water to wash out the diglyme. Distillation yielded 44.1 g. of 1-decanol, b.p. 226–230; a yield of 93%. Refractionation gave 40.3 g. of 1-decanol, b.p. 227–229° at 739 mm., $n^{20}D$ 1.4370, a yield of 85%.

Similar procedures were utilized to convert 1-hexene, 2-hexene and 2,4,4-trimethyl-2-butene to the corresponding alcohols. The results are summarized in Table V.

Triglyme and tetrahydrofuran may also be utilized as reaction media.

In addition to the procedure described above, it is possible to treat the reaction mixture from the oxidation with solid sodium hydroxide to form a lower layer containing the boron and an upper layer containing the solvent (diglyme, triglyme or tetrahydrofuran) and the alcohol. Separation of this layer, drying over magnesium sulfate, and distillation permits recovery of the alcohol in satisfactory purity. In this procedure, the availability of diglyme (b.p. 160°) and triglyme (b.p. 216°) makes it possible to select that solvent which will facilitate separation from the alcohol in the distillation. Tetrahydrofuran is particularly effective in many cases because of its high solvent ability for diborane and its low boiling point.

Hydroboration with Sodium Borohydride–Boron Trifluoride Etherate.—In a 500-ml. three-necked round-bottom flask fitted with a mechanical stirrer, a pressure-equilibrated dropping funnel, nitrogen inlet and outlet, was placed 42.0 g. of 1-decene (0.300 mole), 50 ml. of diglyme and 0.090 mole of sodium borohydride (90 ml. of a 1.00 *M* solution in diglyme). In the dropping funnel was placed 17.0 g. (0.120 mole) of freshly distilled boron trifluoride etherate in 25 ml. of diglyme. The apparatus was flushed out with nitrogen, and then a slight static pressure of the gas was maintained as the boron trifluoride etherate solution was added to the stirred solution over a period of 1 hour. During this time the flask was cooled by running water. The reaction mixture was permitted to stand at room temperature for a second hour, the separatory funnel replaced by a reflux condenser, and the reaction mixture hydrolyzed by 20 ml. of water. When hydrogen was no longer evolved, 40 ml. of 3 *N* sodium hydroxide was added, and the oxidation carried out by adding 40 ml. of 30% hydrogen peroxide in small batches, at such a rate that a gentle reflux was maintained. The reaction mixture was allowed to cool, treated with ice-water, and the alcohol taken up in ether. The ether extracts were washed with ice-water to remove diglyme and the product recovered by distillation. There was obtained 43.7 g. of 1-decanol, b.p. 227–229° at 743 mm., a yield of 92%. Data on related syntheses are summarized in Table VII.

Small Scale Hydroboration Studies.—The apparatus was similar to the generator and reactor described above except for size (50 ml.). The system was flushed with nitrogen. In the generator flask was placed 25 mmoles of boron trifluoride etherate in diglyme (10 ml. of a 2.5 *M* solution) and in the dropping funnel was placed 9.9 mmoles of sodium borohydride (9.9 ml. of a 1.00 *M* solution in diglyme). In the reaction vessel (constructed from an 8″ test-tube fitted with a 24/40 ground joint and a sealed in fritted glass inlet tube) was placed 15 ml. of diglyme and 18 mmoles of the olefin under study. The bubbler top was attached and secured by springs. In the wash bottle was placed 25 ml. of acetone. The system was again flushed briefly with nitrogen and the flow reduced almost to zero. The generator was stirred magnetically and the sodium borohydride solution added dropwise. The diborane generated passed through the sintered glass bubbler into the olefin. After addition of the sodium borohydride was complete, the generator was warmed to 60–70° for a few minutes and a slow stream of nitrogen utilized to drive the residual diborane into the reaction flask.

At the end of the reaction time, 10 ml. of ethylene glycol was added to destroy residual hydride, and the gas evolved, passed through a cold trap, was collected in gas burets over water.

The acetone in the wash bottle was diluted with water, mannitol added, and the boric acid in solution determined by titration with standard sodium hydroxide to the phenolphthalein end-point.

The residual hydride in the reaction mixture, together with three times the milliequivalents of boron found in the acetone, gave the total number of millimoles of hydride not utilized in the reaction. A blank determination, with no olefin in the reaction flask, gave the number of mmoles of hydride available for reaction. The difference was taken as the number of mmoles of hydride which had reacted with the 18 mmoles of olefin in the reaction flasks. Because of low solubility, it proved impractical to include tetraphenylethylene in these studied. The results of these experiments are summarized in Table I.

Related experiments utilizing tetrahydrofuran as solvent are given in Table II. Because of the greater solubility of diborane in tetrahydrofuran then in diglyme, the time required for the diborane generation could be greatly shortened. Note the minor amounts of boron found in the acetone trap.

Essentially the same procedure was utilized for the experiments in Table III in which excess olefin (40 mmoles) was allowed to react with diborane (6.0 mmoles).

In the experiments in which sodium borohydride–boron trifluoride etherate was used directly for the reaction with olefin, the procedure was simpler. Two 50-ml. round-bottom flasks, provided with magnetic stirrers and with stoppers, were dried and flushed with nitrogen. Into each was placed 7.2 mmoles of sodium borohydride (7.2 ml. of a 1.00 *M* solution in diglyme). To one flask was added a weighed sample of the olefin (10–12 mmoles). The other flask was utilized as a blank. Into each of these stirred flasks was then slowly added 4.0 mmoles of boron trifluoride etherate (2.0 ml. of a 2.0 *M* solution in diglyme). A water-bath at 25° was used to maintain the temperature. At the end of the reaction time, the flasks were removed from the bath, 10 ml. of ethylene glycol added, and the hydrogen evolved measured. The difference between the hydrogen evolved by the blank and that evolved by the reaction mixture was taken as the hydride utilized by the olefin.

To determine the yield of organoborane in these experiments, the reaction mixtures were extracted three times with ethyl ether. The combined ether extracts were washed with a small amount of water in order to remove any inor-

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[21] L. Rosenblum, THIS JOURNAL, **77**, 5016 (1955).

[22] R. Köster, *Ann.*, **618**, 31 (1958).

ganic boron which might be present. Part of the ether was then distilled and the residue was treated with 5.0 ml. of 2 *N* sodium hydroxide and 5.0 ml. of 30% hydrogen peroxide added in small amounts. The reaction mixture was refluxed for 5 minutes on the water-bath, cooled, and titrated for boric acid. The yield of organoborane was equated to the yield of boric acid obtained in this procedure.

The results are summarized in Table VI.

Acknowledgment.—We wish to express our appreciation to Dr. Walter Korytnyk who carried out several of the experiments listed in Tables I and III, permitting a more extensive examination of the scope of the hydroboration reaction.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Organoboranes. I. Isomerization and Displacement Reactions of Organoboranes. A Convenient Procedure for the Conversion of Internal Olefins into Primary Alcohols

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RECEIVED MAY 15, 1959

The hydroboration of 2-hexene yields an organoborane which, oxidized directly without prior isolation, yields 2- and 3-hexanol in equimolar amounts. However, if the organoborane is heated in refluxing diglyme (160°) for four hours prior to oxidation, the product obtained is essentially pure 1-hexanol. In the same manner 2-octene, mixed 2-, 3-, 4- and 5-decenes, and a similar mixture of tetradecenes have been converted into 1-octanol, 1-decanol and 1-tetradecanol. It is proposed that the isomerization of the organoborane proceeds through a sequence of eliminations to form olefin and dialkylborane, followed by readditions, until the borane has been completely converted into the more stable tri-*n*-alkylborane. In confirmation of this mechanism is the observation that treatment of a trialkylborane with a higher olefin readily liberates the lower olefin with the concurrent formation of a new trialkylborane. In this way, tri-*n*-pentylborane, refluxed with 1-hexene, 1-octene and 1-decene, yields 1-pentene and, in turn, tri-*n*-hexyl-, tri-*n*-octyl- and tri-*n*-decylborane. 2-Octene, in the presence of organoborane as a catalyst, has been partially isomerized in a fractionating column to 1-octene.

The hydroboration of olefins provides a new, simple synthetic route to the organoboranes.[2] The ready availability[2] and high reactivity[3] of the organoboranes suggest that these compounds should have wide utility in organic synthesis and may well become a valuable adjunct to the organomagnesium compounds for such purposes. Accordingly, we have undertaken a systematic investigation of the chemistry of the organoboranes. The present paper is the first of a group which will present our results on the utility of these intermediates in organic syntheses.

Originally, in our hydroboration studies,[2] we isolated the organoboranes from the reaction mixture and then oxidized the products with alkaline hydrogen peroxide to obtain the alcohol. In this way we observed that the hydroboration of 2-pentene yields a tri-*sec* -pentylborane, b.p. 81–82° at 2 mm., with oxidation of this distilled material yielding 63% 2-pentanol and 37% 3-pentanol (infrared analysis).

Later we developed a simplified procedure in which the hydroboration product could be oxidized *in situ*, without isolation. In this procedure, the organoborane from 2-pentene yielded 2- and 3-pentanol in essentially equimolar amounts. During the earlier distillation a partial shift of the boron atom from the 3- to the 2-position of the alkyl group had occurred. Isomerization of a 2-alkylborane to a 1-alkylborane was first reported by Hennion, McCusker, Ashby and Rutkowski in their attempt to synthesize tri-*t*-butylborane by the reaction of *t*-butylmagnesium chloride with boron trifluoride.[4] Instead of the expected product, the organoborane contained both isobutyl and *t*-butyl groups.[5,6] They also reported that tri-*sec*-butylborane could be converted into tri-*n*-butylborane by heating under reflux (200–215°) for 20 hours.

In the course of our studies we observed that the isomerization proceeded far more rapidly in diglyme solution, usually being complete in 2 to 4 hours refluxing in that solvent (b.p. 160°).[7] Since the organoborane is conveniently synthesized in diglyme solution, it is evident that a simple conversion of internal olefins to terminal organoboranes and to primary alcohols is feasible. Accordingly, we undertook a study of this possibility.

Results and Discussion

The hydroboration of 2-pentene in diglyme solution[2] yields the corresponding tri-*sec*-pentylborane. Oxidation with alkaline hydrogen peroxide without isolation yields an equimolar mixture (infrared analysis) of 2- and 3-pentanol, b.p. 116–119° at 745 mm. On the other hand, if the diglyme solution of the hydroboration product is first heated for 4 hours under reflux, and then oxidized, the product is essentially pure 1-pentanol, b.p. 136–137° at 742 mm.

In a similar manner, 1-hexene yields 1-hexanol, b.p. 155–157° at 743 mm., whereas 2-hexene, yields an equimolar mixture of 2- and 3-hexanol,[8] b.p. 136–138° at 750 mm. After subjecting the

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[1] Post-doctorate research assistant, 1955–1957, on grants provided by The Upjohn Co., Parke, Davis and Co., and Merck and Co.

[2] (a) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6423 (1959); (b) **81**, 6428 (1959).

[3] H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, **61**, 105 (1938); J. R. Johnson, M. G. Van Campen, Jr., and O. Grummitt, *ibid.*, **61**, 111 (1938); J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., *ibid.*, **61**, 115 (1938); J. R. Johnson and M. G. Van Campen, Jr., *ibid.*, **61**, 121 (1938).

[4] E. Krause and P. Nobbe, *Ber.*, **64**, 2112 (1931).

[5] 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.

[6] G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, THIS JOURNAL, **79**, 5190 (1957).

[7] A preliminary Communication reporting this observation was published: H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[8] We are indebted to Dr. George Zweifel for this analysis utilizing gas chromatography.