

ORGANIC AND BIOLOGICAL CHEMISTRY

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

Hydroboration. I. The Reaction of Olefins with Sodium Borohydride-Aluminum Chloride. A Convenient Route to Organoboranes and the Anti-Markownikoff Hydration of Olefins

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The clear solution of sodium borohydride-aluminum chloride in diglyme reacts readily with olefins at room temperature to form the corresponding organoboranes, as indicated by the equation: $9\text{RCH}=\text{CH}_2 + \text{AlCl}_3 + 3\text{NaBH}_4 \rightarrow 3(\text{RCH}_2\text{CH}_2)_3\text{B} + \text{AlH}_3 + 3\text{NaCl}$. The reaction appears to be generally applicable and has been utilized to convert ethylene, propylene, 1- and 2-pentene, 1- and 2-hexene, 1-octene, 1-decene, 1-tetradecene, 2-methyl-2-butene, 3,3-dimethyl-1-butene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, styrene, α -methylstyrene, α,α -diphenylethylene, cyclopentene and cyclohexene to the organoboron derivatives. Moreover, several typical olefinic derivatives, such as allyl ethyl ether, vinyl ethyl ether, allyldimethylamine and allyl chloride have been demonstrated to react. Olefins containing reducible groups, such as ethyl cinnamate and ethyl oleate, undergo hydroboration of the double bond concurrently with reduction of the ester grouping. Aluminum borohydride in ether solvents likewise reacts readily at room temperature with olefinic double bonds. In these hydroborations, the boron atom adds to the less substituted carbon atom, with the hydrogen atom adding to the more substituted carbon atom of the double bond. The organoboranes are readily oxidized by alkaline hydrogen peroxide to the corresponding alcohols. Consequently, hydroboration followed by oxidation provides a convenient route for the anti-Markownikoff hydration of double bonds.

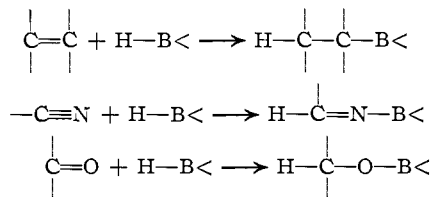
The addition of aluminum chloride to sodium borohydride in diglyme provides a clear solution with markedly greater reducing properties than those exhibited by sodium borohydride itself.² In the course of investigating the full applicability of this reagent for reducing various functional groups, we noted that olefins reacted readily at room temperature with the formation of organoboranes.³

It had been noted earlier that olefins could be converted to organoboranes by reaction with diborane or with aluminum borohydride.⁴⁻⁶ However, the reactions involved either elevated temperatures or long reaction times and did not appear to offer promise for a useful synthetic route. The discovery that sodium borohydride-aluminum chloride converts olefins rapidly and essentially quantitatively into organoboranes at room temperature offered real promise for a convenient synthetic procedure. Consequently, a detailed study of the reaction was undertaken.

Subsequently we observed that in ether solvents diborane adds rapidly and quantitatively to olefins.⁷ Similarly, sodium borohydride in the presence of boron halides readily transforms olefins into organoboranes.⁷ Consequently, there are now available several alternative procedures which permit the conversion of olefins into the corresponding organoboranes, rendering these reactive substances readily available as intermediates in organic synthesis. In the present paper we describe the

utilization of hydroboration followed by oxidation with alkaline hydrogen peroxide⁸ as a convenient procedure for the anti-Markownikoff hydration of double bonds.

The addition of the boron-hydrogen bond to carbon double and triple bonds appears to be a reaction of wide generality.⁷ Moreover, the addition of diborane to the carbon-oxygen double bond of the carbonyl group has long been known⁹ and its addition to the carbon-nitrogen triple bond of nitriles recently has been demonstrated.¹⁰



In view of its wide applicability, it appears desirable to have a convenient term to refer to this general addition of the hydrogen-boron bond to multiple linkages. The term hydroboration is suggested. The present paper is the first of a series of studies dealing with this general reaction and its applicability in organic synthesis.

Results

In preliminary experiments, the scope of the reaction was examined by treating a solution of the reagent ($3\text{NaBH}_4 + \text{AlCl}_3$) in diglyme with approximately 50% of the quantity of olefin corresponding to the available hydride.¹¹ After 3 hours at room temperature, the solution was

(8) J. R. Johnson and M. G. Van Campen, Jr., *THIS JOURNAL*, **60**, 121 (1938).

(9) H. C. Brown, H. I. Schlesinger and A. B. Burg, *ibid.*, **61**, 673 (1939).

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

(11) It is convenient to discuss the reagent in terms of the concentration of available hydride, as indicated by hydrogen evolution on hydrolysis. Thus, a 1.0 M solution of sodium borohydride is 4.0 M in hydride, while a 1.0 M solution of aluminum borohydride is 12.0 M in hydride.

(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).

(3) A preliminary communication of this observation was published: H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 2582 (1956).

(4) D. T. Hurd, *ibid.*, **70**, 2053 (1948).

(5) R. S. Brokaw, E. J. Badin and R. N. Pease, *ibid.*, **72**, 1793 (1950); R. S. Brokaw and R. N. Pease, *ibid.*, **72**, 3237, 5263 (1950); A. T. Whatley and R. N. Pease, *ibid.*, **76**, 835 (1954).

(6) F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 2755 (1950); F. G. A. Stone and W. A. Graham, *Chemistry & Industry*, 1181 (1955).

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

hydrolyzed and the hydrogen evolved was measured. The addition of hydride was estimated from the loss of active hydride from solution. The results of several typical experiments are summarized in Table I.

TABLE I

REACTION OF REPRESENTATIVE OLEFINS WITH SODIUM BOROHYDRIDE-ALUMINUM CHLORIDE IN DIGLYME

Olefin	Olefin, mmoles	Hydride, mmoles	Temp., °C.	Time, hr.	Hydride used, mmoles	Hydride/compd. Calcd.	Exptl.
1-Hexene	6.40	19.9	25	3.0	4.8	1.0	0.8
	7.48	18.9	75	1.0	7.1	1.0	1.0
1-Octene	8.13	20.3	25	0.5	8.7	1.0	1.1
	14.1	19.3	75	1.0	13.9	1.0	1.0
Styrene	7.59	19.9	25	1.0	7.1	1.0	0.9
	8.12	19.2	75	1.0	8.3	1.0	1.0
Cyclohexene	8.21	18.9	75	1.0	8.2	1.0	1.0
2,4,4-Tri-	4.24	20.4	25	3.0	3.9	1.0	0.9
methyl-2-	4.36	22.7	75	1.0	4.4	1.0	1.0
pentene							

In these experiments an excess of hydride was used. It appeared that the use of an excess of olefin would provide information both as to the ability of the reagent to react with the olefin in question and with regard to the number of hydrides in the reagent capable of reacting with the olefin under the reaction conditions. Accordingly 3.0 mmoles of sodium borohydride, 1.0 mmole of aluminum chloride and 24.0 mmoles of olefin were mixed and allowed to stand either at room temperature or at 75°. The amount of hydride added was estimated from the hydrogen evolved in the hydrolysis of the reaction product. The results are summarized in Table II.

TABLE II

REACTION OF EXCESS OLEFIN WITH SODIUM BOROHYDRIDE-ALUMINUM CHLORIDE IN DIGLYME^a

Olefin	Temp., °C.	Time, hr.	Hydride used, mmoles
1-Tetradecene	25	1.0	6.6
		3.0	7.1
		75	8.0
1-Octene	25	1.0	9.1
		3.0	9.4
1-Hexene	25	1.0	8.9
		3.0	9.5
1-Pentene	75	0.5	8.2
		75	8.3
2-Pentene	75	1.0	8.0
		3.0	9.2
Styrene	75	1.0	8.6
		3.0	9.1
2,4,4-Trimethyl-1-pentene	25	1.0	8.9
		3.0	9.1
2,4,4-Trimethyl-2-pentene	25	3.0	5.5
		75	6.7
Cyclohexene	25	1.0	6.6
		3.0	11.7
Cyclopentene	25	1.0	12.1
		3.0	7.1
	75	3.0	7.9
		1.0	8.6

^a 24.0 mmoles of olefin, 3.0 mmoles of sodium borohydride, 1.0 mmole of aluminum chloride.

Experiments also were carried out in which the gaseous olefins, ethylene and propylene, were passed through a sintered glass disk into the reagent. Here also one mmole of hydride disappeared from solution per mmole of olefin absorbed and a maximum of 9 mmoles of olefin reacted per 12 mmoles of active hydride in solution.

These results indicate that most olefins can utilize only 9 of the 12 mmoles of active hydride present in the reaction mixture. Cyclohexene appears capable of utilizing all 12, and the sterically hindered olefin, 2,4,4-trimethyl-2-pentene, appears to utilize only 6.

The solution of sodium borohydride and aluminum chloride is quite clear originally. Addition of an olefin such as 1-octene, results in the precipitation of a white solid as the reaction proceeds. Removal of the clear, supernatant liquid revealed that it contained all of the boron in the reaction mixture in the form of organically bound boron, and only trace amounts of chloride ion and of the residual hydride. It follows that the precipitated solid must contain both the residual hydride and chloride ion, presumably in the form of aluminum hydride and sodium chloride.

It was observed that solutions of aluminum borohydride in ether and in diglyme reacted rapidly and completely with olefins. Here also only 8-9 of the 12 active hydrogens were utilized in reacting with the olefin. It was also confirmed that freshly prepared aluminum hydride, presumably formed in the reaction mixture, fails to add to typical olefins at room temperature. These results are summarized in Table III.

TABLE III

REACTION OF ALUMINUM BOROHYDRIDE AND ALUMINUM HYDRIDE IN ETHER MEDIA WITH OLEFINS AT ROOM TEMPERATURE

Olefin	Olefin, mmoles	Hydrogen compd., mmoles	Hydride, mmoles	Solvent ^a	Time, hr.	Hydride used, mmoles
1-Octene	24.0	Al(BH ₄) ₃	15.0	EE	1.0	10.2
					3.0	10.5
1-Octene	24.0	Al(BH ₄) ₃	18.0	DG	1.0	11.8
					1.0	12.0 ^b
					1.0	11.6 ^c
1-Pentene	30.0	AlH ₃	19.1	EE	1.0	11.3 ^d
					1.0	0.4
Cyclopentene	30.0	AlH ₃	19.3	EE	1.0	.2
Styrene	30.0	AlH ₃	19.3	EE	1.0	.5

^a Ethyl ether (EE), diglyme (DG). ^b Triethylamine added; Al(BH₄)₃/Et₃N, 1:1. ^c Nitrobenzene added; Al(BH₄)₃/C₆H₅NO₂, 1:1. ^d Diphenyl disulfide added; Al(BH₄)₃/(C₆H₅)₂S₂, 1:1.

The reagent then was applied to the hydroboration of several representative olefins on a preparative scale (0.2 to 0.5 mole). The olefin was added over a period of one hour to an excess of the reagent in a flask under nitrogen. After 2-3 hours at room temperature, the flask was warmed on a steam-cone for 0.5 hour to complete the reaction. The reaction mixture was cooled, the flask fitted with a short Vigreux column, and the diglyme removed below 40° (1-2 mm.). The organoborane then was distilled rapidly at 1 mm. from the solid residue,

the distillate being collected in a distilling flask as receiver. This flask was fitted with a short column and the organoborane redistilled at low pressures.¹² A small weighed sample was oxidized with alkaline hydrogen peroxide and the boron determined as boric acid. The results are summarized in Table IV.

TABLE IV
SYNTHESIS OF TRIALKYLBORANES

Olefin	Mole	Reaction product, borane	Yield, ^a g.	%	B.p. °C.	Mm.	Purity, ^b %
1-Octene	0.2	Tri- <i>n</i> -octyl-	19.3	83	144-145	2	98.3
	.2		18.4	79	144-145	2	
1-Hexene	.2	Tri- <i>n</i> -hexyl-	15.5	88	128-130	2	95.0
	.2		15.6	87	124-125	1	
1-Pentene	.2	Tri- <i>n</i> -amyl-	13.2	88	94-95	2	94.0
	.2		13.1	87	94-95	2	
2-Pentene	.2	Tri-2-amyl-	12.3	82	79-80	1	94.4
	.2		12.9	86	81-82	2	
Styrene	.5	Tri-2-phenyl-ethyl-	44.6	83	142-144	1	95.0
α -Methylstyrene	.5	Tri-2-phenyl-propyl-	48.7	80	145-146	1	96.0
Cyclohexene	.2	Tricyclohexyl-	12.4	71	130-131	2	97.6
		hexyl-	12.9	74	131-132	2	
Cyclopentene	.2	Tricyclopentyl-	11.7	79	118-119	2	92.0
		pentyl-	11.6	79	118-119	2	

^a Yield based on olefin; excess hydride utilized: 0.2 mole olefin, 0.1 mole NaBH₄, 0.033 mole AlCl₃. ^b Based on analysis for boron.

In order to establish structures of the organoboranes, the products were oxidized with alkaline hydrogen peroxide. The alcohols isolated were subjected to a careful distillation to establish their composition. In the case of the products from 1- and 2-pentene, infrared examination was utilized to establish the composition of the product. The results are summarized in Table V.

TABLE V
ALCOHOLS REALIZED FROM THE OXIDATION OF ORGANOBORANES

Organo-borane from olefin	Amt. of organoborane, g.	Product	B.p., °C.	Min.	Yield, g.	Composition, %
1-Octene	15.0	1-Octanol	192-193	740	10.1	90
		2-Octanol	179-180	740	0.8	10
1-Hexene	13.3	1-Hexanol	156-157	745	10.7	(~95)
		2-Hexanol				(~5)
1-Pentene	15.0	1-Pentanol	136-137	742	10.8	95 ^a
		2-Pentanol				5 ^a
2-Pentene	14.7	2-Pentanol				63 ^a
		3-Pentanol				37 ^a
Cyclohexene	20.9	Cyclohexanol	158-160	750	18.5	
Cyclopentene	19.2	Cyclopentanol	139-140	740	13.7	

^a From infrared examination.

Conditions were developed which permitted the direct oxidation of the organoborane without isolation. In this procedure, after the hydroboration is over, water is added to hydrolyze residual hydride, and the organoborane is oxidized in the presence of diglyme by addition of alkali and hydrogen peroxide. Diglyme is far more soluble in water than in ether (the distribution coefficient, $C_{\text{water}}/C_{\text{ether}}$, is approximately 10). Consequently, the alcohol is generally recovered readily by adding the reaction mixture to a large excess of water and

(12) The higher boron alkyls exhibit a tendency to lose olefin on extensive fractionation at elevated temperatures: L. Rosenblum, *THIS JOURNAL*, **77**, 5016 (1955).

extracting the alcohol with ether. Alternatively, distillation can be used to isolate the alcohol from the solvent. In this event sodium hydroxide pellets are added to the reaction mixture to give a lower phase containing the inorganic constituents of the reaction and an upper phase consisting of the solvent and the alcohol product. In this procedure it is frequently convenient to utilize triglyme (b.p. 216°) in the reaction, instead of diglyme (b.p. 160°), to permit a more ready separation of the alcohol from the solvent. Operating on a 0.5 molar basis, the alcohol usually is obtained in yields of 80-90%.

TABLE VI
DIRECTIVE CONVERSION OF OLEFINS INTO ALCOHOLS

Olefin	Amt., mole	Alcohol	Yield, %	°C.	B.p., Mm.
1-Hexene	0.50	1-Hexanol	90	156-157	745
1-Decene	.30	1-Decanol	93	225-228	738
Styrene	.50	2-Phenylethanol	81	103-105	14
α -Methylstyrene	.50	2-Phenylpropanol	90	109-111	14
1,1-Diphenylethylene	.50	2,2-Diphenylethanol ^a	86	191-193	20
<i>t</i> -Butylethylene	.10	3,3-Dimethyl-1-butanol ^b	67	140-141	741
2-Methyl-2-butene	.20	3-Methyl-2-butanol ^c	59	109.5-110.5	742
Cyclopentene	.10	Cyclopentanol	80	137-138	740

^a M.p. 64-65°, 71% yield, after recrystallization from petroleum ether. ^b n_D^{20} 1.4132; m.p. of 3,5-dinitrobenzoate, 83.6-84.2°. Gas chromatographic analysis shows only a single peak. There was a small earlier fraction of 3,3-dimethyl-2-butanol of approximately 5%. ^c n_D^{20} 1.4091; m.p. of 3,5-dinitrobenzoate, 75.0-75.5°. Gas chromatographic analysis showed approximately 1% of *t*-amyl alcohol formed in the reaction.

We also examined briefly the applicability of the hydroboration reaction to olefinic derivatives containing substituents, such as allyl ethyl ether, allyl chloride,¹³ cinnamic acid, etc. In all cases reaction was observed. Where the substituent present is itself reducible by the reagent, hydroboration is accompanied by reduction. Where the substituent is not readily reduced, simple hydroboration of the double bond appears to occur. These results are summarized in Table VII.

TABLE VII
HYDROBORATION OF SUBSTITUTED OLEFINS

Compound	Compd., mmoles	Hydride, mmoles	Temp., °C.	Time, hr.	Hydride used, mmoles
Allyl ethyl ether	24.0	12.0	25	1.0	9.1
Vinyl ethyl ether	24.0	12.0	25	1.0	9.8
Allyl chloride	24.0	12.0	25	1.0	11.2
Allyl dimethylamine	23.0	12.0	25		4.1
Ethyl oleate	5.2	19.8	25	0.5	12.5 ^{a,b}
Ethyl cinnamate	6.3	19.8	25	0.5	16.3 ^{a,c}
	6.0	19.8	25	3.0	17.7 ^{a,d}
Cinnamic acid	3.08	20.4	25	0.5	13.1 ^{a,e}

^a Calculated for hydroboration plus reaction; ^b 15.6, ^c 18.9, ^d 18.0, ^e 12.3.

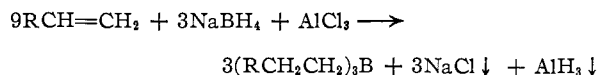
Discussion

The reagent, sodium borohydride-aluminum chloride in diglyme solution, appears to be generally applicable for the conversion of olefinic compounds to organoboron derivatives. The wide scope of

(13) A detailed study of the hydroboration of allyl chloride (and vinyl chloride) has been published recently: M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).

the reaction is indicated by the olefins which have been demonstrated to react in the present study: ethylene, propylene, 1- and 2-pentene, 1- and 2-hexene, 1-octene, 1-decene, 1-tetradecene, *t*-butylethylene, 2-methyl-2-butene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, styrene, α -methylstyrene, 1,1-diphenylethylene, cyclopentene and cyclohexene.

In all cases the reaction proceeded readily, largely in accord with the equation



Only in the case of highly hindered olefins, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, does the reaction take a course which indicates conversion to dialkylborane derivative, rather than to the usual trialkylborane product. Presumably, in these cases the large steric requirements of the olefin renders completion of the final stage relatively slow and difficult.¹⁴

The corresponding reaction with cyclohexene differs from those of the olefins in involving a complete utilization of the hydride in the reagent. This indicates that cyclohexene reacts further to form tricyclohexylaluminum in solution as well as tricyclohexylborane. This observation appears to be in contradiction with the results of a study of the addition of diethylaluminum hydride to cycloolefins.¹⁵ In that study, cyclohexene appeared to be considerably less reactive than cyclopentene and other cyclic olefins. Unfortunately time did not permit further examination of the phenomenon in the present study.

Although we did not attempt a detailed examination of the effect of substituents, the ready reaction of the reagent with allyl ethyl ether, vinyl ethyl ether, allyl chloride, allyldimethylamine, ethyl oleate, ethyl cinnamate and cinnamic acid indicates that the reaction may be general, complicated only by the tendency of the reagent to reduce certain functional groups.²

It was pointed out earlier that the reagent exhibits some of the characteristics of a solution of aluminum borohydride in ether.² This is supported by the observation that aluminum borohydride in ether solvents readily converts olefins at room temperatures to the corresponding organoborane. Sodium chloride is essentially insoluble in diglyme. The formation of a clear solution from sodium borohydride and aluminum chloride indicates that only minor amounts of aluminum borohydride can be present. If aluminum borohydride is indeed the reactive intermediate, it must be regenerated as it is utilized in the reaction.

If aluminum borohydride is the active intermediate, it may be pertinent to consider the apparent marked difference in reactivity between its reaction with olefins at 140° and the easy reaction at room temperature observed in this study. In the case of diborane we have observed that ethers

markedly catalyze the reaction with olefins.⁷ It is known that ethers form addition compounds with aluminum borohydride.¹⁶ Consequently, it must be the ether complexes which are present in solution and it is probable that the ether plays an important role in this reaction similar to that which it plays in the hydroboration reaction utilizing diborane.

The addition of the hydrogen-boron bond to olefins in this reaction occurs in an anti-Markownikoff direction. Thus, terminal olefins such as 1-tetradecene, 1-octene, 1-hexene, *t*-butylethylene and α -methylstyrene give organoboranes which are oxidized to the corresponding primary alcohols with no more than approximately 5% of the isomeric alcohol identified in the reaction. Even in the case of an internal olefin, such as 2-methylbutene, the addition occurs to give the anti-Markownikoff product, 3-methyl-2-butanol. No significant selectivity is exhibited by internal olefins, such as 2-pentene.¹⁷

The ready conversion of *t*-butylethylene to 3,3-dimethyl-1-butanol and of 1,1-diphenylethylene to 2,2-diphenylethanol indicates that the reaction proceeds without rearrangement, even in systems which are sensitive to such rearrangements. This procedure should be particularly useful in hydrating olefinic molecules where it is desirable to retain the carbon structure.

Experimental Part

Materials.—Diglyme (dimethyl ether of diethylene glycol) and triglyme were obtained from the Anslu Chemical Co. and purified as described earlier.¹⁸ Sodium borohydride (98%) from Metal Hydrides, Inc., was used without purification. Commercial aluminum chloride was purified by sublimation and stored in sealed tubes. Solutions of the reagent were prepared as described earlier.²

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, b.p. 41–42°, was prepared by decomposing the xanthate ester of pinacolyl alcohol.¹⁹ Dr. K. W. Greenlee also provided a generous sample of this olefin. 1,1-Diphenylethylene, b.p. 104–106° at 1 mm., was prepared by the dehydration of diphenylcarbinol.²⁰ The olefins were dried, distilled, and central cuts collected for use in the hydroboration experiments. The substituted olefins were Distillation Products chemicals, purified by distillation or recrystallization before use.

Determination of Hydride Utilization.—The general procedure adopted for the hydride utilization studies at 25 and at 75° is described. Into a number of dried 50-ml. round

(16) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *THIS JOURNAL*, **62**, 3421 (1940).

(17) The identification of 2- and 3-pentanol in a ratio of 63:37 from the oxidation of the organoborane from 2-pentene would appear to indicate a moderate selectivity between the two positions of this internal double bond. However, this experiment was carried out early in our studies, before we had recognized the possibility of isomerization of the organoborane in the distillation procedure; G. F. Hennon, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *ibid.*, **79**, 5190 (1957); H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957).

More recent experiments in which the organoborane is oxidized directly, without distillation, indicates a 50–50 yield of 2- and 3-isomers from the 2-olefin; work in progress with Dr. George Zweifel.

(18) H. C. Brown, E. J. Mead and B. C. Subba Rao, *THIS JOURNAL*, **77**, 6209 (1955).

(19) I. Schurman and C. E. Boord, *ibid.*, **55**, 4930 (1933).

(20) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc. New York, N. Y., p. 226.

(14) A detailed consideration of the stoichiometry of the hydroboration reaction is presented in the following paper (p. 6428).

(15) K. Ziegler, H. G. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 91 (1954).

bottomed flasks were placed 3.00 mmoles of sodium borohydride (3.00 ml. of a 1.0 *M* solution in diglyme) from a buret equipped with a reservoir. To this was added the calculated quantity of aluminum chloride in diglyme, the flasks stoppered and mixed. Then to each of the flasks was added 24 mmoles of olefin with vigorous swirling and cooling and the flasks were immersed in baths at 25 or 75° as desired.

A number of experiments were carried out in which the olefin and sodium borohydride were mixed in the flasks, with subsequent addition of the aluminum chloride solution. No significant differences in results were observed.

At the end of the reaction time, one blank reaction mixture (without olefin) and one actual reaction mixture were removed, the contents hydrolyzed by adding 10 ml. of 2 *N* hydrochloric acid through a pressure equalized separatory funnel, and the gas evolved was passed through a cold trap (to remove volatile olefins) and collected in a gas buret over water. The difference in the hydrogen evolved by the blank and the reaction mixture yields the hydride utilized by the olefin.

Hydroborations with Aluminum Borohydride.—Aluminum hydride was prepared by treating lithium aluminum hydride in ether with the theoretical quantity of aluminum chloride.²¹ The clear ether solution of aluminum hydride was decanted from the precipitated lithium chloride and treated with diborane to convert the aluminum hydride into aluminum borohydride.²² A standard solution of aluminum borohydride in ether (1.25 *M*) was used to hydroborate 1-octene, following the reaction by measurement of residual hydride. Nitrobenzene, triethylamine and phenyl disulfide had no effect on the hydroboration reaction.

A diglyme solution of aluminum borohydride was prepared by adding diglyme to the above solution, removing the ether under reduced pressure.

Reaction of Aluminum Hydride with Olefins.—Aliquots of an ether solution of aluminum hydride, prepared as above, were treated with a number of olefins for 1 hour, and then hydrolyzed to determine residual hydride. Typical results are summarized in Table III.

Reaction Products of the Hydroboration Reaction.—To a number of flasks containing 10.0 mmoles of sodium borohydride and 3.3 mmoles of aluminum chloride in diglyme, there were added 50 mmoles of 1-octene. After 12 hours at room temperature, the contents were centrifuged to separate the liquid from the precipitate. The precipitate was again washed with a small quantity of diglyme, and centrifuged. The clear liquids were combined. Total organic boron was determined in one set, hydride in another. The analysis revealed no hydride and only traces of chloride in the liquid layer, with 9.8 mmoles of boron (as boric acid) present (98%) in this layer. The precipitate was hydrolyzed. There was present 10.2 mmoles of hydride, 3.38 mmoles of aluminum (8-hydroxyquinoline), yielding $\text{Al}_{1.00}\text{H}_{3.02}$.

Preparation of Trialkylboron.—In the original experiments, the olefin was treated with the reagent, the reaction mixture was hydrolyzed, and the organoborane was taken up in ether, washed, dried and distilled. It proved difficult to carry out these manipulations without some exposure of the organoborane to oxygen with a consequent loss in purity and yield. Consequently, the following procedure was adopted.

Into a 250-ml. round-bottom flask provided with a nitrogen inlet, dropping funnel, reflux condenser and magnetic stirrer there were introduced 0.100 mole of sodium borohydride (100 ml. of a 1 *M* solution in diglyme) and 0.033 mole of aluminum chloride (20 ml. of a 1.66 *M* solution in diglyme). The system was flushed with dry nitrogen and a slight static pressure of nitrogen maintained. The flask was immersed in water, and the olefin, 0.200 mole, was added through the separatory funnel over a period of one hour. After 2-3 hours at room temperature, the contents were warmed gently on a steam-cone for 0.5 hour to complete the reaction. The reaction flask was cooled, fitted with a short Vigreux column and fractionated under reduced pressure, 1-2 mm., to remove the solvent (below 40°). Then the higher boiling organoborane was distilled rapidly at 1 mm., collecting the material in a flask suitable for redistillation. The product then was refractionated carefully. The data are summarized in Table IV.

(21) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *THIS JOURNAL*, **69**, 1199 (1947).

(22) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).

In order to determine the purity, a 1-g. sample of the organoborane was weighed, placed in a 250-ml. erlenmeyer flask fitted with a condenser, 25 ml. of 30% hydrogen peroxide added, and then treated with 5.0 ml. of 2 *N* sodium hydroxide.²³ A vigorous reaction ensued. When this had ceased, the flask was heated on a steam-cone for 20 minutes. After cooling, the contents were analyzed for boric acid by titration with base in the presence of mannitol.

Oxidation of Trialkylboranes.—The oxidation of the organoboranes was carried out by adding small quantities of 30% hydrogen peroxide and 2 *N* sodium hydroxide to the stirred reaction flask at such a rate that the contents of the flask were maintained at a gentle reflux. The results are summarized in Table V.

Direct Hydroboration and Oxidation.—The hydroboration of olefins followed by oxidation of the reaction product without isolation provides a far more convenient means of proceeding from the olefin to the desired alcohol. These procedures are typical.

To a stirred solution of 0.25 mole of sodium borohydride (200 ml. of 1.25 *M* solution in diglyme) and 0.84 mole of aluminum chloride (50 ml. of 1.7 *M* solution in diglyme) in a 1-l. flask, flushed with nitrogen and maintained under a slight static pressure of the gas, 0.50 mole of α -methylstyrene (59.1 g.) was added over a period of 0.5 hour. The reaction was allowed to proceed without external heating for 3 hours, and the flask was then heated on a steam-cone for 1 hour, with occasional swirling.²⁴ The hot reaction mixture was hydrolyzed by the slow addition of 20 ml. of water (hydrogen evolved) and then 100 ml. of 3 *N* sodium hydroxide, yielding a homogeneous solution. The separatory funnel was replaced by a water-cooled condenser and 68.0 g. (20% excess) of 30% aqueous hydrogen peroxide was added slowly, at a rate sufficient to maintain a gentle reflux. After addition, stirring was continued for another hour, and the flask was then cooled and diluted with ice-water. The alcohol was separated, and the aqueous layer extracted with several small portions of ether. The ether extracts were added to the alcohol, washed with water to remove diglyme, and distilled. There was obtained 60.6 g. of 2-phenyl-1-propanol, b.p. 109-111° at 14 mm., a yield of 89.7%.

An identical procedure was used to hydroborate 0.5 mole (90.5 g.) of 1,1-diphenylethylene and to oxidize the reaction product. Distillation of the product yielded 86.4 g. of 2,2-diphenylethanol, b.p. 192-194° at 20 mm., a yield of 87%. Recrystallization from petroleum ether gave the product, m.p. 64-65, in an over-all yield of 71%.

In a 200-ml. flask fitted with a dropping funnel and a condenser were placed 0.050 mole of sodium borohydride (50.0 ml. of a 1.00 *M* solution in triglyme) and 0.017 mole of aluminum chloride (10.0 ml. of a 1.70 *M* solution in triglyme). The flask was flushed with nitrogen and maintained under a slight static pressure of the gas. To the stirred solution, 6.81 g. (0.100 mole) of cyclopentene was added over a period of 0.5 hour. The reaction was allowed to proceed for 3 hours at room temperature and the flask then was heated on a steam-cone for 0.5 hour. Water, 10 ml., was added to destroy residual hydride. After hydrogen evolution had ceased, 20 ml. of 3 *N* sodium hydroxide was added, followed by 13.6 g. (20% excess) of 30% hydrogen peroxide at a rate sufficient to maintain a gentle reflux. The flask was cooled to room temperature and 15 g. of sodium hydroxide pellets was added. The organic layer was separated by decantation and then the lower layer in the flask was washed with two 20-ml. portions of ether. The combined organic extracts were dried over magnesium sulfate and distilled in a Todd micro column. Cyclopentanol, b.p. 137.5-138° at 740 mm., n_D^{20} 1.4519, was obtained in a yield of 6.9 g., 80% yield.

The procedure is particularly advantageous for the preparation of small quantities of alcohols whose volatility permits them to be distilled directly away from the less volatile diglyme or triglyme. This procedure also was utilized for the hydroboration of *t*-butylethylene and 2-methyl-2-butene. In the latter case, the heating period on the steam-cone was omitted to avoid possible isomerization of the organoborane product.

(23) R. Belcher, D. Gibbons and A. Sykes, *Microchem. Acta*, **40**, 76 (1952).

(24) In view of the tendency toward isomerization exhibited by *sec*- and *t*-alkylboranes, this final heating should be avoided in the hydroboration of internal olefins.

The results are summarized in Table VI.

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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

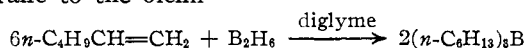
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Rigorously purified diborane and olefins react only slowly at room temperature. However, the presence of traces of ethers results in a rapid reaction which usually is complete in a matter of minutes at room temperature. Consequently, the rapid addition 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; tri-substituted 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



This rapid addition of diborane to olefins appeared to offer a new, useful synthetic route to the organoboranes and their derivatives.⁷ Accordingly,

(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**, 1138 (1957).

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 hydride⁸ 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

(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."