acid was extracted with ether. A small amount of phenothiazine was kept present during all operations to inhibit air oxidation and polymerization. The ether solution was dried over magnesium sulfate and concentrated on the steam-bath. On cooling, ethyleneboronic acid crystallized, yield 0.25 g. (35%). This product was recrystallized twice from ether–pentane, with addition of a trace of phenothiazine to the solution each time, and the volatile ethyleneboronic acid was dried less than 5 min. at 0.1 mm. and room temperature, m.p. 84–85°, polymerization following melting within a few seconds; infrared spectrum, significant bands,[19,22] in chloroform, cm.$^{-1}$: O–H stretch, 3635(m); C=C stretch, 1605(m); vinyl C–H bend, 965(ms) and 1000(m), with overtone, 1940(w).

Anal. Calcd. for $C_2H_5BO_2$: C, 33.42; H, 7.01; B, 15.05. Found: C, 33.44; H, 7.36; B, 15.36.

Propene-2-boronic acid was prepared in a similar manner, m.p. 97–98°, polymerizes. Two attempts to prepare an analytical sample yielded impure material.

Anal. Calcd. for $C_3H_7BO_2$: C, 41.94; H, 8.21; B, 12.60. Found: C, 40.49, 40.71; H, 7.82, 8.19; B, 13.02, 12.43.

Phenothiazine inhibited air oxidation and polymerization of propene-2-boronic acid, but hydroquinone was practically ineffective. If about a gram of the purified boronic acid without inhibitor was dried under vacuum and then exposed to air, after about a minute the material became hot, turned brown, and polymerized. The ultraviolet spectrum of propene-2-boronic acid in water or in isoöctane showed only end absorption; in water (Beckman DU): ϵ_{225} 56, ϵ_{220} 170, ϵ_{210} 3000; infrared spectrum, significant bands,[19,22] cm.$^{-1}$, in chloroform: O–H stretch, 3635(m); C=C stretch, 1610(m); =CH_2 bend, 940(ms) (partially masked by chloroform); unassigned, 980(ms), 850(mw), 1700(w), 1845(ww), 1890(ww); in KBr: OH stretch, 3100–3450(ms); C=C stretch, 1615(m); =CH_2 bend, 930(m); unassigned, 875(m), 1702(m), 2050(w).

The *o*-phenylenediamine derivative of ethyleneboronic acid was prepared by the usual method[15b] but purified by sublimation at 50° (0.07 mm.), yield 60%, m.p. 116–124°. An analytical sample was resublimed, m.p. 122–124°; infrared spectrum, significant bands,[19,22] in Nujol, cm.$^{-1}$: N–H stretch, 3375(m); C=C stretch, 1595(m); vinyl C–H bend, 1010(m) and 950(ms), possible overtones, 1750(w), 1810(w), 1850(w). Instead of the strong bands characteristic of B–O groups,[22] a complex system of medium bands attributable to the aromatic system was observed in this region.

Anal. Calcd. for $C_8H_9BN_2$: C, 66.73; H, 6.30; B, 7.51, N, 19.46. Found: C, 67.01; H, 6.52; B, 7.83; N, 19.49.

PULLMAN, WASH.

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

Hydroboration. V. A Study of Convenient New Preparative Procedures for the Hydroboration of Olefins

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The simple hydroboration procedure previously developed, the addition of boron trifluoride etherate to a mixture of sodium borohydride and olefin in diglyme solution, has been expanded to alternative procedures involving other solvents (ethyl ether, tetrahydrofuran and triglyme), other hydride sources (lithium borohydride, potassium borohydride, lithium aluminum hydride, lithium hydride, sodium hydride, pyridine-borane and trimethylamine-borane) and other Lewis acids, (boron trifluoride, boron trichloride, aluminum chloride plus methyl borate, aluminum chloride, titanium tetrachloride, hydrogen chloride, sulfuric acid and alkyl halides). In the course of these studies the practicality has been demonstrated of a number of convenient new hydroboration procedures, utilizing various solvents, hydride sources and appropriate acids.

The hydroboration reaction provides a convenient new route from olefinic and acetylenic derivatives to organoboranes[4,5] and to the many derivatives to which organoboranes can be converted.[6]

In our original study[4] we utilized the action of aluminum chloride on a mixture of olefin and sodium borohydride in diglyme[7] solution to achieve hydroboration of the olefin at temperatures of 25–75° (1).

$$9RCH{=}CH_2 + 3NaBH_4 + AlCl_3 \longrightarrow 3(RCH_2CH_2)_3B + 3NaCl + AlH_3 \quad (1)$$

Later we discovered that diborane adds to olefins in ether solvents with remarkable ease at 25°, and that hydroboration could be achieved rapidly and quantitatively by adding boron trifluoride etherate to a solution of sodium borohydride and olefin in diglyme[5] (2).

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3 \longrightarrow 4(RCH_2CH_2)_3B + 3NaBF_4 \quad (2)$$

This procedure is a highly convenient one and we have utilized it in the extensive studies of the hydroboration reactions on which we have been engaged. However, it appears that the unavailability of the solvent abroad has resulted in difficulties in applying the reaction to synthetic problems. Thus Dulou and Chrétien-Bessière reported that in order to circumvent this difficulty they generated diborane from the reaction of lithium aluminum hydride with boron trifluoride in ether solution[8] and passed the gas into an ether solution of the olefin.[9] Sondheimer and his co-workers found it possible to avoid the external generation of diborane by adding lithium aluminum hydride to a solution of the olefin and boron trifluoride in ether solution.[10]

Since the original discovery of the alkali metal

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[4] H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956).

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

[6] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247, 1512 (1959); H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959); M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958); J. B. Honeycutt, Jr., and J. M. Riddle, *ibid.*, **81**, 2593 (1959).

[7] Diglyme is diethylene glycol dimethyl ether; triglyme, triethylene glycol dimethyl ether.

[8] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

[9] R. Dulou and Y. Chrétien-Bessière, *Bull. soc. chim.*, **9**, 1362 (1959).

[10] S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

hydride route to diborane and the alkali metal borohydrides,[11] we have been exploring the interaction of various Lewis acids of boron with these hydrides and borohydrides.[12] As a consequence, considerable information has accumulated with regard to these reactions. Therefore, it appeared desirable to apply this information to explore the applicability of alternative convenient procedures, based on other solvents and reagents, for the hydroboration reaction.[13]

It has been observed that organoboranes, such as tri-*sec*-butylborane, undergo slow isomerization at temperatures of 200–210°.[14] However, under hydroboration conditions, such isomerization is far more facile, occurring rapidly at temperatures in the range of 100–125°.[15] Since it is usually desirable in organic synthesis to realize the organoborane directly from a specific olefin, without isomerization of the product, we directed our studies to hydroborations which could be completed in a reasonable time at temperatures of 25°. We adopted 75° as the higher limit of practicality for such hydroborations.

The solvents utilized were ethyl ether, tetrahydrofuran, diglyme, triglyme (for potassium borohydride) and benzene (for amine-boranes). As hydride sources, we examined lithium borohydride, sodium borohydride, potassium borohydride, lithium hydride, sodium hydride, pyridine-borane[16] and trimethylamine-borane.[17] Finally, we utilized boron trifluoride etherate, boron trichloride etherate, aluminum chloride, aluminum chloride plus methyl borate, titanium tetrachloride, hydrogen chloride, sulfuric acid and alkyl halides to convert the hydride sources into active reactants.

Results

1-Octene was adopted as the standard olefin for hydroboration. A standard procedure was usually followed: 100 mmoles of 1-octene was mixed with 110 mmoles of "hydride" (10% excess) in sufficient solvent to make the volume 70 cc. Through a dropping funnel was added 30 cc. of a solution of the acid in a convenient solvent, generally ether, over a period of one hour maintaining the temperature at 25°. At this point a sample was removed with a hypodermic syringe and analyzed for residual 1-octene by vapor phase chromatography. The reaction mixture was again analyzed after standing one hour at 25°. If the reaction was still incomplete, it was heated to reflux for ethyl ether and tetrahydrofuran, and to 75° for diglyme and analyzed after one hour and at regular intervals thereafter. From time to time, the results were checked by oxidizing the reaction mixture with alkaline hydrogen peroxide and analyzing for 1- and 2-octanol (formed from 1-octene in the ratio 94:6).

Lithium Borohydride.—Lithium borohydride is readily soluble in ethyl ether, tetrahydrofuran and diglyme. Consequently, it was possible to examine the utility of this material for hydroborations in a number of solvents.

Utilizing boron trifluoride etherate in the mole ratio $3LiBH_4/4BF_3$, corresponding to eq. 2, the reaction was observed to be essentially complete immediately following the addition of the boron trifluoride etherate in one hour at 25° (Table I).

TABLE I

HYDROBORATIONS BASED ON LITHIUM BOROHYDRIDE[a]

				Extent of reaction, %[d] after		
Solvent[b]	$LiBH_4$, mmoles	Acid[c] used	Acid, mmoles	Addn. period, 1 hr., 25°	Reacn. period, 1 hr., 25°	Heat.[e] period, 1 hr.
EE	27.5	BF_3	36.6	92	98	
THF	27.5	BF_3	36.6	88	93	
DG	27.5	BF_3	36.6	98	98	
EE	27.5	BF_3	9.2	90	87	
THF	27.5	BF_3	9.2	99	99	
DG	27.5	BF_3	9.2	58	65	90
EE	27.5	BCl_3	9.2	99	99	
THF	27.5	BCl_3	9.2	99	99	
DG	27.5	BCl_3	9.2	93	92	
EE	27.5	$AlCl_3$,	9.2			
		$B(OCH_3)_3$	9.2	60	77	77
THF	27.5	$AlCl_3$,	9.2			
		$B(OCH_3)_3$	9.2	65	76	91
DG	27.5	$AlCl_3$,	9.2			
		$B(OCH_3)_3$	9.2		67	92
EE	37	$AlCl_3$	12.2	52	60	92
THF	37	$AlCl_3$	12.2	48	62	62
DG	37	$AlCl_3$	12.2	40	51	93[f]
EE	37	$TiCl_4$[g]	9.2		95	
THF	37	$TiCl_4$[g]	9.2		46	(74)[h]
EE	37	HCl	37	95	95	
THF	37	HCl	37	93	95	
EE	37	H_2SO_4	18.5	92	92	
THF	37	H_2SO_4	18.5	99	99	
EE	37	EtBr	37		30	34
THF	37	EtBr	37		19	(74)[i]
EE	37	$C_6H_5CH_2Cl$	37		0	(20)[j]
THF	37	$C_6H_5CH_2Cl$	37		2	(5)[k]

[a] 100 mmoles of 1-octene in approximately 100 ml. of hydroboration mixture. [b] Ethyl ether, EE; tetrahydrofuran, THF; diglyme, DG. [c] Added in ethyl ether (25 ml.) except where otherwise indicated. [d] Based on V.P.C. analysis for residual 1-octene. [e] Reflux for ethyl ether and tetrahydrofuran; 75° for diglyme. [f] After 4 hr. heating. [g] Added as the pure liquid, over 0.5 hour. [h] After 5 hours at 25°. [i] After 19 hours at 25°. [j] After 10 hours at 25°. [k] After 7 hours at 25°.

It is known that in ethyl ether at 25° lithium borohydride will react with boron trifluoride in the ratio $3LiBH_4/1BF_3$.[18]

Accordingly, we explored briefly the applicability of this ratio in the hydroboration reaction (3).

$$12RCH{=}CH_2 + 3LiBH_4 + BF_3 \longrightarrow 4(RCH_2CH_2)_3B + 3LiF \quad (3)$$

In ethyl ether and tetrahydrofuran the reaction proceeded satisfactorily, but in diglyme the reac-

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[11] H. I. Schlesinger, H. C. Brown, *et al.*, THIS JOURNAL, **75**, 186 (1953).

[12] A summary of these studies was presented in the form of a Section Lecture at the XVII International Congress of Pure and Applied Chemistry in Munich, 1959. This summary should appear soon in the published lectures of the Congress.

[13] A preliminary Communication dealing with this topic has appeared: H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 4106 (1959).

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

[15] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957), and unpublished research with Dr. George Zweifel.

[16] M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

[17] E. C. Ashby, THIS JOURNAL, **81**, 4791 (1959).

[18] J. R. Elliott, E. M. Boldebuck and G. F. Roedel, *ibid.*, **74**, 5047 (1952), and unpublished studies of John A. Snover.

tion is not complete in the usual time at 25° and higher temperatures are necessary to drive the reaction to completion. In view of the rapidity and reliability of the procedures utilizing sufficient boron trifluoride to form lithium fluoroborate, the latter would appear preferable for laboratory syntheses.

Boron trichloride does not form a complex chloroborate in ether solvents. Consequently, in this case there is no ambiguity as to the required stoichiometry of the reaction (4).

$$12RCH{=}CH_2 + 3LiBH_4 + BCl_3 \longrightarrow 4(RCH_2CH_2)_3B + 3LiCl \quad (4)$$

In the case of boron trichloride the reactions are complete immediately following the addition of the boron trichloride to the reaction mixture.

As a reagent boron trichloride suffers from the disadvantage that it is a gas and it reacts rapidly with ethers such as tetrahydrofuran and diglyme.[19,20] Although the reaction with ethyl ether is slower, so that it may be conveniently handled in this solvent, the solutions should be freshly prepared before use.

A mixture of aluminum chloride and methyl borate might be considered to be the equivalent of boron trichloride. In ethyl ether, a 77% yield was realized, whereas in tetrahydrofuran and diglyme we observed yields of better than 90% after one hour of heating (5).

$$12RCH{=}CH_2 + 3LiBH_4 + B(OCH_3)_3 + AlCl_3 \longrightarrow 4(RCH_2CH_2)_3B + Al(OCH_3)_3 + 3LiCl \quad (5)$$

The use of aluminum chloride alone results in the utilization of only three of the four hydrides in the borohydride ion[4] (6).

$$9RCH{=}CH_2 + 3LiBH_4 + AlCl_3 \longrightarrow 3(RCH_2CH_2)_3B + AlH_3 + 3LiCl \quad (6)$$

Accordingly, we increased the amount of lithium borohydride to take care of this stoichiometry. The reaction was essentially complete after one hour heating under reflux in ethyl ether, but required four hours at 75° in diglyme.

Titanium tetrachloride is a liquid material, relatively easily handled. Accordingly, we explored the utility of this Lewis acid in the hydroboration reaction. The titanium tetrachloride formed a crystalline yellow solid in ether solution. Consequently, it was added as the pure liquid to the reaction mixture in ethyl ether and in tetrahydrofuran. Hydroboration of 1-octene appeared to be essentially complete in ethyl ether after one hour at room temperature. Unfortunately, the reaction is accompanied by the formation of dark solids which interfere with the oxidation by alkaline hydrogen peroxide.

The use of hydrogen chloride dissolved in ethyl ether affords a convenient means of carrying out the hydroboration reaction. Such solutions are stable for long periods of time (2 to 3 months), they are readily standardized by titration, and the hydroboration reaction with lithium borohydride in either ethyl ether or tetrahydrofuran is essentially quantitative immediately following the addition (7).

$$3RCH{=}CH_2 + LiBH_4 + HCl \longrightarrow (RCH_2CH_2)_3B + H_2 + LiCl \quad (7)$$

We also observed that concentrated sulfuric acid, dissolved in ether to give a 1.5 *M* solution, reacted readily with the hydroboration mixture in both ethyl ether and tetrahydrofuran. The ready availability of sulfuric acid and the ease with which it can be weighed and the solution prepared give this procedure a marked advantage in convenience (8).

$$6RCH{=}CH_2 + 2LiBH_4 + H_2SO_4 \longrightarrow 2(RCH_2CH_2)_3B + 2H_2 + Li_2SO_4 \quad (8)$$

Sodium borohydride in diglyme solution reacts relatively rapidly with methyl chloride at 25°.[20] There would be obvious advantages in being able to add the acid in the form of a liquid, easily weighed organic halide to achieve hydroboration (9).

$$3RCH{=}CH_2 + LiBH_4 + R'X \longrightarrow (RCH_2CH_2)_3B + R'H + LiX \quad (9)$$

However, we observed that the reactions with ethyl bromide and with benzyl chloride are relatively slow in ethyl ether or in tetrahydrofuran. The corresponding reactions with sodium borohydride in diglyme are considerably faster.

The results realized in these hydroborations are summarized in Table I.

Sodium Borohydride.—Sodium borohydride is readily soluble in diglyme,[21] but is essentially insoluble in either ethyl ether or tetrahydrofuran. Consequently, we explored in detail the relative efficacy of the various acids in bringing about hydroboration in the diglyme-sodium borohydride solutions and then examined for several selected acids their possible utility in bringing about hydroboration with sodium borohydride suspensions in tetrahydrofuran and ethyl ether.

Boron trifluoride etherate reacted readily with a solution of sodium borohydride and 1-octene in diglyme. The yield was 99% immediately following completion of the addition of the reagent at 25°.

On the other hand, only trace amounts of reaction were observed in treating a suspension of sodium borohydride in ethyl ether with boron trifluoride etherate. Unexpectedly, the same reaction involving a suspension of sodium borohydride in tetrahydrofuran proceeded quite well, giving 72% reaction after one hour at room temperature and 98% reaction in six hours. It therefore appears that the solubility of sodium borohydride in tetrahydrofuran, although relatively small, is sufficient to bring about the desired reaction.

In the earlier experiment the boron trifluoride etherate had been added in ether solution. In view of the above results, it appeared desirable to avoid the presence of relatively large amounts of ethyl ether in the reaction mixture. Accordingly, the reaction was repeated in tetrahydrofuran, but in this case the boron trifluoride etherate was added as a solution in 25 cc. of tetrahydrofuran. The reaction proceeded quite smoothly, giving 79% reaction immediately following completion of addition and 99% reaction after one hour at room temperature.

This particular modification should prove highly convenient for use with sodium borohydride in cases

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[19] J. D. Edwards, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1470 (1955).

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

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

where diglyme is not available or where it is desirable to avoid the use of a high boiling solvent.

It appeared desirable to explore further possibilities for bringing about the hydroboration reaction in ethyl ether. The addition of catalytic quantities (27.5 mmoles) of diglyme to the ether suspension of sodium borohydride did bring about a slow reaction in ethyl ether—54% in 18 hours. The small quantity of diglyme likewise facilitated the reaction in tetrahydrofuran suspension, resulting in a yield of 94% after completion of the addition stage.

The stoichiometry of these reactions is represented by eq. 2.

It has been noted that potassium borohydride will react with lithium chloride in tetrahydrofuran to form a solution of lithium borohydride.[22] Unfortunately, no reaction is observed between sodium borohydride and lithium chloride in ethyl ether.[22] However, we had noted that sodium borohydride will react with zinc chloride in ethyl ether solution to form an ether solution of zinc borohydride. Accordingly, sodium borohydride was stirred with the calculated quantity of zinc chloride for 1.5 hours. Analysis of the ether indicated the presence of 97% of the calculated quantity of borohydride in solution. To such a reaction mixture, freshly prepared 1-octene was added and treated with boron trifluoride etherate. The yield was 89% after one hour at room temperature and 98% after one-hour heating (10).

$$2NaBH_4 + ZnCl_2 \xrightarrow[\text{ether}]{\text{ethyl}} Zn(BH_4)_2 + 2NaCl$$

$$24RCH{=}CH_2 + 3Zn(BH_4)_2 + 8BF_3 \longrightarrow 8(RCH_2CH_2)_3B + 3Zn(BF_4)_2 \quad (10)$$

Finally, we observed that catalytic quantities of zinc chloride would also facilitate reaction. Thus treatment of a suspension of sodium borohydride with 10% of the stoichiometric quantity of zinc chloride for 1.5 hours, followed by addition of the 1-octene and the usual hydroboration procedure, resulted in 94% reaction immediately following the addition of the boron trifluoride etherate.

Boron trichloride in ethyl ether, added to the olefin and sodium borohydride in diglyme, results in an essentially quantitative reaction during the addition. However, only minor reaction occurs with ethyl ether and tetrahydrofuran suspensions. Because of the reactivity of the boron trichloride with ethers, we did not explore the effect of more extensive reaction periods or higher temperatures.

As was pointed out earlier, a mixture of aluminum chloride and methyl borate may be considered a substitute for boron trichloride.[23] It was observed that excellent conversion of the olefin to the organoborane could be achieved by this reagent in one hour at 75°.

The use of aluminum chloride produced a 94% yield after one hour at 75°. In tetrahydrofuran the yield was poorer, 52%, under the same conditions. However, here also the addition of catalytic quantities of diglyme improved the conversion to 86%. In ethyl ether the reactions were incomplete, both in the presence and absence of the catalytic quantities of diglyme.

The addition of titanium tetrachloride to the typical hydroboration reaction mixture in diglyme resulted in the formation of a black solution with a blue precipitate. After three hours at room temperature, 93% of the 1-octene had reacted.

The addition of hydrogen chloride in ethyl ether (1 *M*) to the solution of olefin and sodium borohydride in diglyme results in a rapid conversion of the olefin to the organoborane: 94% immediately following the addition. Addition of hydrogen chloride to suspensions of sodium borohydride in ethyl ether resulted in only minor conversion of the olefin.

Although hydroboration of the olefin could not be achieved by treatment of sodium borohydride suspended in tetrahydrofuran with hydrogen chloride, it was possible to bring about a reaction between hydrogen chloride and sodium borohydride in this medium in the absence of the 1-octene. In this way a solution of diborane in tetrahydrofuran can be prepared in yields of 80%, and the hydroboration achieved by addition of the olefin to the solution.

It was also possible to achieve hydroboration in tetrahydrofuran by using a catalytic quantity of diglyme, running the reaction at 0°, and adding the hydrogen chloride as a solution in tetrahydrofuran. Unfortunately, this reaction proved to be erratic, with the hydroboration frequently coming to a halt prior to completion for no apparent reason.

Finally, the convenient reagent, sulfuric acid in ether (1.5 *M*), readily brought about the hydroboration of 1-octene by sodium borohydride in diglyme. A yield of 89% was realized immediately following the addition of the acid solution.

The use of methyl iodide resulted in essentially quantitative hydroboration of the 1-octene after one hour at 25°. This is a highly convenient form in which to add the "acid" component. In order to ascertain whether the sodium iodide present in the reaction mixture would interfere with the oxidation stage, we oxidized the reaction mixture with alkaline hydrogen peroxide. There was realized a yield of 79% of 1-octanol. The reaction was accompanied by some oxidation of the iodide and it is probable that the yield could be improved by the use of a larger excess of hydrogen peroxide.

The corresponding reactions with ethyl bromide and benzyl chloride proved to be much slower. Thus benzyl chloride brought about a conversion of 79% only after 20 hours at 75°.

These results are summarized in Table II.

Potassium Borohydride.—Potassium borohydride is essentially insoluble in diglyme, tetrahydrofuran and ethyl ether. No significant reaction was observed between boron trifluoride and potassium borohydride in ethyl ether or in tetrahydrofuran. In diglyme there was observed a 39% conversion after one hour at room temperature, but the yield was not improved at 75°.

Consequently, we explored the possibility that the reaction would proceed more satisfactorily in triglyme.[7] In this solvent we observed the hydroboration to be 83% complete after addition of the

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(22) R. Paul and N. Joseph, *Bull. soc. chim. France*, 550 (1952); R. Paul and N. Joseph, *ibid.*, 758 (1953).

(23) In unpublished studies Dr. B. C. Subba Rao demonstrated that diborane could be generated at 100° from sodium borohydride in diglyme by means of this reagent in yields of 80% or better.

TABLE II

HYDROBORATIONS BASED ON SODIUM BOROHYDRIDE[a]

Solvent[b]	$NaBH_4$, mmoles	Acid,[c] used	Acid, mmoles	Extent of reaction, %,[d] after: Addn. period, 1 hr., 25°	Reacn. period, 1 hr., 25°	Heat.[e] period, 1 hr.
DG	27.5	BF_3	37	99	99	
EE	27.5	BF_3	37	0	0	(0)[f]
THF	27.5	BF_3	37		72	(98)[g]
THF	27.5	BF_3[h]	37	79	99	
EE(DG)[i]	27.5	BF_3	37		8	(54)[j]
THF(DG)[i]	27.5	BF_3	37	94	99	
EE($ZnCl_2$)[k]	27.5	BF_3	37	86	89	98
EE($ZnCl_2$)[l]	27.5	BF_3	37	94		
DG	27.5	BCl_3	9.2	98		
EE	27.5	BCl_3	9.2	6	21	
THF	27.5	BCl_3	9.2	2		
DG	27.5	$AlCl_3$				
		$B(OCH_3)_3$	9.2	80	85	91
DG	37	$AlCl_3$	12.2	50	48	95
EE	37	$AlCl_3$	12.2		8	9
THF	37	$AlCl_3$	12.2	18	27	52
EE(DG)[i]	37	$AlCl_3$	12.2	8	15	23
THF(DG)[i]	37	$AlCl_3$	12.2	40	45	86
DG	37	$TiCl_4$	9.1		(93)[m]	
DG	37	HCl	37	94		
EE	37	HCl	37		6	
THF	37	HCl	37		7	
THF[n]	40	HCl	34		(88)[o]	
THF(DG)[i]	37	HCl	37[p]		20–80	
DG	37	H_2SO_4	18.5	89	91	
DG	37	CH_3I[q]	37	78	95	
DG	37	C_2H_5Br[q]	37	25	40	53
DG	37	$C_6H_5CH_2Cl$[r]	37		(40)[s]	
DG	37	$C_6H_5CH_2Cl$[r]	37			(79)[t]

[a,b,c,d,e] See corresponding footnotes in Table I. [f] After 19 hours at 25°. [g] After 6 hours at 25°. [h] Boron trifluoride etherate added in tetrahydrofuran. [i] 27.5 or 37 mmoles of diglyme, equivalent to the sodium borohydride used, added to the suspension. [j] After 18 hours at 25°. [k] Ether suspension of sodium borohydride stirred in 13.8 mmoles of zinc chloride for 1.5 hours prior to reaction. [l] Ether suspension stirred with catalytic quantity of zinc chloride (1.4 mmole, 10%) for 1.5 hours prior to reaction. [m] After 3 hours at 25°. [n] Generation of diborane, followed by hydroboration. [o] Reaction run at 0°. [p] Hydrogen chloride added as a 1 *M* solution in tetrahydrofuran. [q] Added in 18 ml. of diglyme. [r] Added as the pure liquid. [s] After 20 hours at 25°. [t] After 20 hours at 75°.

boron trifluoride etherate (in triglyme solution) and 91% complete after one hour at room temperature. Consequently, hydroborations can be conveniently accomplished with potassium borohydride in triglyme as the solvent.

We also explored the applicability of other acids to potassium borohydride in triglyme suspension. Aluminum chloride in ether solution produced a 50% conversion of 1-octene in one hour at 25°. No increase in yield was observed on heating. Hydrogen chloride in ether produced a 47% yield after one hour at 25°. It is probable that these yields could be improved by adding the acid in triglyme solution, but this possibility was not investigated experimentally.

It was observed by Paul and Joseph that potassium borohydride undergoes exchange with lithium chloride in the presence of tetrahydrofuran.[22] It appeared that this metathesis reaction should permit the utilization of potassium borohydride for hydroboration in tetrahydrofuran.

To test this possibility, lithium chloride and potassium borohydride were stirred in tetrahydrofuran for three hours at room temperature. To the reaction mixture was added 100 mmoles of 1-octene and the hydroboration carried out in the usual manner by the addition of boron trifluoride etherate. The conversion of olefin was 72% immediately following the addition and 83% after one hour at room temperature. We explored the possibility that the reaction could be carried out without the initial equilibration period. However, under these conditions the reaction proved to be much more sluggish. Evidently, the presence of the reactants affects the exchange of the lithium chloride with the suspended potassium borohydride.

Potassium borohydride does not exchange with lithium chloride in ethyl ether. Consequently, this expediency cannot be adopted to utilize ethyl ether as a solvent for hydroborations based on the potassium salt. However, Joseph recently has reported that zinc chloride in ethyl ether catalyzes the generation of diborane from potassium borohydride and boron trifluoride etherate.[24] Consequently, it is probable that the use of zinc chloride would permit hydroborations with potassium borohydride to be practical in ethyl ether, in the same way that the zinc salt facilitates the corresponding reaction with sodium borohydride. However, we did not test this possibility experimentally.

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(24) N. Joseph, XVII International Congress of Pure and Applied Chemistry, Munich, September, 1959.

TABLE III

HYDROBORATIONS BASED ON POTASSIUM BOROHYDRIDE[a]

Solvent[b]	KBH_4, mmoles	Acid,[c] used	Acid, mmoles	Extent of reaction, %[d], Addn. period, 1 hr., 25°	Reacn. period, 1 hr., 25°	Heat,[e] period, 1hr.
EE	27.5	BF_3	37	0	0	0
THF	27.5	BF_3[f]	37	6	10	(42)[g]
DG	27.5	BF_3[h]	37	33	39	42
TG[i]	27.5	BF_3	37		35	41
TG	27.5	BF_3[j]	37	83	91	
TG	37	$AlCl_3$	12.2		50	50
TG	37	HCl	12.2		47	51
THF(LiCl)[k]	27.5	BF_3	37	72	83	
THF(LiCl)[l]	27.5	BF_3	37	13	39	(53)[m]

[a,b,c,d,e] See corresponding footnotes in Table I. [f] Added as a solution of boron trifluoride etherate in 25 ml. of tetrahydrofuran. [g] After 20 hours at 25°. [h] Added as a solution of boron trifluoride etherate in 25 ml. of diglyme. [i] Triglyme. [j] Added as a solution of boron trifluoride etherate in 25 ml. of triglyme. [k] Equilibrated with 27.5 mmoles of lithium chloride and 52 ml. of tetrahydrofuran for 3 hours at 25°. [l] No equilibration period. [m] After 13 hours at 25°.

The experimental results are summarized in Table III.

Lithium Aluminum Hydride.—Sondheimer and his co-workers have demonstrated that 1-octene and similar olefins can be hydroborated conveniently by a mixture of lithium aluminum hydride and boron trifluoride etherate in ethyl ether. We have also observed that boron trichloride and a 1:1 molar mixture of methyl borate and aluminum chloride serve to achieve hydroborations with this hydride (Table IV). One minor disadvantage with this system should be mentioned. The use of lithium aluminum hydride results in the formation of a voluminous precipitate of aluminum hydroxide which complicates somewhat the isolation of the organoborane or the oxidation product.

The results are summarized in Table IV.

Amine-boranes.—Diborane forms stable addition compounds with tertiary amines and these products recently have been utilized for hydroborations. Thus, Hawthorne utilized pyridine-borane in diglyme solution at temperatures of 100° for 14 hours to achieve hydroboration of terminal olefins,[16] whereas Ashby utilized trimethylamine-borane and triethylamine-borane for such hydroborations at temperatures of 100 to 200°.[17] In view of our objectives, it appeared desirable to explore whether these materials could be utilized to achieve hydroboration at temperatures of 75° or below.

It has been reported that diborane can be prepared by treatment of the amine-boranes with boron trifluoride.[25] However, somewhat unexpectedly, we discovered that the liberation of diborane from these addition compounds by boron trifluoride etherate is by no means easy.

TABLE IV

HYDROBORATIONS BASED ON MISCELLANEOUS HYDRIDE SOURCES[a]

Solvent[h]	Hydride used	Hydride, mmoles	Acid[c] used	Acid, mmoles	Extent of reaction[d] %	Time, hr.	Temp., °C.
EE	$LiAlH_4$	28	BCl_3	34	95	1	0
EE	$LiAlH_4$	30	$AlCl_3,B(OCH_3)_3$	40	95	1	0
EE	$(CH_3)_3N:BH_3$	37	BF_3	37	5	2	28
EE	$(CH_3)_3N:BH_3$	37	BCl_3	37	5	2	28
EE	$(CH_3)_3N:BH_3$	37	$AlCl_3$	37	5	2	28
EE	$C_5H_5N:BH_3$	37	BF_3	37	5	2	28
Bz	$C_5H_5N:BH_3$	73	BF_3[e]	37	4	6	
Bz	$C_5H_5N:BH_3$	37	BF_3[e]	37	30	3	
					50	6	
					90	16	
Bz	$C_5H_5N:BH_3$	73	BF_3[e]	37	90	6	
Bz	$C_5H_5N:BH_3$	37	None		10	6	
					40	16	
Bz	$C_5H_5N:BH_3$	73	None		25	6	
Bz	$(CH_3)_3N:BH_3$	37	BF_3[e]	37	15	16	
DG	NaH	158	BF_3[f]	146	99	1	25
THF	NaH	165	BF_3[f]	146	99	1	25
EE	NaH	173	BF_3[f]	146	18	1	25
DG	LiH	158	BF_3[f]	37	25	1	25
THF	LiH	158	BF_3[f]	37	25	1	25
EE	LiH	173	BF_3[f]	37	18	1	25
DG	LiH	158	BF_3[f]	146	95	1	25
THF	LiH	158	BF_3[f]	146	95	1	25
EE	LiH	173	BF_3[f]	146	93	2	41[g]

[a,b,c,d] See corresponding footnotes in Table I. [e] Etherate in benzene solution. [f] Pure etherate added. [g] Reflux.

Thus treatment of trimethylamine-borane in ether solution with boron trifluoride does not result in the liberation of diborane. Similarly, treatment of a solution of 1-octene and trimethylamine-borane in ether with boron trifluoride etherate resulted in no detectable reaction of the 1-octene after two hours at 25°. After 24 hours under reflux (46°), there was observed only 15% reaction. Similar results were obtained with pyridine-borane.

The use of boron trichloride or aluminum chloride did not alter the situation.

It appeared possible that the ether solvent was inhibiting the reaction.[26] Therefore benzene was

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(25) G. W. Schaeffer and G. D. Barbaras, U. S. Patent 2,533,696 (December 12, 1950); R. Köster and K. Ziegler, *Angew. Chem.*, **69**, 94 (1957).

adopted as the solvent and the reaction of the amine-boranes with 1-octene examined in this reaction medium.

At 25° there appeared to be approximately 5% reaction in six hours between pyridine-borane and 1-octene under the influence of boron trifluoride etherate. At 75° there was observed 50% reaction in six hours, 90% reaction in 16 hours. The reaction course is indicated by eq. 11.

$$3RCH{=}CH_2 + C_5H_5N{:}BH_3 + BF_3{:}O(C_2H_5)_2 \longrightarrow (RCH_2CH_2)_3B + C_5H_5N{:}BF_3 + (C_2H_5)_2O \quad (11)$$

Under the same conditions, but in the absence of the boron trifluoride etherate, the reaction proceeded to 10% of completion in six hours, 40% completion in 16 hours. Doubling the initial concentration of the pyridine-borane results in an increased conversion of the olefin in the same reaction time.

Trimethylamine-borane appears to be considerably less reactive than pyridine-borane, with only 15% conversion of the 1-octene observed after 16 hours at 75°, as compared to 90% for pyridine-borane under the same conditions.

The experimental data are summarized in Table IV. From these results, it appears that the amine-boranes are less convenient than the borohydrides for the hydroboration of olefins under mild conditions.

Alkali Metal Hydrides.—Sodium hydride reacts with boron trifluoride to produce diborane.[11,20] In diglyme solution, in the presence of 1-octene, reaction readily proceeds to give a 99% conversion of the olefin (12).[27] In tetrahydrofuran the reaction likewise proceeded to completion in one hour at room temperature. However, in ethyl ether the reaction proved sluggish, with only 18% reaction indicated under these conditions.

$$6RCH{=}CH_2 + 6NaH + 8BF_3 \longrightarrow 2(RCH_2CH_2)_3B + 6NaBF_4 \quad (12)$$

Lithium hydride reacted readily in all three solvents. However, the use of boron trifluoride etherate in the ratio $3LiH/BF_3$ resulted in only 20 to 25% reaction. Use of sufficient boron trifluoride to form lithium fluoroborate, $LiBF_4$, resulted in essentially complete conversions.

These results are summarized in Table IV.

Discussion

This study demonstrates that the hydroboration reaction can be realized with a wide variety of reagents and solvents.

The ready solubility of lithium borohydride in ethyl ether and tetrahydrofuran, as well as other ether solvents, gives it obvious advantages for the hydroboration reaction. Boron trifluoride etherate, hydrogen chloride or sulfuric acid in ether solution gives essentially quantitative yields in one hour at room temperature. Moreover, these acids are readily available in pure form. Consequently, hydroboration procedures based on these reactions appear to be the most favorable of those examined utilizing lithium borohydride. The sole disadvantage at the present time is the relatively high cost of lithium borohydride.

Sodium borohydride is readily soluble in diglyme and the reactions with boron trifluoride etherate, hydrogen chloride or sulfuric acid proceed rapidly and quantitatively at room temperature. These reactions are the procedures of choice in cases where diglyme (or triglyme) is available. In cases where the presence of sodium iodide in the reaction medium would not be deletorious, the use of methyl iodide to bring about the hydroboration reaction offers unusual convenience.

Should it be necessary or desirable to avoid the use of diglyme, the hydroboration readily can be achieved by the action of boron trifluoride etherate upon a suspension of sodium borohydride in tetrahydrofuran. Alternatively, a solution of diborane in tetrahydrofuran can be generated by treating a suspension of sodium borohydride at 0° with hydrogen chloride. The hydroboration reaction then is achieved by adding the olefin to this solution.

Finally, it is possible to utilize ethyl ether as the solvent by introducing 10 mole % of anhydrous zinc chloride to catalyze the reaction between sodium borohydride and boron trifluoride etherate in ethyl ether.

Potassium borohydride is utilized readily with boron trifluoride etherate in triglyme suspension. Tetrahydrofuran can be utilized conveniently with this borohydride by carrying out a prior equilibration with lithium chloride to form a solution of lithium borohydride in tetrahydrofuran.[22] The latter solution can be utilized for hydroboration with any of the acids previously established as suitable for lithium borohydride itself.

The reaction of lithium aluminum hydride with boron trifluoride etherate in ethyl ether solution appears to be a convenient procedure utilizing a readily available solvent.[10] In the event boron trifluoride etherate is not available, an equimolar mixture of aluminum chloride and methyl borate provides a readily available substitute.

The amine-boranes appear to be less satisfactory hydride sources for the low temperature hydroboration of olefins. However, in the absence of either the simple metal hydrides or the complex hydrides previously reviewed, pyridine-borane can be utilized in benzene solution with boron trifluoride etherate at 75° to achieve hydroboration.

Finally, lithium hydride in ethyl ether, tetrahydrofuran or diglyme, and sodium hydride, in tetrahydrofuran or diglyme react readily with boron trifluoride etherate. The major disadvantage is the relatively large amount of boron trifluoride which must be used and the resulting presence of large amounts of lithium or sodium fluoroborates in the reaction mixtures.

The wide applicability of different hydride sources, solvents, and acids demonstrated in this study should facilitate the application of the hydroboration reaction to synthetic organic chemistry.

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(26) The reaction of pure boron trifluoride with pyridine-borane proceeds at 25°, but the reaction is much slower than one would anticipate for a simple acid–base displacement reaction. This phenomenon is under study by Mr. Gerald J. Klender.

(27) We are indebted to Dr. B. C. Subba Rao for some early studies of this reaction.

Experimental Part

Materials.—Diglyme, triglyme, tetrahydrofuran, ethyl ether and benzene were all purified by distillation from lithium aluminum hydride following procedures described in earlier papers.[20,21]

Lithium borohydride (95%), sodium borohydride (98%) and potassium borohydride (97%), and lithium aluminum hydride all from Metal Hydrides Inc., were used without purification. Solutions of these hydrides in the appropriate solvents were prepared with the careful exclusion of moisture and the solutions standardized by analysis for active hydrogen, as well as for boron and the alkali metal. Pyridine-borane and trimethylamine-borane from Callery Chemical Co. were utilized without further purification. Sodium hydride was the 50% suspension in oil from Metal Hydrides Inc. Lithium hydride was 200 mesh solid from the Lithium Corporation.

Boron trifluoride etherate (The Matheson Co., Distillation Products Co.) was distilled in an all-glass apparatus and was utilized shortly after the distillation. Boron trichloride from a cylinder (Matheson) was passed into anhydrous ethyl ether at 0°. The solution was standardized by hydrolyzing an aliquot and titrating the hydrochloric acid formed, followed by titration of the boric acid in the presence of mannitol. It was observed that the titer for hydrochloric acid decreased with time, so only freshly prepared solutions were used. (The stability was considerably less than that observed previously for similar solutions prepared and handled in the high vacuum apparatus.)[20]

Aluminum chloride (J.T. Baker, analyzed) was purified by sublimation in an all-glass system. The solid material, weighed, was dissolved in ethyl ether. Methyl borate from Metal Hydrides Inc. was freshly distilled, b.p. 65–66° at 748 mm. Titanium tetrachloride (J. T. Baker, analyzed) was used without purification. Anhydrous zinc chloride was prepared following the procedure of Pray.[28]

Hydrogen chloride was generated by introducing concentrated hydrochloric acid into concentrated sulfuric acid. The dry gas was passed into the solvent at 0° with careful protection of the system from moisture. The solutions were standardized by titration of aliquots. The ether solution proved to be stable over 2 to 3 months. The titer of the tetrahydrofuran solutions decreased significantly over a period of one week. Consequently these solutions were freshly prepared before use.

1-Octene was Phillips pure grade, 99%, $n^{20}\text{D}$ 1.4088. It was used without purification. The remaining chemicals were standard laboratory research chemicals whose purity was checked by distillation, determination of the refractive index, or V.P.C. examination before use.

Analysis.—The decrease in concentration of 1-octene in the reaction mixture was followed by vapor phase chromatographic (V.P.C.) examination. In the majority of the experiments, cyclohexane, at one-fifth the initial concentration of 1-octene, was used as an internal standard. An Aerograph instrument with a Ucon polar column, 5 ft., at 75° and 8 p.s.i. of helium was utilized. The precision of the analysis was tested with a number of synthetic mixtures. We were able to reproduce the known compositions to approximately ±2%.

General Procedure.—The apparatus consisted of a 100 ml., 3-neck flask equipped with a 200-mm. reflux condenser, a 60-ml. pressure equalized separatory funnel, a thermometer well and a magnetic stirrer. The flask was equipped with a short side arm fitted with a rubber serum cap to permit removal of samples by means of a hypodermic syringe. The apparatus was dried in an oven and assembled with minimum exposure to the atmosphere. To this flask was added an aliquot of a standard solution of 1-octene (100 mmoles) and cyclohexane (20 mmoles) in an appropriate solvent. To this solution was added an aliquot of the standardized hydride solution, generally 10% excess over that required for the stoichiometric reaction (see eq. 1–12). The volume was adjusted to 70 ml. by addition of solvent. In the separatory funnel was placed the acid, equivalent to the hydride used, usually dissolved in sufficient ethyl ether to give 30 ml. of solution.

The system was flushed with dry nitrogen and then the acid solution was added over a period of one hour. The temperature was maintained at approximately 25° by means of a water-bath. When the addition was complete, a sample of the solution was removed and examined for residual 1-octene by V.P.C. analysis. After a second hour at 25°, another sample was removed. If the reaction was not yet complete, the reaction mixture was heated under reflux (~40° for ethyl ether solutions, ~58° for tetrahydrofuran solutions) or maintained at 75° for diglyme and triglyme solutions.

In cases where the hydrides were insoluble, weighed samples of the solid compounds were introduced directly into the flasks. Lithium hydride was weighed under the appropriate solvent and the mixture transferred into the flask. The sodium hydride in oil was utilized without attempting to remove all of the oil.

Hydroboration in Ethyl Ether with Lithium Borohydride–Boron Trifluoride.—A solution of 18.8 g. (200 mmoles) of norbornene and 1.98 g. (90 mmoles) of lithium borohydride in 100 ml. ether at 0° was treated over a period of 1 hour with 17 g. (120 mmoles) of boron trifluoride etherate. After a second hour at 0°, 5 ml. of water was added to destroy residual hydride, 21 ml. of sodium hydroxide added, and the product oxidized with 21 ml. of 30% hydrogen peroxide added slowly over a period of 1 hour through the dropping funnel. The solution was washed with water, the ether layer dried over magnesium sulfate, and the ether distilled to recover the product. After recrystallization from petroleum ether, b.p. 30 to 60°, and sublimation, there was obtained 15.9 g. of norborneol, m.p. 123–124°, 70% yield.

Hydroboration in Tetrahydrofuran with Lithium Borohydride–Sulfuric Acid.—In a three-neck 500-ml. round-bottom flask, equipped with a reflux condenser, thermometer and a dropping funnel, was placed 2.62 g. (120 mmoles) of lithium borohydride, 33.6 g. (300 mmoles) of 2,4,4-trimethyl-1-pentene ($n^{20}\text{D}$ 1.4807) and 170 cc. of tetrahydrofuran. In the dropping funnel was placed a solution of 5.88 g. (60 mmoles) of concentrated sulfuric acid in 42 cc. of ether. After flushing with nitrogen, the acid was added over a period of 1 hour to the lithium borohydride–olefin solution, maintaining the temperature at 25°. After a second hour at room temperature, there was added 32 ml. of a 3 N solution of sodium hydroxide, followed by the slow addition of 32 ml. of 30% hydrogen peroxide. The tetrahydrofuran–ether layer was washed with water and dried over magnesium sulfate. The ether and tetrahydrofuran were removed. After distillation, there was obtained 31.6 g. of 2,4,4-trimethyl-1-pentanol, b.p. 165–166° at 748 mm., $n^{20}\text{D}$ 1.4274, 81% yield.

Hydroboration in Tetrahydrofuran with Sodium Borohydride–Boron Trifluoride Etherate.—The sodium borohydride was pulverized before use. To a well stirred suspension of 3.4 g. (90 mmoles) of this pulverized sodium borohydride in 150 cc. of tetrahydrofuran containing 25.2 g. (300 mmoles) of 4-methyl-1-pentene ($n^{20}\text{D}$ 1.3830) there was added 17 g. (120 mmoles) of boron trifluoride etherate in 20 cc. of tetrahydrofuran over a period of 1 hour, maintaining the temperature at 25°. After a second hour at 25°, 32 ml. of a 3 N solution of sodium hydroxide was added, and the product oxidized with 32 ml. of 30% hydrogen peroxide which was added slowly over a period of 1 hour. The solution was washed with water, the tetrahydrofuran layer dried over magnesium sulfate, and the tetrahydrofuran distilled to recover the product. After distillation, there was obtained 24.5 g. of 4-methyl-1-pentanol, b.p. 151–153° at 735 mm., $n^{20}\text{D}$ 1.4140, a yield of 80%.

Hydroboration in Tetrahydrofuran with Sodium Borohydride–Hydrogen Chloride.—To a well-stirred suspension of 3.0 g. (80 mmoles) of pulverized sodium borohydride and 100 ml. of tetrahydrofuran at 0° was added over a period of 2 hours 45 ml. of 1.5 M hydrogen chloride (67 mmoles) in tetrahydrofuran, freshly prepared. To the resulting solution of diborane in tetrahydrofuran (nitrogen atmosphere) was added over a period of 1 hour 22.4 g. (200 mmoles) of 1-octene. The product was oxidized and isolated by the customary procedures. There was obtained 21 g. of 1-octanol, b.p. 98–100° at 23 mm., $n^{20}\text{D}$ 1.4295, a yield of 80%.

Hydroboration in Ethyl Ether with Sodium Borohydride–Zinc Chloride (10%)–Boron Trifluoride.—In the usual apparatus was placed 1.09 g. (27.7 mmoles) of sodium borohydride, 0.177 g. (1.30 mmoles) of anhydrous zinc chloride and 52 cc. of ethyl ether. The reaction mixture was stirred for 1.5 hours. During this time the suspended sodium borohydride underwent an obvious change, becoming very finely divided. To this reaction mixture were added 11.2 g. (100 mmoles) of 1-octene and 1.68 g. (20 mmoles) of cyclohexane.

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[28] A. R. Pray, *Inorg. Syntheses*, **6**, 153 (1957).

Then 4.2 g. (37 mmoles) of boron trifluoride etherate in 25 ml. of ether was added over a period of one hour. The yield, based on V.P.C. analysis for residual 1-octene, was 94%.

Hydroboration in Tetrahydrofuran with Potassium Borohydride–Lithium Chloride–Boron Trifluoride.—In the reaction flask were placed 1.48 g. (27.5 mmoles) of pulverized potassium borohydride, 1.17 g. (27.5 mmoles) of pulverized lithium chloride (dried at 120° under vacuum) and 52 cc. of tetrahydrofuran. The heterogeneous mixture was stirred for 3 hours at room temperature. (In other experiments analysis of the solution for soluble borohydride indicated conversions of 80 to 90% under these conditions.) To the flask were now added the 100 mmoles of 1-octene and 20 mmoles of cyclohexane. Through the dropping funnel was added 36.6 mmoles of boron trifluoride etherate in 25 cc. of tetrahydrofuran over a period of one hour. After a second hour at room temperature, V.P.C. analysis for 1-octene indicated the yield to be 83%.

Hydroboration in Tetrahydrofuran with Sodium Hydride–Boron Trifluoride.—The sodium hydride oil suspension analyzed for 47% sodium hydride by hydrolysis and measurement of the hydrogen produced.

Sodium hydride, 8.5 g. of the oil suspension (47% analysis, 165 mmoles), was weighed in the reaction flask under 27 cc. of tetrahydrofuran. To the flask was added 11.2 g. (100 mmoles) of 1-octene and 1.68 g. (20 mmoles) of cyclohexane with 50 ml. additional of tetrahydrofuran. Through the dropping funnel was added 18.8 cc. (146 mmoles) of boron trifluoride etherate over a period of 1 hour. There was an obvious exothermic reaction and the solid suspension changed in amount and in color (from dark gray to a very light gray.) After one hour, V.P.C. examination showed 99% of the 1-octene had reacted.

Hydroboration Experiments with Amine-boranes.—In the usual reaction flask was placed 80 ml. of dry benzene, 11.2 g. (100 mmoles) of 1-octene and 37 mmoles of the amine-borane (pyridine-borane or trimethylamine-borane). Experiments were carried out both with and without the addition of 37 mmoles of boron trifluoride etherate. The temperature was maintained at 75°. Samples were removed and analyzed by V.P.C. From the decrease in the peak-height the amount of 1-octene reacted was determined. (No internal standard was used, so the analyses are probably not more reliable than ±5%.) At the end of the reaction, the mixture was hydrolyzed by adding 20 ml. of 6 *N* hydrochloric acid. The hydrogen evolved corresponded to the V.P.C. analyses within the indicated precision.

We attempted to run similar experiments in diglyme as solvent. However, our V.P.C. analyses were erratic. We believe that the difficulty is due to reaction of the olefin with the amine-borane on the hot-stage of the instrument, before the diglyme is vaporized.

Acknowledgments.—We are indebted to the Office of Ordnance Research, to the Ethyl Corporation and to Metal Hydrides, Inc., for the financial assistance which made this study possible. We wish to acknowledge also the assistance of the Ansul Chemical Co. in making available supplies of diglyme and triglyme.

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Ethylenimine Ketones. XV. Absorption Spectra and Stereostructure

BY NORMAN H. CROMWELL, RONALD E. BAMBURY AND JULES L. ADELFANG

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A detailed examination of spectroscopic data previously gathered as well as of several new measurements of the infrared and ultraviolet absorption spectra of various arylaroylethylenimines, aroylethylenimines and some related α-aminoketones has led to the following new conclusions: (1) In the solid ground state aroylethylenimines and *cis*-arylaroylethylenimines have a non-conjugated *gauche* conformation, (2) in CCl_4 solutions these ethylenimine ketones exist as mixtures of non-conjugated *gauche* and conjugated *cisoid* rotational isomers, (3) *trans*-arylaroylethylenimines have a conjugated *cisoid* conformation in the ground state in the solid form and in solution, (4) α-aminoketones show conformational isomerism in CCl_4 solution which is similar to that which has been demonstrated for α-halogenated ketones and (5) the ethylenimine ring transmits an electrical effect of a β-phenyl group to the α-carbonyl group in the excited state of the *trans*-arylaroylethylenimines as measured by shifts in ultraviolet absorption spectra, but *p*-substituted groups in the β-phenyl group do not extend the conjugation. Sterically dependent polarity factors responsible for the conformational isomerism shown by these diverse compounds, and the transmission of electrical effects by the ethylenimine ring are discussed.

In a series of papers,[1] beginning in 1951, we have reported on studies of the infrared and ultraviolet absorption spectra of several series of ethylenimine ketones, epoxy ketones and cyclopropyl ketones and discussed the nature of and steric requirements for the electrical interaction of these various three-rings with the carbonyl group. These studies led to the discovery of a practical general method of assigning the geometrical configurations at carbon for the *cis*- and *trans*-arylaroylethylenimines,[1a,c,h] methylaroylethylenimines,[1d] arylacetylethylenimines,[1i] arylaroylethylene oxides[1e] and arylaroylcyclopropanes.[1f,j]

The nature of the electrical interaction between the three-ring and the carbonyl group which results in the latter's increased polarization has been described[1c] as a type of hyperconjugation which results from orbital overlap of the *bent bonds* of the three-rings with the π-orbitals of attached unsaturated groups. The geometrical isomer which shows an inhanced degree of carbonyl associated light absorption in the ultraviolet and/or infrared ranges of the spectrum has been found to possess the *trans* structure.[1]

The steric requirement for maximum three-ring carbonyl hyperconjugation has been assessed[1b,g] to be that *the p-orbitals of attached groups must be free to orient themselves so that their axes approach a parallel relation to the plane of the three-ring and a near symmetrical arrangement with respect to the bent bonds.*

Recently a further consideration of the spectroscopic data which have been gathered to date for these various three-ring carbonyl compounds and

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[1] (a) N. H. Cromwell, *et al.*, THIS JOURNAL, **73**, 1044 (1951); (b) N. H. Cromwell and G. V. Hudson, *ibid.*, **75**, 872 (1953); (c) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952); (d) N. H. Cromwell and R. J. Mohrbacher, THIS JOURNAL, **75**, 6252 (1953); (e) N. H. Cromwell and R. A. Setterquist, *ibid.*, **76**, 5752 (1954); (f) R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957); (g) R. D. Campbell and N. H. Cromwell, *ibid.*, **79**, 3456 (1957); (h) N. H. Cromwell and G. D. Mercer, *ibid.*, **79**, 3815 (1957); (i) N. H. Cromwell and R. P. Cahoy, *ibid.*, **80**, 5524 (1958); (j) N. H. Cromwell, R. E. Bambury and R. P. Barkley, *ibid.*, **81**, 4294 (1959).