means that at some stage, prior to the chlorine atom elimination reaction, the original stereochemical structure is lost. This might happen at the stage of the activated complex if the addition proceeds *via* the same transition state in both isomers, or it might be caused by a free rotation around the C–C axis of the original olefinic carbon atoms in the c-$C_6H_{11}C_2Cl_2H_2$ radical if there is a different transition state in the two cases.

Another question which arises is whether the chlorine atom splitting reaction leading to the formation of the *cis* and *trans* forms of c-$C_6H_{11}CHCClH$ proceeds *via* a single or two distinct transition states. This question cannot be answered on the basis of our results.

Selective Reductions. XV. Reaction of Diborane in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups

Herbert C. Brown, Peter Heim,[1a] and Nung Min Yoon[1b]

Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana 47907. *Received September 10, 1969*

Abstract: The rates and stoichiometry of the reaction of diborane in tetrahydrofuran solution with selected organic compounds containing representative functional groups were examined under standardized conditions in order to compare its reducing characteristics with those of other selective reducing agents similarly examined and to establish the scope of its applicability as a selective reducing agent. The rate of evolution of hydrogen from active hydrogen compounds varied considerably with the nature of the functional group and the structure of the hydrocarbon moiety. Most aldehydes and ketones are reduced rapidly to the alcohol stage. However, the reduction of benzophenone is considerably slower. Norcamphor is reduced with much higher stereospecificity than is realized with the usual complex hydrides, yielding 2% *exo*-, 98% *endo*-norbornanol. *p*-Benzoquinone is reduced to hydroquinone at a moderate rate, whereas the reaction with anthraquinone is quite sluggish. Carboxylic acids are rapidly reduced, whereas the corresponding acid chlorides react much slower. Aliphatic acid esters are reduced at a moderate rate, whereas the reactions of aromatic esters are much slower. The reactions of diborane with epoxides are relatively slow and complex, yielding only 48% of butyl alcohols from the simplest epoxide examined, 1,2-butylene oxide, and none of the anticipated simple alcohols from 1-methyl-1,2-cyclohexene oxide. Tertiary amides and nitriles are reduced readily to the corresponding amines, whereas the reduction of primary amides is much slower. Azobenzene undergoes reduction to aniline, whereas 1-nitropropane, nitrobenzene, and azoxybenzene are stable to the reagent under the standard conditions. Cyclohexanone oxime, phenyl isocyanate, and pyridine N-oxide react with diborane at moderate rates, whereas pyridine forms an addition compound but fails to indicate further reaction. Finally dimethyl sulfoxide is reduced at a moderate rate to dimethyl sulfide. However, the other sulfur derivatives examined, disulfide, sulfide, and tosylate, are inert to the reagent under the standard conditions.

Diborane has proved to be a most versatile reagent for the hydroboration of olefins, dienes, and acetylenes,[2] making organoboranes readily available for synthetic purposes.[3] Previous explorations have also revealed that diborane is a powerful hydrogenating agent for functional groups.[4]

In these preliminary exploratory studies[4] we noted many unusual reducing characteristics of diborane, quite different from those we have observed for aluminum hydride,[5] lithium aluminum hydride,[6] and its alkoxy derivatives.[7,8] In particular, it appeared that diborane, as a Lewis acid, functions as an "acidic" reducing agent,[4b] in marked contrast to the behavior of sodium borohydride or the alkoxy aluminohydrides[7,8] which function as "basic" reducing agents.

For example, acyl halides are rapidly reduced by all of the aluminum hydrides[6–8] as well as by sodium borohydride. However, reduction of acyl halides by diborane is remarkably slow.[4a] On the other hand, carboxylic acids are rapidly reduced by diborane,[4b,c] with the rate comparable to that exhibited by the exceedingly powerful reducing agent, lithium aluminum hydride. This reactivity toward the mild reagent, diborane, is in marked contrast to the behavior of the other mild reagents, lithium tri-*t*-butoxyaluminohydride and sodium borohydride, neither of which reduce carboxylic acids under the usual mild standard conditions (THF, 0°).

(1) (a) Postdoctorate research associate, 1962–1964, on research grants supported by the Atomic Energy Commission, AT(11-1)-70, and the National Institute of Health, GM 10937; (b) graduate research assistant, 1963–1967, and postdoctorate research associate, 1967–1969, on Research Grants DA-31-124, ARO(D)-117, and -453 supported by the U. S. Army Research Office (Durham).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(3) (a) H. C. Brown, *Accad. Naz. Lincei*, 73 (1968); (b) H. C. Brown, *Accounts Chem. Res.*, 2, 65 (1969).

(4) (a) H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Amer. Chem. Soc.*, 61, 673 (1939); (b) H. C. Brown and B. C. Subba Rao, *ibid.*, 82, 681 (1960); (c) H. C. Brown and W. Korytnyk, *ibid.*, 82, 3866 (1960).

(5) H. C. Brown and N. M. Yoon, *ibid.*, 88, 1464 (1966).

(6) H. C. Brown, P. M. Weissman, and N. M. Yoon, *ibid.*, 88, 1458 (1966).

(7) H. C. Brown and P. M. Weissman, *ibid.*, 87, 5614 (1965).

(8) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, 1, 430 (1963).

These unique reducing characteristics, turned up in our original exploratory studies,[4] persuaded us of the desirability for making a systematic study of the reducing characteristics of diborane. We have recently described such systematic studies of the approximate rates and stoichiometries of the reactions of aluminum hydride,[5] lithium aluminum hydride,[6] lithium trimethoxyaluminohydride,[7] and lithium tri-*t*-butoxyaluminohydride,[8] all in tetrahydrofuran solution (THF) at 0° with a standard list of compounds representative of the more common functional groups. Accordingly, we decided to undertake a similar study of the reducing properties of diborane, utilizing the same standard list of compounds and the same standard conditions (THF, 0°). In cases where a reaction occurred, but was slow to proceed to completion at 0°, it was also run at 25° in order to establish the stoichiometry. Glpc examination of hydrolyzed reaction mixtures was made to establish the structure of the product in those cases where this might be in question, in spite of the established stoichiometry. No attempt was made to force sluggish reactions, since we were interested primarily in those reactions which proceed rapidly and completely and would be useful especially for our program of making possible the selective reduction of particular groups in the presence of other substituents.

Results and Discussion

Procedure for Rate and Stoichiometry Studies. The procedure adopted was to add 12.5 mmol of the organic compound to 16.6 mmol of borane (BH_3) in sufficient tetrahydrofuran to give 50 ml of solution. This makes the reaction mixture 0.33 *M* in borane (*i.e.*, 1.00 *M* in hydride) and 0.25 *M* in the compound under examination. The solution was maintained at 0° and aliquots were removed at appropriate intervals and analyzed for residual hydride. In this manner it was possible to establish both the rate at which reduction proceeds and the stoichiometry of the reaction, *i.e.*, the number of hydrides utilized per mole of compound when the reaction comes to an effective halt.

Alcohols, Phenols, Amines, and Thiols. The alcohols, phenols, and thiols examined all liberated hydrogen quantitatively. On the other hand, *n*-hexylamine liberated only 0.13 equiv of hydrogen slowly over 12 hr.

It is interesting that the rate of hydrogen evolution for the alcohols decreases in the order: primary > secondary > tertiary. This is in agreement with the usual interpretation that the acidity of the hydroxylic hydrogen in these alcohols decreases in this order.[9] Such a trend could not be observed with the aluminohydrides, all of which evolve hydrogen instantly and quantitatively.[10] On the other hand, sodium borohydride reacts quite rapidly with methanol, but relatively slowly with ethanol or water, and is remarkably stable in isopropyl alcohol.[11]

In view of the much slower reaction with phenol, it is not possible to argue solely for a mechanism involving reaction of the borane with the acidic hydrogen. The results can be rationalized by prior coordination of BH_3 with alkoxy oxygen, followed by hydrogen evolution (eq 1).

$$R\text{–}OH + BH_3 \longrightarrow R\text{—}\overset{H}{\overset{+}{O}}\text{:}\overset{H}{\underset{H}{B}}\text{:}H \longrightarrow R\text{—}OBH_2 + H_2 \quad (1)$$

In the cases of phenol, *n*-hexylamine, and the thiols, it is apparent that two factors, the acidity of hydrogen as well as the ability of the donor atom to share its electron pair, must be influencing the rate of the reactions. Thus, the slow rate of hydrogen evolution exhibited by phenol must be attributed to its weakly basic character which opposes formation of the prior addition compound postulated for the alcohol reaction (eq 1). On the other hand, *n*-hexylamine readily forms such an addition compound. The slow evolution of hydrogen here must be a result of the much lower acidity of the hydrogen atoms attached to nitrogen.

The results are summarized in Table I. The rates of hydrogen evolution are compared in Figures 1 and 2.

Table I. Reaction of Diborane with Representative Active Hydrogen Compounds in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Hexanol	0.25	0.98	0.98	0
	0.5	1.0	1.0	0
	1.0	1.0	1.0	0
Benzyl alcohol	0.25	0.92	0.92	0
	0.5	0.98	0.98	0
	1.0	1.0	1.0	0
3-Hexanol	0.25	0.88	0.88	0
	0.5	0.94	0.94	0
	1.0	0.98	0.98	0
	1.5	1.0	1.0	0
3-Ethyl-3-pentanol	0.25	0.2	0.2	0
	0.5	0.29	0.29	0
	1.0	0.41	0.41	0
	1.5	0.50	0.50	0
	3.0	0.71	0.71	0
	6.0	0.86	0.86	0
	12.0	1.00	1.00	0
Phenol	0.25	0.17	0.17	0
	0.5	0.32	0.32	0
	1.0	0.48	0.48	0
	1.5	0.60	0.60	0
	3.0	0.84	0.84	0
	6.0	0.96	0.96	0
	12.0	1.00	1.00	0
n-Hexylamine	1.0	0.04	0.04	0
	6.0	0.11	0.11	0
	12.0	0.13	0.13	0
	20.0	0.13	0.13	0
1-Hexanethiol	0.5	0.50	0.50	0
	1.0	0.74	0.74	0
	3.0	0.93	0.93	0
	6.0	0.95	0.95	0
	12.0	1.0	1.0	0
Benzenethiol	0.5	0.95	0.95	0
	1.0	1.00	1.00	0

[a] 12.5 mmol of compound was added to 16.6 mmol of borane (50 mmol of hydride) in 50 ml of solution 0.25 *M* in compound and 1.00 *M* in hydride. [b] Millimoles/millimole of compound.

In the reactions of alcohols with diborane, we did not observe any additional hydride utilization suggesting hydrogenolysis.[12] However, it has been reported that

(9) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 7.

(10) With lithium tri-*t*-butoxyaluminohydride, we observed only partial hydrogen evolution. However, this was due to other factors.[8]

(11) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 77, 6209 (1955).

(12) Hydrogenolysis of alcohols, using "mixed hydrides" have been extensively studied. See J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964), and references therein.

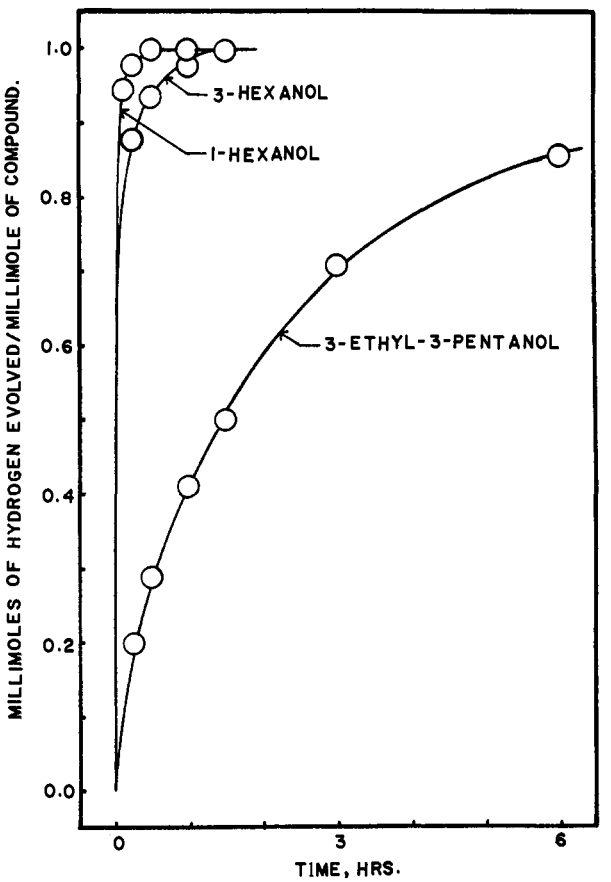


Figure 1. Rates of hydrogen evolution from representative primary, secondary, and tertiary alcohols.

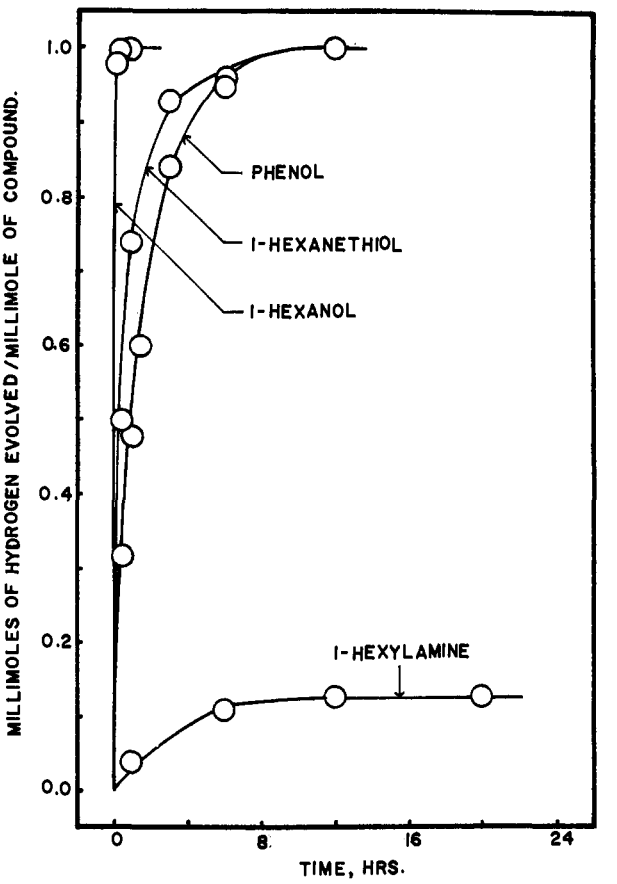


Figure 2. Rates of hydrogen evolution from various active hydrogen compounds.

those benzylic alcohols which can form carbonium ions readily are transformed by diborane into the corresponding hydrocarbons in the presence of boron trifluoride. Moreover, in the case of 4-dimethylaminobenzaldehyde, the corresponding hydrocarbon was obtained in 70% yield with diborane only, in the absence of boron trifluoride.[13]

Aldehydes and Ketones. The aldehydes and ketones examined all consumed one hydride, indicating reduction to the corresponding alcohols. The reduction of norcamphor appears to be unusually stereoselective, forming 2% *exo*- and 98% *endo*-norbornanol, in contrast to the 11:89 distribution realized with lithium aluminum hydride.[14] The high stereospecificity realized with diborane is comparable to that previously achieved with lithium trimethoxyaluminohydride.[14] The rate of reduction of benzophenone was considerably slower than the other ketones, probably a consequence of the combined steric and electronic effects of the phenyl groups.

Cinnamaldehyde consumed a total of 2.1 hydrides, presumably one for the double bond, one for the carbonyl group, and 0.1 for rehydroboration after elimination.[15]

(13) E. Breuer, *Tetrahedron Lett.*, 1849 (1967).
(14) H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, 87, 5620 (1965).
(15) Cinnamyl alcohol, when allowed to react with diborane, gave, along with expected glycols, large amounts of monoalcohols. See K. Kratzl and P. Claus, *Monatsh. Chem.*, 94, 1140 (1963). However, by using disiamylborane to reduce the carbonyl groups, followed by diborane for hydroboration, the elimination was largely avoided, giving the glycol (after oxidation) in yields as high as 92%: H. C. Brown and R. M. Gallivan, Jr., *J. Amer. Chem. Soc.*, 90, 2906 (1968).

The results are summarized in Table II. The rates of three representative carbonyl compounds are compared in Figure 3.

Table II. Reaction of Diborane with Representative Aldehydes and Ketones in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproaldehyde	0.25	0	0.55	0.55
	0.5	0	0.92	0.92
	1.0	0	0.97	0.97
	2.0	0	1.00	1.00
Benzaldehyde	0.25	0	1.00	1.00
	0.5	0	1.00	1.00
2-Heptanone	0.25	0	0.60	0.60
	0.5	0	0.80	0.80
	1.0	0	1.00	1.00
	2.0	0	1.00	1.00
Norcamphor	1.0	0.03	0.99	0.96
	6.0	0.03	0.99	0.96
Acetophenone	0.25	0	0.67	0.67
	0.5	0	0.82	0.82
	1.0	0	0.91	0.91
	2.0	0	1.00	1.00
Benzophenone	0.25	0	0.12	0.12
	0.5	0	0.22	0.22
	1.0	0	0.34	0.34
	2.0	0	0.49	0.49
	6.0	0	0.80	0.80
	24.0	0	1.00	1.00
Cinnamaldehyde	0.25	0	1.66	1.66
	0.5	0	1.85	1.85
	1.0	0	2.10	2.10
	2.0	0	2.10	2.10

[a,b] See corresponding footnotes in Table I.

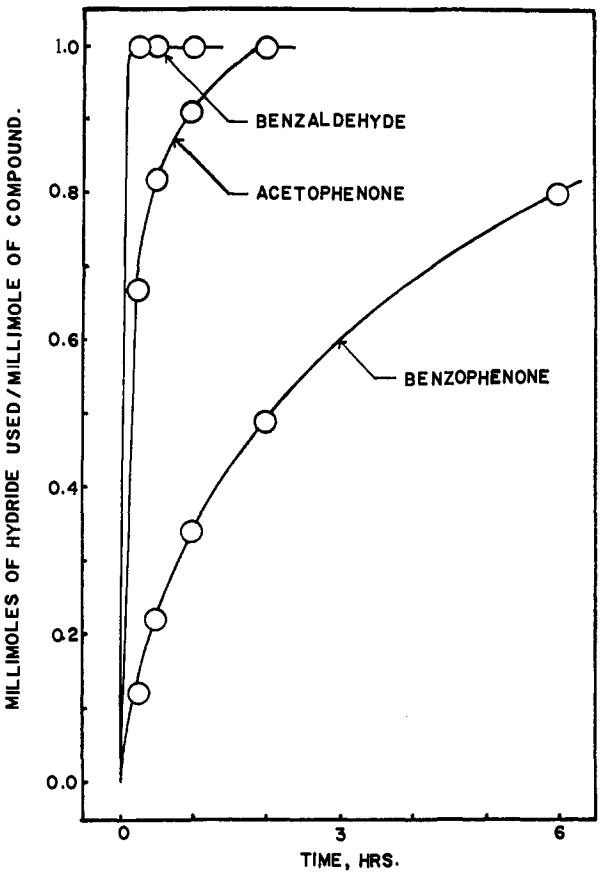
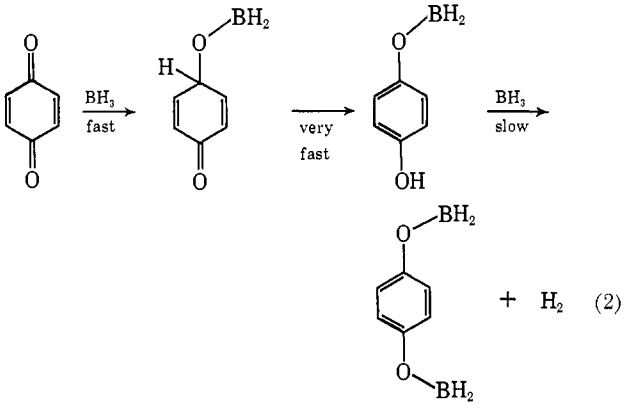


Figure 3. Rates of reduction of carbonyl compounds.

Quinones. *p*-Benzoquinone reacted slowly, using two hydrides, one for reduction and the other for hydrogen evolution. This stoichiometry corresponds to reduction to hydroquinone.[6] Indeed, we isolated a nearly quantitative yield of hydroquinone. The probable mechanism is indicated in eq 2. On the other



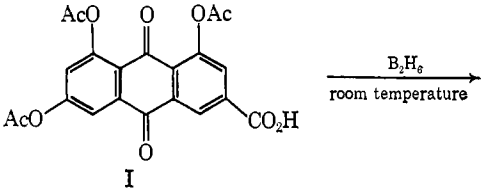
hand, anthraquinone was reduced very slowly, showing only one hydride uptake in 7 days without hydrogen evolution. This compound is only sparingly soluble in tetrahydrofuran. However, two hydrides were consumed readily both with lithium aluminum hydride[6] and aluminum hydride[5] in spite of the low solubility.[16]

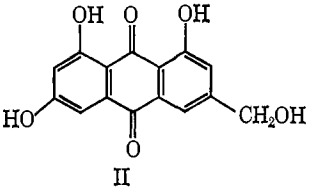
(16) It has been reported that anthraquinone is readily reduced at room temperature by sodium borohydride in pure diglyme to anthrahydroquinone: D. S. Bapat, B. C. Subba Rao, M. K. Unni, and K. Venkataraman, *Tetrahedron Lett.*, No. 5, 15 (1960). This is in apparent contradiction to an earlier report.[17]

(17) G. S. Panson and C. E. Weill, *J. Org. Chem.*, 22, 120 (1957).

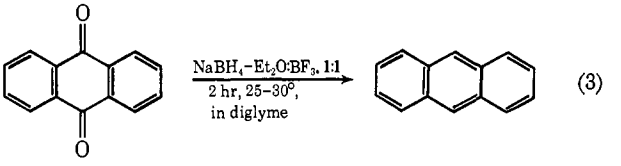
Consequently, it is probable that the slow reaction of diborane with anthraquinone is a result of the very weak donor properties of the reagent and is related to the relatively slow rate observed for benzophenone.

The slow reaction of diborane with the anthraquinone structure has been utilized to achieve the selective reduction of I to II in 60% yield by avoiding the presence of excess reagent.[16] It is also of interest that





diborane and boron trifluoride (actually sodium borohydride in the presence of excess boron trifluoride) achieves the reduction of anthraquinone and its derivatives to the corresponding anthracenes[16] (eq 3).



(3)

The results of the present study with these representative quinones are summarized in Table III.

Table III. Reaction of Diborane with Representative Quinones in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
p-Benzoquinone[c]	0.5	0.26	1.10	0.84
	1.0	0.40	1.60	1.20
	6.0	0.90	1.95	1.05
Anthraquinone[c]	6.0	0	0.06	0.06
	168.0	0	0.95	0.95

[a,b] See corresponding footnotes in Table I. [c] Compounds were added as solids.

Carboxylic Acids and Derivatives. The reaction with caproic acid is exceedingly fast, even at 0°, being essentially complete within 15 min. The aromatic acid, benzoic, is somewhat slower, requiring 12 to 24 hr at 0° to go to completion. Both reactions consume three hydrides, one for hydrogen evolution and the other two for reduction. The reaction with acetic anhydride proceeds at a moderate rate. On the other hand, the corresponding reactions for the two cyclic anhydrides, succinic and phthalic, are much slower, showing only 1.32 and 0.87 hydride uptake in 48 hr out of the 4 expected for complete reduction.

Under our standard conditions the rates of reduction of both the aliphatic acid chloride, caproyl chloride, and the aromatic acid chloride, benzoyl chloride, are

Table IV. Reaction of Diborane with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproic acid	0.25	1.00	2.96	1.96
	0.5	1.00	2.94	1.94
	1.0	1.00	2.96	1.96
Benzoic acid	0.25	1.00	1.08	0.08
	1.0	1.00	1.98	0.98
	3.0	1.00	2.46	1.46
	12.0	1.00	2.95	1.95
	24.0	1.00	3.0	2.0
Acetic anhydride	0.25	0	1.50	1.50
	0.5	0	2.10	2.10
	1.0	0	2.58	2.58
	3.0	0	3.20	3.20
	12.0	0	3.64	3.64
	24.0	0	3.82	3.82
Succinic anhydride	0.5	0	0.05	0.05
	3.0	0	0.23	0.23
	12.0	0	0.5	0.5
	24.0	0	0.85	0.85
	48.0	0	1.32	1.32
Phthalic anhydride	1.0	0	0.08	0.08
	3.0	0	0.19	0.19
	12.0	0	0.45	0.45
	24.0	0	0.64	0.64
	48.0	0	0.87	0.87
Caproyl chloride	6.0	0	0.18	0.18
	12.0	0	0.37	0.37
	24.0	0	0.63	0.63
	48.0	0	1.13	1.13
Benzoyl chloride	6.0	0	0.12	0.12
	12.0	0	0.35	0.35
	24.0	0	0.60	0.60
	48.0	0	0.98	0.98

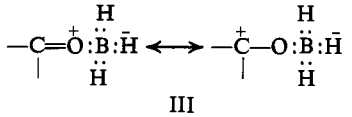
[a,b] See corresponding footnotes in Table I.

quite slow, being only approximately 50% complete in 48 hr.

These results are summarized in Table IV.

It has been reported that acid chlorides containing relatively electronegative substituents are reduced more readily by diborane than the parent acid chlorides.[18] Thus the observed rates are reported to be, in decreasing order, $CCl_3COCl > CH_2ClCOCl \gg CH_2ClCH_2COCl \gg C_2H_5COCl \geq C_3H_7COCl \geq CH_3COCl > C_6H_5COCl$.

This is puzzling for in our early work,[4a] where no solvent was used, we observed that the reaction of diborane with acetyl chloride and phosgene was very slow. On the other hand, aldehydes and ketones, such as acetaldehyde, trimethylacetaldehyde, and acetone, reacted very rapidly. Yet the introduction of chlorine substituents into the alkyl residue, as in chloral, completely altered the high reactivity of the parent aldehyde, and chloral failed to exhibit any reactivity toward diborane. We were able to correlate the donor properties of these carbonyl groups toward boron trifluoride with their reactivity toward diborane and proposed that the diborane reaction involved an initial formation of a borane addition compound (III) which was subsequently converted to products.



III

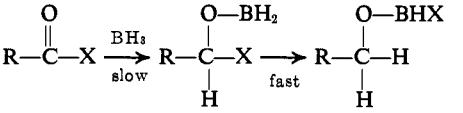
(18) S. L. Ioffe, V. A. Jartakovskli, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 622 (1964).

Evidently there is a marked difference in the effect of electronegative substituents in these original experiments involving no solvent and the effect of such substituents in the experiments carried out by Ioffe and his coworkers.[18] The latter used the present solvent, tetrahydrofuran, for their reductions with diborane. We have observed that diborane possesses an appreciable conductivity in this solvent. This conductivity has been attributed to a small amount of unsymmetrical ionization of diborane[19] (eq 4). Consequently, the ap-

$$2THF{:}BH_3 \rightleftharpoons (THF)_2BH_2^+ BH_4^- \quad (4)$$

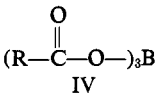
parent discrepancy between our early experiments and those of Ioffe and his coworkers as to the effect of electronegative substituents on the rates of reduction of carbonyl derivatives may be merely a reflection of a change in mechanism brought about by the use of tetrahydrofuran as a solvent. In this solvent, the more highly substituted acid chlorides may be undergoing nucleophilic attack by the small concentration of borohydride anion produced by the self-ionization of diborane, rather than the more usual electrophilic attack by the Lewis acid, BH_3.

We also treated caproic acid, benzoic acid, succinic anhydride, phthalic anhydride, and benzoyl chloride at 25° with the stoichiometric amount of reagent to produce the corresponding aldehydes (*i.e.*, 2 equiv of hydride per mole of acid and 1 equiv of hydride per mole of anhydride or acid chloride). Phthalic anhydride yielded 20% aldehyde, but the remaining derivatives revealed no measurable formation of aldehyde. These results suggest that the first hydride transfer must be slower than the second one (eq 5).



(5)

As was pointed out earlier,[4b] the fast reduction of carboxylic acids by diborane opens up the possibility of reducing this group selectively in the presence of many other substituents, or to protect it from such reduction by transforming it temporarily into an acyl halide or ester function. We are exploring such applications, as well as the unusual chemistry of the triacyloxyborane (IV), evidently the first intermediate in these reductions.[4b]



IV

Esters and Lactones. Ethyl caproate and γ-butyrolactone are reduced relatively slowly, requiring 12–24 hr for the uptake of two hydrides required for conversion to the corresponding alcohol. Phenyl acetate is reduced even more slowly. The aromatic derivatives, ethyl benzoate and phthalide, react even more sluggishly, exhibiting only 4–6% uptake of hydride after 24 hr. It is evident that resonance of the aromatic ring with the carbonyl group, either in benzophenone or ethyl benzoate, renders that group less susceptible to electrophilic attack by the borane species.

(19) H. C. Brown and W. J. Wallace, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, No. 9N; W. J. Wallace, *Dissertation Abstr.*, 22, 425 (1961).

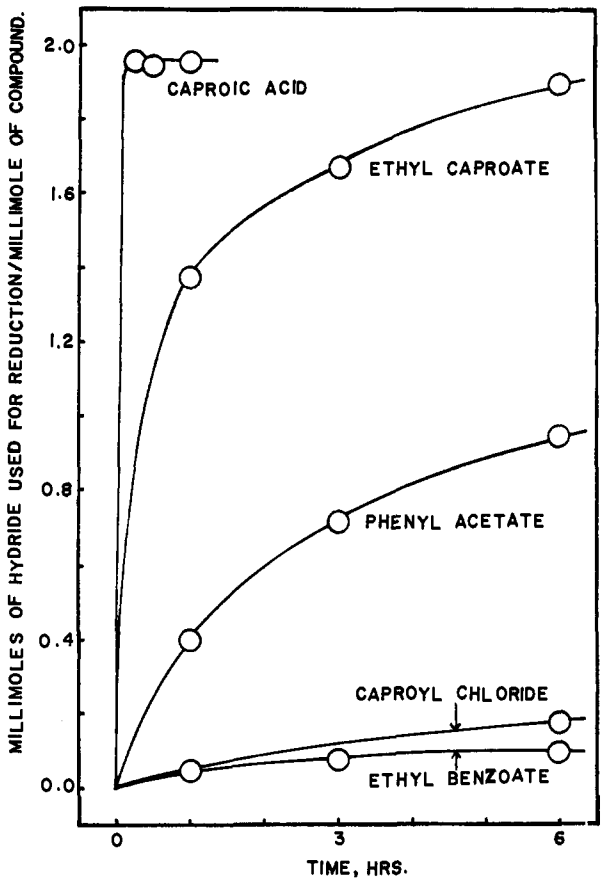


Figure 4. Rates of reduction of representative acids and their derivatives.

The unusually fast reaction of isopropenyl acetate could be explained by the fast hydroboration of the double bond,[2] which is followed by facile elimination,[20] and rapid reduction of resulting acyloxyborane and olefin.

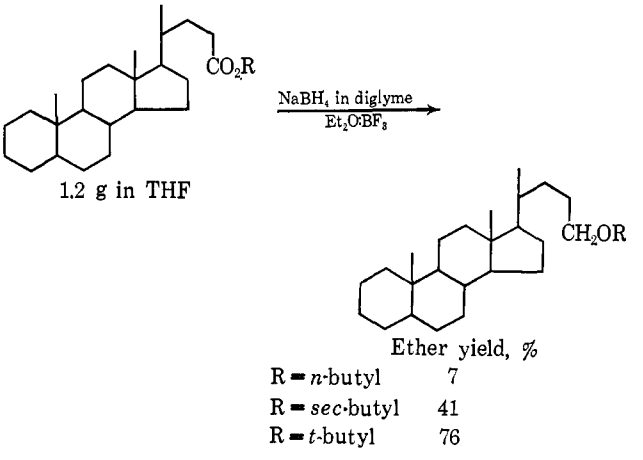
The results are summarized in Table V.

Here also no aldehyde formation could be detected during the reduction of esters to alcohols, showing that no stable intermediate is formed. The mechanism[21] should be similar to those of the acyl derivatives, already discussed (here, RC(=O)X in eq 5 is RC(=O)OR′).

Table V. Reaction of Diborane with Representative Esters and Lactones in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Ethyl caproate	1.0	0	1.38	1.38
	3.0	0	1.68	1.68
	6.0	0	1.90	1.90
	12.0	0	1.98	1.98
	24.0	0	2.00	2.00
Ethyl benzoate	1.0	0	0.05	0.05
	3.0	0	0.08	0.08
	6.0	0	0.10	0.10
	12.0	0	0.15	0.15
	24.0	0	0.18	0.18
Phenyl acetate	1.0	0	0.40	0.40
	3.0	0	0.72	0.72
	6.0	0	0.95	0.95
	12.0	0	1.28	1.28
	24.0	0	1.67	1.67
γ-Butyrolactone	1.0	0	0.58	0.58
	3.0	0	1.62	1.62
	6.0	0	1.83	1.83
	12.0	0	1.93	1.93
	24.0	0	2.00	2.00
Phthalide	6.0	0	0.08	0.08
	12.0	0	0.11	0.11
	24.0	0	0.13	0.13
Isopropenyl acetate	1.0	0	3.16	3.16
	3.0	0	3.60	3.60
	12.0	0	3.80	3.80
	24.0	0	3.95	3.95

[a,b] See corresponding footnotes in Table I.



Ether yield, %

R = *n*-butyl	7
R = *sec*-butyl	41
R = *t*-butyl	76

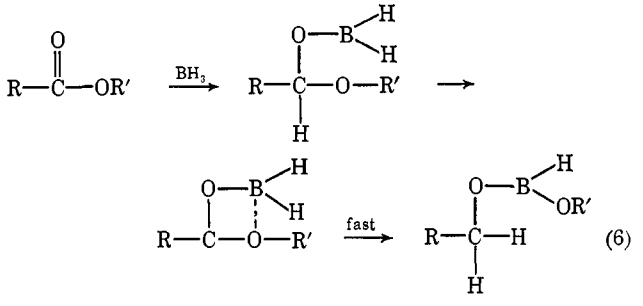
The vast range in the rates of reductions of several representative acids and their derivatives is indicated in Figure 4.

Epoxides. The rate of reduction of epoxides is quite slow. Thus the simplest epoxide, 1,2-butylene oxide, required 3 days to complete the uptake of one hydride. The reduction of cyclohexene oxide is equally slow. Even though the hydride uptake was nearly one, after 48 hr at 25°, corresponding to the hydride uptake for quantitative reduction, glpc analysis showed only 48% of butanols (96% 2-, 4% 1-) from 1,2-butylene oxide, and 44% of cyclohexanol from cyclohexene oxide. The reactions are also complex for styrene oxide and 1-methyl-1,2-cyclohexene oxide, although in a different manner. Thus, in the case of styrene oxide, the hydride

(20) We previously suggested a *cis*-elimination mechanism for a β-acetoxyorganoborane. See H. C. Brown and O. J. Cope *J. Amer. Chem. Soc.*, **86**, 1801 (1964), and ref 15.

(21) Attention is called to our previous study[4a] where attempts to isolate the monoalkoxyborane failed and, instead, polymer-like crystalline substances were obtained. It is probable that this polymerization occurs by coordination of the boron atom of one molecule to the oxygen atom of another.

The unstable intermediate under discussion has these two coordinating moieties in the same molecule (eq 6).



(6)

In this connection it is interesting to note that the three isomeric butyl esters of 5β-cholanic acid were reduced to the corresponding ethers with diborane in the presence of a large excess of boron trifluoride: G. R. Petit and D. M. Piatak, *J. Org. Chem.*, 27, 2127 (1962).

uptake went beyond the stoichiometric point (one hydride per mole of epoxide for conversion to alcohol), indicating instead 1.84 hydride uptake in 24 hr at 0° and 2.13 in 6 hr at 25°. The glpc analysis showed only 28% of 2-phenylethanol for the latter reaction.[22]

On the other hand, the reaction of 1-methyl-1,2-cyclohexene oxide was accompanied by hydrogen evolution, exhibiting 0.6 hydrogen evolution and 0.98 hydride utilized for reduction in 72 hr at 0°. At room temperature, 0.96 hydrogen evolution and 0.96 hydride utilized for reduction were realized in 24 hr. However, glpc analysis of the hydrolyzed reaction mixtures showed no appreciable amount of the expected alcohols, 1- and 2-methylcyclohexanols. Instead we obtained a 60–70% yield (isolated) of 1-methylol-2-cyclohexanols after oxidation. However, the presence of sodium borohydride changes the reaction path drastically, giving a quantitative yield of alcohols (26% 1-, and 74% *cis*-2-methylcyclohexanol[23]).

The presence of boron trifluoride also changes markedly the reaction of epoxides with diborane. For example, in the presence of catalytic quantities of boron trifluoride styrene oxide is reduced by diborane quantitatively to 2-phenylethanol.[24]

A detailed study of the reduction of epoxides by a wide range of hydride reducing agents has been completed by Dr. N. M. Yoon and will be reported shortly.

The present results on the uncatalyzed reaction of representative epoxides with diborane in tetrahydrofuran are summarized in Table VI.

Table VI. Reaction of Diborane with Representative Epoxides in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1,2-Butylene oxide	1.0	0.04	0.09	0.05
	3.0	0.04	0.15	0.11
	6.0	0.04	0.22	0.18
	12.0	0.04	0.37	0.33
	24.0	0.04	0.52	0.48
	48.0	0.04	0.78	0.74
	72.0	0.04	0.99	0.95
	48[c]	0.04	1.19	1.15[d]
Styrene oxide	1.0	0.04	0.35	0.31
	3.0	0.04	0.74	0.70
	6.0	0.04	0.99	0.95
	12.0	0.04	1.49	1.45
	24.0	0.04	1.89	1.85
	6.0[e]	0.06	2.19	2.13[e]
Cyclohexene oxide	1.0[c]	0.04	0.11	0.07
	3.0[c]	0.04	0.27	0.23
	12.0[c]	0.04	0.64	0.60
	24.0[c]	0.04	0.85	0.81
	48.0[c]	0.05	0.94	0.89[f]
1-Methyl-1,2-cyclohexene oxide	3.0	0.24	0.56	0.32
	6.0	0.34	0.72	0.38
	12.0	0.45	1.02	0.57
	24.0	0.56	1.32	0.76
	48.0	0.60	1.48	0.88
	72.0	0.60	1.58	0.98
	24.0[c]	0.96	1.92	0.96[g]

[a,b] See corresponding footnotes in Table I. [c] At 25°. [d] 48% yield of butanols (4% 1-, and 96% 2-). [e] 28% yield of 2-phenylethanol. [f] 44% yield of cyclohexanol. [g] ~0% yield of 1- and 2-methylcyclohexanols.

Amides and Nitriles. Primary amides are reduced very slowly, exhibiting about 50% reduction after 48 hr at 0°. The reactions evolve hydrogen rapidly, but such hydrogen evolution stops well before 2 mol are realized (1.1 mmol of hydrogen per mmol of compound was observed for caproamide and 1.4 mmol for benzamide under the standard conditions.)

However, the rates of reaction of disubstituted amide are considerably faster, exhibiting quantitative hydride uptake (two) in 24 hr, both for N,N-dimethylcaproamide and N,N-dimethylbenzamide.

Nitriles were also relatively slow under these conditions. However, by using a larger excess of diborane and higher temperatures (refluxing THF, 65°), it was possible to obtain excellent yields of amines both from amides[25-27] and from nitriles.[4b]

It is evident from the successes already realized[4a,25-27] that it should be possible to achieve these reductions in the presence of many types of the less reactive functional groups. Consequently, diborane promises to be highly useful for such selective reductions.

The results are summarized in Table VII.

The possibility of achieving a partial reduction of the two primary amides and the two nitriles by treating them with a controlled quantity of the reagent was briefly explored. However, in no case could the presence of aldehydes be detected following hydrolysis of the reaction mixtures. This indicates that the possible intermediates, such as imines, must react much more rapidly than the parent compound.

Diborane reacts relatively rapidly with primary amides to liberate hydrogen (Table VII). It is probable that the resulting borane–amide species are polymeric and account for the far slower rate of reduction of the primary amides as compared to the tertiary amides. Even in the case of the tertiary amides, the tertiary amines produced will react with diborane to produce tertiary amine–boranes of much lower activity.[28]

The reaction of diborane with nitriles produces the corresponding N,N,N-trialkylborazoles [29] (eq 7). Consequently, isolation of the amine requires hydrolysis of the intermediate borazole. Indeed, in all cases involving reduction of these nitrogen intermediates the relatively stable boron–nitrogen intermediates must be sub-

(22) It has been reported that in 12 days reaction at room temperature, 41% of 2-phenylethanol, 1% of 1-phenylethanol, and 24% of 2-*n*-butoxy-2-phenylethanol were obtained. See D. J. Pasto, C. C. Cumbo, and J. Hickman, *J. Amer. Chem. Soc.*, **88**, 2201 (1966).

(23) H. C. Brown and N. M. Yoon, *ibid.*, **90**, 2686 (1968).

(24) H. C. Brown and N. M. Yoon, *Chem. Commun.*, 1549 (1968).

(25) H. C. Brown and P. Heim, *J. Amer. Chem. Soc.*, **86**, 3566 (1964). A detailed study of such reductions has been completed and will shortly be reported.

(26) Diborane has been successfully utilized for the reduction of N-substituted fluoroacetamide derivatives to the corresponding fluoroethylamines in cases where lithium aluminum hydride and lithium aluminum hydride–aluminum chloride cause hydrogenolysis of the fluorine–carbon bond: Z. B. Papanastassiou and R. J. Bruni, *J. Org. Chem.*, **29**, 2870 (1964); see also E. R. Bissell and M. Finger, *ibid.*, **24**, 1256 (1959), and G. R. Pettit, S. K. Gupta, and P. A. Whitehouse, *J. Med. Chem.*, 10, 692 (1967).

(27) The successful application of diborane for the reduction of the tertiary amide group in the presence of (i) the carbamate moiety and (ii) the ester moiety has been achieved: (a) W. V. Curran and R. B. Angier, *J. Org. Chem.*, **31**, 3867 (1966); (b) M. J. Kornet, P. A. Thio, and S. I. Tan, *ibid.*, **33**, 3637 (1968). Finally, it has proven possile to reduce 1,2-diacylhydrazines to 1,2-dialkylhydrazines, so that the reduction of the tertiary amide grouping without rupture of the nitrogen–nitrogen hydrazine bond is demonstrated: H. Feuer and F. Brown, Jr., *ibid.*, in press.

(28) Alkylamine–borane reduces acyl halides, aldehydes, and ketones, but is inert to esters, carboxylic acids, and amides; see H. Nöth and H. Beyer, *Ber.*, **93**, 1078 (1960).

(29) H. J. Emeleus and K. Wade, *J. Chem. Soc.*, 2614 (1960).

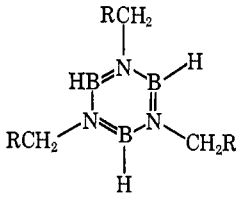
Table VII. Reaction of Diborane with Representative Amides and Nitriles in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproamide	1.0	0.80	1.38	0.58
	3.0	1.10	1.60	0.5
	6.0	1.10	1.66	0.56
	12.0	1.10	1.84	0.74
	24.0	1.10	2.00	0.90
	48.0	1.10	2.10	1.00
Benzamide	1.0	1.34	1.80	0.46
	3.0	1.38	2.14	0.76
	6.0	1.38	2.25	0.87
	24.0	1.38	2.44	1.06
	48.0	1.38	2.58	1.20
N,N-Dimethyl-caproamide	1.0	0	1.08	1.08
	3.0	0	1.50	1.50
	6.0	0	1.82	1.82
	12.0	0	2.00	2.00
	24.0	0	2.00	2.00
N,N-Dimethyl-benzamide	1.0	0	0.72	0.72
	3.0	0	1.15	1.15
	6.0	0	1.38	1.38
	12.0	0	1.72	1.72
	24.0	0	2.00	2.00
	48.0	0	2.00	2.00
Capronitrile	12.0	0	0.60	0.60
	24.0	0	0.90	0.90
	48.0	0	1.25	1.25
	72.0	0	1.53	1.53
	120.0	0	1.94	1.94
Benzonitrile	12.0	0	0.70	0.70
	24.0	0	1.03	1.03
	48.0	0	1.56	1.56
	72.0	0	1.90	1.90
	80.0	0	1.97	1.97

[a,b] See corresponding footnotes in Table I.

jected to acidic hydrolysis to recover the desired amines.[25]

$$3\ RCN + 3\ BH_3 \longrightarrow \text{(7)}$$



Nitro Compounds and Their Derivatives. 1-Nitropropane, nitrobenzene, and azoxybenzene fail to react with diborane in any reasonable time at standard conditions. Azobenzene is reduced at a moderate rate, utilizing two hydrides with hydrogen evolution. This stoichiometry indicates reduction to aniline. Aniline was identified in the reaction mixture after the usual hydrolysis. However, only 50% of the expected aniline could be isolated. Possibly, relatively stable boron–nitrogen intermediates are formed.

The inertness of diborane toward the nitro group is presumably related to the very weakly basic properties of that group. We pointed out previously that even the highly reactive aldehyde group becomes inert as highly electronegative substituents reduce the donor properties of the carbonyl oxygen, as in chloral.[4a] On the other hand, salts of nitroalkanes are readily reduced to hydroxylamines.[30] Presumably, the formation of the anion provides a point of attack for the electrophilic borane species.

(30) H. Feuer, R. S. Bartlett, B. F. Vincent, Jr., and R. S. Anderson, *J. Org. Chem.*, **30**, 2880 (1965).

Table VIII. Reaction of Diborane with Nitro Compounds and Their Derivatives in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Nitropropane	96.0	0	0	0
Nitrobenzene	20.0	0	0	0
Azobenzene	1.0	0	0.85	0.85
	3.0	0	1.43	1.43
	6.0	0	1.62	1.62
	12.0	0	1.78	1.78
	24.0	0	1.93	1.93
	48.0	0	2.00	2.00
Azoxybenzene	12.0	0	0	0
	24.0	0	0.05	0.05

[a,b] See corresponding footnotes in Table I.

The results are summarized in Table VIII.

Although we did not include any nitroso derivatives in our standard list, it has recently been established that aromatic nitroso compounds are readily reduced at 25° to the corresponding amines by diborane.[31] On the other hand, aliphatic *gem*-nitronitroso and *gem*-chloronitroso derivatives are converted to the corresponding N-alkylhydroxylamines.[31]

Other Nitrogen Compounds. Cyclohexanone oxime is reduced slowly and only a part of the expected hydrogen was liberated. When the order of addition was reversed (diborane added to the compound) the reaction involved the utilization of two hydrides, one for hydrogen evolution and one for reduction. N-Cyclohexylhydroxyamine is formed in good yield. Such reduction of oximes under mild conditions provides an excellent synthetic route to the corresponding N-substituted hydroxylamines.[32]

It is not clear whether in this reduction the acidic hydrogen reacts first, followed by addition of the boron–hydrogen moiety to the carbon–nitrogen double bond,[32] or whether the addition is the prior step.[33]

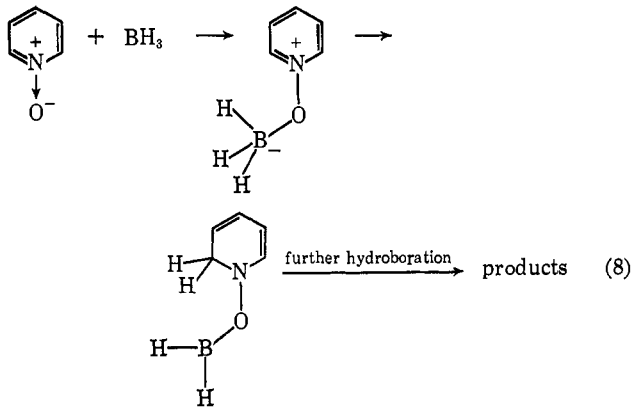
At higher temperatures (125°) oximes and hydroxylamines are reduced by diborane to the corresponding amines. On the other hand, oxime ethers and oxime esters are reduced readily, even at 25°, to give the corresponding amines.[34]

Phenyl isocyanate consumes two hydrides in moderate rate. However, the third hydride is consumed very slowly. Pyridine forms the borane addition compound, but shows no further utilization of hydride. On the other hand, pyridine N-oxide is reduced at a moderate rate, exhibiting an uptake of hydride of 2.03 in 3 hr and 2.76 in 48 hr. The ir spectra of the product revealed evidence for attack of the aromatic ring. We also observed immediate precipitation when the N-oxide was added to the diborane solution. These observations suggest the pathway shown in eq 8.

The results are summarized in Table IX.

Sulfur Compounds. Diborane did not react with disulfides, aromatic and aliphatic sulfide, sulfone, or cyclohexyl tosylate under our standard conditions. Sulfonic acids evolved only hydrogen and showed no indication of reduction. The only compound of all the

(31) H. Feuer and D. M. Braunstein, *ibid.*, **34**, 2024 (1969).
(32) H. Feuer, B. F. Vincent, Jr., and R. S. Bartlett, *ibid.*, **30**, 2877 (1965).
(33) S. L. Ioffe, V. A. Tartakovskii, A. A. Medvedeva, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1537 (1964).
(34) H. Feuer and D. M. Braunstein, *J. Org. Chem.*, **34**, 1817 (1969).



(8)

sulfur derivatives tested which reacted was dimethyl sulfoxide. The formation of dimethyl sulfide was verified by glpc analysis. The results are summarized in Table X.

Table IX. Reaction of Diborane with Other Nitrogen Compounds in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Cyclohexanone oxime	3.0	0.08	0.38	0.3
	6.0	0.16	0.50	0.34
	12.0	0.35	0.90	0.55
	24.0	0.53	1.32	0.79
	48.0	0.56	1.78	1.22
Phenyl isocyanate	1.0	0	1.72	1.72
	3.0	0	1.83	1.83
	6.0	0	1.87	1.87
	24.0	0	2.05	2.05
	c		2.9[c]	2.9[c]
Pyridine	48.0	0	0	0
Pyridine N-oxide[d]	1.0	0	1.48	1.48
	3.0	0	2.03	2.03
	12.0	0	2.62	2.62
	24.0	0	2.67	2.67
	48.0	0	2.76	2.76

[a,b] See corresponding footnotes in Table I. [c] After 14 days. [d] Precipitate was formed, so that each measurement was a separate run.

Table X. Reaction of Diborane with Representative Sulfur Derivatives in Tetrahydrofuran at 0°

Compd[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Di-*n*-butyl disulfide	24.0	0	0	0
Diphenyl disulfide	72.0	0	0	0
Phenyl *n*-propyl sulfide	40.0	0	0	0
Dimethyl sulfoxide	1.0		0.3	
	6.0	0.4	0.85	0.45
	12.0	0.57	1.15	0.58
	24.0	0.71	1.42	0.71
	48.0	0.83	1.60	0.77
Diphenyl sulfone	24.0	0	0	0
Methanesulfonic acid	0.5	1.0	1.0	0
	1.0	1.0	1.0	0
p-Toluenesulfonic acid monohydrate	0.5	2.82	2.82	0
	1.0	2.90	2.90	0
	3.0	2.97	2.97	0
	12.0	2.98	2.98	0
Cyclohexyl tosylate	40.0	0	0	0

[a,b] See corresponding footnotes in Table I.

Conclusions

The reducing properties of diborane are now thoroughly characterized. In the reduction of polyfunctional molecules, one can proceed with reasonable confidence that certain groups will not be attacked by diborane in the course of the other reducing groups.[35] We believe these systematic studies of the reducing characteristics of diborane, thexylborane,[36] and disiamylborane,[37] together with the related studies of the aluminohydrides,[5-8] will serve not only to help make a science out of selective reduction, but also to open up major possibilities for mechanism studies of interesting aspects of these reductions.

Experimental Section

Materials. The compounds used were from the same collection utilized in the earlier studies.[5-8] The standard solution of diborane was prepared following the procedures described previously,[38] and stored in the cold room. Analysis at regular intervals revealed no measurable change in the hydride concentration over several weeks at the cold room temperatures (−2−4°).

Stability of Diborane Solution in Tetrahydrofuran (THF). The stability of diborane solutions in THF was examined by following the change in hydride concentration with time. The results at 25, 50, and 65° (refluxing THF) are summarized in Table XI. (The losses in refluxing THF are probably largely the result of escape of of the gas from the solution due to decreased solubility.)

Table XI. Stability of Diborane in Tetrahydrofuran at Various Temperatures

	Time, hr						
Temp, °C	0	0.5	1.0	3.0	6.0	12.0	24.0	48.0
25	0.98[a]	0.98	0.98	0.98	0.98	0.96	0.95	
	(100)[b]	(100)	(100)	(100)	(100)	(98)	(97)	
50	1.03	1.03	1.01	0.99	0.99	0.94	0.86	
	(100)	(100)	(98)	(96)	(96)	(91)	(83.5)	
65[c]	0.97	0.59	0.47	0.37	0.31	0.32	0.34	
	(100)	(61)	(48.5)	(38)	(32)	(33)	(35)	

[a] Millimoles of "hydride" per milliliter of solution. [b] Figures in parentheses are percentage of concentration, compared with initial (0 hr) concentration. [c] The solution was refluxed.

Behavior of THF Solution of Diborane toward Air. A standard solution of diborane in THF (approximately 1.00 *M* in hydride) was prepared and subjected to the following tests at room temperature.

1. A 5-ml aliquot of the above solution was removed by syringe and discharged through air into an evaporating dish. The solution did not catch fire, indicating that the solution is not spontaneously inflammable.

2. A 5-ml aliquot of the above solution was placed in an evaporating dish and allowed to stand exposed to the open air. A slow gas evolution (presumably hydrogen) was observed, and evaporation of solvent was complete in about 1 hr, leaving a white residue (presumably boric acid) which exhibited no hydride activity on treatment with water.

3. A flask and a condenser (protected by a drying tube) were flushed with dry air. Fifty milliliters of a standard solution (1.0 *M* in hydride) was introduced into the flask and allowed to stand ex-

(35) It is necessary to caution the reader that we have explored only the reactivities of representative groups in common structures. It is evident that by modifications of structure it is often possible to vary the reactivity of any group over a wide range. Consequently, it is necessary to exercise judgment in applying the average reactivities that we have defined in the present study to new situations.

(36) H. C. Brown, P. Heim, and N. M. Yoon, manuscript in preparation.

(37) H. C. Brown, D. B. Bigley, S. K. Arora, and N. M. Yoon, manuscript in preparation.

(38) G. Zweifel and H. C. Brown, *Org. Reactions*, 13, 1 (1963).

Table XII. Loss of Hydride from Diborane Solution in THF in the Presence of Air at Room Temperature

	Time, hr						
	0	0.5	1.0	3.0	6.0	24.0	48.0
M in H^-	0.97	0.94	0.91	0.88[a]	0.86	0.71	0.46
% H^-	(100)	(97)	(94)	(91)	(89)	(73)	(48)

[a] The solution became slightly turbid.

posed to the dry air with constant stirring. Aliquots were removed and analyzed for residual hydride. The observed decrease in the hydride concentration is summarized in Table XII.

Procedure. All reductions were carried out under a dry nitrogen atmosphere, using hypodermic syringes to transfer solutions. In a 100-ml flask fitted with a side arm capped by a rubber septum (to permit introduction and removal of material with a hypodermic syringe) was placed 45 ml of a solution of diborane in THF (50 mg-ions of H^-). The flask was immersed into an ice bath. The reaction mixture was diluted with 5 ml of THF containing 12.5 mmol of the compound to be reduced. For the reaction of alcohols, mercaptans, amines, and acids, the reaction flask was attached to a gas meter. At different time intervals, 5-ml samples were withdrawn and quenched in glycerol–water (1:3) or in concentrated hydrochloric acid (for sulfur- and nitrogen-containing compounds). The hydrogen evolved was measured volumetrically. The reaction was continued until two or more analyses indicated a constant utilization of hydride. In the case of relatively slow reductions, the reactions were also run at 25° to establish that a definite stoichiometry could be achieved.

Reduction with Isolation of Product. In a number of cases, the reduction was carried out as described above for the established yield and stoichiometry. However, the reaction mixtures were then worked up to isolate and characterize the reduction products. Several representative examples are described to illustrate the procedures.

Reduction of *p*-Benzoquinone to Hydroquinone. To a 45-ml solution of BH_3 in THF (50 mg-ions of H^-), 1.351 g of *p*-benzoquinone (12.5 mmol) was added as a solid. After 48 hr, an uptake of 2 mg-ions of hydride per mmol of compound could be detected by hydrolyzing the milky and viscous reaction mixture with water.

The hydrolyzed material was evaporated to dryness under reduced pressure. Then 10 ml of dry methanol was added and the solution was evaporated to dryness again. This procedure was repeated for several times to remove the boric acid as methyl borate. Following this treatment, 1.36 g of a slightly colored crystalline residue was recovered. Flame analysis showed only traces of boron. (The expected amount of hydroquinone for 100% yield was 1.37 g.) The crude product was recrystallized from water and 1.12 g, a yield of 82%, of *p*-hydroquinone, mp 170–171°, was obtained.

Reduction of Azobenzene to Aniline. To a 45-ml solution of BH_3 in THF, containing 50 mg-ions of hydride, 2.28 g of azobenzene (12.5 mmoles) in 5 ml of THF was added. The reaction mixture was allowed to stand for 48 hr at 0°. Then 40 ml of the solution was hydrolyzed with 10 ml of concentrated HCl (17.2 mmol of hydrogen evolved). After removing the THF under reduced pressure, 3 N sodium hydroxide solution was added. The strongly basic solution was extracted with ether (3 times) and the extract dried over anhydrous magnesium sulfate. After filtration, dry hydrogen chloride was passed through for about 20 min. A white precipitate formed. After filtration, the residue, 2.21 g, was treated with alcohol and filtered again. A white crystalline residue was obtained which did not melt up to 280°. The filtrate was evaporated to dryness and yielded 1.34 g (10.3 mmol) of aniline hydrochloride, mp 180–185° (after sublimation, mp 197°); yield, 51%.

Azobenzene was treated with diborane as described above in a ratio 1 H^- to 1 azobenzene. About 50% of the pure starting material was recovered, and 25% of the aniline hydrochloride was obtained.

Reduction of Dimethyl Sulfoxide to Dimethyl Sulfide. To a 45-ml solution of BH_3 in THF, containing 50 mmol of hydride, 0.9765 g of dimethyl sulfoxide (12.5 mmol) in 5 ml of THF was added at 0°. The solution was allowed to stand at 0° for 48 hr (80% reduction).

A 5-ml sample of the reaction mixture was hydrolyzed in 3 ml of water for several hr.

Potassium carbonate, 5 g, was then added (saturation). The upper layer was checked by glpc analysis (tricresyl phosphate column, 5% on chromasorb W). The product was compared with a standard solution (2.5 mmol of dimethyl sulfide in 10 ml of THF). A 78% yield of the expected dimethyl sulfide was found (after 80% reaction by stoichiometry), corresponding to an overall yield of 97%.

Reduction of Various Representative Functional Derivatives with the Stoichiometric Amount of Hydride to Get Aldehyde. The reduction of phenyl acetate is described as representative. In a 100-ml flask were injected 3.3 ml of 2 M borane (20 mg-ions of H^-) solution and 11.8 ml of THF. The temperature was kept at 0°, and 5 ml of THF, containing 20 mmol of phenyl acetate (2.723 g), was added under stirring to the diborane–THF solution.

The reaction mixture was checked for aldehyde by treating 2.5-ml samples with 2,4-dinitrophenylhydrazine. The reaction was continued until no more hydrogen was evolved by hydrolysis, indicating that all of the available hydride had been utilized for reduction.

Anodic Oxidation Pathways of Aromatic Amines. IV. Diphenylamine Systems in Aqueous Acid Solution[1]

Donald W. Leedy and Ralph N. Adams

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044. *Received July 10, 1969*

Abstract: The overall anodic oxidation pathways of diphenylamine systems in aqueous solutions have been examined. The nature and extent of the chemical reactions which follow the electron transfers are summarized. Products of these reactions are unequivocally established by various chemical and spectrophotometric methods and some rate data are presented.

Previous studies of the anodic oxidation of tertiary amines have emphasized the role of coupled chemical reactions following the initial electron transfer. The present results, in brief, summary form, illustrate that such follow-up reactions also dominate the overall electrooxidation of diphenylamine systems.

Earlier studies of diphenylamines have been concerned with effects of structure on $E_{1/2}$, ease of oxidation, and antioxidant behavior.[2,3] Brief reports of the

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