Hydroboration. XXV. The Hydroboration of 3-Butenyl Derivatives Containing Representative Substituents

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Abstract: The study of the hydroboration of 3-butenyl derivatives, $CH_2=CHCH_2CH_2X$, where X represents Me, OMe, OPh, OH, OAc, Cl, NH_2, SMe, as well as some related carboxylic esters, $CH_2=CHCH_2CO_2R$, was undertaken in order to ascertain the problems that might be introduced by the presence of such groups. No major difficulties were encountered. In contrast to the corresponding allylic and crotonic derivatives, which lead to the formation of thermally unstable organoboranes that eliminate rapidly, the 3-butenyl derivatives yield stable organoboranes which can be readily oxidized to alcohols or subjected to other reactions. The yields of alcohols in the hydroboration–oxidation procedure are quite satisfactory, in the range of 75 to 100%. The 6 to 7% of 2 derivatives, formed in the usual hydroboration of 1-alkenes, is increased somewhat by the presence of the electronegative substituents, rising to a maximum of 18%. The formation of this minor product can be greatly reduced, to 1–2%, by the use of disiamylborane for the hydroboration stage. Consequently, hydroboration of such olefins containing functional substituents provides a simple route to organoboranes containing such functional substituents, making readily available for the first time organometallics with functional substituents for use in organic synthesis.

The remarkably facile reactions of olefins, acetylenes, and dienes with a variety of hydroborating agents, such as diborane, disiamylborane, thexylborane, dicyclohexylborane, and diisopinocampheylborane, have opened up a new, highly convenient route to a large variety of organoboranes.[2–4] The ability of the organoboranes to undergo versatile chemical transformations is giving them increasing possibilities in organic syntheses. Thus, under the influence of heat they readily isomerize to place the boron atom at the terminal position.[5a] Treatment with another olefin causes a transfer of the boron atom, liberating an olefin.[5b] This permits the contrathermodynamic isomerization of olefins.[5a,b] Further, at relatively elevated temperatures they cyclize,[5c] or react further to form polycyclic derivatives.[5d] Protonolysis with carboxylic acids affords the corresponding alkanes.[5e] Oxidation with alkaline hydrogen peroxide gives the alcohol,[3] and oxidation with chromic acid provides the ketone.[5f] Reaction with chloramine or O-hydroxylaminesulfonic acid gives the amine.[5g] Treatment with base and appropriate metal oxides yields other organometallics.[5h] Alkaline silver nitrate causes coupling of the alkyl and and alicyclic groups.[5i] Reaction with various ylides achieves homologation.[5j] Finally, carbonylation[5k] can be directed to provide excellent syntheses of tertiary alcohols,[5l] secondary alcohols,[5m] ketones,[5m] methylol derivatives,[5n] carboxylic acids,[5o] ring ketones,[5p] and polycyclics.[5q]

Perhaps one of the more intriguing features about this development is the observation that many unsaturated molecules containing functional substituents are readily hydroborated and converted into the corresponding organoboranes.[2,6] This makes organoboranes with functional substituents readily available, and presumably many other organometallics.[5h] For the first time the organic chemist faces the possibility of designing his synthesis on organometallics involving building blocks containing a wide variety of functional groups.

Although many individual compounds containing functional groups have now been hydroborated,[2,6] no systematic study has yet appeared. Accordingly, it appeared desirable to undertake such a study. In the present paper we report our results on the hydroboration of 3-butenyl derivatives, where the position of the double bond might be expected to cause difficulty because of the possibility for reaction *via* a cyclic intermediate. In the following paper we report our results on the hydroboration of 2-butenyl (crotyl) and related derivatives, where major directional effects introduce special characteristics into the hydroboration reaction.[7]

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Finally, in the third paper, we explore the hydroboration of 1-butenyl and related vinylic derivatives.[8]

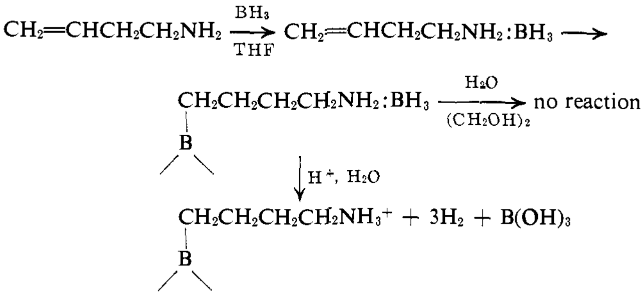
Results and Discussion

Stoichiometry Studies with Diborane. The following compounds were selected for study: 4-methoxy-1-butene, 4-phenoxy-1-butene, 4-hydroxy-1-butene, 4-acetoxy-1-butene, 4-chloro-1-butene, 4-amino-1-butene, 4-thiomethoxy-1-butene, and the methyl, ethyl, and *t*-butyl esters of 3-butenoic acid. Diborane in tetrahydrofuran was utilized for the hydroboration.

In the related study of the allylic derivatives,[6a,b] we found it highly informative to examine the stoichiometry of the reaction of diborane with the derivative. Thus a simple hydroboration takes up 1.00 "hydride"/mol of olefin. However, any side reaction, such as reduction of a funtional group, or elimination–rehydroboration,[6a,b] shows up in the form of an increased utilization of hydride. Accordingly, we treated each of the above compounds with a known excess of diborane in tetrahydrofuran at 0°. The reaction mixture was maintained at 0° and the course of the reaction followed by hydrolysis of an aliquot at appropriate intervals of time. From the amount of hydrogen evolved in the analysis, it was possible to determine the amount of "hydride" which had been utilized for hydroboration and reduction.

The hydroboration of the methyl and phenyl ethers, the thioether, and the chloride proceeded normally, with a consumption of 1 equiv of hydride/mol of compound. In the case of 3-buten-1-ol, there was an initial vigorous reaction with the liberation of 1 mol of hydrogen/mol of alcohol, and the product (probably the dialkoxyborane ($(RO)_2BH$[9])) then underwent normal hydroboration utilizing a second equivalent of hydride. With the hydroxyl group protected as the acetate, there was no evolution of hydrogen, but the hydride consumption exceeded 1 equiv/mol of compound (1.45 in 1 hr, 1.9 in 4 hr, 2.6 in 8 hr, and 2.94 equiv in 24 hr). A total of 3 equiv of hydride/mol of compound would be required for hydroboration of the double bond and reduction of the acetoxy group to the alcohol stage. Fortunately, this side reaction could be circumvented. The use of the theoretical quantity of diborane leads to the preferential hydroboration of the double bond and little or no reduction of the acetoxy group occurs.

The reaction of excess diborane with 4-amino-1-butene indicated a hydride consumption of 4.0 equiv of hydride/mol of compound when the hydrolysis was performed with the usual aqueous ethylene glycol. However, addition of acid to the hydrolysis mixture liberated additional hydrogen, corresponding to the presence of 3.0 hydrides, revealing a true uptake of only 1.00 equiv/mol of unsaturated amine. It therefore appears that the amine must form an amine borane, probably prior to the hydroboration of the double bond. This amine borane is stable to the usual hydrolysis mixture,[10] but is hydrolyzed by acid (I).



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The reaction of diborane with a number of unsaturated methyl esters was previously studied in detail.[6a] It was found that a slow addition of the theoretical quantity of diborane in tetrahydrofuran to a concentrated solution of the unsaturated ester at ice-bath temperatures effected selective hydroboration of the double bond without significant reduction of the ester group. These results were confirmed with the ethyl and *t*-butyl ester, so that this procedure will evidently work satisfactorily for various alkyl esters. The results of these stoichiometry studies are reported in Table I.

Table I. Stoichiometry and Oxidation Results for the Reaction of Diborane in Tetrahydrofuran with Various 3-Butenyl Derivatives

Compound	Hydride[a] 24 hr, 0°	Alcohol[b,c] yield, %	Addn to the 3 posn, %
1-Pentene	1.00	96	7
4-Methoxy-1-butene	1.01	100	11
4-Phenoxy-1-butene	1.04	86[d]	13
4-Hydroxy-1-butene	2.06[e]	75	14
4-Acetoxy-1-butene	2.94[f]	81	16
4-Chloro-1-butene	1.00	89	18
4-Amino-1-butene	1.03	74	16
4-Thiomethoxy-1-butene	0.95	88	13
Methyl 3-butenoate	2.85[f]	73	17
Ethyl 3-butenoate	2.2[f,g]	78	17
t-Butyl 3-butenoate		79	16

[a] Equivalents of hydride utilized per mole of compound. [b] After oxidation with alkaline hydrogen peroxide. [c] Yield by glpc analysis except where otherwise indicated. [d] Yield by isolation. [e] Includes 1 equiv of hydride utilized to form hydrogen during hydroboration. [f] Includes hydride utilized to reduce ester group. [g] 5 hr.

Directive Effects. The hydroboration of simple 1-alkenes with diborane proceeds to place 93–94% of the boron on the terminal position, with a minor amount of the boron, 6–7%, appearing at the 2 position.[2] In the hydroboration of allyl derivatives the relative amount of the boron going to the 2 position greatly increases, rising to as high as 40% for allyl chloride and 45% for allyl tosylate.[6a] This shift in the distribution is evidently a result of the inductive influence of the electronegative substituents.

While the effect should evidently be smaller in the corresponding 3-butenyl derivatives, it was desirable to know more precisely the amount of the minor product to be anticipated for different substituents. Accordingly, each of the compounds was hydroborated and oxidized with alkaline hydrogen peroxide, and the alcohols formed were analyzed for total yield and for the relative amounts of primary and secondary alcohols. The results are summarized in Table I.

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(7) H. C. Brown and R. W. Gallivan, Jr., *J. Am. Chem. Soc.*, **90**, 2906 (1968).

(8) H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

(9) Unpublished research with D. B. Bigley.

(10) A control experiment with *n*-butylamine confirmed that it deactivated toward the usual hydrolytic medium 3.0 hydrides/mol of amine.

In general, the yields must be considered quite good, in the range of 73 to 100%. The lower yields (Table I) are primarily observed where the product is a diol or an amino alcohol, or a hydroxy ester, with consequent difficulties in achieving a quantitative transfer from the aqueous system to the dry solvent required for glpc analysis.

In the case of the allylic derivatives, the yields occasionally dropped off greatly, due to hydroboration in the 2 position and the great tendency exhibited by these derivatives to undergo elimination.[6a,b] Such difficulties were absent with the 3-butenyl compounds. As far as we could ascertain, the organic derivatives are quite stable and exhibit no tendency under these conditions to undergo secondary reactions.[11]

The formation of the secondary derivatives lies in the range of 11 to 18% (Table I). As anticipated, the formation of this minor isomer is less than that observed in the corresponding allylic derivatives,[6a,b] but considerably larger than the 6 to 7% observed with the 1-alkene. Consequently, the directive effect of the substituent is significant in the four-carbon system.

Hydroboration with Disiamylborane. The formation of minor products in the range of 11 to 18% can introduce difficulties in the isolation of the major component in a pure state. Accordingly, we decided to examine the effect of hydroboration with disiamylborane[4] to see whether this would provide a satisfactory solution for derivatives of this kind. The results are summarized in Table II.

Table II. Hydroboration–Oxidation of Various 3-Butenyl Derivatives with Disiamylborane in Tetrahydrofuran

Compound	Alcohol yield, %	Addn to the 3 posn, %
1-Pentene	95	1.3
4-Methoxy-1-butene	92	2.0
4-Phenoxy-1-butene	88	2.0
4-Hydroxy-1-butene	91	2.0
4-Acetoxy-1-butene	89	1.4
4-Chloro-1-butene	99	1.0
4-Amino-1-butene	83	2.4
4-Thiomethoxy-1-butene	94	1.7
Methyl 3-buteneoate	84	2.0
Ethyl 3-butenoate	90	2.2

It is apparent that the use of disiamylborane for the hydroboration greatly reduces the formation of the minor isomer.

Conclusions

It was pointed out earlier that these derivatives are in an ideal position to undergo secondary reactions through cyclization reactions involving the initially formed monoalkylborane. Indeed, the hydroboration of ethyl 3-butenoate under standard conditions resulted in major attack on the ester grouping, a feature that was absent in hydroborating a mixture of 1-hexene and ethyl butyrate.[12] Consequently, the fact that these derivatives can be successfully hydroborated, without significant interference by the functional groups, makes it highly probable that other isolated double bonds, equally remote or more remote in aliphatic chains or alicyclic rings, can be successfully hydroborated.

α,β-Unsaturated derivatives and vinyl derivatives represent other problems, and these are considered in the following papers.[7,8]

It should be pointed out that once the organoborane containing a functional group is formed, it is necessary to know whether the group will interfere in the subsequent transformations of the organoborane.[5] The present study, as well as earlier ones,[4,6a,b] make it clear that the alkaline hydrogen peroxide oxidation is highly specific for the carbon–boron bond, with no case thus far reported of interference with the oxidation by any functional group. We are currently exploring the amination, coupling, and carbonylation reactions, in order to ascertain whether there is any interference by functional groups in these reactions.

Experimental Section

Materials. Both tetrahydrofuran and diglyme were distilled over lithium aluminum hydride, the latter under vacuum.[13] Stock solutions of diborane[3,14] and disiamylborane[3] in tetrahydrofuran were prepared and stored at 0° in a cold room. 2-Methyl-2-butene (Phillips, 99%), for the preparation of the disiamylborane, was distilled from lithium aluminum hydride and stored under nitrogen.

3-Buten-1-ol was obtained from Columbia Organic Chemicals Co. and the 4-acetoxy-1-butene was obtained from the alcohol by treatment with acetyl chloride in the presence of pyridine. 4-Chloro-1-butene was prepared from the alcohol by treatment with thionyl chloride.[15] 4-Phenoxy-1-butene was obtained by refluxing the chloride with an alcoholic solution of sodium phenolate, and 4-thiomethoxy-1-butene by treatment of the halide with the sodium salt of methyl mercaptan. 4-Methoxy-1-butene was prepared by the action of methyl iodide on sodium butenoxide, following the general procedure described for *n*-butyl methyl ether.[16]

Attempts to reduce allyl cyanide to the amine by lithium aluminum hydride led to the formation of much polymeric material and only minor amounts of the amine.[17] Consequently, we prepared the amine from the alcohol *via* the benzenesulfonate ester, converted to the azide, and then reduced with lithium aluminum hydride.[18] 3-Buteneoic acid (Columbia Organic Chemicals Co.) was converted into the methyl, ethyl, and *t*-butyl esters by standard procedures.

The various compounds used were purified by appropriate methods and were indicated to be at least 99% pure by glpc. The infrared and pmr spectra confirmed their identity. The physical constants of the individual compounds are summarized in Table III.

Analysis by Glpc. An F & M Model 300, temperature-programmed gas chromatograph, fitted with appropriate columns, was used for most of the analyses. In some cases a Perkin-Elmer 226 temperature-programmed capillary unit was used to check on the homogeneity of the starting materials and products.

The methoxybutanols were analyzed on a 4-ft column of Carbowax 20M, 20% on Firebrick, and the phenoxybutanols were analyzed on a 4-ft column of Carbowax 20M, 5% on Chromosorb W. Carbowax-alkaline, 20% on acid-washed Chromosorb W 60–80

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[11] Indeed, the organoborane from 3-butenyl chloride has been distilled in a vain attempt to achieve cyclization: P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).

[12] See Figure 1 of ref 6a, p 1796.

[13] It has been reported that explosions have occurred in this purification of diglyme. See M. F. Hawthorne, *J. Am. Chem. Soc.*, **87**, 4585 (1965). In the past 10 years our associates must have distilled hundreds of liters of diglyme without experiencing any difficulty of this kind. Possibly the difference arises from the fact that we utilize only a slight excess of lithium aluminum hydride over that required to react with the active hydrogen impurities and avoid carrying the distillation close to the point of dryness.

[14] We also have used for some of the preparative studies the 1 *M* solution of borane in tetrahydrofuran currently available from Ventron, Inc., Metal Hydrides Division.

[15] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

[16] A. Vogel, *J. Chem. Soc.*, 616 (1948).

[17] We have since discovered that allyl cyanide is smoothly reduced to 4-amino-1-butene by aluminum hydride in tetrahydrofuran (research in progress with N. M. Yoon).

[18] E. Renk and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 878 (1961).

Table III. Summary of Physical Data for the 3-Butenyl Derivatives

Compound	Bp, °C (mm)	n^{20}D
4-Methoxy-1-butene	68–69 (750)	1.3976
4-Phenoxy-1-butene	92 (12)	1.5128
4-Hydroxy-1-butene[a]	112 (750)	1.4420
4-Acetoxy-1-butene	124 (750)	
4-Chloro-1-butene	75 (741)	1.4232
4-Amino-1-butene	77–78 (750)	1.4254
4-Thiomethoxy-1-butene	121–122 (724)	1.4704
3-Butenoic acid[a]	71 (12)	1.4248
Methyl 3-butenoate	106 (745)	
Ethyl 3-butenoate	119 (745)	1.4102
t-Butyl 3-buteneoate	88 (150)	

[a] Columbia Organic Chemicals Co.

(obtained from Lachat Chemicals Inc., Chicago, Ill.), was found to be excellent for the aminobutanols. The other products were conveniently analyzed on a 4-ft column of silicone oil 703–4% sorbitol, 1% on HMDS Chromosorb 60–80. For the preparative runs, the same column materials were employed, with appropriate changes in column size and conditions. The capillary columns used with the 226 instrument were 150 ft in length, coated with Carbowax 20M or 4 Con LBX 550 (R column).

The identification of the products was carried out by comparison of the retention times with authentic samples, or by actual isolation of the peak by preparative gas chromatography, followed by characterization by infrared and pmr spectroscopy.

General Procedure. The hydroboration reactions were carried out in an atmosphere of nitrogen and in glassware that had been flame dried prior to use. The hydroboration flask was usually a 100- or 200-ml, round-bottomed flask provided with a thermometer well, a pressure-equalized addition funnel, a serum-capped outlet tube for introducing and withdrawing samples by means of a hypodermic syringe, and a water-cooled reflux condenser. Magnetic stirring was invariably employed, and the reaction flask was cooled externally with crushed ice when necessary.

The active hydride analysis of the diborane and disiamylborane stock solutions, as well as the analyses for the residual hydride in the stoichiometry studies, was determined by removing aliquots with a calibrated syringe and injecting the aliquots into ethylene glycol–water mixtures. The hydrogen evolved was collected and measured in a gas buret.

Stoichiometry Studies. The following procedure is representative of the stoichiometry studies involving diborane. 4-Thiomethoxy-1-butene, 2.04 g, 20 mmol, in 10 ml of tetrahydrofuran solution, was added at 0° over 5 min to 30 ml of a solution of diborane in tetrahydrofuran containing 20 mmol of BH_3, 60 mequiv of H^-. The reaction mixture was maintained at 0° for2 4 hr. Zero time was taken at 5 min after the addition of the unsaturated compound. At appropriate intervals of time, 4-ml aliquots were removed with a hypodermic syringe and hydrolyzed by adding to a 40% aqueous solution of ethylene glycol. The hydrogen evolved was measured in a gas buret over water and the amount of unreacted hydride present was calculated.

The same procedure was followed for all the various compounds examined and the results are reported in Table I. In the case of 4-amino-1-butene, the amount of borane used was twice the usual amount (6 H^- per molecule of amine). As mentioned earlier, in this case it was necessary to acidify the hydrolyzing medium (5 ml of 3 *M* hydrochloric acid was added). The hydrogen evolved during the addition of 3-buten-1-ol to the diborane solution was measured with a wet test meter, and the amount of diborane was increased (4 H^- per molecule of alcohol) to provide the usual excess following this initial reaction.

In the corresponding studies with disiamylborane, the same general procedure was employed, using 60 mmol of disiamylborane for 20 mmol of the unsaturated derivative.

Hydroboration of 4-Methoxy-1-butene with Diborane. To 10 ml of a solution of 4-methoxy-1-butene (1.72 g, 20 mmol) in tetrahydrofuran was added a solution of borane in tetrahydrofuran (7.5 mmol of BH_3 in 4.8 ml) at 0° over 10 min. The mixture was stirred for 2 hr at 0°. The residual hydride was destroyed by the addition of a few drops of water. The hydrogen evolved, 2.0 mmol, indicated that 1 mol of the compound had consumed 1.02 equiv of hydride. The organoborane was oxidized by the addition of 5 ml of 2 *N* sodium hydroxide, followed by 2.5 ml of 30% hydrogen peroxide (24 mmol) at 20°, stirring for 1 hr at room temperature. 3-Methoxy-1-propanol, 1.95 g, 21.8 mmol, was added to serve as an internal standard. Potassium carbonate was added to saturate the aqueous phase. The organic phase was separated, dried over anhydrous potassium carbonate, and analyzed by glpc. An 89% yield of 4-methoxy-1-butanol, 17.8 mmol, and 11% of 4-methoxy-2-butanol, 2.2 mmol, was indicated.

Hydroboration of 4-Methoxy-1-butene with Disiamylborane. A solution of disiamylborane in tetrahydrofuran, 12 mmol in 8.8 ml, was added over 10 min to 5 ml of an ice-cold solution of 4-methoxy-1-butene, 0.888 g, 10.2 mmol, in tetrahydrofuran. The reaction mixture was stirred for 1 hr at 0° and for 2 hr at 20°. Decomposition of the residual hydride with water indicated a hydride uptake of 10.4 mmol. Oxidation with 6 ml of 5 *N* sodium hydroxide and 3.5 ml of 30% hydrogen peroxide (35 mmol), followed by analysis as described above, showed 90.4% yield of 4-methoxy-1-butanol, (9.14 mmol) and 1.8% of 4-methoxy-2-butanol (0.182 mmol).

Hydroboration of 4-Phenoxy-1-butene. The diborane experiment yielded an 86% yield of phenoxybutanols, bp 104–106° (0.5 mm). Analysis by glpc indicated 13.2% of the secondary alcohol appearing as a peak prior to the large primary peak.

The disiamylborane experiment indicated an 87.8% yield of 4-phenoxy-1-butanol and 1.6% of the isomer. The primary alcohol was isolated by preparative glpc: n^{19}D 1.5210 (lit.[19] n^{27}D 1.520).

Hydroboration of 3-Buten-1-ol. The diborane experiment indicated 64.0% 1,4-butanediol and 10.5% 1,3-butanediol. A standard solution of the diol was utilized as an external standard.

Disiamylborane provided 89.4% 1,4-butanediol and 1.9% 1,3-butanediol. The product, isolated by preparative glpc, exhibited n^{20}D 1.4465 (lit.[20] n^{20}D 1.4467).

Hydroboration of 4-Amino-1-butene. Diborane provided 71.0% 4-amino-1-butanol and 13.3% 4-amino-2-butanol. Disiamylborane gave 81.5% 4-amino-1-butanol and 2% 4-amino-2-butanol. The product was isolated by distillation in 74% yield,bp 60–62° (1 mm), and gave infrared, pmr, and elementary analysis in agreement with the assigned structure.

Hydroboration of 4-Thiomethoxy-1-butene. The unsaturated sulfide, 2.03 g, 19.9 mmol, was hydroborated with disiamylborane, 22 mmol, following the general procedure. Oxidation produced 92.7% 4-thiomethoxy-1-butanol and 1.7% 4-thiomethoxy-2-butanol. The major product, isolated by preparative glpc, exhibited n^{19}D 1.4870.

Anal. Calcd for $C_5H_{12}OS$: C, 50.0; H, 10.0; S, 26.7. Found: C, 50.26; H, 10.30; S, 26.47.

Hydroboration of 4-Chloro-1-butene and 3-Butenoic Acid Esters. The hydroboration of these derivatives has been described previously.[6a]

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(19) C. Marvel and A. Tanenbaum, *J. Am. Chem. Soc.*, **44**, 2648 (1922).

(20) W. Kirmer and G. Richter, *ibid.*, **51**, 2505 (1929).