

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

Hydroboration. XXI. The Reaction of Unsaturated Alkyl Chlorides and *p*-Toluenesulfonates with Diborane and Disiamylborane¹

BY HERBERT C. BROWN AND KESTUTIS A. KEBLYS²

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The hydroboration of 1-chloro-4-pentene, 1-chloro-3-butene, and 4-pentenyl tosylate with diborane in tetrahydrofuran proceeds normally with the uptake of 1 equivalent of borane per mole of unsaturated compound. The products do not undergo cyclization with alkali, but are readily oxidized by alkaline hydrogen peroxide to the corresponding α,ω -chlorohydrins and α,ω -hydroxyalkyl tosylates. The electronegative substituent exerts an appreciable directive effect, as shown by the formation of an 82:18 ratio of primary:secondary isomers from 1-chloro-3-butene, in contrast to the 94:6 ratio observed in simple 1-alkenes. Allyl chloride and allyl tosylate, under the same hydroboration conditions, react with 1.42 and 1.55 equivalents of borane, respectively. This is due to the strong directive effects of the substituents, which place 40% of the boron in the secondary position in the case of the chloride and 45% in the case of the tosylate. Rapid elimination to form propylene, followed by hydroboration, accounts for the excess reagent utilized. The use of disiamylborane circumvents these difficulties. Oxidation of the disiamylborane derivatives of 1-chloro-4-pentene, 1-chloro-3-butene, and 4-pentenyl tosylate produces the corresponding hydroxy derivatives essentially free of the secondary isomers. Similarly, allyl chloride and allyl tosylate take up only slightly more than 1 mole of reagent. Treatment of the reaction product with alkali produces cyclopropane in 80% yield. In spite of the rapid cyclization under alkaline conditions, oxidation under controlled addition of alkali proceeds satisfactorily to give trimethylene chlorohydrin.

In the past twenty papers, a systematic survey has been reported of convenient procedures for achieving hydroboration^{3a,b,e} and of some of the more interesting characteristics of the hydroboration of representative olefins,^{3f,g,i,n,o} dienes,^{3l} and acetylenes^{3k} with diborane and some of its derivatives,^{3n,s} such as thexylborane,^{3p} disiamylborane,^{3h,j,m} and diisopinacampheylborane.^{3r,s,t} These studies have opened up a new and convenient route to a variety of organoboranes which exhibit great promise as versatile intermediates in organic synthesis.⁴

In these initial studies the emphasis has been on the exploration of the hydroboration reaction with representative hydrocarbon olefins, dienes, and acetylenes. However, considerable information is now available on the reaction of diborane with various functional groups,^{3c,d} and it has been apparent for some time that the hydroboration reaction should be readily applicable to unsaturated derivatives containing many different types of functional groups. The simple synthesis and availability of a relatively reactive organometallic containing a wide variety of functional groups is a new development in chemistry, of considerable interest and promise, and should extend significantly the synthetic usefulness of the hydroboration reaction.

The present paper initiates a systematic survey of the applicability of the hydroboration reaction to un-

saturated derivatives containing representative functional groups.

It should be pointed out that over the past several years there have been numerous individual applications of the hydroboration reaction to structures containing functional substituents.⁵ However, with the exception of some relatively extensive explorations in the steroid series,⁶ these have largely consisted of individual applications, where the primary objective was usually the synthesis of a specific product⁷⁻⁹ rather than the definition of the full scope of the hydroboration reaction.

The hydroboration of olefin derivatives bearing functional groups which are not reduced by diborane and which are not situated on the double bond should proceed without difficulty. A simple hydroboration, analogous to those observed in representative alkenes, should be anticipated for compounds such as unsaturated chlorides and tosylates. No attempts to hydroborate unsaturated tosylates have been reported previously. However, a number of hydroborations of unsaturated alkyl halides has been described.¹⁰⁻¹³ In some cases, useful applications of these hydroboration reactions have been achieved. For example, the γ -chloropropylboranes, produced in the hydroboration of allyl chloride, undergo cyclization to cyclopropane under the influence of alkali,^{11,13} and undergo protonolysis to *n*-propyl chloride on treatment with propionic acid.¹⁴

The present paper reports the results of a study of the hydroboration of several representative unsatu-

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(2) Research assistant on an XR Grant provided by the Purdue Research Foundation.

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rated chlorides and tosylates by diborane and disiamylborane, and an examination of the behavior of the products toward alkali and alkaline hydrogen peroxide.

Results and Discussion

Hydroboration with Diborane.—In order to establish whether unsaturated alkyl chlorides and tosylates could be converted into the corresponding organoboranes in good yield, without concurrent reaction with the substituent, the compounds selected (1-chloro-4-pentene, 1-chloro-3-butene, allyl chloride, 4-pentenyl tosylate, and allyl tosylate) were treated with an excess of diborane in tetrahydrofuran solution at 0°. Aliquots were removed at various intervals and analyzed for residual hydride.¹⁵

The reactions with 1-chloro-4-pentene, 1-chloro-3-butene, and 4-pentenyl tosylate all proceeded smoothly, with the consumption of only 1 mole of hydride per mole of olefin present (Table I). Evidently, the chloride and tosylate substituents do not participate in the reaction. On the other hand, it was observed that allyl chloride took up 1.42 molar equivalents of hydride, and that allyl tosylate took up 1.55 molar equivalents. Evidently, in these cases the substituents are participating in the reaction.

These results of the stoichiometry of the reaction of diborane with these derivatives are summarized in Table I.

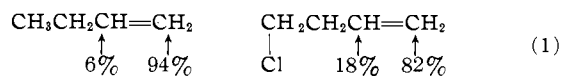
TABLE I

STOICHIOMETRY OF THE REACTIONS OF REPRESENTATIVE UNSATURATED ALKYL CHLORIDES AND TOSYLATES WITH DIBORANE AND DISIAMYLBORANE IN TETRAHYDROFURAN AT 0°

Compound	Time, hr.	Moles of hydride utilized per mole of compound	
		Diborane	Disiamylborane
1-Chloro-4-pentene	1.0	1.05	1.04
	2.0	1.03	0.95
	4.0	1.41	
1-Chloro-3-butene	7.0	1.42	1.06
	1.0		1.04
Allyl chloride	1.0	1.23	
	2.0	0.96	0.93
4-Pentenyl tosylate	0.5	0.96	0.93
	2.0	0.96	0.93
Allyl tosylate	0.5	1.52	1.07
	1.0	1.58	1.07
	6.0	1.55	1.10

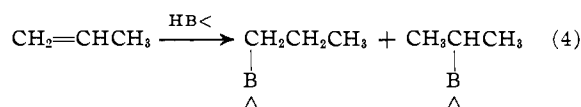
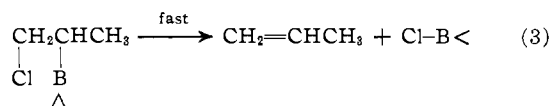
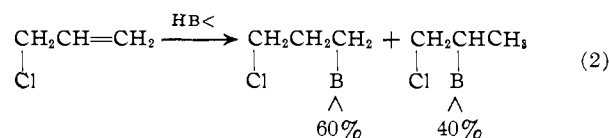
The organoborane from 4-pentenyl tosylate underwent the usual oxidation by alkaline hydrogen peroxide to give 5-hydroxypentyl tosylate in 92% yield. The product presumably contained a small quantity of the isomeric 4-hydroxy derivative, but the difficulty of working with this relatively unstable material of low volatility prevented a satisfactory analysis. Similarly, the organoborane from 1-chloro-3-butene was oxidized to a mixture of the corresponding isomeric chlorohydrins in 89% yield. The ratio of primary to secondary isomers, as determined by gas chromatographic analysis, was 82:18, in contrast to the 94:6 ratio observed in the 1-alkenes.^{3g} This indicates that the chlorine substituent exerts a significant directive influence on the addition of borane to the double bond (1).

(15) It is convenient to discuss the stoichiometry of hydroboration reaction in terms of the "hydride" utilized by the olefin. Thus, 1 mole of borane, BH₃, yields 3 moles of hydrogen on hydrolysis, corresponding to the presence of three "hydrides." Addition of 1 mole of olefin results in the uptake of 1 mole of "hydride." Hydrolysis then results in the evolution of only 2 moles of hydrogen, indicating the presence of only 2 moles of residual "hydride."



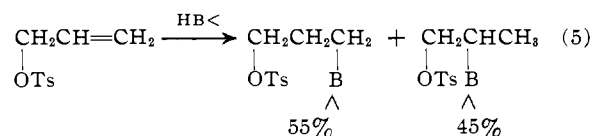
Treatment of the hydroboration product of allyl chloride with sodium hydroxide yielded cyclopropane in 51% yield. Oxidation of the residual alkaline reaction mixture yielded 38% 1-propanol and 2% 2-propanol.

Both the high uptake of hydride and the large yield of the by-products can be accounted for in terms of the reaction sequence suggested by Binger and Koester.¹³ The chlorine substituent exerts a powerful directive influence on the hydroboration of the neighboring double bond, causing 40% of the boron to become attached to the secondary position (2). A rapid elimination of the neighboring boron and chlorine atoms occurs, yielding propylene (3), which then undergoes hydroboration to give the usual 94:6 distribution of the primary and secondary boron derivatives (4).



Treatment of the hydroboration product of allyl tosylate with base yielded cyclopropane in a yield of only 43%. Oxidation of the alkaline reaction mixture yielded 43% 1-propanol and 2% 2-propanol.

Consequently, the reaction sequence in the case of allyl tosylate must parallel that for allyl chloride, with the one exception that the tosyl group apparently exerts a more powerful directive influence on the hydroboration stage, placing 45% of the boron at the secondary position (5).



These results are summarized in Table II.

TABLE II

PRODUCTS OBTAINED *via* ALKALINE HYDROLYSIS AND OXIDATION OF THE ORGANOBORANES PRODUCED IN THE REACTIONS OF DIBORANE AND DISIAMYLBORANE WITH ALLYL CHLORIDE AND ALLYL TOSYLATE IN TETRAHYDROFURAN AT 0°

Product	Yield, %			
	Diborane		Disiamylborane	
	Chloride	Tosylate	Chloride	Tosylate
Cyclopropane	51	43	82	78
Propylene	0	0	2	Trace
1-Propanol	38	43	1	5
2-Propanol	2	2	0	0

Hydroboration with Disiamylborane.—It was observed previously that the use of disiamylborane as a hydroborating agent greatly reduces the formation of the by-product secondary derivative in the hydroboration of terminal hydrocarbon olefins.^{3h} Accordingly,

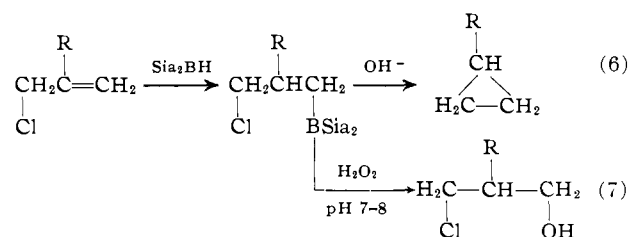
its applicability to the present problem was explored. Studies of the stoichiometry of the reaction of disiamylborane (in excess) with the five unsaturated chlorides and tosylates under investigation all indicated an essentially 1:1 reaction between the reagent and the olefinic derivative. Only in the case of allyl chloride and allyl tosylate was there indicated a slightly greater than molar uptake of reagent, 1.06 and 1.10, respectively (Table I).

Moreover, the use of disiamylborane reduced considerably the amount of secondary isomers formed from the higher derivatives. Oxidation of the resulting organoboranes gave the corresponding primary hydroxy compounds, virtually uncontaminated by the secondary isomers. Thus, the organoborane from 1-chloro-4-pentene and disiamylborane was oxidized to 5-chloro-1-pentanol. A yield of 98% was indicated by gas chromatographic analysis and an 88% yield of product was isolated. Examination of the isolated product indicated the complete absence of the secondary isomer. Similarly, the 1-chloro-3-butene-disiamylborane adduct was oxidized to 4-chloro-1-butanol in 98% yield. A quantitative yield of 5-hydroxypentyl tosylate was realized in the corresponding conversion of 4-pentenyl tosylate.

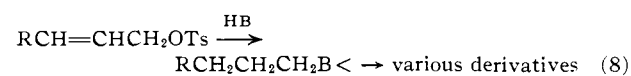
Several attempts to cyclize the disiamylborane derivatives of 1-chloro-3-butene, 1-chloro-4-pentene, and 4-pentenyl tosylate by treatment with alkali failed to yield detectable amounts of cyclobutane or cyclopentane.

The reaction products from disiamylborane and allyl chloride or allyl tosylate were converted readily into cyclopropane by treatment with alkali in yields of 78–82%. Moreover, oxidation of the residual reaction mixture indicated the presence of only minor amounts of by-product organoboranes (Table II).

Finally, we demonstrated that it was possible to circumvent this cyclization in the case of γ -chloropropylideneborane to achieve oxidation to trimethylenechlorohydrin in 77% yield. The reaction was accomplished by adding the alkali concurrently with the hydrogen peroxide to the organoborane reaction mixture at 5 to 10°, maintaining the pH of the reaction mixture at 7–8. Consequently, it appears possible to proceed at will from the allyl derivatives to the corresponding cyclopropanes (6) or the chlorohydrins (7).



Conclusions.—One implication of the present study is that it should be possible to utilize the strong directive effect of the tosyl group to achieve the following general transformation (8) in essentially quantitative yield.



This possibility is currently under investigation.¹⁶

(16) Research in progress with Dr. O. J. Cope and R. M. Gallivan.

Finally, it appears that the hydroboration of unsaturated chlorides and tosylates offer no unusual difficulties, except in cases where the strong inductive influence of the electronegative substituent may bring about an undesirable directive influence on the addition to a neighboring double bond. In such cases the use of disiamylborane frequently serves to circumvent the difficulty.

Experimental

Materials.—Tetrahydrofuran and diglyme were distilled from lithium aluminum hydride. Boron trifluoride ethyl etherate was treated with a small quantity of ethyl ether and distilled under reduced pressure from a few pieces of calcium hydride. Sodium borohydride from Metal Hydrides, Inc. (98%), was used without purification. Diborane and disiamylborane stock solutions in tetrahydrofuran were prepared following procedures described previously.^{11,m} 2-Methyl-2-butene was distilled from lithium aluminum hydride and stored under nitrogen. Hydrogen peroxide, Fisher reagent grade, 15 to 35% solutions, was analyzed periodically by density determination.¹⁷ Allyl chloride, from the Matheson, Coleman and Bell Co., was redistilled and stored under nitrogen at 5°. Other unsaturated chlorides were prepared from the corresponding alcohols and thionyl chloride by known methods.¹⁸

Allyl tosylate was prepared by treating allyl alcohol with tosyl chloride in presence of aqueous base, a method described by Drahowzal,¹⁹ and purified by distillation at 0.15 mm.

4-Pentenyl tosylate was prepared by treating 4-penten-1-ol with tosyl chloride dissolved in ether in presence of pyridine, following the procedure described by Drahowzal.²⁰ The material was purified by distillation at 0.1 mm.

Anal. Calcd. for C₁₂H₁₆O₂S: C, 59.98; H, 6.71; S, 13.35; Cl, 0.0. Found: C, 60.10; H, 6.89; S, 13.08; Cl, 0.37.

The physical constants of the starting materials are summarized in Table III.

TABLE III
SUMMARY OF DATA FOR COMPOUNDS USED

Compound ^a	Source	B.p., °C. (mm.)	n _D ²⁰	n _D ²⁰ (lit.)
Allyl alcohol	Fisher	...	1.4133	1.4135
3-Buten-1-ol	Columbia	...	1.4218	1.4224
4-Penten-1-ol	Columbia	...	1.4303	1.4309
Allyl chloride	Matheson	45 (755)	1.4150	1.4157
1-Chloro-3-butene	...	75 (741)	1.4232	1.4233
1-Chloro-4-pentene	...	104 (748)	1.4306	1.4297
Allyl tosylate	...	102 (0.15)	1.5214	1.5209
4-Pentenyl tosylate	...	114–116 (0.1)	1.5133	...

^a At least 99% pure by gas chromatography (except for tosylates).

Analysis by Gas Chromatography.—Aerograph Model A90-S instrument (Wilkins Instrument and Research Co.) was used for most gas chromatographic analyses. Tetra- and pentamethylene chlorohydrins were analyzed on a 5-ft. column, packed with 10% Carbowax 1540 on Fluoropak, operated at 100–110°. These chlorohydrins decomposed on columns packed with Chromosorb supports. Decomposition was also noted when column temperatures exceeded 110°. Cyclopropane and propylene were analyzed using a 22-ft. column packed with 12% silver nitrate and 33% benzyl cyanide on Chromosorb, operated at room temperature. Standard columns packed with Carbowax 1540 or Ucon Polar on Chromosorb-W were used for other analyses.

General Procedures.—All glassware used in hydroboration experiments was dried and purged with dry nitrogen before use. Most hydroboration reactions were carried out using two-neck, 100-ml., round-bottom flasks fitted with a thermometer well, a rubber-capped inlet tube, and a magnetic stirrer. All hydroboration reactions were carried out in tetrahydrofuran and in an atmosphere of nitrogen.

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Active hydride content of diborane and disiamylborane stock solutions was determined by injecting small samples into an ethylene glycol-diglyme mixture and measuring the hydrogen evolved. The same method was used to determine the amount of unreacted hydride in the stoichiometric studies.

Cyclopropane was isolated by passing a slow stream of nitrogen through refluxing reaction mixtures and condensing the gas in a series of Dry Ice-cooled traps. The quantity of cyclopropane formed was measured by a simplified vacuum line technique.

Stoichiometry of the Reactions with Diborane.—Allyl chloride (6.14 g., 80.2 mmoles) was added to 75.0 ml. (80.3 mmoles) of 1.07 *M* borane²¹ solution in 20 min. at 0° and stirred 7 hr. at 0°. Samples were withdrawn at various time intervals and injected into ethylene glycol-diglyme solution in order to determine the amount of unreacted hydride.

The same procedure was used to determine the stoichiometry of the reaction of diborane with allyl and 4-pentenyl tosylates. The results of these experiments are listed in Table I.

Stoichiometry of the Reactions with Disiamylborane.—Allyl chloride (1.686 g., 22.0 mmoles) was added in 3 min. at 0° to 35.0 ml. (44.4 mmoles) of 1.27 *M* disiamylborane solution. The reaction mixture was stirred at 0° for 1 hr. and then hydrolyzed with 3 ml. of water in order to determine the amount of unreacted hydride. The experiment was repeated, allowing the reaction to proceed for 3 and 7 hr. before hydrolysis.

The same procedure was used to determine the stoichiometry of the reaction between allyl tosylate and disiamylborane. The results of these experiments are listed in Table I.

Reaction of Allyl Chloride with Diborane.—Allyl chloride (3.75 g., 49.0 mmoles) was added to 50.0 ml. (49.5 mmoles) of 0.990 *M* borane solution at 0° and was stirred 1 hr. at 25°. After excess hydride was destroyed with water, 30 ml. of 3 *M* sodium hydroxide was added at 15–35°. The solution was then refluxed 3 hr. at 64–66° in order to remove the gaseous products, which were collected and measured by standard procedures. There was obtained 24.9 mmoles, a 51% yield, of cyclopropane, which was free of propylene.

The reaction mixture was cooled, then oxidized with 4.3 ml. (50 mmoles) of 35% hydrogen peroxide. After separation of layers, the aqueous phase was saturated with potassium carbonate and extracted with three 20-ml. portions of ether. The organic layer was combined with the ether extracts, dried over magnesium sulfate and Drierite, and then analyzed by gas chromatography. There was found 18.8 mmoles, a 38% yield, of 1-propanol, and 0.9 mmoles, a 2% yield, of 2-propanol.

Another experiment was carried out using 59.5 mmoles of allyl chloride and 22.0 mmoles of borane. After hydrolysis with aqueous sodium hydroxide, cyclopropane and propylene were obtained in 42 and 12% yields, respectively. After oxidation, 1-propanol was obtained in 26% yield. There was found 15% of unreacted allyl chloride.

Reaction of Allyl Chloride with Disiamylborane. (a) **Cyclization.**—Allyl chloride (2.10 g., 27.4 mmoles) was added to 33.0 ml. (39.9 mmoles) of 1.21 *M* solution of disiamylborane at 0° and stirred 1 hr. at 23–26°. Excess hydride was destroyed with 2 ml. of water. Then 18 ml. of 3 *M* sodium hydroxide was added at 0° in 30 min. The mixture was stirred 3 hr. at 0°. Periodic examination by gas chromatography showed that cyclization was complete in about 2 hr. Cyclopropane was isolated and measured by standard procedures. There was found 22.4 mmoles, an 82% yield, of cyclopropane, and 0.6 mmole, a 2.2% yield, of propylene. After oxidation and standard work-up, 0.26 mmole, a 1% yield, of 1-propanol was found.

In a duplicate experiment, an 83% yield of cyclopropane and a 2% yield of propylene was obtained.

When the alkaline hydrolysis was carried out at 25–67°, cyclopropane was obtained in 72% yield. After oxidation, 1,3-propanediol was obtained in 13% yield.

(b) **Oxidation.**—Allyl chloride (3.0 g., 39.2 mmoles) was added to 37.0 ml. (47.7 mmoles) of 1.29 *M* disiamylborane solution and was stirred for 1 hr. at 25°. The reaction mixture was then oxidized with 15.7 ml. (145 mmoles) of 33% hydrogen peroxide, added in 1 hr. at 5–10°. The mixture was kept at pH 7–8 by concurrent addition of 8.4 ml. of 3 *M* sodium hydroxide. The oxidized mixture was then treated with 5 g. of potassium carbonate, and the layers were separated. The aqueous layer was saturated with potassium carbonate and extracted with ether.

The organic layer and the extracts were combined, dried over magnesium sulfate and Drierite, and analyzed by gas chromatography. There was found 30.0 mmoles, a 77% yield, of trimethylenechlorohydrin. No 2-hydroxy isomer was detected.

Hydroboration of 1-Chloro-3-butene. (a) **Diborane.**—To 15.0 ml. (15.0 mmoles) of 1.0 *M* borane solution was added at 0° 2.75 g. (30.4 mmoles) of 1-chloro-3-butene. The solution was stirred 2 hr. at 0°, then hydrolyzed with 2 ml. of water. There was evolved 13.6 mmoles of hydrogen. Thus 1.03 moles of hydride had been consumed per mole of chlorobutene.

The solution was oxidized by adding concurrently at 15–25° 3.3 ml. (36.5 mmoles) of 34% hydrogen peroxide and 3.7 ml. of 3 *M* sodium hydroxide. The products were extracted with ether, as described before. Gas chromatographic analysis showed 22.2 mmoles, a 73% yield, of 4-chloro-1-butanol, and 4.9 mmoles, a 16% yield, of 4-chloro-2-butanol.

(b) **Disiamylborane.**—To 20.0 ml. (31.2 mmoles) of 1.56 *M* disiamylborane solution was added at 0° 1.98 g. (21.8 mmoles) of 1-chloro-3-butene. The solution was stirred 2 hr. at 0°, and then hydrolyzed with 2 ml. of water. There was evolved 10.5 mmoles of hydrogen. Thus 0.95 mole of disiamylborane had been consumed per mole of chlorobutene.

Then, 9.1 ml. (101 mmoles) of 34% hydrogen peroxide and 7.0 ml. of 3 *M* sodium hydroxide were added simultaneously at 20–30°. The oxidized mixture was worked up and analyzed as before. There was found 21.3 mmoles, a 98% yield, of 4-chloro-1-butanol. Only a small amount (about 1%) of the 2-hydroxy isomer was found.

Preparation of 5-Chloro-1-pentanol.—To 75.0 ml. (105 mmoles) of 1.40 *M* disiamylborane solution was added at 0° in 10 min. 10.42 g. (99.7 mmoles) of 1-chloro-4-pentene. The solution was stirred 3 hr. at 0°, then hydrolyzed with water, and oxidized by a simultaneous addition of 31 ml. (340 mmoles) of 33% hydrogen peroxide solution and 35 ml. of 3 *M* sodium hydroxide. After stirring 10 min. at 25°, the mixture was treated with 3 g. of potassium carbonate, and the layers were separated. The aqueous layer was saturated with potassium carbonate and extracted three times with 30 ml. of ether. The combined organic phase was dried over magnesium sulfate, filtered, and made up to 250 ml. A 15.0-ml. aliquot was removed, dried over Drierite, and analyzed by gas chromatography. There was found 5.87 mmoles, a 98% yield, of 5-chloro-1-pentanol.

The remaining 235 ml. of ether solution was evaporated *in vacuo* at room temperature. The residue was distilled rapidly at 1–0.3 mm. into a Dry Ice-cooled receiver. Redistillation of the flash distillate gave 10.0 g., an 88% yield, of 5-chloro-1-pentanol, collected at 65–66° at 1.5 mm., n_D^{20} 1.4540 (lit.²² b.p. 103° at 8 mm., n_D^{20} 1.4518).

Reaction of Allyl Tosylate with Diborane.—Allyl tosylate (8.78 g., 41.4 mmoles) was added to 40.0 ml. (40.4 mmoles) of 1.01 *M* borane solution at 0°. The solution was stirred 3 hr. at 0° and then hydrolyzed with water. Next, 28 ml. of 3 *M* sodium hydroxide was added in 35 min. and stirred for 1 hr. at 0°. Gaseous products were isolated and measured by standard procedures. There was obtained 17.7 mmoles, a 43% yield, of cyclopropane, demonstrated free of propylene. The reaction mixture was then oxidized with 42 mmoles of hydrogen peroxide, saturated with potassium carbonate, and extracted with ether. Analysis by gas chromatography showed 17.9 mmoles, a 43% yield, of 1-propanol and 0.8 mmole, a 2% yield, of 2-propanol.

Reaction of Allyl Tosylate with Disiamylborane. **Cyclization.**—Allyl tosylate (5.74 g., 27.0 mmoles) was added to 25.0 ml. (40.5 mmoles) of 1.62 *M* disiamylborane solution at 0°, stirred for 10 min. at 0° and for 1 hr. at 25°. Excess hydride was destroyed by adding 2 ml. of water. Then 18 ml. of 3 *M* sodium hydroxide was added at 0° over 27 min. The resulting mixture was stirred for 1 hr. at 0°. Gaseous products were isolated and measured by standard procedures. There was obtained 20.9 mmoles, a 78% yield, of cyclopropane, and approximately 0.02 mmole of propylene.

The reaction mixture was then oxidized with hydrogen peroxide, saturated with potassium carbonate, and extracted with ether. Analysis by gas chromatography showed 1.3 mmoles, a 5% yield, of 1-propanol and approximately 5–10% yield of 1,3-propanediol.

The experiment was repeated allowing the reaction to proceed 6 hr. at 0° before addition of alkali. There was obtained a 77%

(21) In tetrahydrofuran solutions diborane exists as the borane derivative: B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955).

(22) S. M. McElvain and T. P. Carney, *J. Am. Chem. Soc.*, **68**, 2596 (1946).

yield of cyclopropane, a 0.2% yield of propylene, and a 4% yield of 1-propanol.

Preparation of 5-Hydroxypentyl Tosylate.—To 8.6 ml. (8.5 mmoles) of 0.987 *M* borane solution was added at 0°, 4.82 g., (20.1 mmoles) of 4-pentenyl tosylate. The solution was stirred 1 hr. at 0°, and then oxidized by adding 2.4 ml. of 3 *M* sodium hydroxide and 2.2 ml. (24 mmoles) of 33% hydrogen peroxide at 10–25°. The oxidized mixture was diluted with 15 ml. of ether, and the layers were separated. The aqueous layer was extracted twice with 10 ml. of ether. The organic layer was combined with the extracts, washed with 1 *M* sodium hydroxide, water, and saturated sodium chloride, and then dried over magnesium sulfate at 0°. The solvent was evaporated *in vacuo*, and the residue was stripped at 0.1 mm. to constant weight (4 hr. at 25°). There was obtained 4.78 g., a 92% yield, of 5-hydroxypentyl tosylate, a viscous, opaque oil.

Anal. Calcd. for C₁₃H₁₈O₄S: C, 55.8; H, 7.02; S, 12.4. Found: C, 55.3; H, 7.09; S, 12.1.

In another experiment 18.7 g. (77.9 mmoles) of 4-pentenyl tosylate was added at 0° to 59.0 ml. (85.0 mmoles) of 1.44 *M* disiamylborane solution. After stirring for 3 hr. at 0°, 25 ml.

(275 mmoles) of 33% hydrogen peroxide and 23 ml. of 3 *M* sodium hydroxide were added simultaneously at 10–23°. The oxidized mixture was treated with 5 g. of potassium carbonate, and the layers were separated. The aqueous layer was saturated with potassium carbonate and extracted with ether. The combined organic phase was dried over magnesium sulfate at 0°. The solvent was evaporated *in vacuo* at room temperature, and the residue was stripped to constant weight at 0.1 mm. (7 hr. at 25°). There was obtained 20.5 g., a 102% yield, of crude 5-hydroxypentyl tosylate, a viscous, opaque oil.

Anal. Calcd. for C₁₃H₁₈O₄S: C, 55.8; H, 7.02; S, 12.4. Found: C, 57.4; H, 7.55; S, 11.9.

No further purification was attempted because the hydroxypentyl tosylate decomposed slowly at room temperature. The crude material (19.2 g.) was treated with 21 ml. of 2,6-lutidine and heated 7 hr. at 100–140°. There was collected 3.97 g., a 62% yield, of liquid, *n*_D²⁰ 1.4223, which was shown by gas chromatography to be 99% pure tetrahydropyran.²³

(23) D. D. Reynolds and W. O. Kenyon, *J. Am. Chem. Soc.*, **72**, 1593 (1950).

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

Hydroboration. XXII. The Reaction of Unsaturated Esters with Diborane and Disiamylborane¹

BY HERBERT C. BROWN AND KESTUTIS A. KEBLYS²

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The treatment of several representative ω -unsaturated esters with excess diborane in tetrahydrofuran at 0° results in both addition to the carbon-carbon double bond and concurrent reduction of the ester group. Oxidation of the products with alkaline hydrogen peroxide yields mixtures of hydroxy esters and diols. Under standard conditions the extent of reduction of the ester grouping decreases with increasing number of carbon atoms between the ester grouping and the double bond: ethyl 3-butenolate > ethyl 4-pentenolate > ethyl 10-undecenoate. It is proposed that a major side reaction is reduction of the ester group intramolecularly by the monoalkylborane formed in the initial addition of borane to the double bond. The use of the theoretical quantity of diborane added to a concentrated solution of the unsaturated ester minimizes the side reaction and produces the organoborane in good yield. Oxidation produces the ω -hydroxy esters, accompanied by smaller quantities of the secondary isomers. The use of disiamylborane for the hydroboration circumvents the partial reduction of the ester group and essentially eliminates the formation of the secondary isomer. The ω -carboethoxyalkylboranes fail to undergo a base-catalyzed cyclization to cyclic ketones. The reactions of diborane and disiamylborane with ethyl acrylate are relatively complex, apparently the result of a strong directive influence of the carboethoxy group which directs the boron predominantly to the α -position of the ester, followed by a transfer of the boron to the neighboring oxygen of the carbonyl group.

The development of hydroboration, the reaction of olefins, dienes, and acetylenes with diborane and diborane derivatives, has opened up a new and convenient route to a variety of organoboranes.^{3–6} Owing to their ability to undergo numerous chemical transformations, the organoboranes promise to become important intermediates in organic synthesis.⁷ The extension of hydroboration to functional derivatives of olefins and acetylenes would not only provide access to new types of organoboranes, but would also extend significantly the synthetic usefulness of the hydroboration reaction.

In the preceding publication we examined the hydroboration of unsaturated alkyl chlorides and tosylates.⁸ These derivatives represent substituents normally inert to diborane under hydroborating conditions.⁹

(1) Based upon a thesis submitted by K. A. Keblys in 1962 to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Research assistant on an XR Grant provided by the Purdue Research Foundation.

(3) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).

(4) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

(5) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961).

(6) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

(7) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp. 59–80.

(8) H. C. Brown and K. A. Keblys, *J. Am. Chem. Soc.*, **86**, 1791 (1964).

Of far greater significance is the achievement of the hydroboration of unsaturated derivatives containing substituents capable of undergoing reduction by diborane. In the present paper we examine the practicality of achieving the selective hydroboration of unsaturated carboxylic esters, while avoiding or minimizing concurrent reduction of the ester grouping.

Apart from its more general implications, it is evident that such a study is of interest in demonstrating the possibility of synthesizing organoboranes containing carboethoxy substituents. It is evident that were the hydroboration step feasible, one would have readily available a wide range of carboethoxy derivatives containing a reactive center on which one could operate to introduce other substituents, such as the hydroxy group,⁷ to convert into other organometallics, such as the mercury derivative,¹⁰ or to join to other groupings *via* carbon-carbon bonds.¹¹

Although esters are reduced by diborane,⁹ the rate of reduction appears to be considerably slower than the

(9) H. C. Brown and B. C. Subba Rao, *ibid.*, **82**, 681 (1960); research in progress with Dr. P. Heim.

(10) J. B. Honeycutt, Jr., and J. M. Riddle, *ibid.*, **82**, 3051 (1960).

(11) H. C. Brown, N. C. Hébert, and C. H. Snyder, *ibid.*, **83**, 1001 (1961); H. C. Brown and C. H. Snyder, *ibid.*, **83**, 1001 (1961); H. C. Brown, C. Verbrugge, and C. H. Snyder, *ibid.*, **83**, 1002 (1961).