

(1–2%) of ethyl 3-hydroxybutyrate. Only traces of diols were detected.

Ethyl 4-Hydroxybutyrate.—Disiamylborane solution was prepared *in situ* using 65.0 ml. (75.3 mmoles) of 1.16 *M* borane solution and 10.6 g. (151 mmoles) of 2-methyl-2-butene. To this solution was added 7.65 g. (67.0 mmoles) of ethyl 3-butenolate at 0°, stirring for 1 hr. at 0° and 30 min. at 25°. The solution was hydrolyzed with 3 ml. of water, then oxidized with 35 ml. of 1 *M* sodium hydroxide, added simultaneously at 20–26°. The oxidized mixture was diluted with 50 ml. of ether, and the layers were separated. The aqueous layer was extracted with 100 ml. of ether. The organic layer was combined with the extracts, washed with 15 ml. of 1% sodium carbonate, 15 ml. of saturated sodium sulfite, and 15 ml. of saturated sodium chloride, and then dried over magnesium sulfate. The solvent and most of the siamyl alcohol were evaporated *in vacuo* at room temperature. The residue was distilled rapidly at 0.1 mm. into an ice-cooled receiver. Redistillation of the flash distillate gave 6.7 g., a 76% yield, of ethyl 4-hydroxybutyrate, collected at 43–44° at 0.15 mm., n_D^{20} 1.4294. The product was 98% pure by gas chromatography.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.32; H, 9.24.

The 3,5-dinitrobenzoate derivative of the product, recrystallized from ether–hexane, melted at 63.0–63.8° (reported²⁶ m.p. 62–63°).

Ethyl 5-Hydroxyvalerate.—By the procedure described above, ethyl 4-pentenoate (11.2 g., 87.2 mmoles) was treated with 96 mmoles of disiamylborane. Distillation gave 9.92 g., a 78% yield, of ethyl 5-hydroxyvalerate, collected at 64–65° at 0.1 mm., n_D^{20} 1.4342 (reported²⁷ b.p. 114° at 14 mm.).

Ethyl 11-Hydroxyundecanoate.—Similarly, ethyl 10-undecenoate (10.8 g., 51 mmoles) was treated with 57 mmoles of disiamylborane. Distillation gave 9.52 g., an 81% yield, of ethyl 11-hydroxyundecanoate, collected at 111.0–112.5° at 0.1 mm., n_D^{20} 1.4478.

(26) S. Okamura, M. Masumura, and T. Horie, *Yuki Gosei Kagaku Kyokai Shi*, **17**, 419 (1959); *Chem. Abstr.*, **53**, 17958c (1959).

(27) R. Robinson and L. H. Smith, *J. Chem. Soc.*, 371 (1937).

Anal. Calcd. for $C_{13}H_{26}O_3$: C, 67.78; H, 11.38. Found: C, 67.66; H, 11.68.

Reaction of 3-Butenoyl Chloride with Disiamylborane.—To disiamylborane, prepared *in situ* from 25.0 ml. (15.2 mmoles) of 0.608 *M* borane solution and 2.14 g. (30.3 mmoles) of 2-methyl-2-butene, was added at 0° 1.58 g. (15.1 mmoles) of 3-butenoyl chloride. The solution was stirred for 2 hr. at 0°, and then treated with 1.03 g. (15.2 mmoles) of sodium ethoxide and 5 ml. of ethanol. After stirring 10 min. at 0–10°, the solution was oxidized by a simultaneous addition of 55 mmoles of hydrogen peroxide and 7.5 ml. of 1 *M* sodium hydroxide. After standard work-up, the analysis by gas chromatography showed 8.4 mmoles, a 56% yield, of ethyl 4-hydroxybutyrate.

Attempted Cyclizations.—The organoborane, prepared *in situ* from 12.2 mmoles of ethyl 3-butenolate and 14 mmoles of disiamylborane in tetrahydrofuran, was treated with 0.97 g. of sodium ethoxide and 1.3 ml. of ethanol. The resulting solution was stirred for 7 hr. at 25°. No cyclobutanone was obtained. After oxidation, a 49% yield of ethyl 4-hydroxybutyrate was found. The experiment, was repeated, allowing the solution to reflux for 7 hr. at 65°. Again no cyclobutanone was detected. After oxidation, a 38% yield of ethyl 4-hydroxybutyrate was found. In another experiment, after addition of sodium ethoxide, the solvent was evaporated, and the residue heated *in vacuo* for 20 hr. at 100–200°. The distillate, collected in a Dry Ice-cooled trap, contained no cyclobutanone.

The organoborane, prepared *in situ* from 36.5 mmoles of ethyl 4-pentenoate and 14.2 mmoles of borane, was treated with 28.4 mmoles of sodium ethoxide. The resulting solution was stirred for 3 hr. at 23° and 4 hr. at 67°. Examination by gas chromatography showed no cyclopentanone. The solvent was then evaporated, and the residue heated *in vacuo* for 10 hr. at 150–170°. No cyclopentanone was found in the –80° traps.

The organoborane, prepared *in situ* from 27.6 mmoles of 3-butenoyl chloride and 30.5 mmoles of disiamylborane, was treated with 44 mmoles of tetramethylethylenediamine. The mixture was stirred 24 hr. at 25°, then heated 7 hr. at 67°. No cyclobutanone was detected.

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

Hydroboration. XXIII. Directive Effects in the Hydroboration of Representative Allyl Derivatives. The Elimination Reaction of β -Substituted Organoboranes

BY HERBERT C. BROWN AND O. J. COPE¹

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The hydroboration of representative allyl derivatives was examined in order to observe the effect of the substituent on the direction of addition of diborane to the double bond. The per cent addition of the boron to the secondary carbon atom decreases with decreasing electronegativity of the substituent: allyl tosylate, 45%; chloride, 40%; acetate, 35%; benzoate, 25%; borate, 18%; phenyl ether, 32%; phenyl thioether, 22%; ethyl ether, 19%; alcohol, 24%. Whereas the secondary boron derivatives derived from allyl tosylate, chloride, benzoate, and acetate undergo a spontaneous elimination to propylene during the hydroboration of the allyl derivative, the borate, phenoxide, and ethoxide derivatives survive the hydroboration reaction at 0°. However, at elevated temperatures (refluxing tetrahydrofuran, 64°) the elimination reaction is essentially complete within 2 hr. in the case of these derivatives. A base-catalyzed elimination at room temperature was observed for the secondary hydroboration product of allyl phenyl ether. This controlled elimination reaction of β -substituted organoboranes should find useful application in organic synthesis. The hydroboration of representative allyl derivatives with disiamylborane greatly reduces the formation of the secondary isomer and permits conversion of the allyl compounds into desirable products in very high yield.

The present investigation is a logical extension of an earlier study of directive effects in the hydroboration² of simple olefins.³ In the case of terminal olefins, the addition of boron takes place predominantly on the terminal carbon atom of the double bond. This was explained in terms of polarization of the double bond by the alkyl substituent, increasing the electron

density at the terminal carbon atom and thereby favoring the attachment of the electrophilic boron atom at that position.³

The introduction of electron-withdrawing functional groups at the allyl position brings about a marked increase in the addition of boron to the secondary carbon atom of the double bond.⁴ Thus, in the hydroboration of allyl tosylate and allyl chloride, 45 and 40%, respectively, of the boron adds to the nonterminal position.

(1) Postdoctorate research associate on Research Grant DA-ARO(D)-31-124-G106 supported by the U. S. Army Research Office (Durham).

(2) For a summary of the main characteristics of the hydroboration reaction and its application to organic synthesis, see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

(4) H. C. Brown and K. A. Kebly, *ibid.*, **86**, 1791 (1964).

The ratio of secondary alcohol (or product derived from the elimination reaction of the β -substituted secondary organoborane) to primary alcohol was taken as the ratio of the two isomeric organoboranes produced in the hydroboration step.

Experiments with allyl ethyl ether appeared to show a small, but significant, variation in the isomer ratio with changing ratios of diborane to substrate. Accordingly, in order to eliminate this possible factor, the hydroborations were carried out by using a standard excess of reagent—three hydrides per mole of allyl derivative, except for allyl acetate and benzoate, where five hydrides per mole were utilized.

The products identified and the yields realized in the hydroboration-oxidation of the various allyl derivatives are summarized in Table I.

It is apparent in the case of the acetate that hydroboration was accompanied by reduction of the ester moiety. We explored the possibility that hydroboration might be achieved selectively, without reduction of the ester group, by adding the theoretical quantity of diborane to the ester. However, the following products were realized: allyl acetate, 48%; 1,3-propanediol monoacetate, 34%; 1-propanol, 13%; ethanol, 13%. The presence of unchanged allyl acetate along with 1-propanol and ethanol shows that the elimination reaction must be faster than the hydroboration stage, and that the products of the elimination reaction must compete very favorably with the allyl ester for the available hydride.

In the case of allyl benzoate, the addition of 1.25 equivalents of hydride (thus allowing for the observed 25% elimination) yielded the following product distribution: allyl benzoate, 5%; 1,3-propanediol monobenzoate, 65%; benzoic acid, 23%; benzyl alcohol, 3%; 1-propanol, 20%. In this case, the propylene formed in the elimination stage competes with allyl benzoate for the available hydride, but reduction of the benzoic acid moiety does not.

In the case of allyl alcohol, it was observed that the addition of 1 equivalent of diborane to the alcohol in tetrahydrofuran at 0° liberated 0.89 equivalent of hydrogen. Evidently, 11% of the double bonds had undergone hydroboration. Addition of a second equivalent of diborane resulted in the evolution of the remaining hydrogen (0.11 equivalent).

Hydroboration with Disiamylborane.—The use of disiamylborane avoids many of the complications observed with diborane. Thus allyl acetate, allyl ethyl ether, and allyl phenyl thioether react with only 1 mole of the reagent. Evidently, reduction of the acetate grouping is not a factor here.¹¹ Moreover, only minor amounts of the secondary derivatives are observed (~2%). Consequently the use of disiamylborane provides a convenient means of converting these allyl derivatives into the corresponding organoboranes and into the products into which these organoboranes may be transformed.²

The experimental results are summarized in Table II.

The Elimination Reaction.—Although the hydroboration of allyl borate, alcohol, phenyl ether, ethyl ether, and phenyl thioether had utilized but one hydride per mole of olefin, the oxidation products re-

TABLE II
STOICHIOMETRY AND OXIDATION PRODUCTS FOR THE
HYDROBORATION OF ALLYL DERIVATIVES WITH
DISIAMYLBORANE IN TETRAHYDROFURAN AT 0°

Allyl compound	Hydride utilized ^a	Addition to 2-position, %	Oxidation products	Yield, ^b %
Acetate	0.99	2	1,3-Propanediol monoacetate	95
			1-Propanol	2
Ethyl ether	0.98	2	3-Ethoxy-1-propanol	92
			1-Ethoxy-2-propanol	2
Phenyl thio-ether	0.97	None obsd.	3-Phenylthio-1-propanol	86

^a Equivalents of hydride per equivalent of allyl compound.

^b Moles of product per mole of allyl compound.

vealed the presence of small quantities of 1-propanol, from 1 to 5% (Table I). This suggested that the elimination reaction, so evident in the chloride,^{4,5} tosylate,⁴ benzoate, and acetate, might also be occurring as a relatively slow, secondary reaction under the mild conditions (0°) utilized for the hydroboration. If so, it should be possible to accelerate the elimination reaction at higher temperatures, thereby causing it to proceed at a convenient rate for observation.

Accordingly, allyl phenyl ether, allyl ethyl ether, and allyl borate were hydroborated in tetrahydrofuran at 0°, utilizing a 50% excess of hydride. An aliquot was removed and oxidized, and the ratio of primary to secondary alcohols was established by gas chromatographic examination. Meanwhile, the tetrahydrofuran solutions of the organoboranes were rapidly brought to room temperature and maintained there as aliquots were removed at suitable time intervals. These were oxidized by the standard procedure and analyzed for the ratio of secondary to primary isomers. The change in this ratio was taken as an estimate of the amount of the elimination which had occurred during the time interval.

It was observed that the elimination reaction was fastest with the borate, rising from 30% in 1 hr., to 77% in 3, to 97% in 20. The ethyl ether derivative was considerably slower, exhibiting only 50% elimination in 20 hr. under these conditions.

The elimination reaction proceeds quite rapidly at 64° (refluxing tetrahydrofuran), being essentially complete in 1 hr.

It was established, by the use of internal standards, that under all of the elimination conditions examined the primary isomer was not affected—its concentration remaining essentially constant.

These results are summarized in Table III.

In order to ascertain whether the excess hydride was playing any part in the elimination, the study was repeated using only the theoretical quantity of hydride to achieve hydroboration. Under these conditions there was observed only 23% elimination in 20 hr. at 25° for allyl borate, in contrast to the 97% observed for the reaction in the presence of excess hydride. Similarly, allyl ethyl ether under these conditions exhibited only 20% elimination, in contrast to the 51% realized with excess hydride. Moreover, these reactions were not complete in 1 hr. at reflux (Table III).

Cagliotti and Cainelli have noted that acetic acid and acetic anhydride facilitate the elimination reaction in certain organoborane derivatives produced in their hydroboration experiments.⁶ Accordingly, we repeated

(11) It had been previously demonstrated that disiamylborane does not reduce either carboxylic esters or acids under these conditions: H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, **83**, 486 (1961).

tosylate. However, the latter is an excellent leaving group. At first sight it appears surprising that acetate and benzoate are also such very effective leaving groups. However, it may be that in the case of these derivatives the availability of a simple cyclic mechanism, similar to that postulated for the *cis* pyrolysis of alkyl acetates,¹³ provides a highly favorable reaction path for the elimination reaction.

The use of disiamylborane as the hydroborating agent for allyl acetate resulted, as anticipated, in almost exclusive addition to the terminal carbon atom. Evidently, the role of the electronic effect of the substituent in directing boron to the nonterminal atom is largely nullified by the large steric effect of the substituent. A minor amount of addition to the secondary position (~2%) apparently occurs, resulting in elimination and the ultimate formation of a small amount of 1-propanol (Table II).

The use of disiamylborane thus provides a useful general method for the preparation of the half-esters of diols from the corresponding unsaturated ester, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{OCOR}$.

Allyl Alcohol and Allyl Borate.—The treatment of allyl alcohol with the theoretical quantity of diborane results in a predominant evolution of hydrogen, with only minor participation of the double bond. Consequently, the first stage of the reaction results in the transformation of the allyl alcohol into allyl borate, and it is logical to consider the behavior of these two derivatives as a unit.

In view of argument that allyl alcohol is largely transformed into allyl borate before it undergoes hydroboration of the double bond, one may wonder why allyl alcohol yields 24% attack at the 2-position, whereas allyl borate exhibits only 18% addition of the boron to this position. In these experiments the allyl alcohol and allyl borate were added to an excess of the hydroborating agent. Under these conditions, it is probable that intermediates, such as $\text{CH}_2=\text{CHCH}_2\text{-OBH}_2$ and $(\text{CH}_2=\text{CHCH}_2\text{O})_2\text{BH}$, form and participate in the reaction, rather than the allyl borate produced in the absence of an excess of diborane. In view of the lower steric influence of the mono- and diallylboranes, as well as their altered inductive influences, it is not unreasonable that there should be realized somewhat different distributions in the two systems.

It is very important that hydroboration can be achieved in these derivatives without significant elimination, with elimination possible in a controlled later stage. This opens some interesting possibilities in synthetic work.^{6,14}

Allyl Ethers and Thioethers.—The principal products in the hydroboration-oxidation of both allyl phenyl ether and allyl ethyl ether are the corresponding mono-phenyl and monoethyl ethers of 1,2- and 1,3-propanediols. The increased addition at the secondary carbon atom of the double bond in the case of the phenyl ether (32 vs. 19% for the ethyl ether) is in the direction to be anticipated for the relative inductive ($-I$) effects of the phenoxy and ethoxy groups.

(13) D. Y. Curtin and D. B. Kellon, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

(14) L. Cagliotti, G. Cainelli, G. Maina, and A. Selva, Congress of Chemistry of the Swiss and Italian Chemical Societies, Naples, Italy, May, 1962.

The amount of elimination taking place under the hydroboration conditions utilized appears to be quite small. However, attention should be called to the base-catalyzed elimination reaction observed in the case of the phenyl derivative. One can either take advantage of this to destroy selectively the minor component prior to oxidation, or to circumvent it by oxidation with simultaneous addition of the hydrogen peroxide and base.

The smaller addition of boron to the secondary position of allyl phenyl thioether, 22%, is also in accord with the reduced inductive influence of the thiophenyl grouping. The observation that hydroboration does not involve any attack of the carbon-sulfur bond, and that the boron-carbon bond can be oxidized selectively by alkaline hydrogen peroxide has important implications for synthetic work with sulfur derivatives.¹⁵

Finally, disiamylborane achieves the conversion of both allyl ethyl ether and allyl phenyl thioether to 3-ethoxy-1-propanol and 3-phenylthio-1-propanol, respectively, in excellent yield with a minimum of side products.

Directive Effects.—The available data on directive effects in the hydroboration of propylene carrying various substituents in the allylic position are summarized in Table IV.

TABLE IV
DIRECTIVE EFFECTS IN THE REACTION OF DIBORANE WITH REPRESENTATIVE ALLYL DERIVATIVES

Allyl Compound	Substituent in $\text{ZCH}_2\text{CH}=\text{CH}_2$	Addition to 2-position, %
1-Butene ^a	CH_3-	6
3-Phenyl-1-propene ^a	C_6H_5-	10
Ethyl 4-pentenoate ^b	$\text{C}_2\text{H}_5\text{O}_2\text{CCH}_2-$	17
4-Chloro-1-butene ^b	ClCH_2-	18
Allyl borate	$>\text{BO}-$	18
Allyl ethyl ether	$\text{C}_2\text{H}_5\text{O}-$	19
Allyl phenyl thioether	$\text{C}_6\text{H}_5\text{S}-$	22
(Allyl alcohol) ^d	$(\text{HO}-)$	(24)
Allyl benzoate	$\text{C}_6\text{H}_5\text{CO}_2-$	25
Allyl phenyl ether	$\text{C}_6\text{H}_5\text{O}-$	32
Allyl acetate	CH_3CO_2-	35
Allyl chloride ^b	$\text{Cl}-$	40
Allyl tosylate ^b	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3-$	45
1,1,1-Trifluoropropene ^c	$\text{F}_3\text{C}-$	74

^a Ref. 3. ^b Ref. 4. ^c J. R. Phillips and F. G. A. Stone, *J. Chem. Soc.*, 94 (1962). ^d Allyl alcohol reacts to form allyloxy derivatives of borane before hydroboration of the double bond occurs.

Unfortunately, these studies were not all carried out under identical conditions. Moreover, great accuracy cannot be claimed for individual measurements in view of the indirect procedure which was necessarily employed to establish the relative addition of the boron atom to the primary and secondary positions of the double bond. Nevertheless, the trend is unmistakable. With increase in electron-withdrawing characteristics of the substituent, there results an increase in the percentage addition of boron to the secondary position.

(15) The hydroboration-oxidation of allyl phenyl thioether, among other unsaturated sulfur derivatives, has been reported recently: D. J. Pasto and J. L. Miesel, *J. Am. Chem. Soc.*, **85**, 2118 (1963). These authors prefer to interpret the observed reactions in terms of "transfer reactions involving boron," rather than in terms of the simple elimination reaction here presented. A critical evaluation of this proposal by Pasto and Miesel will be made following completion of a more detailed study of the hydroboration of monocyclic and bicyclic olefinic derivatives now under way.

TABLE V
 SUMMARY OF DATA FOR THE ALLYL COMPOUNDS AND FOR THE ISOMERIC ALCOHOLS

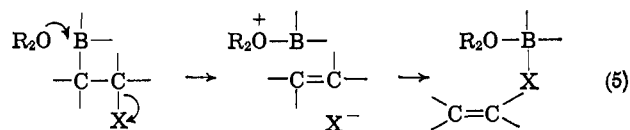
Compounds	Source	B. p., °C. (mm.)	n_D^{20}
Allyl acetate	Eastman (White Label)	102 (745)	1.4048
Allyl benzoate	From allyl alcohol and benzoyl chloride ^a	110 (14)	1.5184
Allyl ethyl ether	Eastman (White Label)	66 (745)	1.3878
Allyl phenyl ether	Eastman (White Label)	71 (10)	1.5220
Allyl phenyl thioether	From allyl chloride and thiophenol ^b	61-62 (1.9)	1.5760
Allyl alcohol	Fisher (reagent)	96 (750)	1.4134
Allyl borate	From boric acid and allyl alcohol ^c	175 (754)	1.4285
1,3-Propanediol	Eastman	104 (7)	1.4397
Monoacetate of 1,3-propanediol	From 3-chloro-1-propanol and silver acetate in dimethylformamide	86 (9) ^d	1.4236
Monobenzoate of 1,3-propanediol	From benzoyl chloride and 1,3-propanediol ^e	148 (3)	1.5200
3-Phenoxy-1-propanol	From phenol and 3-chloro-1-propanol ^f	153 (22.5)	1.5290
3-Ethoxy-1-propanol	From sodium ethoxide and 3-chloro-1-propanol ^g	91 (50)	1.4167
1,2-Propanediol	Eastman	97 (20)	1.4338
1-Phenoxy-2-propanol	From phenol and propylene oxide ^h	129-130 (20)	1.5230
1-Ethoxy-2-propanol	K and K	131 (740)	1.4070
3-Phenylthio-1-propanol	From sodium thiophenoxide and 3-chloro-1-propanol ⁱ	133-134 (2)	1.5817
1-Phenylthio-2-propanol	From thiophenol and propylene oxide ^j	110-112 (2)	1.5730

^a P. B. D. De la Mare, R. A. Scott, and P. W. Robertson, *J. Chem. Soc.*, 509 (1945). ^b D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952). ^c V. K. Kuskov and B. M. Sheiman, *Doklady Akad. Nauk S.S.S.R.*, **106**, 479 (1955) (Engl. transl. p. 83). ^d D. C. Dittmer, W. R. Hentlen, and H. Winicov, *J. Am. Chem. Soc.*, **79**, 4431 (1957). In order to obtain a sample of the half-ester free from glycol, it was necessary to use preparative gas chromatography (silicone-sorbitol column). ^e E. Fischer, *Ber.*, **53**, 1642 (1920). ^f S. Searles and C. F. Butler, *J. Am. Chem. Soc.*, **76**, 56 (1954). ^g M. Okawara, *J. Chem. Soc. (Japan, Ind. Chem. Sect.)*, **55**, 219 (1952); *Chem. Abstr.*, **48**, 7583g (1954). ^h C. D. Hurd and P. Perlit, *J. Am. Chem. Soc.*, **68**, 38 (1946). ⁱ W. R. Kirner and G. H. Richter, *ibid.*, **51**, 3409 (1929). ^j R. D. Schuetz, *ibid.*, **73**, 1881 (1951).

In these allyl derivatives, the directive effect of the substituent must work against the natural tendency of the boron atom to add to the terminal atom of the double bond. In the case of the corresponding crotonyl derivatives $\text{CH}_3\text{CH}=\text{CH}_2\text{CH}_2\text{Z}$, the directive influence of the substituent should be much more powerful, resulting in a dominant addition of the boron to the neighboring 2-position.¹⁶

The Elimination Reaction.—The elimination reactions of the secondary organoboranes from allyl tosylate, chloride, acetate, and benzoate are obviously very fast and occur concurrently with hydroboration. On the other hand, the corresponding elimination reactions from allyl borate, allyl phenyl ether, and allyl ethyl ether are much slower and can be controlled to proceed in a second stage, subsequent to hydroboration.

It is apparent that the first class involves substituents (tosylate, chloride, carboxylate) which are relatively good leaving groups, whereas the second involves substituents (borate, phenoxide, ethoxide) which are relatively poor leaving groups. It is tempting, therefore, to postulate that the elimination is initiated by the heterolysis of the carbon-anion bond, accompanied by a *trans* loss of the boron atom¹⁷ (5).

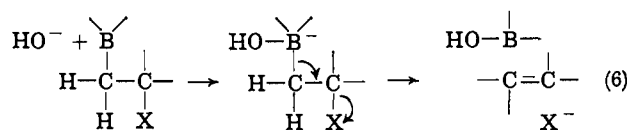


The base-catalyzed elimination of the phenoxide derivative suggests that the elimination may be aided, in the case of poorer leaving groups, by a nucleophilic

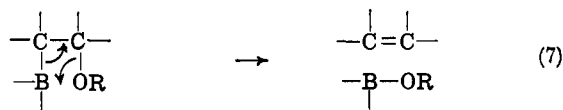
(16) Directive efforts in this system and the elimination reactions of the resulting derivatives are currently under study by Dr. O. J. Cope and Mr. R. M. Gallivan.

(17) This elimination reaction of β -substituted alkylboranes is presumably related to the metal-promoted eliminations of 1,2-dibromides and similar derivatives. For a summary of the literature relating to eliminations of this type, see D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963, pp. 136-140.

attack at the boron atom, to facilitate heterolysis of the boron-carbon bond (6), initiating the reaction.



Finally, an alternative mechanism may be available for poor leaving groups, such as borate, phenoxide, and ethoxide—a *cis* elimination (7).

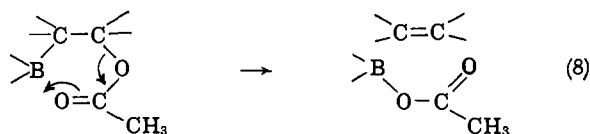


The enhanced rate of elimination indicated by allyl ethyl ether and allyl borate hydroborated with an excess of diborane is consistent with a *cis* elimination. R_2BH is a stronger Lewis acid than R_3B .¹⁸ Consequently, the excess diborane should produce a boron derivative which contains one or more hydrogen atoms attached to boron. This derivative should be more electrophilic and thereby exhibit an enhanced tendency for the boron atom to become united with the neighboring nucleophilic oxygen atom than the fully alkylated borane, produced with the theoretical quantity of diborane.

As was pointed out earlier, the very fast rate of elimination exhibited by the acetate and benzoate groups, in spite of the fact that acetate and benzoate are not normally considered to be very good leaving groups, may be the result of such a *cis* elimination, for which the carboxylate group is particularly effective (8).

It is evident that considerable mechanistic work must be done to attain an understanding of the elimination reaction in these derivatives commensurate with the

(18) H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *J. Am. Chem. Soc.*, **61**, 1078 (1939).



present understanding of the elimination reaction in carbon compounds.¹⁹

Experimental

Materials.—Tetrahydrofuran and diglyme were freshly distilled (the latter under vacuum) from lithium aluminum hydride prior to the preparation of each stock solution of diborane. Boron trifluoride etherate was purified by distillation under vacuum. Sodium borohydride from Metal Hydrides, Inc., was used without further purification.

The source or preparative method and physical constants of the allyl compounds used are incorporated in Table V. In addition, the method of preparation and the physical constants of the alcohols required for the gas chromatographic comparison with the alcohol reaction products are included in this table. All the allyl compounds and the alcohols were examined by gas chromatography prior to use and judged to be 98% pure. The compounds obtained commercially were redistilled from calcium hydride, except for the hydroxylic compounds which were distilled after standing over Drierite for several days. Diborane and bis-3-methyl-2-butylborane stock solutions in tetrahydrofuran were prepared following procedures described previously.²⁰

General Procedures.—All glassware used in these experiments was flame dried and cooled in a stream of dry nitrogen before use. Throughout the course of the hydroboration a positive pressure of nitrogen was kept above the THF solution. The reactions were carried out in 100-ml., two-neck, round-bottom flasks fitted with a thermometer well, an inlet tube (fitted with a silicone rubber septum), and a magnetic stirrer. In those experiments where the solution was refluxed, the flask was also provided with a water-cooled reflux condenser which had been previously flushed with dry nitrogen.

In a typical hydroboration procedure about 20 mmoles of allyl compound was added dropwise from a hypodermic syringe to the solution of diborane (20 mmoles of BH_3 -THF)²¹ in the

(19) E. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(20) G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183, 190 (1962).

ice-cooled flask. The temperature was maintained at 0–5° and the amount of allyl compound added determined by weighing by difference. Addition took about 20–30 min.; after allowing the reaction to stand for a further 30 min., excess hydride was destroyed by the dropwise addition of water. Oxidation was carried out by adding 6.7 ml. of a 3 *M* sodium hydroxide solution (20 mmoles) followed by the dropwise addition of 24 mmoles (a 20% excess) of hydrogen peroxide, keeping the solution cooled in an ice bath. Hydrogen peroxide concentrations were determined from specific gravity measurements. Where ester groupings were present, and in the case of the phenyl ether, addition of base and hydrogen peroxide were carried out simultaneously from two hypodermic syringes. A known weight of internal standard was added at this juncture.

The solution was then saturated with anhydrous sodium carbonate. In order to ensure that any glycols, ethanol, or propanol were completely salted out, it was necessary to add a sufficient excess of potassium carbonate to convert the aqueous layer into a slurry. The tetrahydrofuran layer was decanted off and dried first over anhydrous magnesium sulfate and then over Drierite overnight. The solution was then analyzed by gas chromatography. In order to estimate small quantities of 1-propanol it was necessary fractionally to distill off most of the THF before analysis. In a typical elimination study, 5-ml. aliquots of the reaction mixture were withdrawn and these were oxidized and worked up in exactly the same way as described above.

An Aerograph gas chromatograph Model A90-S (Wilkins Instrument and Research, Inc.) was used for the analyses. The products were identified by a comparison of their retention times with those of authentic samples. A 5-ft. column packed with 20% Carbowax 20M on Chromosorb W was used for the analysis of most of the monohydric alcohols except the phenylthiopropanols. The latter were determined, using a 2-ft. column packed with 2% Carbowax 1540 on Fluoropak 80 at 150°. The propanediols and phenoxypropanols were separated by employing a 5-ft. column packed with *d*-sorbitol (4%) and Dow silicone 703 (16%) on 60–80 mesh firebrick at 125°.

It was shown that the v.p.c. quantitative determinations were reproducible to $\pm 1\%$ ($\pm 2\%$ for the glycols), the results given being the average of three separate analyses. Although it was possible to identify the monobenzoate of 1,3-propanediol using the above columns, the quantitative determination was carried out by first hydrolyzing the ester (by refluxing with aqueous sodium hydroxide) and then analyzing for 1,3-propanediol as before.

(21) The BH_3 -THF solutions used in this work varied from 0.3 to 1.3 *M* in BH_3 .

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Electron-Transfer Processes. I. The Scope of the Reaction between Carbanions or Nitransions and Unsaturated Electron Acceptors^{1,2}

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The scope of the reaction leading to the products of electron transfer between carbanions and nitransions and unsaturated organic molecules has been investigated. Many carbanions and nitransions, particularly those which are dianions, react with unsaturated molecules such as nitroaromatics, azobenzene, and diaryl ketones to form the radical-anions derived from the unsaturates. The same effect was observed with *n*-butyllithium and *n*-butylmagnesium bromide. It is concluded that processes involving one-electron transfer must be important in many reactions involving carbanions.

Introduction

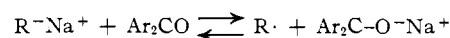
The transfer of an electron from a diamagnetic carbanion to an unsaturated organic molecule was

(1) Reactions of Resonance Stabilized Anions. XII.

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apparently first recognized by Schlenk who found that tritylsodium reacts with benzophenone and other diaryl ketones with characteristic color changes to produce products which upon hydrolysis and air oxidation yield trityl peroxide and the pinacol.⁴



(4) W. Schlenk and R. Ochs, *Ber.*, **49**, 608 (1916); W. Schlenk and E. Bergmann, *Ann.*, **464**, 1 (1928).